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Organomercury, -rhodium and -palladium compounds in organic synthesis

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ORGANOMERCURY, -RHODIUM AND -PALLADIUM COMPOUNDS IN ORGANIC SYNTHESIS

Iowa State University PH.D. 1980

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Organomercury, -rhodium and -palladium compounds in organic synthesis

by

Susan Smith Hershberger

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1980

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DEDICATION

For Jim

QUOTATION

A little Madness in the Spring
Is wholesome even for the King,
But God be with the clown-

Who ponders this tremendous scene-
This whole Experiment of Green-
As if it were his own!

Emily Dickinson

INTRODUCTION

Organo-transition metal compounds are valuable in organic synthesis both as versatile reagents and reactive intermediates. In addition to their often unique reactivity and selectivity, they may function catalytically. Common methods for forming or elaborating organo-transition metal complexes include: oxidative addition, transmetalation, nucleophilic displacement and insertion reactions. The reverse of oxidative addition, reductive elimination may result in carbon-carbon bond formation and is especially interesting to organic chemists. Currently, these classifications represent synthetic mnemonics rather than precise mechanistic descriptions.

In this thesis, the first two modes of organometallic compound formation, oxidative addition and transmetalation are utilized extensively. However, the synthetic implications and applications of these processes and compounds in organic chemistry are emphasized most.

This thesis has two main divisions. In Part I, organomercury compounds react with organorhodium compounds ultimately resulting in carbon-carbon bond formations and the synthesis of methyl-substituted alkenes and arenes, vinyl and phenyl substituted compounds and divinyl and diaryl ketones. In Part II, stable alkylpalladium compounds are formed from vinyl mercurials, palladium chloride and bicyclic olefins.

Although the compounds and their requisite chemistry in Parts I and II are quite different, Parts I and II are not completely unrelated. In both, transmetalation between a relatively unreactive organomercury compound and a transition metal compound produces a more reactive organo-transition metal compound. Primarily, this thesis further demonstrates both the generality of these transmetalations and their potential role in synthetic organic chemistry.

PART I: ALKYLATION OF ORGANOMERCURIALS VIA ORGANORHODIUM SPECIES

I. ORGANORHODIUM CHEMISTRY PERSPECTIVES

Among Group VIII metals, complexes of rhodium are extensively employed in homogeneous catalysis and the synthesis of organic molecules from inorganic and simple organic reactants. A comprehensive review of organorhodium chemistry is completely beyond the scope of this introduction due to both magnitude and diversity. Since this part of the thesis emphasizes organomercury and -rhodium chemistry applied to synthetic organic chemistry, this chapter introduces organorhodium chemistry. A useful perspective of organorhodium chemistry for a synthetic organic chemist might be provided by briefly considering common organorhodium compounds and reactions and subsequently examining carbon-carbon bond formations facilitated by organorhodium compounds.

A common reaction of rhodium compounds is oxidative addition. Oxidative addition is a reaction of coordinatively unsaturated transition metal compounds. The conversion is illustrated (Eq. 1) where M represents a transition compound

$$\mathrm{M} + \mathrm{A{-}B} \longrightarrow \mathrm{A{-}M{-}B} \tag{1}$$

including ancillary ligands and A-B represents a covalent molecule. In this transformation the oxidation state of the metal increases by two. This process is typical of the Group VIII metals: iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, and platinum. Several reviews have appeared.[1-4] These reviews emphasize the scope of the reaction, discussing a variety of metals, and metal ligand systems, a variety of addends and some mechanistic considerations. The tendency of these metals to undergo oxidative addition increases as one descends a triad and as one moves toward the left of the periodic table. The ligand system also modifies the reactivity of the metal; specifically, ligands which increase the electron density on the metal facilitate oxidative addition. If the addend is an organic molecule the adduct contains a transition metal-carbon bond of potential utility in organic synthesis for either functionalization or carbon-carbon bond formation.

One rhodium compound which is coordinatively unsaturated and undergoes numerous oxidative addition reactions is Wilkinson's catalyst, tris(triphenylphosphine)rhodium chloride, $[P(C_6H_5)_3]_3RhCl$. Similar rhodium compounds with other aryl, alkyl, or aryl and alkyl phosphine or arsine ligands react analogously and are considered here also. Some of the varied covalent molecules which oxidatively add to these complexes include: hydrogen (Eq. 2) and halogens,[5-9] hydrogen halides (Eq. 3),[6-11] hydrogen cyanide (Eq. 4)[12] and hydrogen sulfide (Eq. 5) or thiophenols,[12] methyl iodide (Eq. 6),[9,10,13-15] and allyl chlorides (Eq. 7).[10,13] Aryl

$$RhCl[P(C_6H_5)_3]_3 + H_2 \xrightarrow[CH_2Cl_2]{} RhH_2Cl[P(C_6H_5)_3]_2 \cdot CH_2Cl_2 \qquad (2)$$

$$RhCl[P(C_6H_5)_3]_3 + HCl \xrightarrow[CH_2Cl_2]{} RhHCl_2[P(C_6H_5)_3]_2,\ \tfrac{1}{2}CH_2Cl_2 \qquad (3)$$

$$RhCl[P(C_6H_5)_3]_3 + HCN \longrightarrow RhHCl(CN)(HCN)[P(C_6H_5)_3]_2 \qquad (4)$$

$$RhCl[P(C_6H_5)_3]_3 + H_2S \xrightarrow[CH_2Cl_2]{} RhHCl(SH)[P(C_6H_5)_3]_2,\ \tfrac{1}{2}CH_2Cl_2 \qquad (5)$$

$$RhCl[P(C_6H_5)_3]_2 + CH_3I \longrightarrow Rh(CH_3)I_2[P(C_6H_5)_3]_2 \qquad (6)$$

$$RhCl[P(C_6H_5)_3]_3 + H_2C{=}CH{-}CH_2Cl \longrightarrow Rh(CH_2{-}CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2 \qquad (7)$$

iodides and an alkenyl bromide are assumed to oxidatively add to the rhodium(I) species where the chloride of Wilkinson's catalyst is replaced by a methyl (Scheme 1). The oxidative addition adduct was not isolated but reacts further forming methyl arenes and an alkene.[16]

Scheme 1

$$\begin{tikzcd} Rh(CH_3)[P(C_6H_5)_3]_3 + C_6H_6I \arrow[r] & \{Rh(C_6H_5)(CH_3)I[P(C_6H_5)_3]_3\} \arrow[d] \\ & RhI[P(C_6H_5)_3]_3 + C_6H_5CH_3 \end{tikzcd}$$

Acyl halides[10,11,17-29] and aldehydes[5,19,20,30-35] also oxidatively add to Wilkinson's catalyst and other rhodium(I) species. The initially formed acyl rhodium(III) halide or hydride may be stable (Eq. 8) or may isomerize forming an

$$RhCl[P(C_6H_5)_3]_3 + CH_3COCl \longrightarrow RhCl_2(COCH_3)[P(C_6H_5)_3]_2 \qquad (8)$$

alkyl or aryl rhodium carbonyl halide or hydride (Scheme 2). These species may then react further forming alkenes, alkyl or aryl halides, or alkanes (Scheme 3). Oxidative addition of

Scheme 2

$$\begin{tikzcd} RhCl[P(C_6H_5)_3]_3 + CH_3COCl \arrow[r] & \left[RhCl_2(COC_6H_5)[P(C_6H_5)_3]_2\right] \arrow[d] \\ & RhCl_2(CO)(C_6H_5)[P(C_6H_5)_3]_2 \end{tikzcd}$$

Scheme 3

$$RhCl[P(C_6H_5)_3]_3 + RCH_2CH_2CHO \longrightarrow \left[RhClH(COCH_2CH_2R)[P(C_6H_5)_3]_2\right] \longrightarrow$$

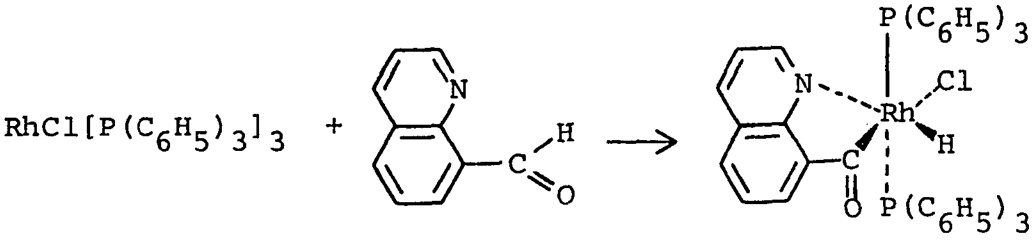
$$\left[RhClH(CO)(CH_2CH_2R)[P(C_6H_5)_3]_2\right] \longrightarrow$$

$$RhCl(CO)[P(C_6H_5)_3]_2 + CH_3CH_2R$$

$$\text{and/or}$$

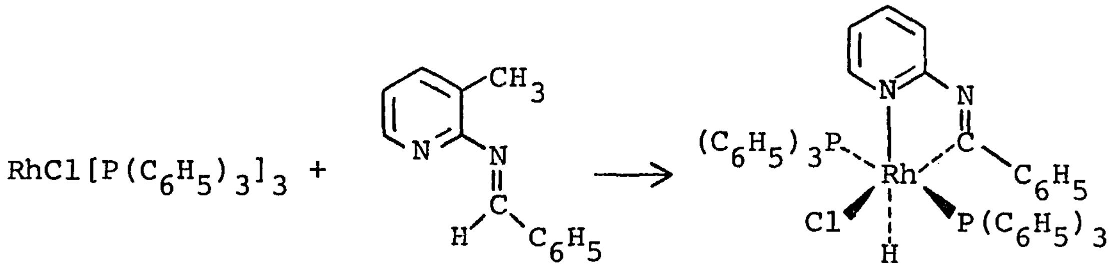
$$H_2C{=}CH_2 + H_2$$

8-quinolinecarboxaldehyde yields a stable chelated rhodium (III) adduct (Eq. 9).[36] The carbon-hydrogen bond of alkimines



(9)

has also been oxidatively added to Wilkinson's catalyst (Eq. 10).[37] Arylsulfonyl chlorides react with Wilkinson's catalyst



(10)

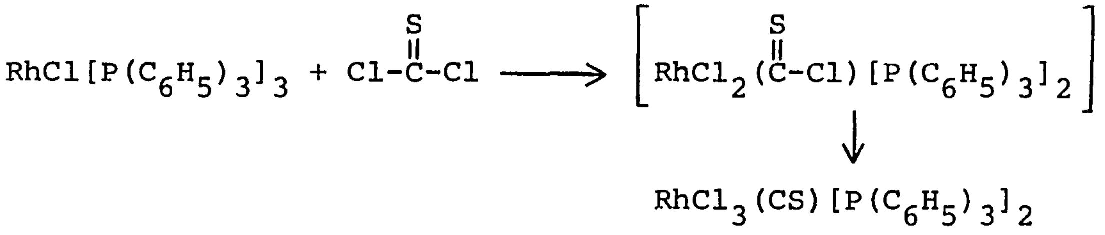
forming aryl chlorides and sulfur dioxide (Scheme 4). An oxidative addition is implied.[38] The synthesis of a rho-

Scheme 4

$$\mathrm{RhCl[P(C_6H_5)_3]_3 + C_6H_5SO_2Cl \longrightarrow \left[RhCl_2(SO_2C_6H_5)[P(C_6H_5)_3]_2\right]}$$
$$\downarrow$$
$$\mathrm{RhCl[P(C_6H_5)_3]_2 + C_6H_5Cl + SO_2}$$

dium(III) thiocarbonyl complex was accomplished by the oxidative addition of thiophosgene followed by ligand migration (Scheme 5).[39] Although Wilkinson's catalyst generally does

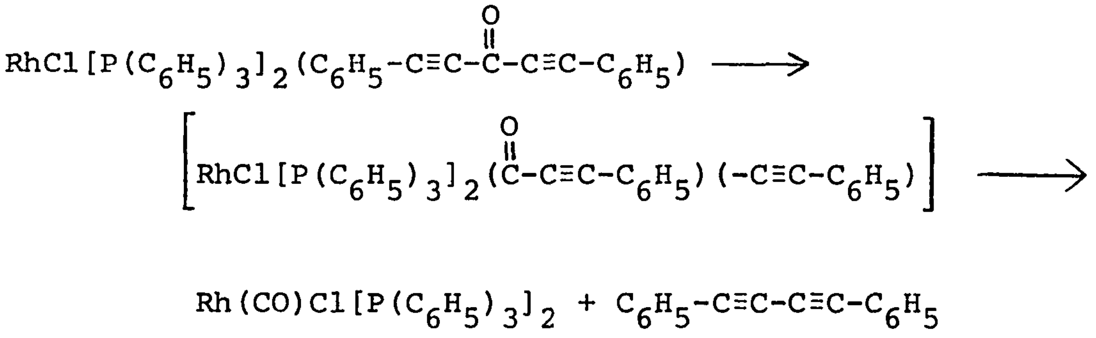
Scheme 5



$$\mathrm{RhCl[P(C_6H_5)_3]_3} + \mathrm{Cl{-}\overset{\overset{S}{\|}}{C}{-}Cl} \longrightarrow \left[\mathrm{RhCl_2(\overset{\overset{S}{\|}}{C}{-}Cl)[P(C_6H_5)_3]_2}\right] \downarrow \mathrm{RhCl_3(CS)[P(C_6H_5)_3]_2}$$

not decarbonylate ketones, dialkynyl ketones have been decarbonylated (Scheme 6). In this case an oxidative addition was implied but not confirmed.[40]

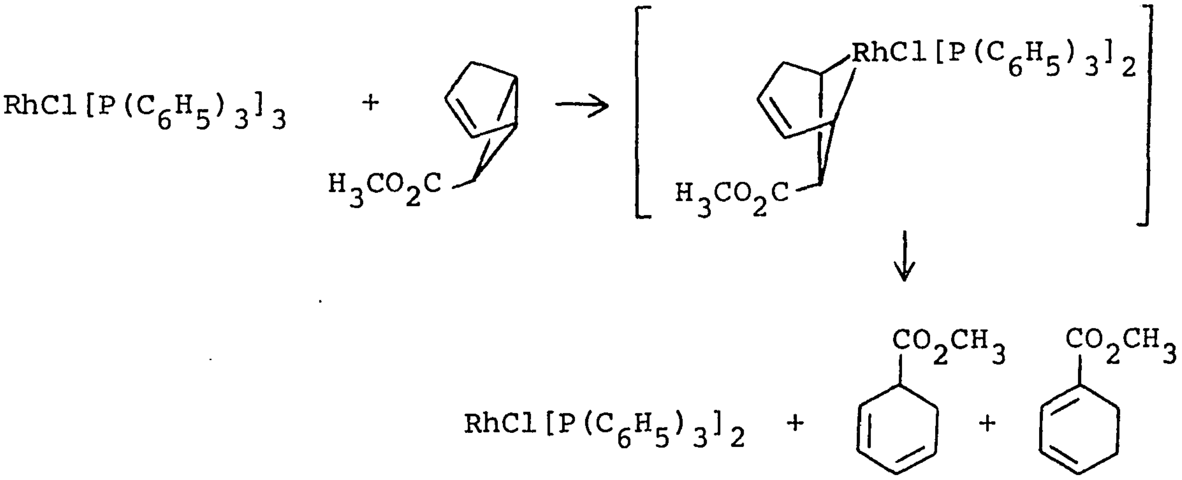
Scheme 6



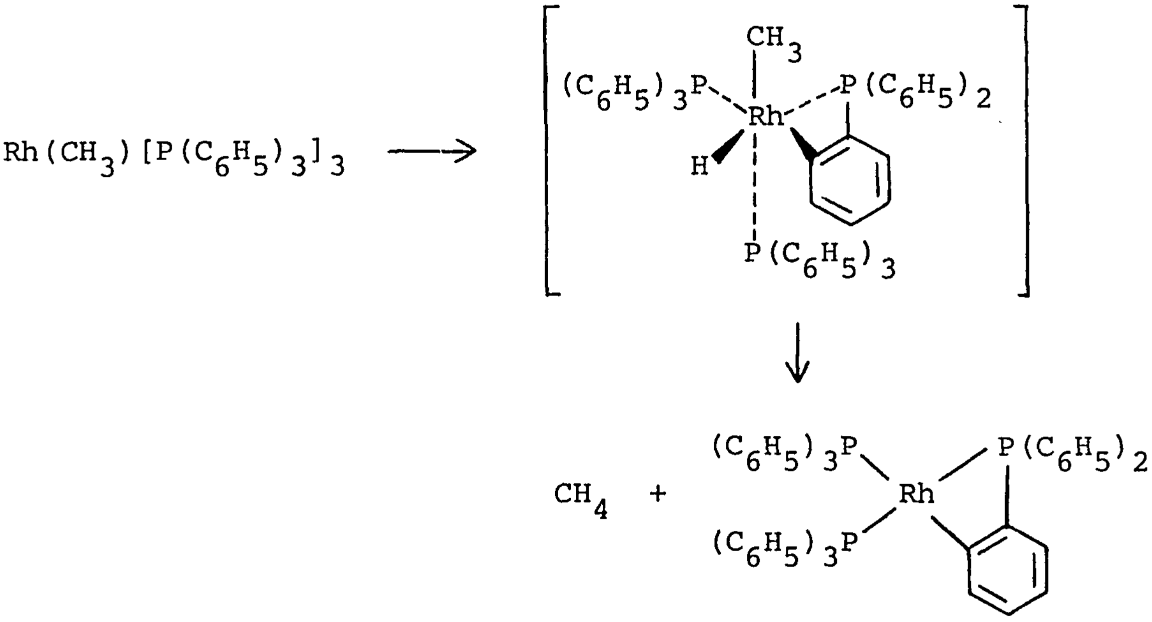
$$\mathrm{RhCl[P(C_6H_5)_3]_2(C_6H_5{-}C{\equiv}C{-}\overset{\overset{O}{\|}}{C}{-}C{\equiv}C{-}C_6H_5)} \longrightarrow \left[\mathrm{RhCl[P(C_6H_5)_3]_2(\overset{\overset{O}{\|}}{C}{-}C{\equiv}C{-}C_6H_5)({-}C{\equiv}C{-}C_6H_5)}\right] \longrightarrow \mathrm{Rh(CO)Cl[P(C_6H_5)_3]_2} + \mathrm{C_6H_5{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_5}$$

Oxidative addition of unsaturated rhodium(I) species occurs with other carbon-hydrogen or carbon-carbon bonds. The carbon-carbon bonds most susceptible to oxidative addition are highly strained carbon-carbon bonds usually in cyclopropyl (Scheme 7) or cyclobutyl systems.[41,42] Oxidative additions involving carbon hydrogen bonds may be distinguished by either a rather acidic hydrogen and/or unique steric accessibility (Schemes 8 and 9).[43-48]

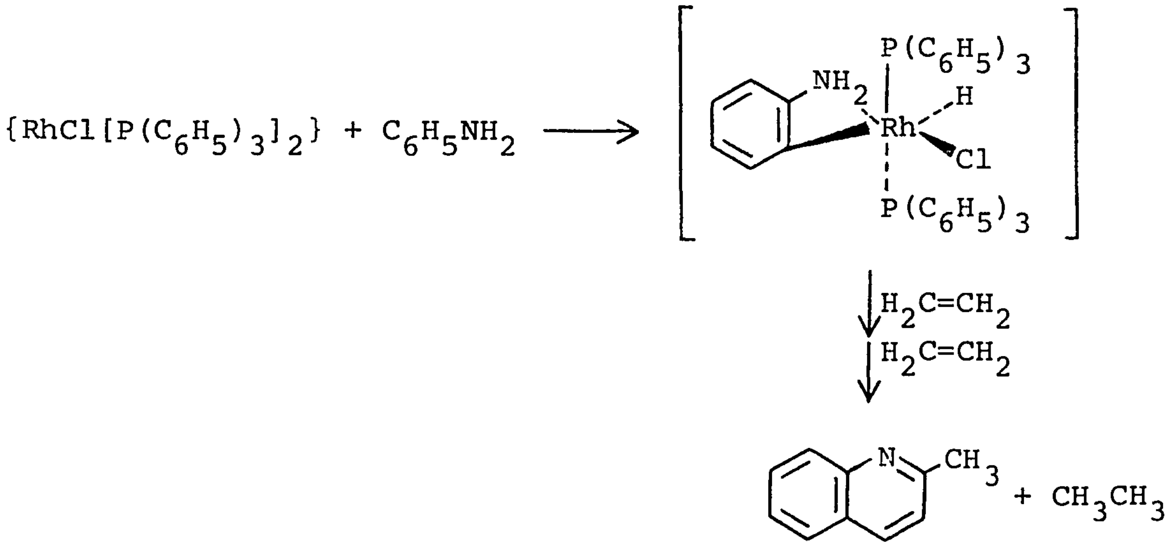
Scheme 7



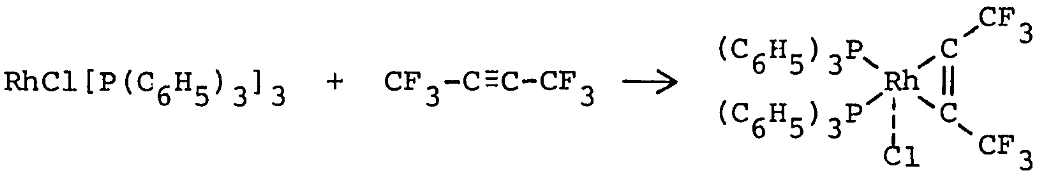
Scheme 8



Scheme 9



Oxidative additions involving Wilkinson's catalyst and double or triple bonded covalent molecules such as: acetylenes (Eq. 11),[49,50] some olefins (Eq. 12),[49] allenes (Eq. 13),[51,52] oxygen (Eq. 14),[9,50,53,54] carbon disulfide (Eq. 15),[55] isocyanates (Eq. 16),[56] and isothiocyanates (Eq. 17),[57-59] as well as strained heterocycles[60] (Scheme 10) are



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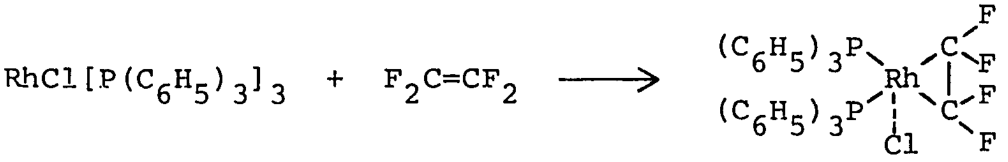
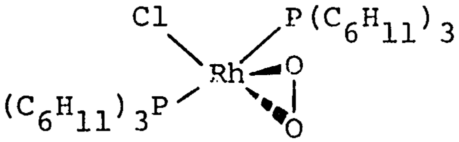


(12)

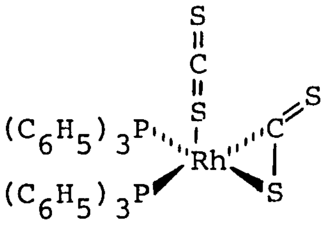
$$RhCl[P(C_6H_5)_3]_3 + \text{excess } H_2C{=}C{=}CH_2 \longrightarrow RhCl(C_3H_4)_5 \qquad (13)$$

$$RhCl[P(C_6H_{11})_3]_2 + O_2 \longrightarrow$$



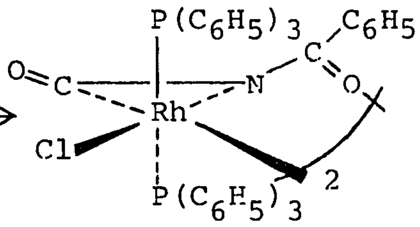
(14)

$$RhCl[P(C_6H_5)_3]_3 + CS_2 \longrightarrow$$



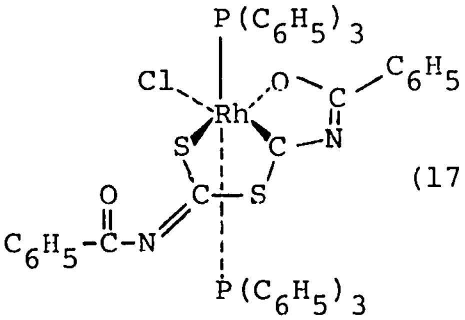
(15)

$$RhCl[P(C_6H_5)_3]_3 + C_6H_5CONCO \longrightarrow$$



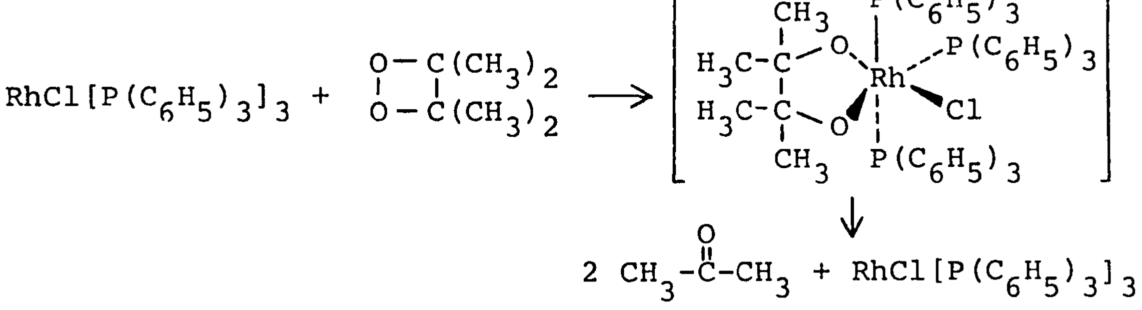
(16)

$$RhCl[P(C_6H_5)_3]_3 + 2\ C_6H_5CONCS \longrightarrow$$

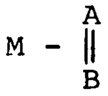


(17)

Scheme 10

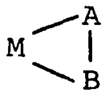


also known. For these oxidative additions there is some dispute whether the adduct is better represented by pi coordination **1** of the unsaturated species or sigma bonded as in a metallocyclopropyl system **2**. One criterion for dis-



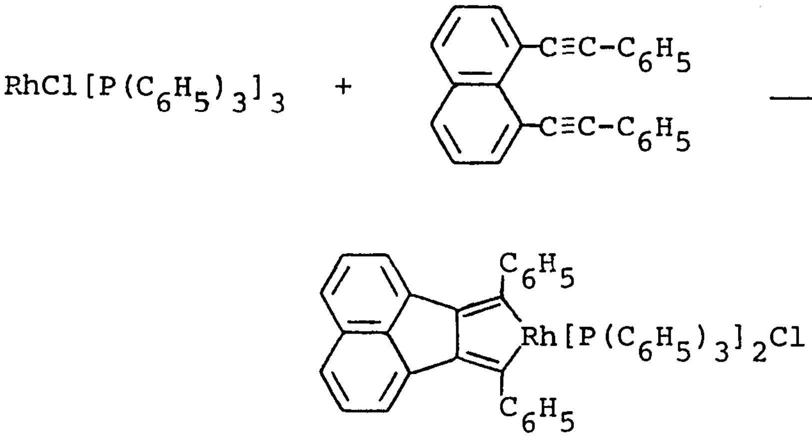
$$M - \overset{A}{\underset{B}{\|}}$$

1



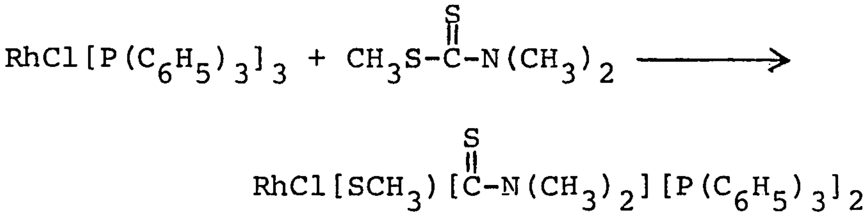
2

tinguishing between these involves spectroscopically observing the other ligands on rhodium.[61,62] An example would be the ligand carbon monoxide.[63] If the C--O stretch in the IR is comparable to that in other rhodium(I) species, pi coordination is preferred and an oxidative addition is considered not to have occurred; whereas, if the C--O stretch in the IR is comparable to other rhodium(III) species, the sigma bonded metallocyclopropyl system is preferred and an oxidative addition is considered to have occurred. The oxidative addition of some diacetylenes is unique since the metallocycle formed contains a ring with a newly formed carbon-carbon bond. 1,4-, 1,5-, 1,6-, and 1,7-Diacetylenes react with Wilkinson's catalyst forming divinylrhodium(III) compounds (Eq. 18).[64-71]



(18)

The oxidative addition of a carbon-sulfur bond has also been reported (Eq. 19).[72] Silicon-hydrogen bonds oxidatively



$$RhCl[P(C_6H_5)_3]_3 + CH_3S\text{-}\overset{S}{\overset{\|}{C}}\text{-}N(CH_3)_2 \longrightarrow RhCl[SCH_3)[\overset{S}{\overset{\|}{C}}\text{-}N(CH_3)_2][P(C_6H_5)_3]_2 \quad (19)$$

add to Wilkinson's catalyst and other rhodium(I) species (Eq. 20).[73] The rhodium(III) hydrosilylation intermediate may react further by inserting into multiple bonded species (Scheme 11).[74-77]

$$RhCl[P(C_6H_5)_3]_3 + Cl_3SiH \xrightarrow[CH_2Cl_2]{} RhClH(SiCl_3)[P(C_6H_5)_3]_2,\ 1/2CH_2Cl_2 \quad (20)$$

Scheme 11

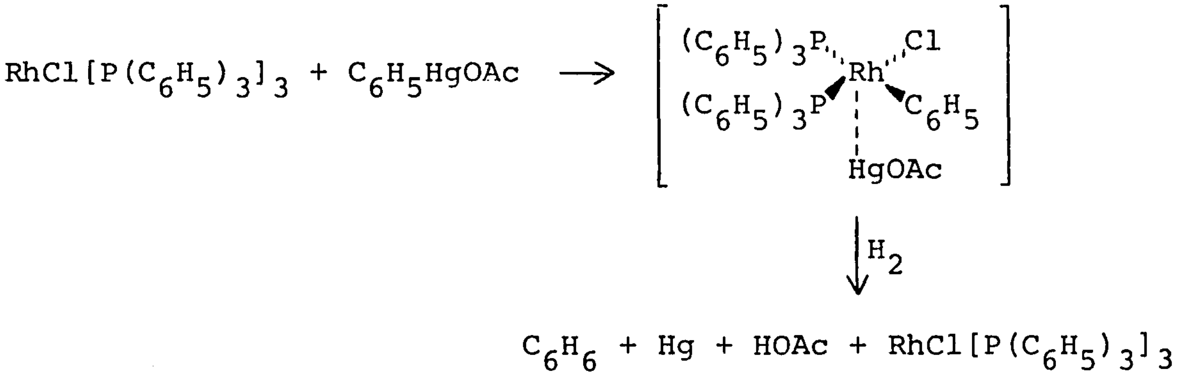
$$\mathrm{RhCl[P(C_6H_5)_3]_3 + (C_6H_5)_3SiH \rightarrow \left[RhClH[Si(C_6H_5)_3][P(C_6H_5)_3]_2\right]}$$

$$\xrightarrow[60^\circ\mathrm{C}]{\mathrm{CH_3CH_2CH_2CH_2CH{=}CH_2}}$$

$$\mathrm{RhCl[P(C_6H_5)_3]_3 + 100\%\ CH_3CH_2CH_2CH_2CH_2CH_2Si(C_6H_5)_3}$$

The oxidative addition of organomercury compounds to rhodium(I) species (Scheme 12) has been assumed several times[78-81] but rhodium-mercury bonded compounds apparently have not been isolated from rhodium(I) compounds and organomercury compounds. However the transmetalation of rhodium(III) compounds is known and accounts for the synthesis of a compound containing a rhodium-mercury bond (Eq. 21)[82] and the

Scheme 12



alkylation of a rhodium(III) compound via an organomercurial (Eq. 22).[26]

$$\mathrm{RhCl_2H[As(CH_3)(C_6H_5)_2]_3 + HgCl_2 \longrightarrow Rh(HgCl)Cl[As(CH_3)(C_6H_5)_2]_3 + HCl} \qquad (21)$$

$$\mathrm{\mathit{mer}\text{-}RhCl_3[P(CH_3)_2(C_6H_5)]_3 + Hg(CH_3)_2 \longrightarrow Rh(CH_3)Cl_2[P(CH_3)_2(C_6H_5)]_3 + CH_3HgCl} \qquad (22)$$

Oxidative additions have been reported with other unsaturated rhodium(I) compounds. Of equal or greater popularity than Wilkinson's catalyst or the $\mathrm{RhClL_3}$ system is the $\mathrm{RhClL'L_2}$ system, where one ligand, L of the alkyl, aryl, or alkyl and aryl phosphine or arsine type is replaced by L' which is also a two electron, pi coordinating ligand similar to carbon monoxide, thiocarbonyl, ethylene or another olefin. Numerous oxidative additions similar to those previously described with Wilkinson's catalyst have been reported using these compounds.[63,83-111]

Another rhodium compound which participates in oxidative addition is the dicarbonyl rhodium chloride dimer, $\mathrm{[Rh(CO)_2Cl]_2}$ or similar $\mathrm{[RhL'_2Cl]_2}$ compounds. Although some additions of the previously mentioned covalent molecules have been reported,[112-120] oxidative additions of strained or other carbon-carbon bonds[121-139] are more numerous with dicarbonyl rhodium chloride or other $[Rh(L')_2Cl]_2$ compounds.

Oxidative additions have also been reported with cyclopentadienylrhodiumbis(triphenylphosphine) or other cyclopentadienyl rhodium ligand compounds, $Rh(Cp)L_2$, $Rh(Cp)LL'$, or $Rh(Cp)(L')_2$, where (Cp) represents the cyclopentadienyl ligand and L and L' are ligands as previously defined. In addition to the oxidative additions already discussed,[140-152] these rhodium compounds may be distinguished by their ability to trimerize acetylenes to arenes. Various rhodium carbocycles and possible intermediates have also been isolated.[153-161]

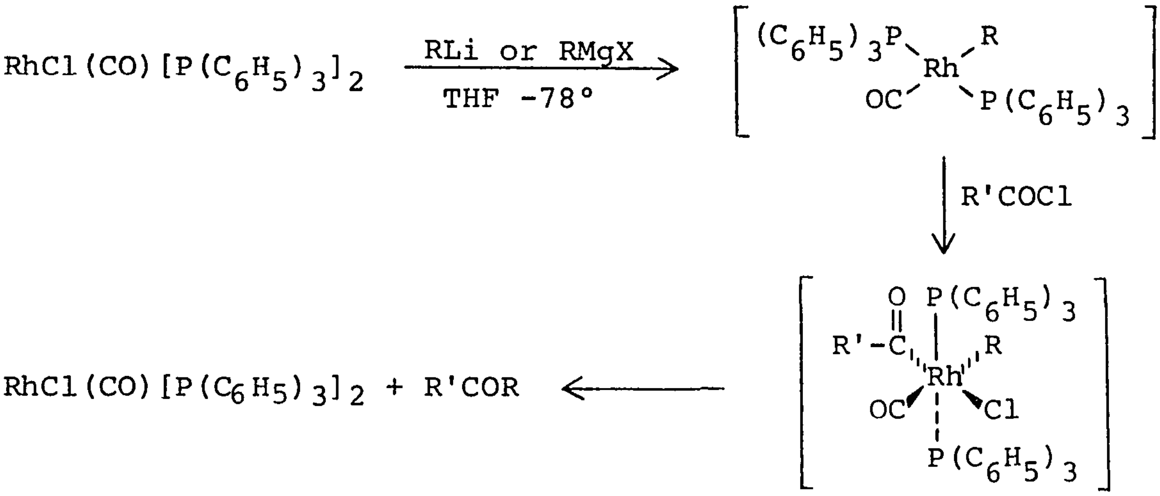
Cationic rhodium compounds are known with cyano, isocyanide, or phosphite ligands. Similar to the previously discussed neutral rhodium(I) compounds, oxidative additions are also known.[162-180] The oxidative addition of alkyl halides is especially noteworthy since these adducts are surprisingly stable and apparently do not undergo beta hydride elimination to the alkene even where possible.

Oxidative additions are also known with rhodium(I) compounds stabilized with nitrogen or sulfur ligand systems. Examples of nitrogen ligand systems include the schiff base ligands, salicylaldimines[181,182] and 2-pyridinalmethylimine,[183] plus polypyrazolylborates,[184,185] 3,3'-(trimethylenediimino)bis(butan-2-one oxime)[186,187] derivatives and polypyrrole macrocycles.[188-189] Malenonitriledithiolate is a bidentate sulfur ligand. With other neutral ligands it forms an anionic rhodium(I) complex which undergoes oxidative addition.[190-192] Oxidative additions are also known with dithiophosphinato complexes of rhodium(I).[193]

Oxidative addition, although presently a catch-all for many different processes, is potentially important for synthetic chemists. Firstly, new metal bonds are formed. Secondly, and subsequently through the influence of reaction conditions and the ancillary ligands of the metal, the reverse reaction, reductive elimination may occur. These processes are most interesting when the molecule eliminated is strikingly different from the molecule which oxidatively added. Rhodium(III) species containing two or more carbon moieties have been demonstrated to undergo reductive elimination. A new carbon-carbon bond is formed and a rhodium(I) species regenerated. Ketones, alkenes, arenes, dienes and biaryls may be produced in these reactions.

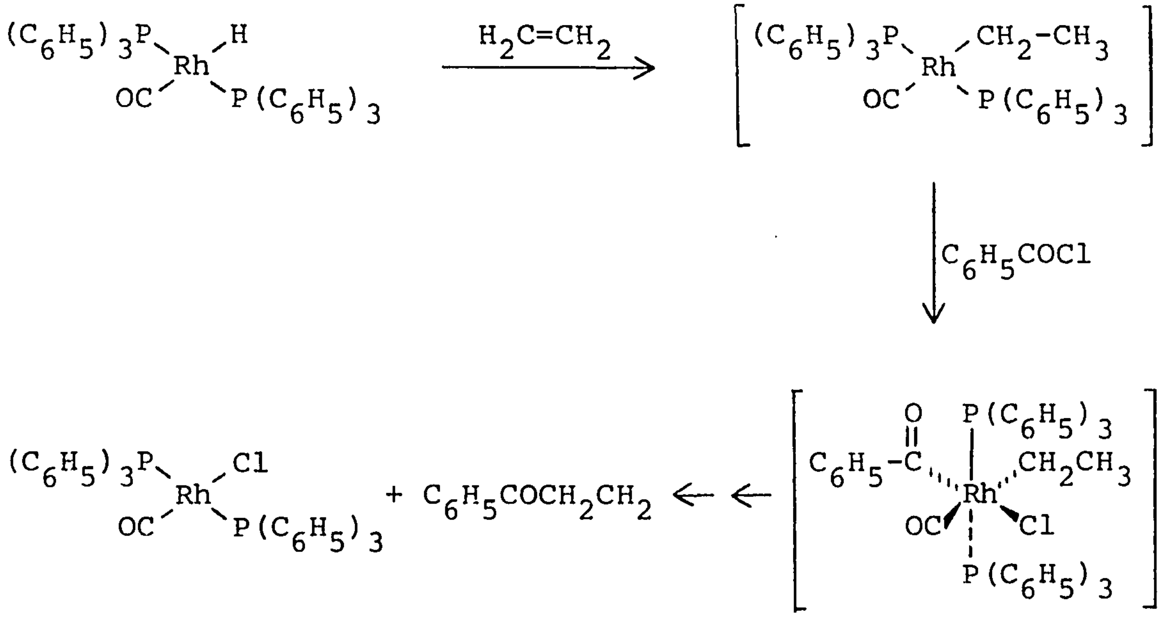
Potentially general ketone syntheses have been investigated. The intermediates in the reaction of an acid chloride and an organorhodium compound form ketones (Scheme 13).[99,105] The organorhodium compound is produced by transmetalation of $RhCl(CO)[P(C_6H_5)_3]_2$ with an organo-lithium or Grignard reagent. The intermediate in the alkene insertion reaction

Scheme 13



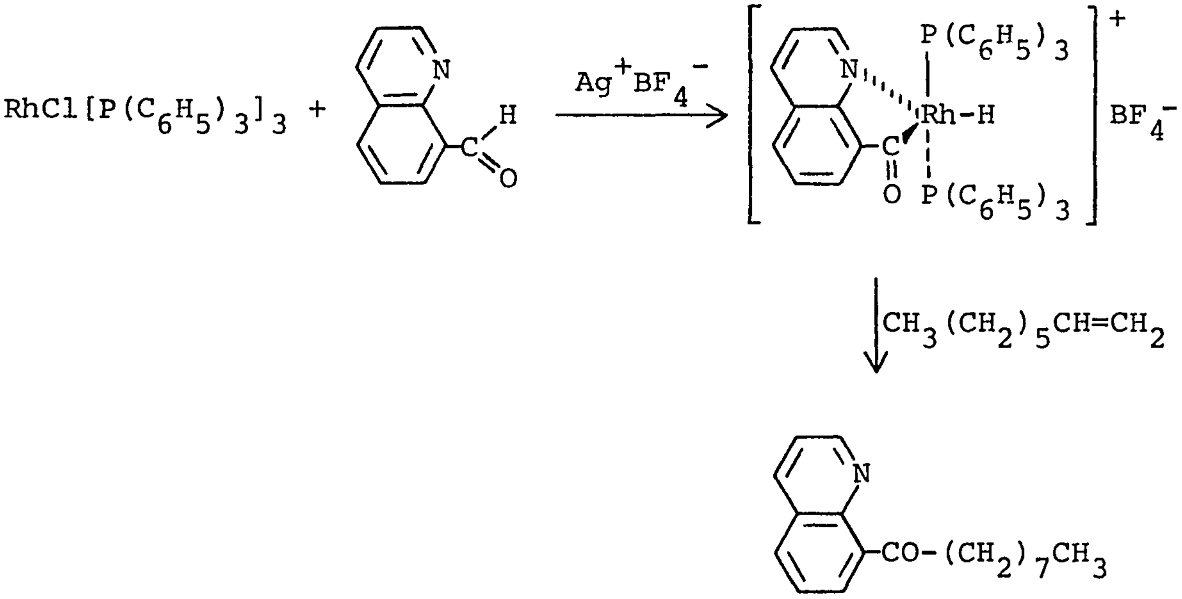
of a rhodium hydride reacts with acid chlorides to also form ketones (Scheme 14).[194] Unfortunately, the yields generally are not high. The insertion of olefins into the rhodium-

Scheme 14

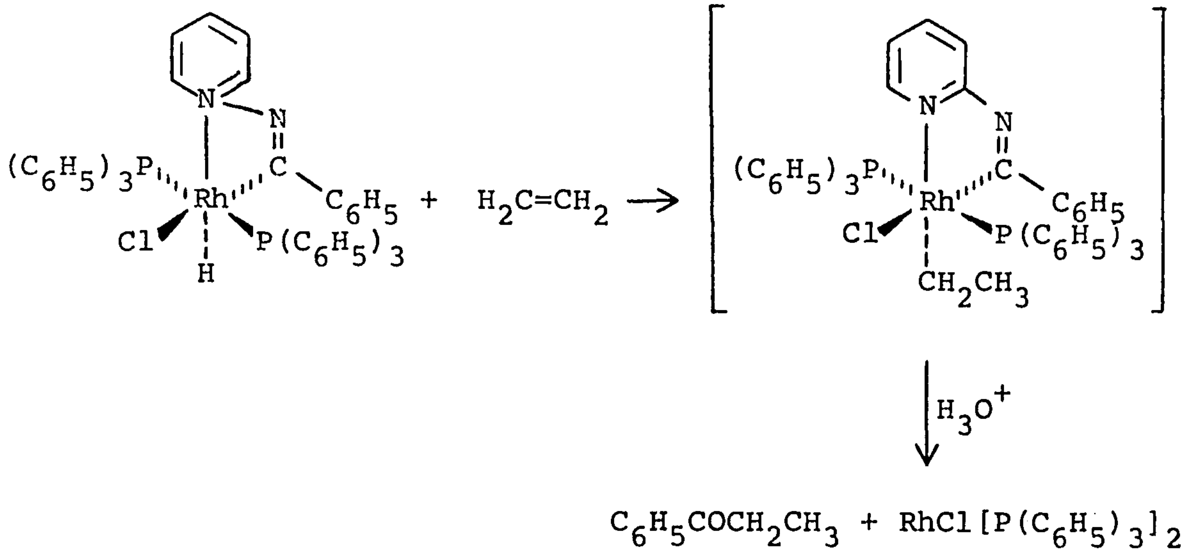


hydrogen bond of the chelated rhodium compounds synthesized by Suggs also produces ketones (Schemes 15 and 16).[36,37]

Scheme 15



Scheme 16

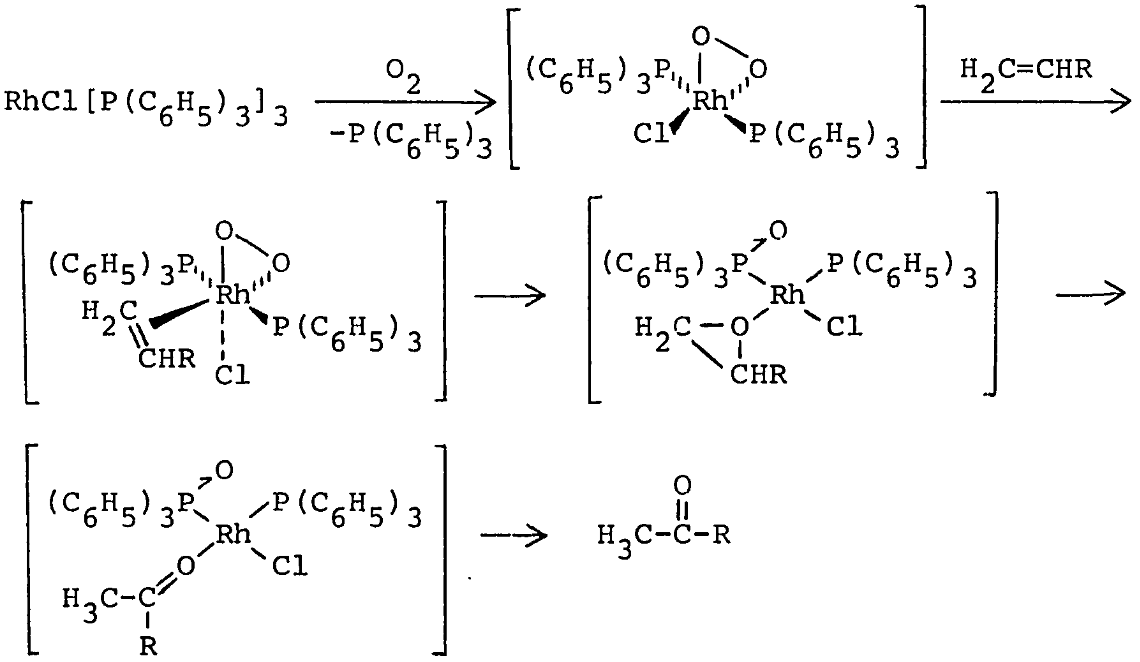


Aryl mercurials transmetalate with rhodium compounds in an atmosphere of carbon monoxide. Diaryl ketones are formed, but the yields are moderate to low (Eq. 23).[78] Transmetalation to rhodium apparently also occurs with organo-copper or -gold cluster compounds. Symmetrical ketones are produced (Eq. 24).[195] Moderately low yields of ketones have been reported in an oxygen mediated reaction of alkenes in the presence of a rhodium catalyst (Scheme 17).[54,196] Less

$$C_6H_5HgCl + CO \xrightarrow[CH_3CN]{\text{cat } RhCl_3\cdot 3H_2O} C_6H_5COC_6H_5 \qquad (23)$$

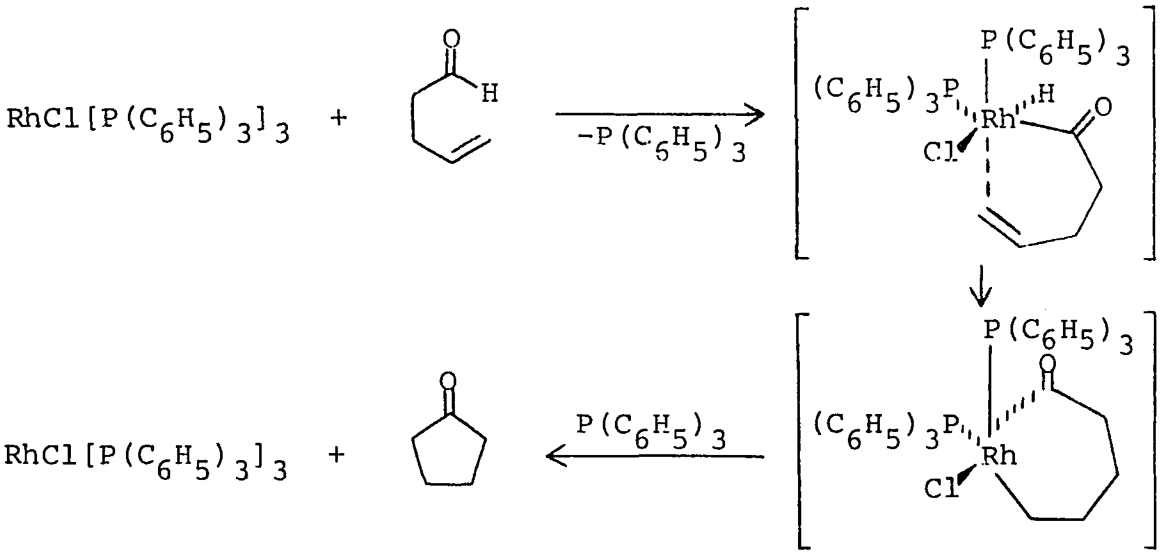
$$(\underline{p}\text{-}CH_3\text{-}C_6H_4)_4Cu_2Li_2\cdot 2TMED + [Rh(CO)_2Cl]_2 \xrightarrow{CO} (\underline{p}\text{-}CH_3C_6H_4)_2CO \qquad (24)$$

Scheme 17

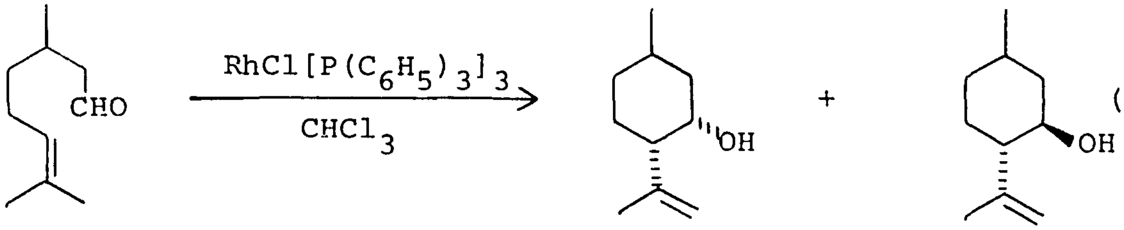


general ketone syntheses sometimes require a unique steric environment. For example, cyclopentanone is a reductive elimination product from an intermediate in the reaction of 4-pentenal and Wilkinson's catalyst (Scheme 18).[197-199]

Scheme 18



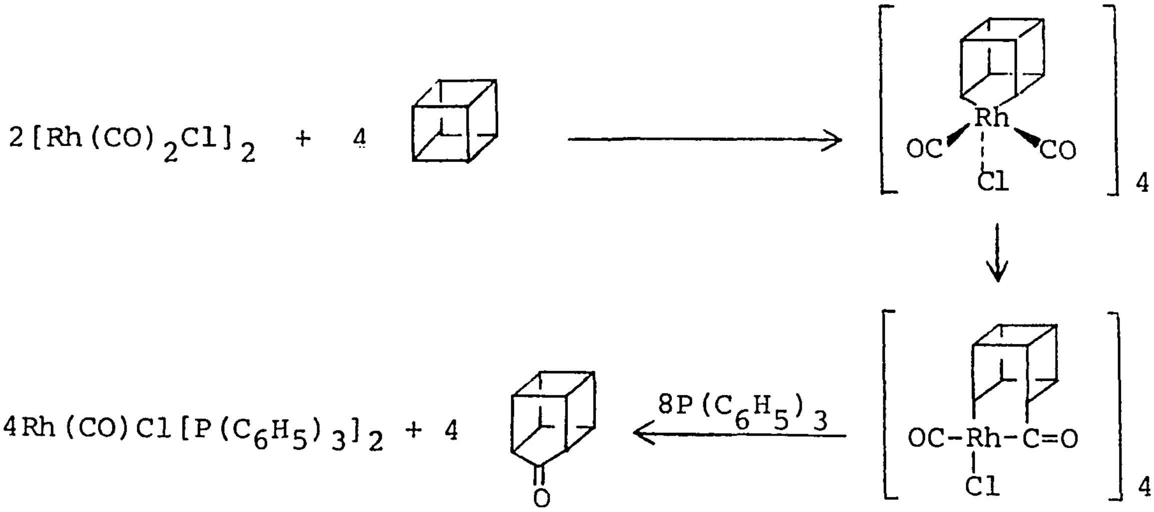
Citronellal, a 1-al-6-ene system has also been cyclized with Wilkinson's catalyst (Eq. 25). However the reaction is not general since the 1-al-5-ene system does not cyclize to cyclohexanone.[200] Triphenylphosphine addition induces the



(25)

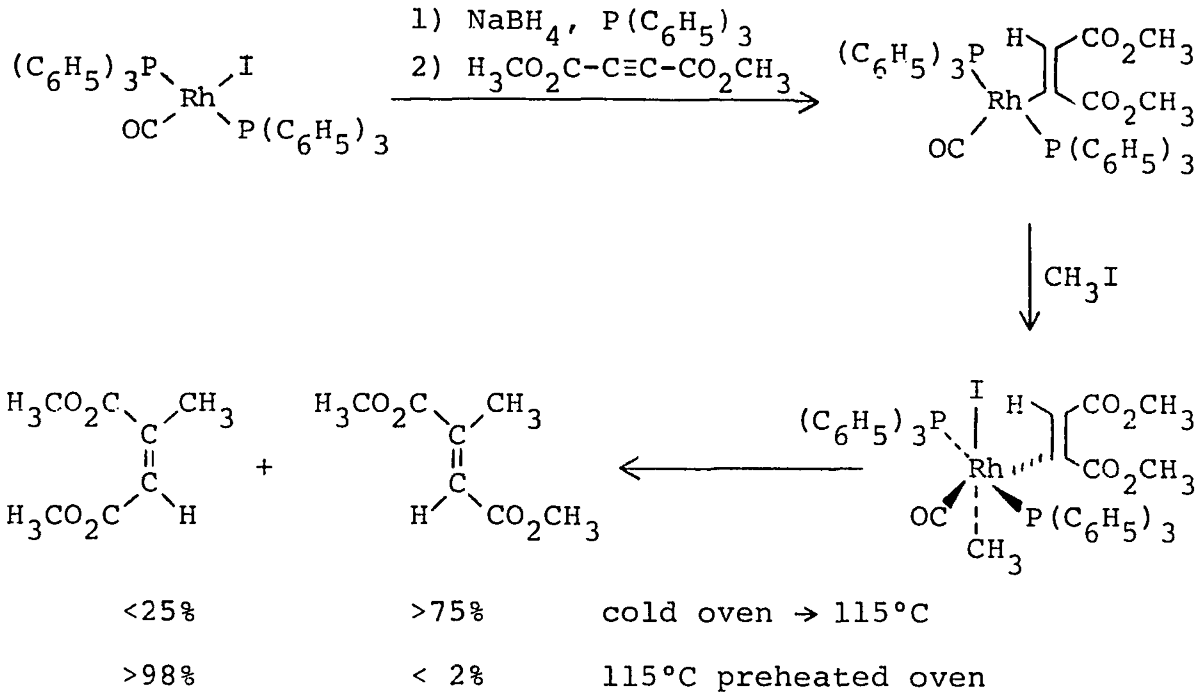
reductive elimination of a cyclic ketone from the intermediate in the reaction of $[Rh(CO)_2Cl]_2$ and cubane (Scheme 19).[129]

Scheme 19

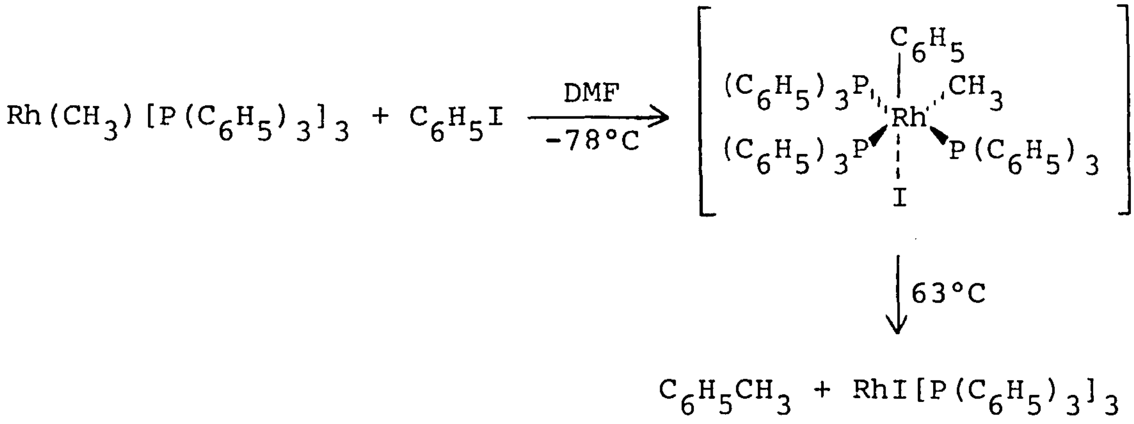


Reductive couplings also result in olefin syntheses. Methylated olefins are produced in the pyrolysis of a rhodium(III) compound substituted with both a vinyl and methyl group (Scheme 20). The stereochemistry of the resulting olefin was dependent upon the pyrolysis conditions.[201] Likewise, the reductive coupling of a rhodium(III) compound substituted with an aryl and a methyl group forms the methyl substituted arene (Scheme 21).[16] An insertion of an olefin into the carbon-metal bond of an organotransition metal compound (Heck Reaction) has also been reported with rhodium

Scheme 20



Scheme 21



(Eq. 26).[202] A methylrhodium compound generated <u>in situ</u> from rhodium trichloride, a reducing agent and methyl iodide has

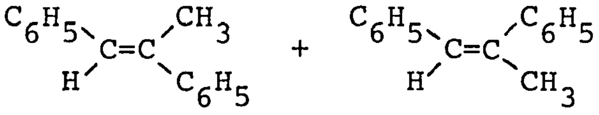
$$C_6H_5HgCl + RhCl_3 \cdot 3H_2O + H_2C{=}CHCO_2CH_3 \rightarrow C_6H_5CH{=}CHCO_2CH_3 \qquad (26)$$

also been reported to insert olefins. Following rhodium-hydride elimination, the end organic product is the methylated olefin (Eq. 27).[203] Methyl stilbenes are the predomi-

$$CH_3I + RhCl_3\cdot 3H_2O + C_6H_5CH{=}CH_2 \xrightarrow[\substack{\text{or } SnCl_2/DMF\\ 100°C}]{\substack{CH_3OH/CH_3OH\cdot CH_3CN\\ 160°C}} \sim 60\%\ C_6H_5CH{=}CHCH_3 \qquad (27)$$

nant product in the reaction of diphenylacetylene and a methylrhodium compound (Eq. 28). The stereochemistry is

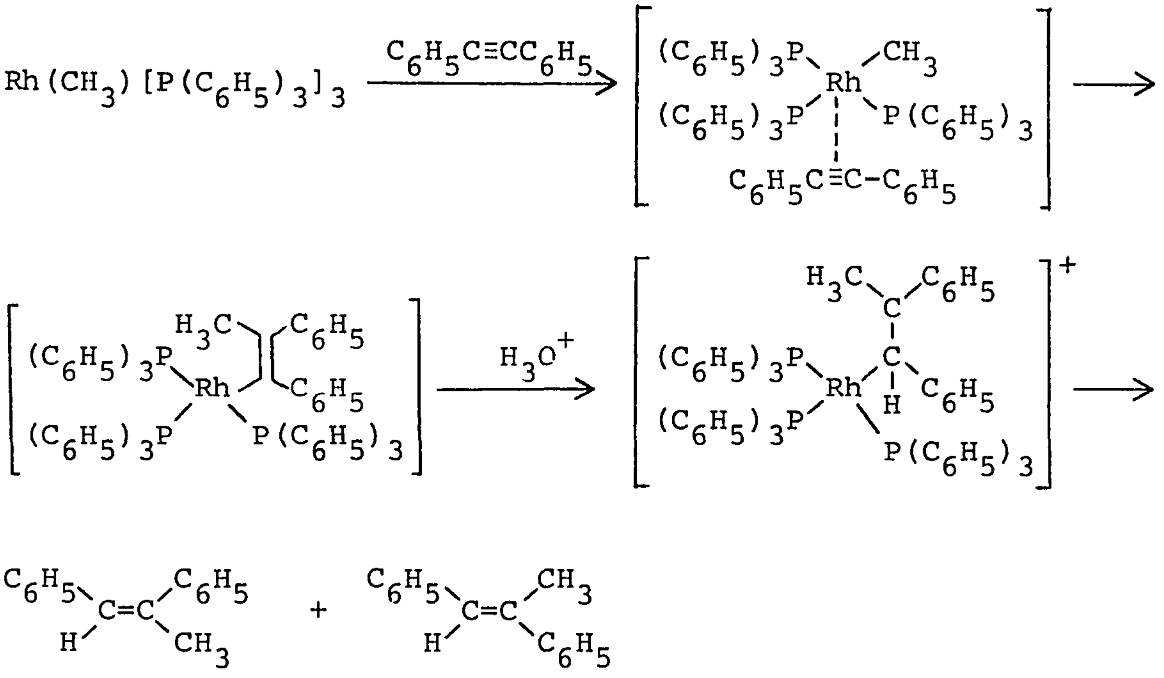
$$C_6H_5C{\equiv}CC_6H_5 \xrightarrow[\substack{Rh(CH_3)[P(C_6H_5)_3]_3\\ RhBr[P(C_6H_5)_3]_3 + CH_3MgBr\\ RhBr_3\cdot 3H_2O + CH_3MgBr}]{} \qquad (28)$$



14.6%	62%
18 %	74%
58.6%	--

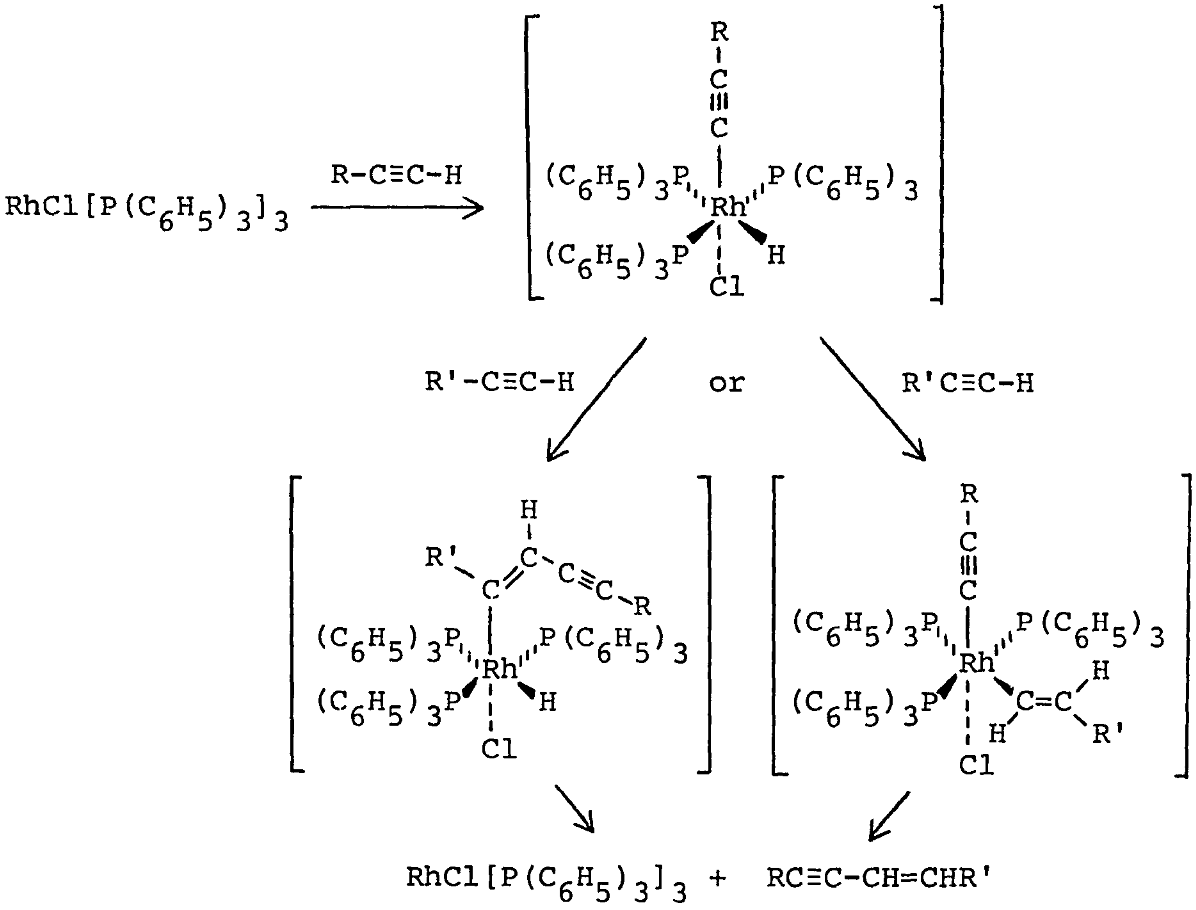
apparently dependent upon the origin of the methylrhodium compound.[204] The pathway proposed by the authors involves an acetylene insertion into the rhodium-carbon bond followed by hydrolysis (Scheme 22). Enynes may be formed from phenyl acetylenes[205] or 3-hydroxy acetylenes[206] in the presence of

Scheme 22



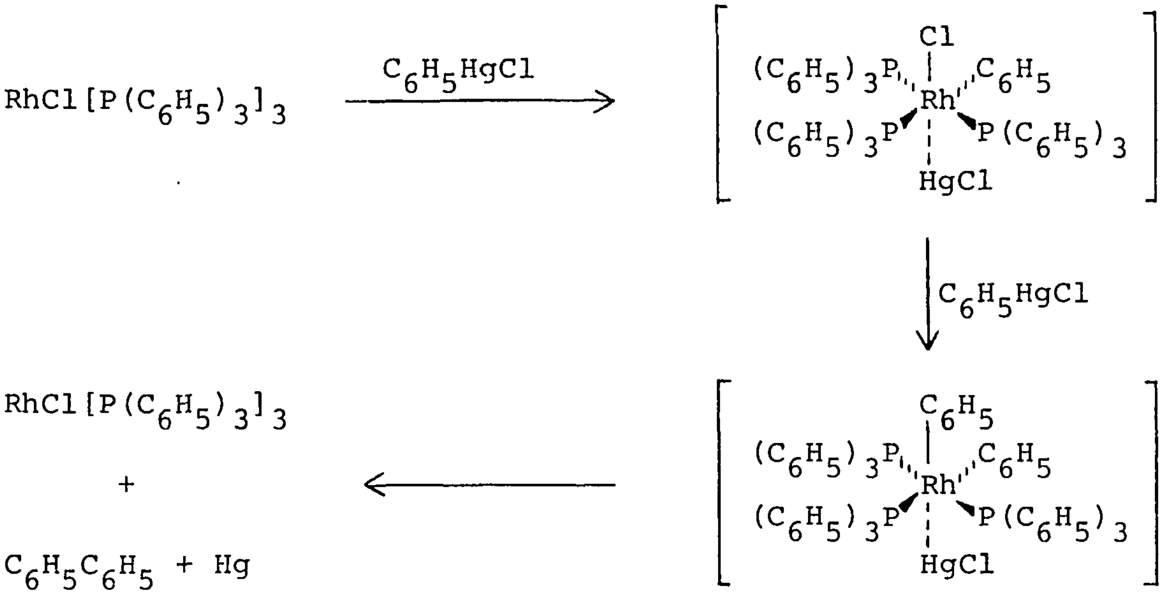
a rhodium catalyst (Scheme 23). One molecule of the acetylene oxidatively adds across the carbon-hydrogen bond of the acetylene. Another acetylene molecule then inserts into the newly formed carbon-rhodium or hydrogen-rhodium bond. A reductive elimination then yields the enyne. With 3-hydroxy acetylenes, presumably the hydroxyl group through hydrogen bonding coordinates and induces the acetylene insertion.

Scheme 23

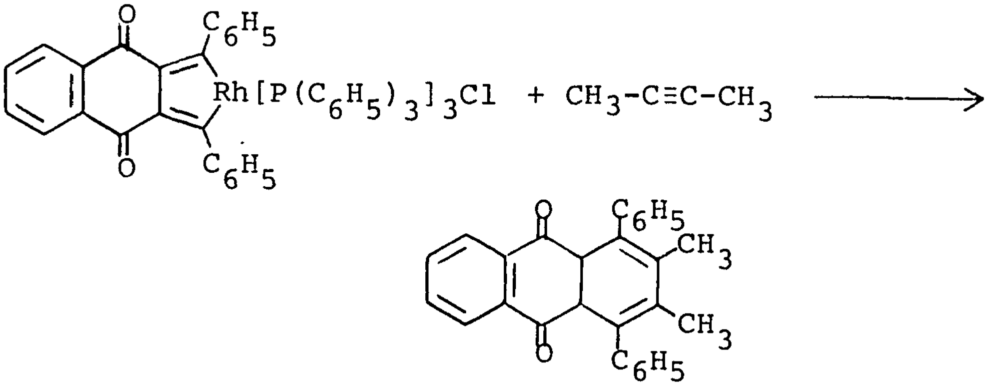


Vinyl-[80] and arylmercurials[80,81] couple forming symmetrical dienes and biaryls in the presence of rhodium(I) catalysts. One of several schemes which may account for the formation of dienes and biaryls consists of, oxidative addition of a vinylmercurial to rhodium(I) species, transmetalation of the resultant rhodium(III) species with a second vinylmercurial, followed by reductive elimination (Scheme 24). Muller's divinylrhodium(III) compounds formed from diacetylenes undergo carbon-carbon bond forming reductive elimina-

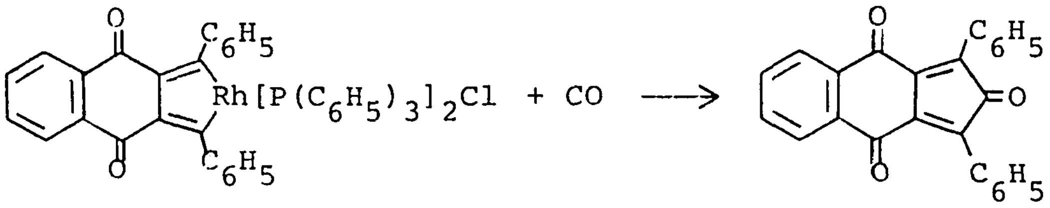
Scheme 24



tions[64,66-68,207-212] upon reaction with acetylenes (Eq. 29), carbon monoxide (Eq. 30), or isonitriles. Rhodium compounds



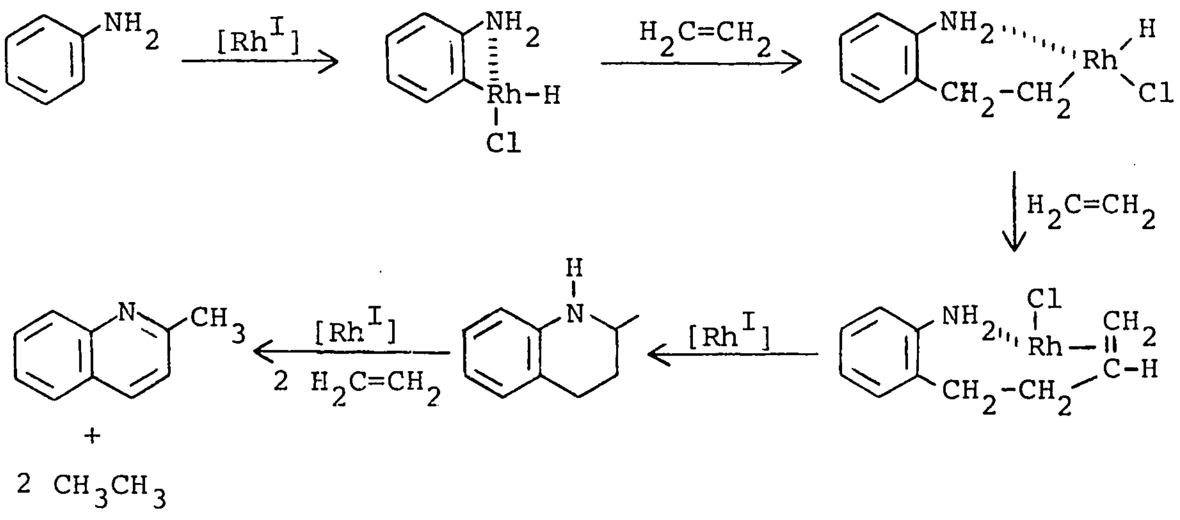
(29)



(30)

also facilitate heterocycle formation.[47] The insertion of ethylene into a rhodium-hydrogen bond is proposed to account for the formation of 2-methylquinoline from aniline and ethylene (Scheme 25).

Scheme 25



Although novel carbon-carbon bond formations mediated by rhodium have been reviewed, and this thesis concentrates on utilizing organorhodium compounds and catalysts as synthetic organic intermediates, rhodium compounds have also been employed in other classic organometallic reactions such as carbonylations, hydroformylation, polymerization, and hydrogenations. Generally, palladium, cobalt, or other metals and catalysts have been preferred. An exception to this might be the synthesis of acetic acid from methanol (Eq. 31).[119] In

$$CH_3OH \xrightarrow[NaI]{Rh(I) \atop CO} CH_3COOH \qquad (31)$$

the following chapter, organorhodium compounds have been utilized to effect the alkylation of organomercury compounds, a conversion which so far is not easily accomplished.

II. METHYLATION OF VINYLMERCURIALS: SYNTHESIS OF METHYL-SUBSTITUTED OLEFINS

A. Introduction

Previously, Larock and Heck have demonstrated that organomercury compounds are viable synthetic reagents in organic chemistry. Acids, esters,[213] symmetrical 1,3-dienes and biaryls,[80] lactones,[214,215] and 1,4-dienes,[216] as well as aryl, methyl, and carboxyl substituted olefins,[217] 3-aryl aldehydes and ketones,[218] allyl arenes,[219] 2-aryl aldehydes and ketones,[220] chlorophenethyl compounds,[221] and diaryl ketones[78] can be synthesized from organomercury compounds through an appropriate transition metal salt or complex. Of the numerous transformations synthetic organic chemists are interested in, one obvious transformation, an alkylation, is missing from the previous list. If the mercury moiety in a vinylmercurial is replaced by an alkyl group, an alkyl-substituted olefin is formed and a specific alkylation performed.

1. General syntheses of alkyl-substituted olefins

The variously substituted olefins in natural products like terpenes, pheromones and steroids challenge and stimulate synthetic organic chemists. Although stereoselectivity in olefin syntheses has been reviewed,[222,223] it remains a popular current research interest. Desirable features for general syntheses of olefins are generation of the double bond regio- and stereospecifically. Classic eliminations often lack these requirements. The Wittig synthesis of olefins from carbonyls yields olefins stereospecifically only with special modifications. However, numerous organometallic compounds generate olefins both regio- and stereospecifically.

A vinyl halide and a primary alkyl halide may be coupled through a vinyl lithium species.[224] Iron[225,226] and nickel[227] assist in the coupling of alkyl Grignards and vinyl halides. Alkyl cuprates[228-230] or alkyl copper species[231,232] and vinyl halides couple to form olefins, as do vinyl cuprates and alkyl or aryl halides.[233-235] Stereospecificity in these syntheses hinges on the vinyl halide or the lithium or Grignard reagent derived from it. A further limitation is the lack of functionality which the required lithium or Grignard reagent tolerates.

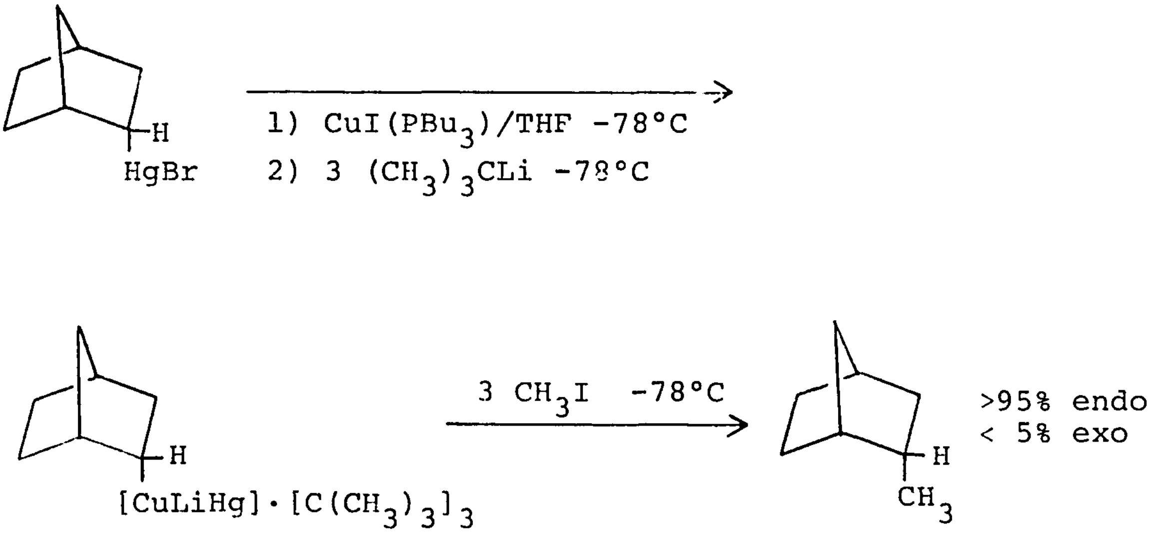
Another approach involves the hydrometalation of an alkyne and subsequent coupling of the vinyl organometallic species to an alkyl moiety. The alkylation conditions are determined by the specific organometallic reagent. Hydroboration of an alkyne with dialkylboranes followed by iodination[236,237] or cyanogen bromide[238] treatment yields the Z or E olefins respectively, substituted with the alkyl group of the borane. Alternatively, the E olefin can be obtained from hydroboration of iodo-acetylenes with a dialkyl borane, conversion to the boronate (with sodium methoxide) and protonolysis.[239] Similarly, the reaction of vinyl lithium reagents with trialkylboranes followed by iodination yields alkyl substituted olefins.[240] Acetylene plus (i-Bu)$_2$AlH or ZrHCl(Cp)$_2$ yields vinylalanes or vinylzirconium derivatives respectively. Aryl, alkenyl- or alkynyl halides couple with these in the presence of ZnCl$_2$ and catalytic amounts of either Pd[P(C$_6$H$_5$)$_3$]$_4$ or Ni[P(C$_6$H$_5$)$_3$]$_4$.[241,242] The vinylalane may also couple with allyl halides in the presence of cuprous chloride.[243] Hydroalumination of an alkyne followed by addition of an alkyl lithium forms a vinyl aluminate intermediate. Coupling then occurs with primary sulfonates and iodides, and allylic, benzylic, and propargylic halides.[244,245]

A carbometalation route is similar to the hydrometalation approach producing a tri- or tetrasubstituted olefin. Alkyl copper species have been demonstrated to carbometalate alkynes. The resulting substituted vinyl copper species may react with alkyl, aryl, and alkynyl halides forming a more highly substituted olefin.[246-249] Carbometalation may also be effected with an organoalane-zirconocene dichloride complex which further reacts with alkenyl, aryl, or alkynyl halides.[250,251] A nickel species catalyzes the carbometalation of silylacetylenes with Grignard reagents.[252] Subsequent addition of vinyl bromide or methyl iodide forms the tetrasubstituted olefins although not regiospecifically. Vinylmercurials are especially attractive organometallic intermediates due to their accessibility from acetylenes via hydroboration and transmetalation, stability, and ease of handling.[253,254] Consequently, a convenient general method for the alkylation of vinylmercurials constitutes an attractive olefin synthesis.

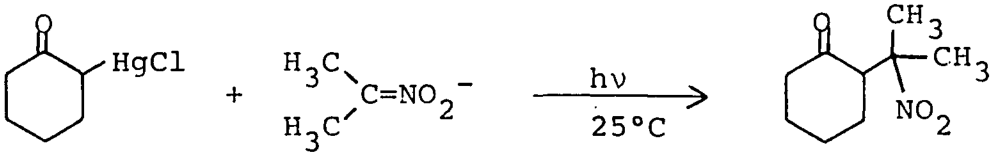
2. Alkylations of organomercurials

Only a couple alkylations of organomercurials have been reported and these unfortunately lack generality. Treatment of an alkylmercurial first with cuprous iodide tributylphosphine followed by tert-butyl lithium forms a scantily characterized copper(I)ate complex of the mercurial which reacts with primary iodides (Scheme 26).[255] Recently, an electron-

Scheme 26

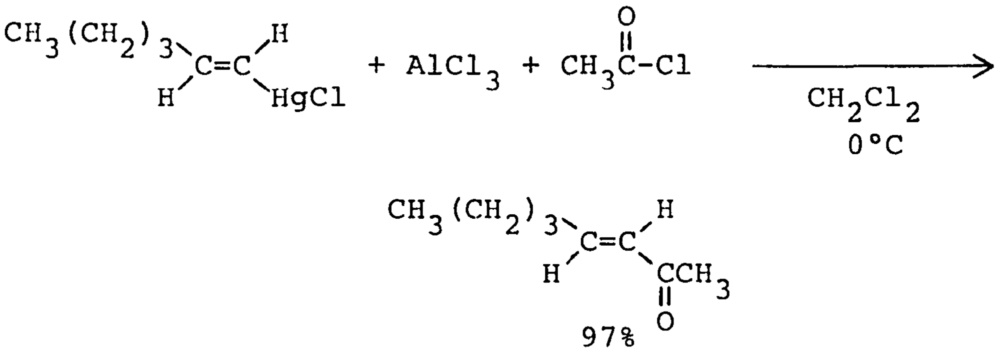


transfer mechanism has been indicated for the coupling of alkylmercurials and nitronates (Eq. 32).[256]



(32)

Although alkylations of organomercurials are quite limited, several electrophilic acylations of organomercurials are known. Some highly activated arylmercuric chlorides react with acid halides to form the corresponding aryl ketones.[257-261] Di-n-alkyl- and diarylmercurials require aluminum halides to promote reaction with acid halides[262,263] or alternatively, $Pd[P(C_6H_5)_3]_4$ catalyzes the reaction of diethyl- or diphenylmercury with acid chlorides.[264] The acylation of vinylmercury chlorides has been thoroughly investigated by Larock and Bernhardt.[265,266] Aluminum chloride with methylene chloride as solvent produces nearly exclusively trans-enones (Eq. 33). Other reagents which



(33)

promote this reaction include aluminum powder, aluminum bromide and titanium tetrachloride. $[Rh(CO)_2Cl]_2$ in methylene chloride and $Pd[P(C_6H_5)_3]_4$ in hexamethylphosphoramide (HMPA) catalyze the production of trans-enones in only moderate yields.

B. Results and Discussion

1. Electrophilic approaches

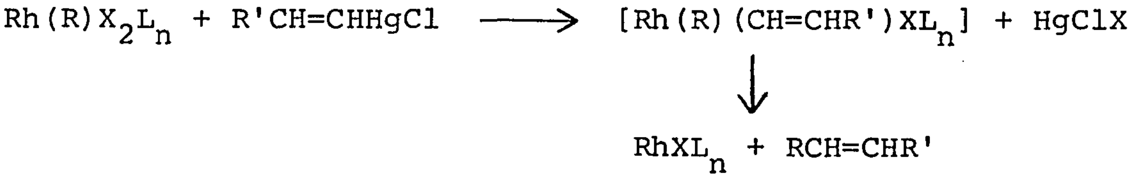
The successful acylation of vinylmercury chlorides with Lewis acids suggested the investigation of alkylations under similar electrophilic conditions. Styrylmercuric chloride was treated with trimethyloxonium tetrafluoroborate in methylene chloride at 0°C. Gas chromatographic analysis indicated that trans-propenyl benzene was not formed. Since the styrylmercurial possesses unusually low solubility, a similar reaction was tried with trans-1-hexenylmercuric chloride. As before, no coupling product, trans-2-heptene was formed. The reaction of trans-1-hexenylmercuric chloride with methyl fluorosulfonate, or aluminum chloride plus methyl iodide in methylene chloride at 0°C was also investigated. Neither of these reactions produced trans-2-heptene, although the latter system yielded chloroiodomethane and diiodomethane.

2. Methylrhodium(III) approach

Since the initial electrophilic approaches were unsuccessful, a transition metal coupling scheme was investigated.

Recalling that a diorganorhodium(III) compound substituted with a vinyl and methyl group forms the methyl olefin upon pyrolysis[201] (Chapter I, Scheme 20), and that vinylmercurials transmetalate with transition metal compounds, the following transformation was envisioned (Scheme 27). This transformation requires a rhodium(III) compound substituted with an alkyl group for coupling and at least one halide for the transmetalation of the vinylmercurial. One possible compound is $Rh(CH_3)I_2[P(C_6H_5)_3]_2$, obtained by treating Wilkinson's catalyst with excess methyl iodide (Eq. 34).[13] In the literature this compound was originally formulated as $Rh(CH_3)ClI[P(C_6H_5)_3]_2(CH_3I)$. Later a crystal structure indicated that the compound is more correctly described as $Rh(CH_3)I_2[P(C_6H_5)_3]_2$.[14] The nmr peak initially assigned to the coordinated methyl iodide was later admitted to be an impurity and its chemical shift actually agrees better with

Scheme 27

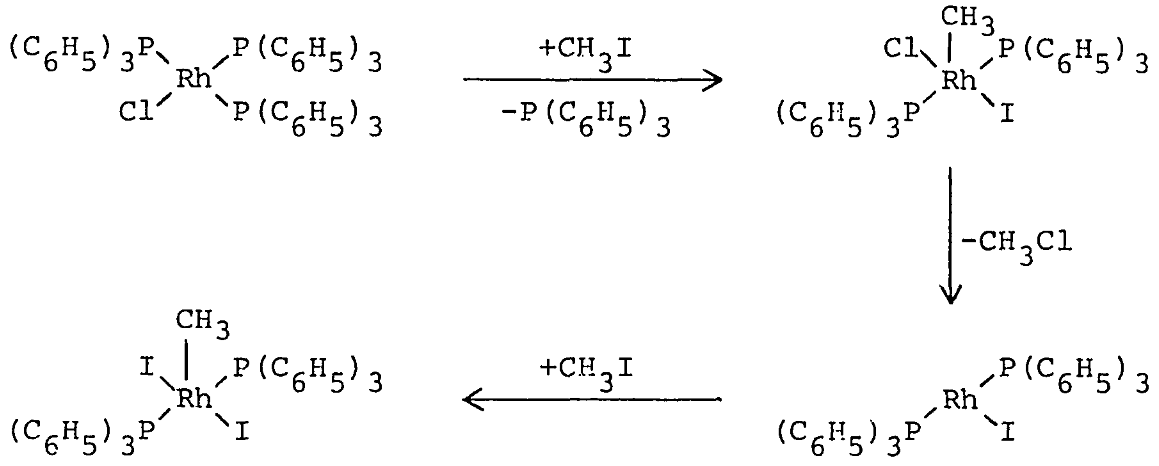


$$\begin{tikzcd}[column sep=small] Rh(R)X_2L_n + R'CH{=}CHHgCl \arrow[r] & {[Rh(R)(CH{=}CHR')XL_n]} + HgClX \arrow[d] \\ & RhXL_n + RCH{=}CHR' \end{tikzcd}$$

$$RhCl[P(C_6H_5)_3]_2 + CH_3I \longrightarrow Rh(CH_3)I_2[P(C_6H_5)_3]_2 \qquad (34)$$

methyl chloride. Successive oxidative additions of methyl iodide and eliminations of methyl chloride may account for the formation of the compound (Scheme 28).

Scheme 28



a. Initial studies The first reactions attempted involved the *in situ* preparation of the methylrhodium(III) compound. Wilkinson's catalyst was treated first with methyl iodide followed after 25 minutes by the addition of *trans*-styrylmercuric chloride with either dichloromethane or hexamethylphosphoramide (HMPA) as the solvent. Gas chromatographic analysis indicated a small amount of propenylbenzene was formed upon heating the HMPA solution (Eq. 35), while none was formed in methylene chloride (Eq. 36). Since the methylrhodium(III) intermediate in these *in situ* preparations never developed its characteristic green color, $Rh(CH_3)I_2$

$$\mathrm{RhCl[P(C_6H_5)_3]_3 \xrightarrow{CH_3I} [Rh(CH_3)I_2[P(C_6H_5)_3]_2 \xrightarrow[HMPA]{C_6H_5CH{=}CHHgCl}} \tag{35}$$

$$\text{small amount } \mathrm{C_6H_5CH{=}CHCH_3}$$

$$\mathrm{RhCl[P(C_6H_5)_3]_3 \xrightarrow{CH_3I} [Rh(CH_3)I_2[P(C_6H_5)_3]_2 \xrightarrow[CH_2Cl_2]{C_6H_5CH{=}CHHgCl}} \tag{36}$$

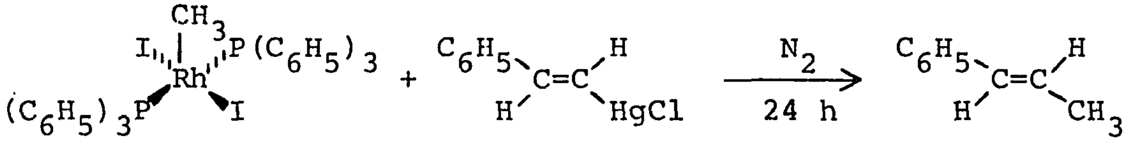
$$\text{no } \mathrm{C_6H_5CH{=}CHCH_3}$$

$[P(C_6H_5)_3]_2$ isolated and purified according to the literature was utilized in subsequent investigations.

The reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and styrylmercuric chloride was attempted under several different reaction conditions (Table I). HMPA as solvent is superior to dichloromethane or tetrahydrofuran (THF). The addition of excess lithium chloride and heating at 70°C also increases the yield noticeably. In the absence of the methylrhodium(III) compound, methyl iodide does not methylate vinylmercurials in HMPA, but the formation of styrene and some 1,4-diphenylbutadiene was observed by GLPC.

b. Syntheses of methyl-substituted olefins After briefly examining different reaction conditions with styrylmercuric chloride, $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ was reacted with other organomercurials under optimal conditions: excess lithium chloride, HMPA, under nitrogen, at 70°C for 24 hours

Table I. Effect of varying reactions conditions on the reaction of styrylmercuric chloride and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$



Added reagents	Solvent	Temperature °C	GLPC Yield, %[a,b]
-	HMPA	25	18
10 LiCl			48
		70	95
	THF	-78 → 25	8
		65	11,16[c]
32 CH_3I	HMPA	70	3[d]

[a] Yield determined using an internal standard.

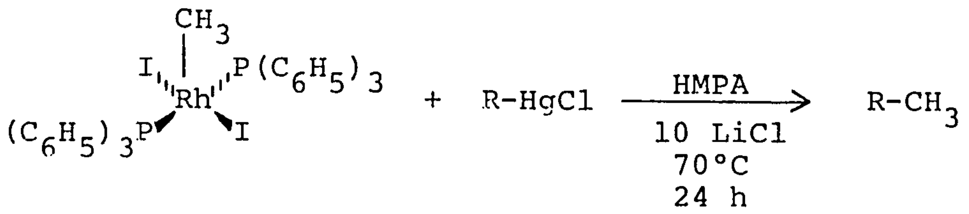
[b] Assumed to be the E-isomer.

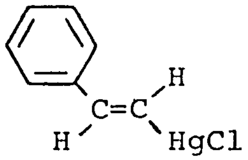
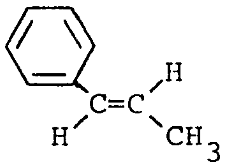
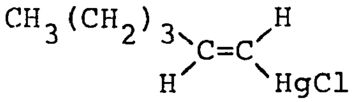
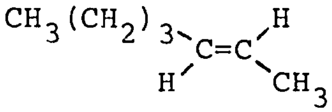
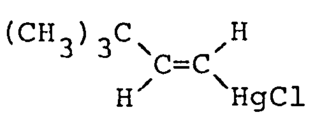
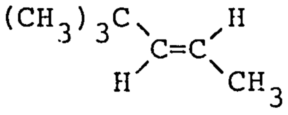
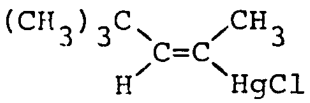
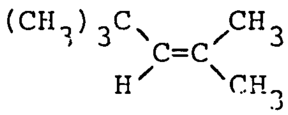
[c] Yield after 1 hour.

[d] No $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ was added.

(Table II). Other terminal vinylmercurials react similarly to styrylmercuric chloride. The stereochemistry of the methyl-substituted olefins produced is not established to be trans, at this time it is merely assumed to be trans. *trans*-1-Hexenylmercuric chloride and *trans*-3,3-dimethyl-1-butenylmercuric chloride react analogously producing 2-heptene and *trans*-4,4-dimethyl-2-pentene respectively. Coupling also occurs with dialkynylmercurials. Bis(3,3-dimethyl-1-butynyl)mercury reacts with the methylrhodium(III) compound producing 4,4-dimethyl-2-pentyne quantitatively. For this dialkynylmercurial the yield is based upon transfer of both organic groups bonded to mercury. Under the same conditions internal vinylmercurials couple with this methylrhodium(III) compound less successfully. *E*-4,4-Dimethyl-2-pentenylmercuric chloride forms the trisubstituted olefin 2,4,4-trimethyl-2-pentene in low yield. Likewise, coupling with *trans*-3-methyl-1,3-butadienylmercuric chloride was also difficult. Although the yields of *trans*-2-methyl-1,3-pentadiene varied from 6 to 53 percent, most yields were low. The coupling of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and an alkylmercurial is completely unsuccessful. The reaction of this methylrhodium(III) and *n*-decylmercuric chloride produced no undecane. GLPC peaks corresponding to 1-decene, *n*-decane, and another unidentified peak of very similar retention time (most probably another isomeric decene or decenes) was observed. Presumably this

Table II. Syntheses of methyl-substituted olefins and acetylenes from the reaction of vinyl- and alkynylmercurials and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$



Mercurial	Product	GLPC Yield,%
		97[a]
		94[a]
		92[a]
		17[b]

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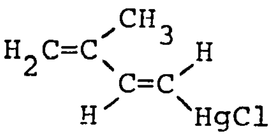
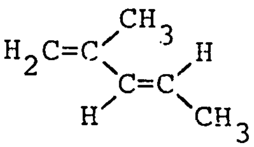
[a] Ether added prior to analysis.

[b] Pentane and water added prior to analysis.

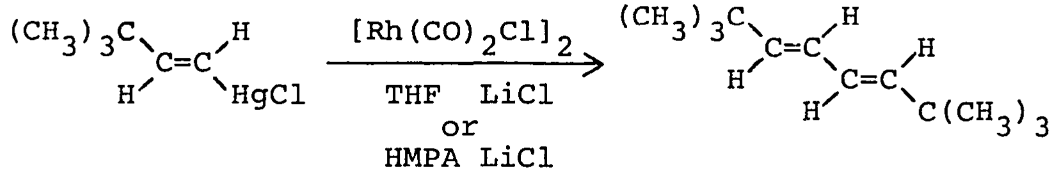
Table II. (continued)

Mercurial	Product	GLPC Yield,%
		~10^{b}
$[(CH_3)_3C-C\equiv C]_2Hg$	$(CH_3)_3C-C\equiv C-CH_3$	$99^{b,c}$
$CH_3(CH_2)_9HgCl$	$CH_3(CH_2)_7CH=CH_2$ + $CH_3(CH_2)_8CH_3$	--

[c] Yield is based upon methylation of both alkynyl groups of the mercurial.

reaction fails due to the possibility of beta-hydride elimination and alkene formation, although the attempted methyl coupling with α-chloromercuri-acetophenone or benzylmercuric chloride was usually unsuccessful also. The reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and arylmercurials is discussed in Chapter III.

The yields for these reactions were determined by gas chromatography using appropriate inert hydrocarbons as internal standards due to the expense of utilizing stoichiometric amounts of a rhodium reagents with a molecular weight of nearly 950. While the observed products were verified by GC-MS as having consistent molecular ions, foregoing the luxury of isolating products has some severe disadvantages. Since the gas chromatographic equipment utilized does not allow the separation of cis and trans olefins such as the heptenes, it is assumed all of the coupling products of a trans vinylmercurial and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ are the corresponding trans methyl-substituted olefins. This assumption is reasonable since the rhodium catalyzed coupling of vinylmercurials yielding symmetrical 1,3-dienes occurs under similar reaction conditions and the trans stereochemistry is retained (Eq. 37).[80] The trans stereochemistry is also retained in the carbonylation and coupling of vinylmercurials yielding divinyl ketones (Chapter V).



(37)

The exclusive use of gas chromatography also causes some ambiguity with respect to the exact experimental conditions necessary for this coupling reaction. There is a distinct systematic difference between the GLPC yields for "quenched" or "unquenched" reactions for the coupling of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and vinylmercurials. The nearly quantitative yields of methyl-substituted olefins from terminal vinylmercurials were obtained by the addition of ether to the reaction mixture and direct GLPC analysis. The yields of 2-heptene and 4,4-dimethyl-2-pentene especially were dramatically decreased if the analysis was not performed immediately after the addition of ether. Alternatively, if pentane and water, or ether and water were added to the reaction mixture, the yields of the methyl-substituted olefins were substantially decreased (Tables III and IV). (The water layer hydrolyzes and dissolves HMPA, the dark unknown rhodium and triphenylphosphine derivatives, and mercuric and lithium chloride while the clear pentane or ether layer extracts the olefin and hydrocarbon standard).

Table III. Comparison of GLPC yield of 2-heptene with time and treatment prior to GLPC analysis

$$\underline{n}\text{-}C_4H_9CH{=}CHHgCl + Rh(CH_3)I_2[P(C_6H_5)_3]_2 \xrightarrow[70°C]{\text{LiCl, HMPA}} \underline{n}\text{-}C_4H_9CH{=}CHCH_3$$

	2-Heptene GLPC Yield,%			
Time, h	Added prior to analysis:	Et_2O	Et_2O/H_2O	C_5H_{12}/H_2O
1				20
3		46	13	27
6				29
9				63
12			15	62
24		94	14	

Table IV. Comparison of GLPC yields of 2-heptene with added reagents and treatment prior to GLPC analysis

$$\underline{n}\text{-}C_4H_9CH{=}CHHgCl + Rh(CH_3)I_2[P(C_6H_5)_3]_2 \xrightarrow[70^\circ C,\ 24h]{HMPA} \underline{n}\text{-}C_4H_9CH{=}CHCH_3$$

Added Reagents	Treatment prior to analysis	2-Heptene GLPC Yield,%
Excess CH_3I	Et_2O	90
	Et_2O/H_2O	18
	C_5H_{12}/H_2O	34
Excess CH_3I and LiCl	Et_2O	73
	Et_2O/H_2O	21
	C_5H_{12}/H_2O	14,13

Although this discrepancy persists, attempts were made toward resolving it. The first possible source of this discrepancy checked was whether or not the reaction was partially occurring on the injector port upon gas chromatographic analysis. The coupling reaction was attempted at several temperatures greater than 70°C, quenched with pentane and water and analyzed. The results are not spectacularly different (Table V) despite the fact HMPA and methyl iodide rapidly darken and decompose at higher temperatures. The lower yields at room temperature suggest that if the coupling reaction occurs on the injector port it does upon preformation of an intermediate complex which is formed nearly completely above 70°C but only partially at lower temperatures. However, since increased yields are not systematically observed with increased reaction temperatures this explanation lacks some credibility. Another perhaps more reasonable source of the discrepancy may be that the coupled olefin is formed nearly quantitatively but then reacts further upon quenching with water. Acid which is quite probably generated (Chapter III) in this system also, might react with the newly formed alkene. Other suspicious reactants toward the alkene might be some unidentified mercury(II) or rhodium(I) species. Before discussing other attempts at resolving this difficulty, some mechanistic aspects should be considered.

Table V. Effect of elevated temperatures and shorter reaction times on the reaction of trans-1-hexenylmercuric chloride and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

$$\underline{n}\text{-}C_4H_9CH{=}CHHgCl + Rh(CH_3)I_2[P(C_6H_5)_3]_2 \xrightarrow{HMPA} \underline{n}\text{-}C_4H_9CH{=}CHCH_3$$

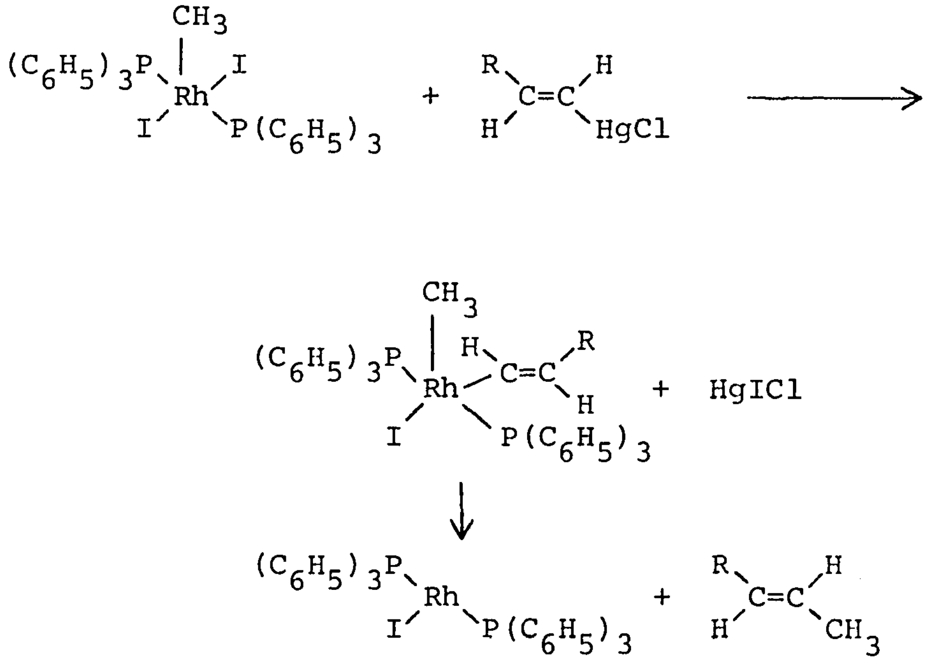
Added reagents	Reaction Temperature °C	Reaction Time min	2-Heptene GLPC Yield,%[a]
--	100	60	9
Excess CH_3I			18
LiCl	125	180	0
CH_3I	125	30	23
		60	20,25,25
CH_3I/LiCl			16
CH_3I		180	57,25
	160	1-2	24,47
		2-3	66,36
		5	27,41,35
		10	24
		15	(92)[b],34
	200	2	29
		8	26

[a] C_5H_{12}/H_2O added prior to analysis.

[b] Initial analysis.

c. Mechanistic considerations The reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and vinylmercurials may be envisioned as involving first a transmetalation forming a diorganorhodium(III) intermediate and the mixed mercuric halide. The diorganorhodium(III) intermediate then reductively eliminates the coupled alkene and a rhodium(I) species (Scheme 29). It is not known which one or whether both of these steps require the added lithium chloride, HMPA, and increased temperatures. Since Schwartz has prepared another diorganorhodium(III) intermediate which may be isolated and only upon pyrolysis forms the methyl-substituted olefin,[201] perhaps this diorganorhodium(III) intermediate might be isolated and the reductive

Scheme 29



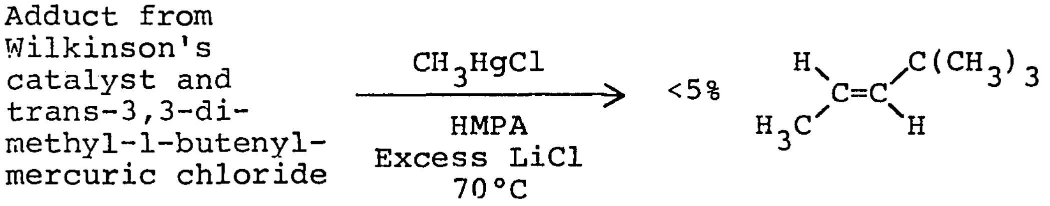
elimination conditions determined. Since HMPA as a solvent does not allow convenient extraction or recovery of organorhodium complexes, the synthesis of the diorganorhodium(III) intermediate was approached by other routes.

One route involved the attempted transmetalation of Wilkinson's catalyst with a vinylmercurial at lower temperatures. Mixing one equivalent of $RhCl[P(C_6H_5)_3]_3$ and one equivalent of trans-3,3-dimethyl-1-butenylmercuric chloride in dichloromethane or THF at -78°C or benzene at 0°C produces a light red orange solid. The characterization of this solid unfortunately is not complete; however, the collected data will be presented. Mass spectral analysis of the solid indicated mercury, the tert-butylvinyl group and triphenylphosphine were present. The presence of these groups strongly suggests rhodium is present also. This much suggests that the vinylmercurial and $RhCl[P(C_6H_5)_3]_3$ did not undergo a simple transmetalation to give $Rh[CH{=}CHC(CH_3)_3][P(C_6H_5)_3]_3$ and mercuric chloride as anticipated, or that $Rh[CH{=}CHC(CH_3)_3][P(C_6H_5)_3]_3$ is not stable in the presence of trans-3,3-dimethyl-1-butenylmercuric chloride under the reaction conditions. The nmr is as informative. The ^1H nmr of different samples (prepared or purified slightly different) consistently showed a multiplet primarily due to the triphenylphosphine hydrogen resonances and 2 tert-butyl singlets, both with a chemical shift different from that of either the vinylmercurial or trans,

trans-2,2,7,7-tetramethyl-3,5-octadiene. In addition, some especially concentrated samples also possessed two multiplets in the vinyl region. While the triphenylphosphine multiplet was difficult to integrate due to its breadth, the vinyl group was difficult to integrate since it is almost buried in the base line and the integration of the 2 tert-butyl singlets were especially variable. Since prospective vinyl hydrogens either appear as a multiplet of doublets or are not apparent, it is more reasonable that the tert-butylvinyl group be bonded to rhodium rather than mercury. Usually the vinyl hydrogens in a vinylmercurial are relatively unaffected with respect to chemical shift by the presence of mercury. The chemical shift of vinyl hydrogens in a vinylrhodium compound are not known since the vinylrhodium compound prepared previously was reported to be too insoluble for nmr measurement.[11] A more complex vinyl pattern would be expected if the vinyl group were bonded to rhodium due to coupling to rhodium and possibly further coupling to phosphorous. The IR confirms approximately the same structural elements. Aromatic and aliphatic carbon-hydrogen stretching is visible. The carbon-carbon double bond stretch at 1580 cm^{-1} is broad with shoulders at 1565 and 1550 cm^{-1}. In trans-3,3-dimethyl-1-butenylmercuric chloride the carbon-carbon double bond stretch is quite sharp at 1580 cm^{-1}[253] and since the aromatic carbon-carbon stretches of triphenylphosphine are very weak from

1400 to 1600 cm^{-1}, the multiplicity of the carbon-carbon stretch in the IR appears to confirm the observed double tert-butyl signal observed in the nmr spectrum. Since the IR spectra of the known rhodium-mercury compound or the IR spectrum of $Rh(CH=CH_2)Cl_2[P(C_6H_5)_3]_2$ except for mention of the carbon-carbon stretch at 1567 cm^{-1}[11] have not been, reported, other possible IR peaks may not be identified from literature comparison. Another piece of physical evidence is an analysis for carbon (61.89%), hydrogen (5.51%), and mercury (14.37%). The analysis for these elements does not acceptably fit any obvious possible formulae considered in the experimental section although some are close, especially $Rh[CH=CHC(CH_3)][HgCH=CHC(CH_3)_3]Cl[P(C_6H_5)_3]_3$. This formula which best agrees with the analytical results, seems least consistent with the observed chemical reactivity. Alternatively mixtures of rhodium species such as $Rh[HgCH=CHC(CH_3)_3][P(C_6H_5)_3]_3$ and $RhCl_3[P(C_6H_5)_3]_2$ or $Rh[CH=CHC(CH_3)_3](HgCl)Cl[P(C_6H_5)_3]_3$ and $Rh[CH=CHC(CH_3)_3][P(C_6H_5)_3]_3$ also fit the analysis and are perhaps are more consistent with the observed reactivity while not agreeing so well with the spectral data especially the nmr with 2 different tert-butyl singlets.

In an attempt to further characterize this unknown compound, it was treated with methylmercuric chloride under the standard coupling conditions--excess lithium chloride, HMPA, and heating at 70°C. Rather surprisingly, the unknown adduct and methylmercuric chloride react, but do not form the methyl-vinyl coupling product since only a very small amount of 4,4-dimethyl-2-pentene is formed (<5%) (Eq. 38).

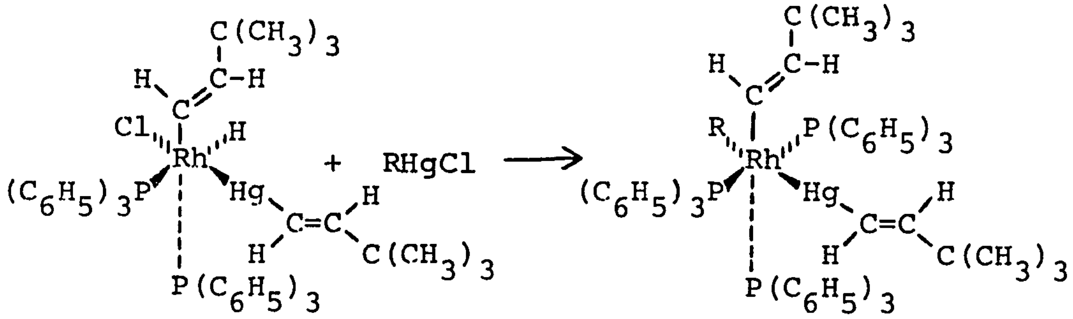


(38)

The major organic product is the symmetrical diene, trans, trans-2,2,7,7-tetramethyl-3,5-octadiene. Presumably the reductive elimination of methyl chloride takes place instead. This is supported by repetition of this reaction, but replacement of methylmercuric chloride with benzylmercuric chloride. In that case the formation of benzyl chloride and again trans, trans-2,2,7,7-tetramethyl-3,5-octadiene were both verified by GC-MS. Some precedent for the reductive elimination of methyl chloride being quite facile is the formation of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ from $RhCl[P(C_6H_5)_3]_2$ and neat methyl iodide.

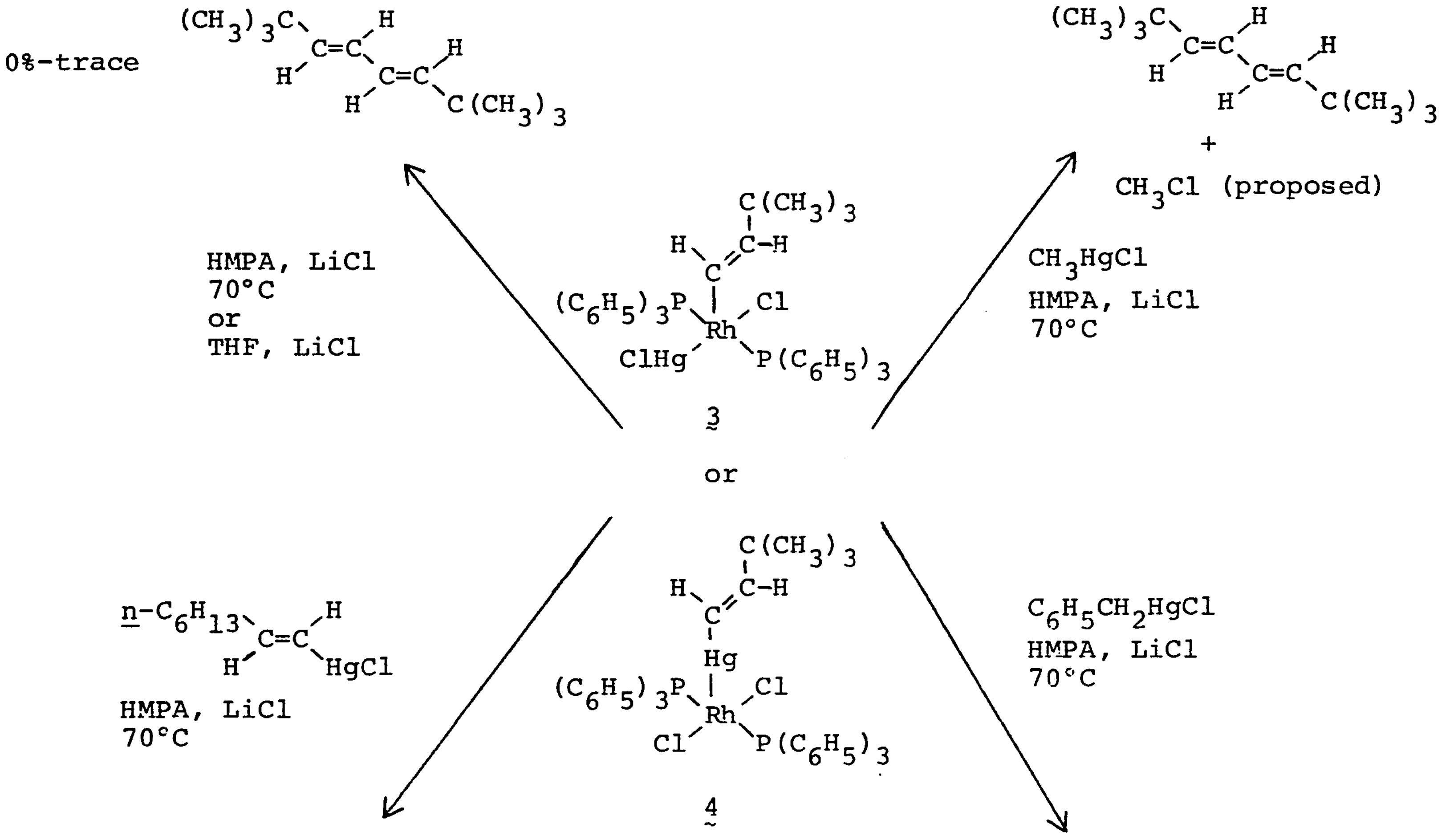
Although the symmetrical diene is the major organic product in the reaction of alkylmercurials and the compound isolated from the low temperature reaction of a vinylmercurial and Wilkinson's catalyst, the isolated compound itself does not form the symmetrical diene under coupling conditions. This compound in either THF and excess lithium chloride or HMPA, excess lithium chloride and heating does not yield trans,trans-2,2,7,7-tetramethyl-3,5-octadiene. However, reaction of the isolated compound and another vinylmercurial, trans-1-octenylmercuric chloride, produces all three possible dienes, the symmetrical dienes, trans,trans-2,2,7,7-tetramethyl-3,5-octadiene and trans,trans-7,9-hexadecadiene, as well as the unsymmetrical diene, trans,trans-2,2-dimethyl-3,5-dodecadiene. Unfortunately, the GLPC conditions did not allow estimation of the ratios of these three dimers. The reactions of the rhodium compound with these different mercurials are outlined in Scheme 30.

Numerous schemes might be proposed to account for the formation of the observed dienes and alkyl halides from the proposed adduct formulae. All of these will not be considered in detail but a few remarks will be made. Although it has not been demonstrated, $Rh[CH{=}CHC(CH_3)_3][HgCH{=}CHC(CH_3)_3]Cl[P(C_6H_5)_3]_3$ would be expected to form trans,trans-2,2,7,7-tetramethyl-3,5-octadiene, mercury and $RhCl[P(C_6H_5)_3]_3$ under coupling reaction conditions and that was not observed. One remote possibility is that an organomercurial might induce the observed reductive couplings from the adduct via transmetalation (Eq. 39). Alternatively, the oxidative addition



(39)

Scheme 30

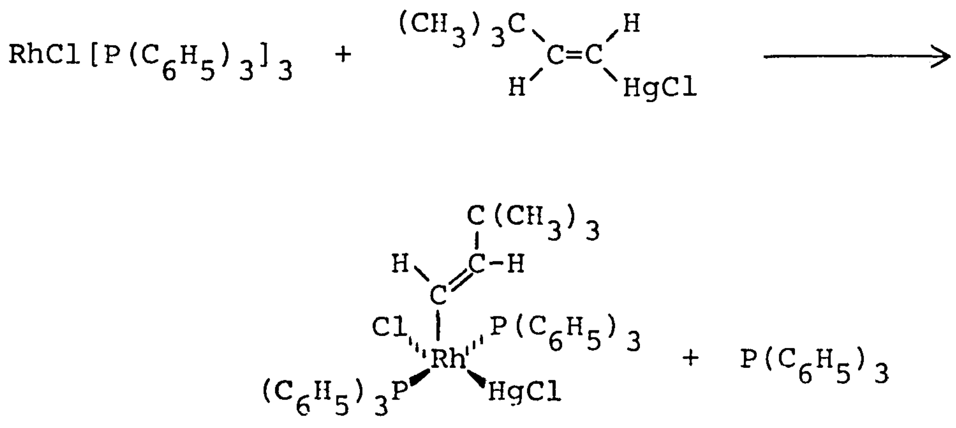

0%-trace
(CH3)3C, H, C=C, H, C=C, H, H, C(CH3)3
HMPA, LiCl
70°C
or
THF, LiCl
(CH3)3C, H, C=C, H, C=C, H, H, C(CH3)3
+
CH3Cl (proposed)
CH3HgCl
HMPA, LiCl
70°C
C(CH3)3
H, C=C-H
(C6H5)3P, Rh, Cl
ClHg, P(C6H5)3
3
or
C(CH3)3
H, C=C-H
Hg
(C6H5)3P, Rh, Cl
Cl, P(C6H5)3
4
n-C6H13, C=C, H, H, HgCl
HMPA, LiCl
70°C
C6H5CH2HgCl
HMPA, LiCl
70°C


(CH3)3C
C=C
H
C(CH3)3
+
n-C6H13
C6H5CH2Cl

of an organomercurial to a rhodium(III) species producing a rhodium(V) species, analogous to a very recent palladium investigation[267] might be considered with subsequent reductive eliminations.

The second of the previously proposed formulae for the adduct formed from Wilkinson's catalyst and a vinylmercurial is a rhodium(I) species, $Rh[HgCH{=}CHC(CH_3)_3][P(C_6H_5)_3]_3$. The observed products can be considered to arise from an oxidative addition of an organomercurial followed by reductive elimination of an alkyl halide or a diene. If reductive elimination of an organomercurial also occurs the symmetrical dienes may be formed.

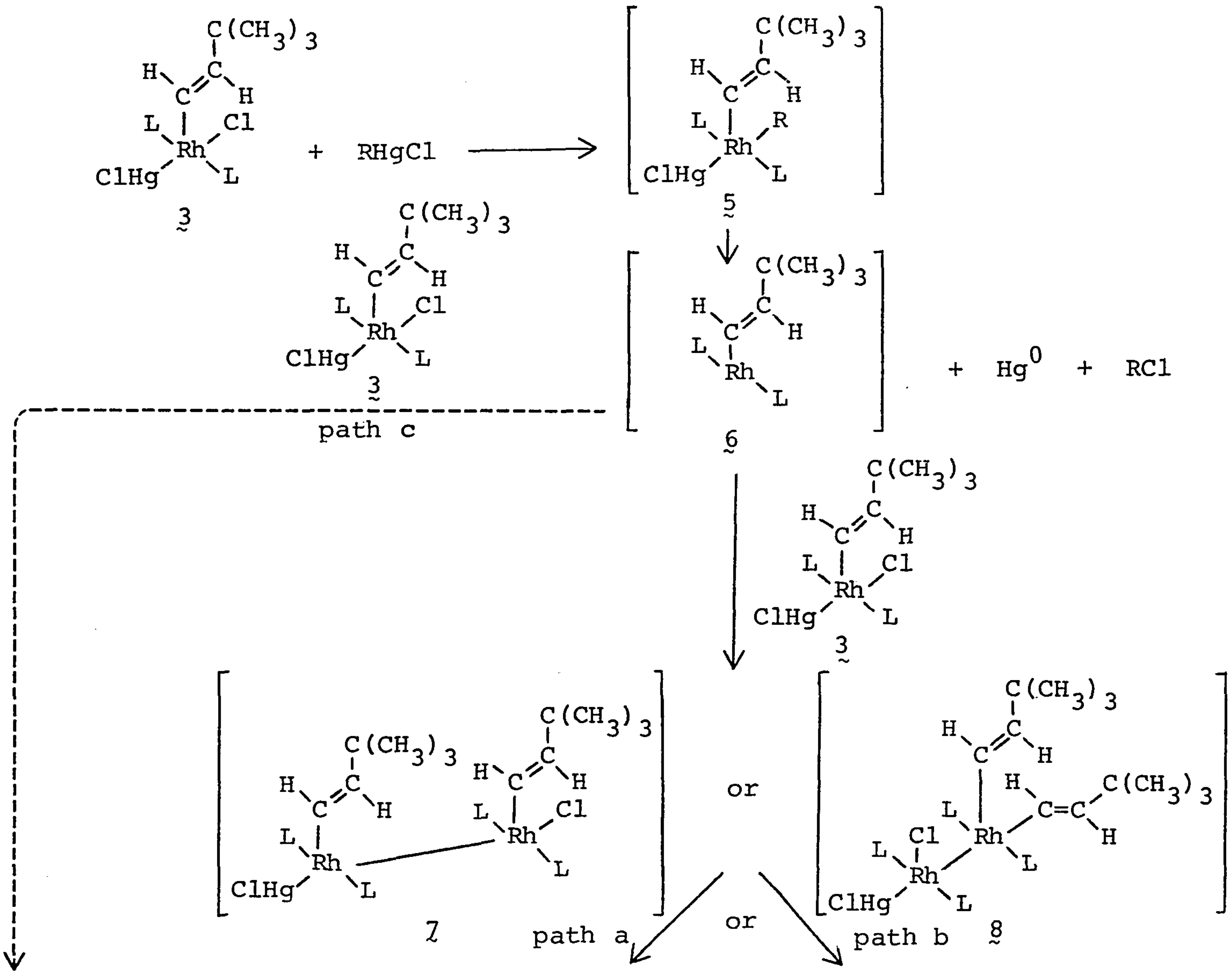
The final possible formula for the adduct formed from Wilkinson's catalyst and a vinylmercurial to be considered is $Rh[CH{=}CHC(CH_3)_3](HgCl)Cl[P(C_6H_5)_3]_3$. It may be formed from the oxidative addition of the vinylmercurial to Wilkinson's catalyst (Eq. 40). Since the adduct does not form the sym-

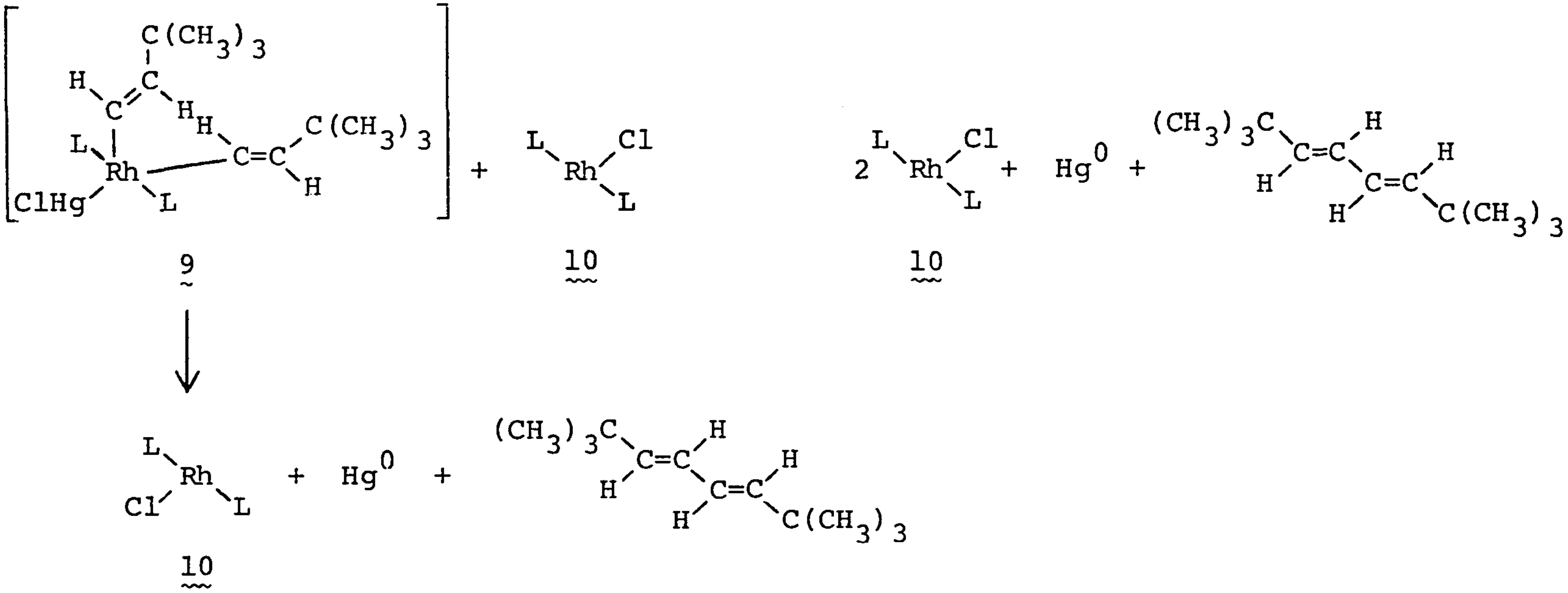


(40)

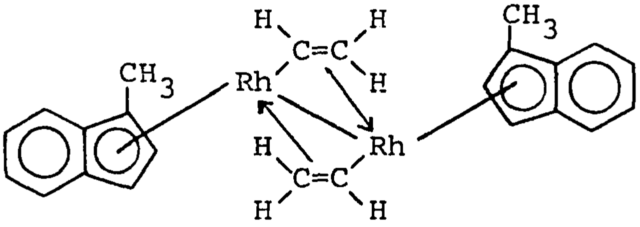
metrical diene under the usual coupling conditions, $Rh[CH{=}CHC(CH_3)_3]Cl(HgCl)[P(C_6H_5)_3]_3$, a rhodium(III) species which might not be expected to reductively eliminate under coupling conditions, is also a reasonable formula. However, $Rh[CH{=}CHC(CH_3)_3]Cl(HgCl)[P(C_6H_5)_3]_3$ as a rhodium(III) species presents less obvious schemes for the formation of the observed dienes and alkyl halides. Schemes 31 and 32 illustrate a couple of possibilities. Scheme 31 accounts for the formation of benzyl or methyl chloride and trans,trans-2,2,7,7-tetramethyl-3,5-octadiene from the reaction of the rhodium adduct and benzyl- or methylmercuric chloride. The transmetalation of this adduct with the organomercurial may form a diorganorhodium(III) mercuric chloride intermediate **5**. Reductive elimination of benzyl or methyl chloride would produce metallic mercury and a rhodium(I) vinyl species **6**. Oxidative addition of the starting rhodium(III) compound would produce intermediate **7** or **8**, respectively. Although the oxidative addition of a rhodium(III) species to another rhodium(I) species is unprecedented, a dinuclear divinylrhodium compound has been isolated recently from the reaction of 2-butyne with $Rh(C_2H_4)_2(\eta^5\text{-}1\text{-}CH_3\text{-}C_9H_6)$ (Eq. 41).[268] Its structure was established by single crystal X-ray diffraction. The similarity of this compound to the proposed intermediate **7** provides some credibility for this process. The reductive elimination of trans,trans-2,2,7,7-tetramethyl-

Scheme 31




9 10 10 10

$$Rh(C_2H_4)_2(\eta^5\text{-}CH_3\text{-}C_9H_6) \quad + \quad CH_3\text{-}C{\equiv}C\text{-}CH_3 \longrightarrow$$

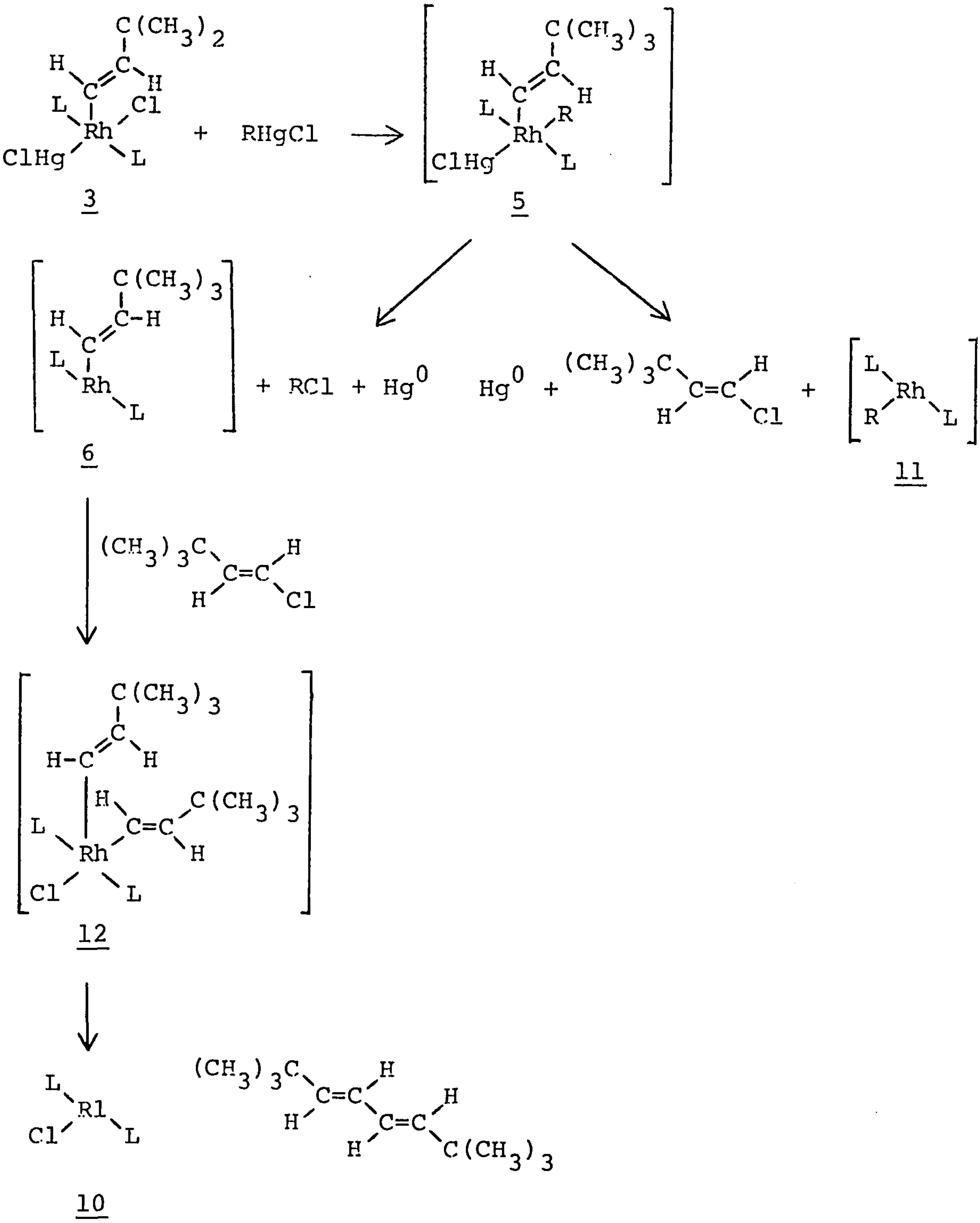


(41)

3,5-octadiene might occur from either of these dinuclear species (path b) or alternatively stepwise reductive eliminations (path a) to mononuclear species 9 and 10 are also possible. Alternatively, a transmetalation sequence (path c) might also produce a mononuclear species 9 from which reductive elimination of the diene might occur. In the illustrated scheme an organorhodium(I) compound transmetalates with an organorhodium(III) compound, 3 forming a diorganorhodium(III) compound 9 and a rhodium(I) halide species, 10.

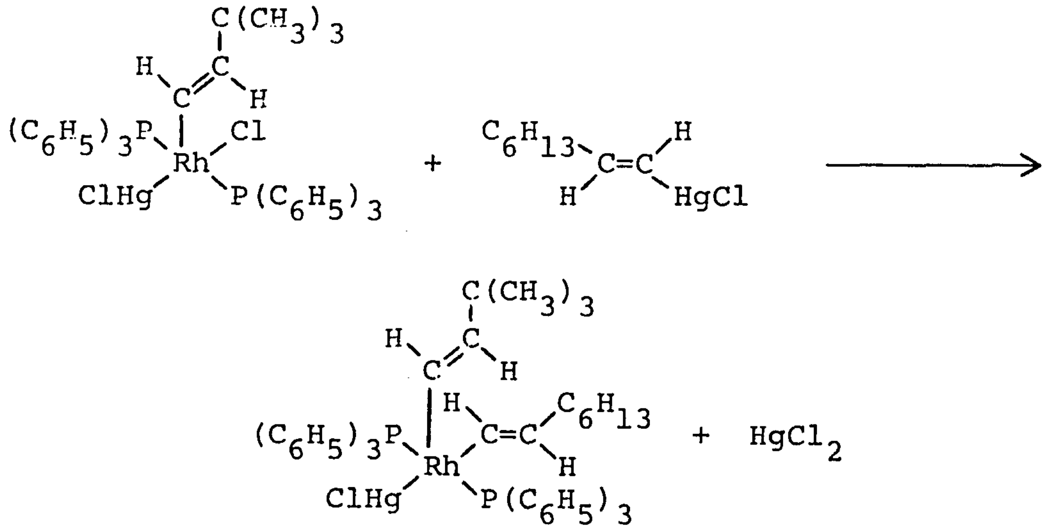
Scheme 32 is another possible route for formation of 2,2,7,7-tetramethyl-3,5-octadiene in the presence of an added mercurial. It involves the previously described transmetalation of the organorhodium(III) compound 3 with an organomercurial producing the diorganorhodium(III) intermediate 5. The reductive elimination of either an alkyl chloride or a vinyl chloride then forms a vinylrhodium(I) compound, 6 or an alkylrhodium(I) compound 11 respectively. The oxidative addition of the vinyl chloride to the vinylrhodium(I) species

Scheme 32



forms a divinylrhodium(III) compound 12 from which reductive elimination of the diene might occur. Organic products perhaps indicative of the fate of the alkylrhodium(I) compound 11 such as methane or ethane, or toluene or bibenzyl were not noticed.

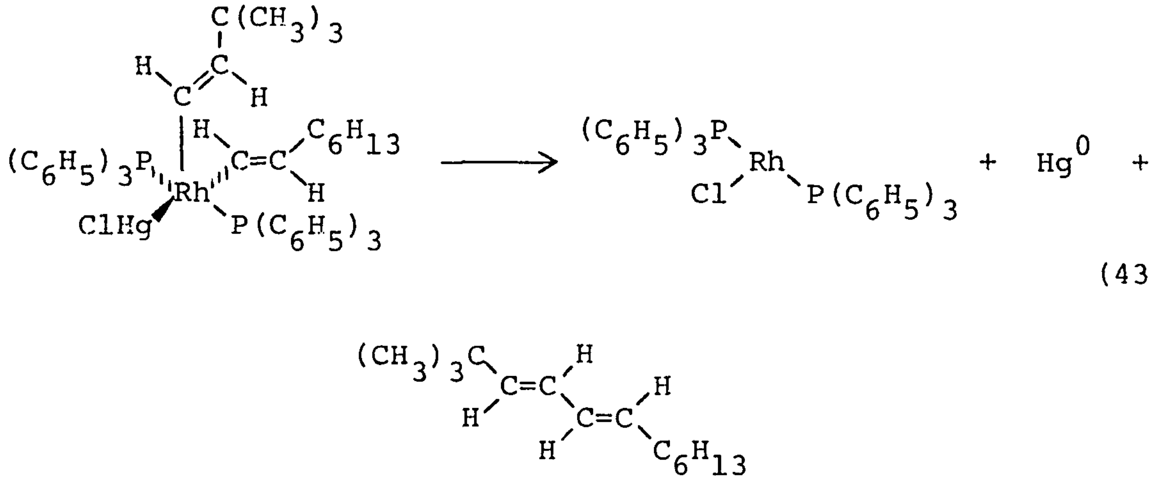
The formation of 2,2,7,7-tetramethyl-3,5-octadiene, 2,2-dimethyl-3,5-dodecadiene and 7,9-hexadecadiene from the reaction of *trans*-1-octenylmercuric chloride and the intermediate isolated from *trans*-3,3-dimethyl-1-butenylmercuric chloride and Wilkinson's catalyst may be explained by schemes similar to 31 or 32. Alternatively, the unsymmetrical divinylrhodium compound 13 formed via transmetalation with the added vinylmercurial (Eq. 42) may undergo rapid exchange forming the two symmetrical divinylrhodium species as well.



(42)

13

These divinylrhodium(III) species might reductively eliminate the observed dienes (Eq. 43). Although the presumed trans-

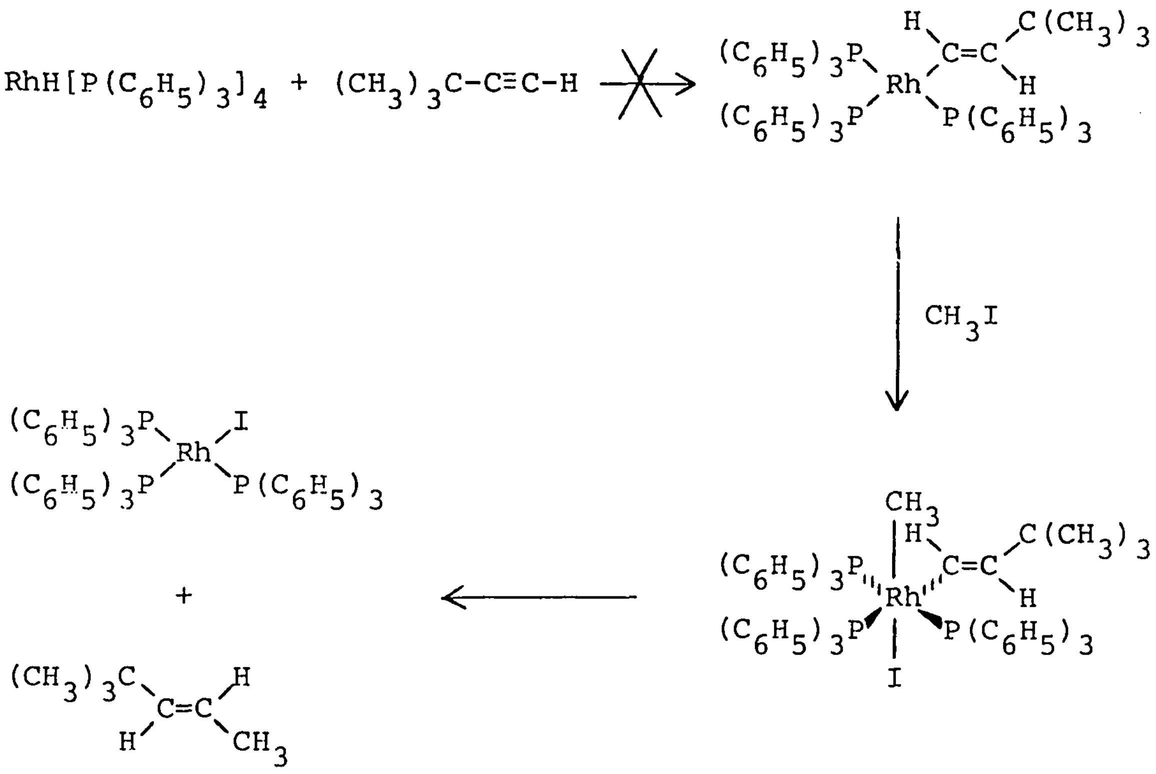


(43)

metalation of Wilkinson's catalyst with an organomercurial failed to produce a vinylrhodium(I) species, for the subsequent oxidative addition of methyl iodide, this investigation perhaps suggests that oxidative addition of the organomercurial to the rhodium(I) species precedes the transmetalation of an organorohdium(III) halide with another organomercurial in the rhodium catalyzed dimerization of vinyl- and arylmercurials or the rhodium catalyzed carbonylation of vinyl- and arylmercurials yielding divinyl and diaryl ketones (Chapter V).

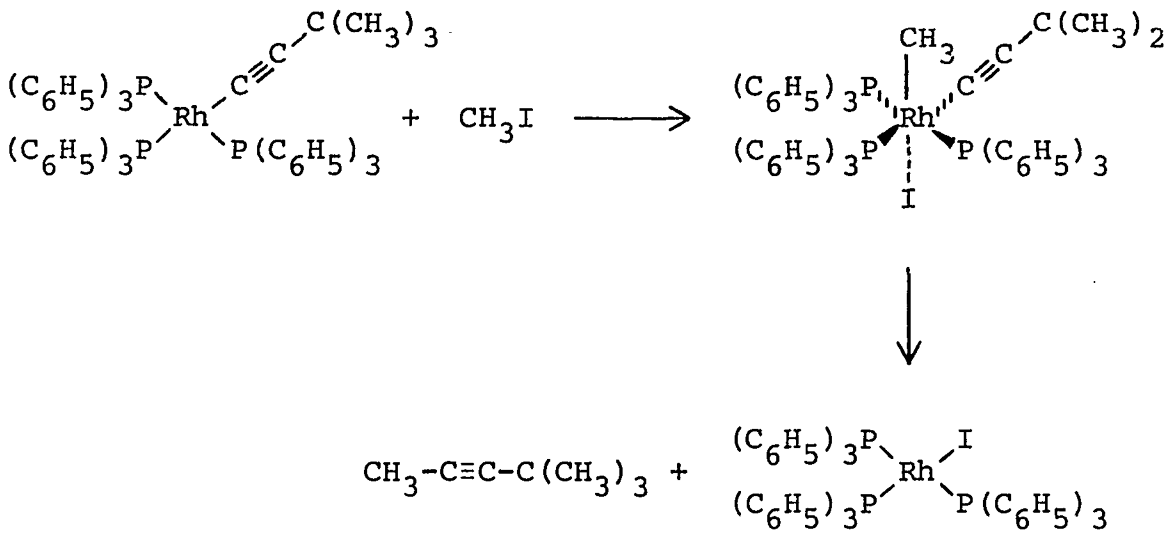
Alternatively, the vinylrhodium(I) precursor for the proposed Rh(CH=CHR)(CH$_3$)Cl[P(C$_6$H$_5$)$_3$]$_2$ intermediate might also be obtained via the insertion of an acetylene into a rhodium hydride (Scheme 33). This reaction was performed as pre-

Scheme 33

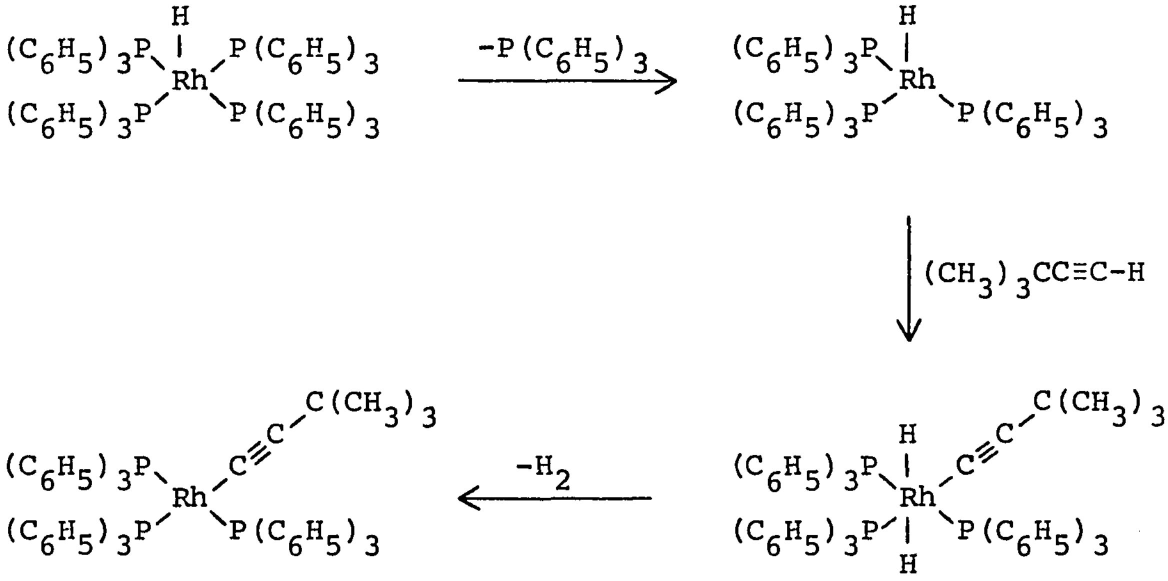


viously reported for phenyl acetylene and $RhH[P(C_6H_5)_3]_4$.[269] However, the crude product did not exhibit distinct vinyl hydrogens in the nmr. Only phenyl type hydrogens were observed, and the triphenylphosphine hydrogens could not be differentiated from the phenyl hydrogens of phenyl acetylene. Consequently, the crude product was purified by column chromatography. However, no rhodium containing species were isolated from the column. Although only the insertion of alkynes containing electron withdrawing groups are reported in the literature, $RhH[P(C_6H_5)_3]_4$ was mixed with 3,3-dimethyl-1-butyne and allowed to stand, sealed over six months during which time the mixture gradually turned darker orange. Initially it was bright yellow-orange. The solid was rinsed thoroughly with ether, but not chromatographed. The nmr of the solid although not containing distinct vinylic hydrogens does have a <u>tert</u>-butyl singlet. The rhodium hydride stretch in the IR is also absent. The reaction of this complex with methyl iodide has been used to help further characterize it. Mixing this supposed vinylrhodium compound with neat methyl iodide at room temperature or mixing it with excess methyl iodide and also excess lithium chloride, HMPA, and heating at 70°C does not form the expected 4,4-dimethyl-2-pentene. Instead 4,4-dimethyl-2-pentyne is formed. Although the formation of this product was not thoroughly investigated, oxidative addition of methyl iodide to a rhodium(I)acetylide followed by reductive elimination may account for the formation of 4,4-dimethyl-2-pentyne (Scheme 34). The rhodium(I)-acetylide might be formed via oxidative addition of 3,3-dimethyl-1-butyne to the rhodium hydride, and subsequent reductive elimination of hydrogen (Scheme 35). Although interesting in its own right, the fact that this methyl-alkynyl coupling occurs neat in methyl iodide at room temperature, or under the standard coupling conditions suggests that

Scheme 34



Scheme 35



perhaps the usual rigorous reaction conditions (excess lithium chloride and HMPA at 70°C) may be more important in the proposed transmetalation step.

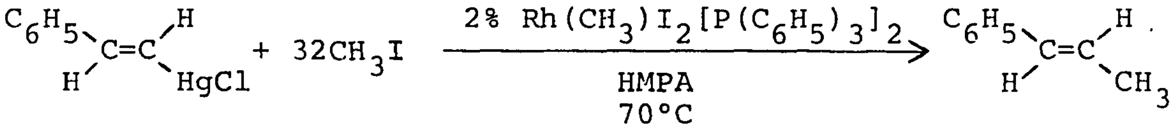
Returning to the scheme initially proposed for this reaction (Scheme 29), the end rhodium product is a rhodium(I) species to which methyl iodide might oxidatively add. Another vinylmercurial may subsequently transmetalate and the reaction continue as previously described. Picturing the reaction in this simple manner suggests this reaction might be catalytic with respect to rhodium.

d. Catalytic attempts The successful catalytic methylation of vinylmercurials depends ultimately on three specific reaction requirements. First, methyl iodide should be the only species to oxidatively add to the rhodium(I) species. Second, the vinylmercurial should participate by transmetalation only and, third, the reductive elimination of the methyl olefin from the intermediate derived from the two previous reactions should be facile. Already, the formation of 4,4-dimethyl-2-pentyne from $Rh[C{-}C{\equiv}C(CH_3)_3][P(C_6H_5)_3]_3$ and methyl iodide at room temperature indicates the reductive methyl-alkynyl coupling and possibly other methyl couplings may be especially facile. Successful catalytic methylation then depends upon the oxidative addition of methyl iodide beating out the oxidative addition of the mercurial.

Disregarding the previously described extraction, work-up and/or analysis difficulties, Table VI illustrates that this methylation is partially catalytic. Unfortunately, some of the vinylmercurial oxidatively adds to the rhodium(I) species as evidenced by the predominant formation of the symmetrical diene, 1,4-diphenylbutadiene from the reaction of styrylmercuric chloride, lithium chloride, methyl iodide, HMPA, and 2% $Rh(CH_3)I_2[P(C_6H_5)_3]_2$. To evaluate the catalytic coupling by the turnover number for methylation (approximately 10 for styrylmercuric chloride) is really not accurate, since the rhodium(I) species present remains catalytically active. The oxidative addition of the vinylmercurial which produces symmetrical dienes[80] competes with the oxidative addition of methyl iodide which produces methyl-substituted olefins. Thus this methylation fails catalytically due to a side reaction consuming one of the reactants, but apparently not deactivating the catalyst.

It is conceivable that mercurials other than vinylmercuric chlorides may be less reactive in the oxidative addition to the rhodium(I) species formed after reductive elimination of the methyl olefin. Table VII illustrates that bis(3,3-dimethyl-1-butynyl)mercury forms higher catalytic yields of the methylated product, 4,4-dimethyl-2-pentyne. Consistent with the stoichiometric reaction, conditions which best promote the catalytic reaction include excess lithium

Table VI. Effect of time, treatment prior to GLPC analysis and lithium chloride on the methylation of styrylmercuric chloride with methyl iodide catalyzed by 2 mole percent $Rh(CH_3)I_2[P(C_6H_5)_3]_2$



Added reagents	Reaction Time h	Treatment prior to analysis	Propenylbenzene GLPC Yield,%
LiCl	1	Pentane/water	17
		Benzene/water	23[a]
--	3	Ether/water	4
LiCl			11
--	12		3[a]
LiCl			24[a]
--		Pentane/water	2
LiCl			16
	24		15[a]
		Benzene/water	19[a]

[a] Presence of 1,4-diphenylbutadiene verified by GLPC.

Table VII. Effect of time and lithium chloride on the methylation of bis(3,3-dimethyl-1-butynyl)-mercury with methyl iodide catalyzed by 2 mole percent $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

$$[(CH_3)_3C\text{-}C{\equiv}C]_2Hg \; + \; 32CH_3I \xrightarrow[\text{HMPA} \atop 70^\circ C]{2\%\ Rh(CH_3)I_2[P(C_6H_5)_3]_2} 2(CH_3)_3C\text{-}C{\equiv}C\text{-}CH_3$$

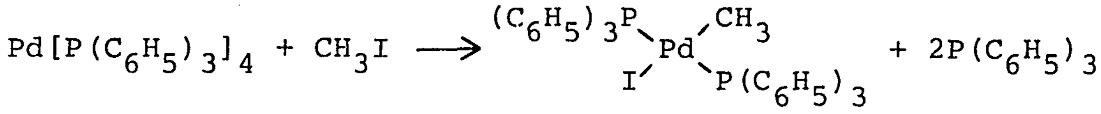
Added reagents	Reaction Time h	4,4-Dimethyl-2-Pentyne GLPC Yield,%[a]
--	8	47
LiCl		52
--	12	16
LiCl		55
--	24	22,35
LiCl		58,65

[a] Pentane and water added prior to analysis.

chloride in HMPA. It was not established whether these improved catalytic yields are due to the bis(organo)mercury moiety or the alkynylmercurial moiety.

e. Other approaches Difficulties with catalyst selectivity prompted a brief survey of some other transition metal compounds since many are also known to undergo similar oxidative additions and reductive eliminations. A rhodium(I) species not containing phosphine ligands, $[Rh(H_2C{=}CH_2)_2Cl]_2$ was hastily investigated, but not pursued since only a trace of methylated olefin was observed.

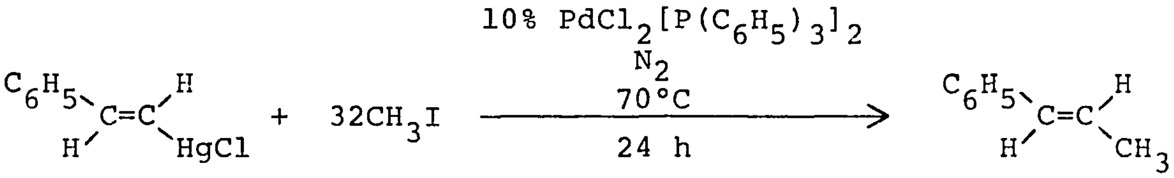
The reaction of methyl iodide and tetrakis(triphenylphosphine)palladium(0) has been briefly communicated (Eq. 44).[270] Attempts to reproduce this reaction produced a black



$$Pd[P(C_6H_5)_3]_4 + CH_3I \longrightarrow \begin{array}{ccc} (C_6H_5)_3P & & CH_3 \\ & Pd & \\ I & & P(C_6H_5)_3 \end{array} + 2P(C_6H_5)_3 \qquad (44)$$

solid which is quite insoluble and difficult to purify. The black material obtained did not possess the reported spectral evidence (nmr), nor did it produce any methylated olefin in the reactions with vinylmercurials with or without excess methyl iodide in HMPA at 70°C. Catalytic in situ attempts from tetrakis(triphenylphosphine)palladium(0) were similarly unsuccessful. However, the reaction with bis(triphenylphosphine)palladium(II) chloride is interesting (Table VIII).

Table VIII. Effect of different reaction conditions on the methylation of styrylmercuric chloride with methyl iodide catalyzed by 10 mole percent $PdCl_2[P(C_6H_5)_3]_2$



Reaction Conditions	Propenylbenzene GLPC Yield,%[a]
Benzene	0
THF	0
HMPA	0
HMPA, excess LiCl	17

[a] 1,4-Diphenylbutadiene was verified by GLPC in all four reactions.

Some 1,4-diphenylbutadiene is formed perhaps via two transmetalations and a subsequent reductive elimination.[271] Methyl iodide also may apparently oxidatively add to the resulting palladium(0) species, which after transmetalation and reductive elimination forms the methyl-substituted olefin. As with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$, the oxidative addition of the vinylmercurial competes with the oxidative addition of methyl iodide maring the synthetic potential of this system also. Perhaps strictly limiting the number of phosphine ligands to two per palladium may be a reason for some success with $PdCl_2[P(C_6H_5)_3]_2$ and failures in the $Pd(P(C_6H_5)_3]_4$ derived systems.

C. Conclusion

The methylation of vinylmercurials via transmetalation with an organotransition metal halide, followed by reductive elimination produces methyl-substituted olefins. Apparently the reductive elimination is quite facile while the transmetalation appears to be promoted by excess lithium chloride and HMPA. The propensity of vinylmercurials to oxidatively add to rhodium(I) phosphine species as well as transmetalate organorhodium(III) halides precludes the employment of catalytic amounts of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ in the presence of methyl iodide. In the following chapter this methylation scheme is extended to arylmercurials and the formation of methyl-substituted arenes.

D. Experimental Section

1. General

Melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. Nmr spectra were obtained on the following commercial spectrometers, Varian A-60, and HA-100, Hitachi-Perkin Elmer R-20B, and Bruker HX-90. All nmr spectra are recorded as parts per million downfield from tetramethylsilane on the δ scale, and presented in the following order: chemical shift, integration, multiplicity, coupling constant in Hz. IR spectra were measured on a Beckman IR 4250 Spectrometer. The intensities of absorptions are abbreviated: s, strong; m, moderate; w, weak; vs, very strong; and vw, very weak. Exact masses were measured on a MS-902 Mass Spectrometer. A Finnegan 4000 Gas Chromatograph-Mass Spectrometer was employed for GC-MS. Gas chromatographic yields were determined using hydrocarbon internal standards on a Varian Model 920 or Series 2700 Aerograph with thermal conductivity detectors. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Several reagents and solvents were always used after the same purification procedure. These are listed in Table IX. All other reagents were used as obtained commercially unless otherwise noted. All the vinylmercurials except _trans_-1-octenylmercuric chloride (m.p. = 105-106°C) were known previously and were prepared as described in the

Table IX. Purification of routine reagents and solvents

Reagent	Purification
DMSO	Distilled from calcium hydride at reduced pressure.
Ether	Distilled from lithium aluminum hydride.
HMPA	Stirred over calcium hydride and distilled under reduced pressure and in the early part of this work stored under nitrogen or in the later part of this work used immediately.
Pentane	Stirred with sulfuric acid, washed with water, dried (anhydrous $MgSO_4$), filtered and distilled from calcium hydride.
THF	Distilled from lithium aluminum hydride.
Triphenylphosphine	Recrystallized prior to use from ethanol.

literature.[213,253,254] Bis(3,3-dimethyl-1-butynyl)mercury was also prepared as described in the literature.[272] Acetylenes were obtained from Farchan, trimethyloxonium tetrafluoroborate from Cationics and methyl fluorosulfonate from Aldrich.

$RhCl[P(C_6H_5)_3]_3$,[273] $RhH[P(C_6H_5)_3]_4$[274], $[Rh(H_2C{=}CH_2)_2Cl]_2$[275] and $Pd[P(C_6H_5)_3]_4$[276] were prepared as described in the literature from $RhCl_3 \cdot 3H_2O$ and $PdCl_2$ generously loaned by Matthey Bishop.

2. The reaction of $(CH_3)_3O^+BF_4^-$ with *trans*-1-hexenylmercuric chloride

0.5 Grams (3.4 mmoles) $(CH_3)_3O^+BF_4^-$ was weighed (dry box) into a 50 ml round bottom flask equipped with a septum inlet, a gas inlet tube and a magnetic stirring bar. The flask was flushed with nitrogen and 0.0381 grams (0.33 mmole mmoles) *n*-octane and 30 ml dichloromethane were added by syringe. After cooling to 0°C, 0.1085 grams (0.34 mmoles) *trans*-1-hexenylmercuric chloride was added all at once while backflushing with nitrogen. A white precipitate was present throughout the reaction. After stirring 24 hours and warming to room temperature, the reaction was quenched with saturated ammonium chloride solution and the dichloromethane solution analyzed by GLPC analysis. No 2-heptene was observed. The reaction was repeated with 0.15 grams (1 mmole) $(CH_3)_3O^+BF_4^-$ and 0.32 grams (1 mmole) *trans*-1-hexenylmercuric chloride in 10 ml dichloromethane and 0.114 grams (0.998

mmoles) n-octane with the same result, no 2-heptene was observed.

3. The reaction of FSO_3CH_3 with trans-1-hexenylmercuric chloride

Under reaction conditions similar to those of $(CH_3)_3O^+BF_4^-$ and trans-1-hexenylmercuric chloride, 0.1144 grams (1 mmole) FSO_3CH_3 (Magic Methyl) was reacted with 0.32 grams (1 mmole) trans-1-hexenylmercuric chloride in 10 ml dichloromethane. GLPC analysis again indicated no 2-heptene was present after either 6 or 12 hours reaction time.

4. The reaction of aluminum chloride, methyl iodide and trans-1-hexenylmercuric chloride

Under reaction conditions similar to those of $(CH_3)_3O^+BF_4^-$ and trans-1-hexenylmercuric chloride, 0.13 grams (1 mmole) $AlCl_3$ and 0.32 grams (1 mmole) trans-1-hexenylmercuric chloride were allowed to react with excess methyl iodide in 10 ml dichloromethane. Although the color changed from yellow to orange to red during the reaction, upon quenching after 24 hours only chloroiodomethane and diiodimethane were observed and confirmed by GLPC and mass spectrometric analysis.

5. Reaction of trans-styrylmercuric chloride and $Rh(CH_3)I_2[P(C_6H_5)_3]_3$ formed in situ from $RhCl[P(C_6H_5)_3]_3$ and methyl iodide

0.0924 Grams (0.1 mmoles) $RhCl[P(C_6H_5)_3]_3$ was weighed into a 10 ml round bottom flask equipped with a septum inlet a condenser with a gas inlet tube and a magnetic stirring bar. After flushing the system with nitrogen, 2 ml (excess) methyl iodide was added by syringe. Although the color darkened within five minutes, it did not develop the reported characteristic bright green color of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$. After stirring at room temperature 25 minutes, the excess methyl iodide was pumped off. Either 1 ml dichloromethane of 1 ml HMPA and 0.0170 grams (0.1 mmoles) n-dodecane was added by syringe. 0.0339 Grams (0.1 mmoles) trans-styrylmercuric chloride was added all at once with nitrogen backflushing. After 1 and 3 hours, GLPC analysis indicated no trans-propenylbenzene was formed in dichloromethane at room temperature, but a small amount of propenylbenzene was formed in HMPA. After heating the HMPA solution at 70°C overnight, GLPC analysis indicated trans-propenylbenzene was formed in less than 10% yield.

6. Synthesis of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

The synthesis of Lawson, Osborn and Wilkinson[13] was modified in the following manner. 1 Gram (1.08 mmoles) $RhCl[P(C_6H_5)_3]_3$ was weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 20 ml methyl iodide was added with vigorous stirring under nitrogen. In 3 to 5 minutes the solution darkens and becomes dark green. After the dark green color forms, the excess methyl iodide is removed (water aspirator) leaving a dark green-brown solid. Failure to begin removing the excess methyl iodide in time results in a red-brown solid which is not easily purified. The gas inlet tube was replaced with a filter frit also attached to another 250 ml round bottom flask with a septum inlet. Under nitrogen the dark green solid was washed and agitated with acetone and filtered leaving a green solid. After 4 to 5 acetone rinses, the rinse is nearly colorless and the solid medium green. The solid was dried, stored under nitrogen and used as is. A typical yield based on $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot CH_3Cl$ is 0.90 grams (0.95 mmole), 88%. Although Lawson, Osborn and Wilkinson reported the recrystallization of this compound from benzene, attempts to recrystallize it from benzene resulted in decomposition.

7. <u>Initial investigations of the coupling between $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and trans-styrylmercuric chloride</u>

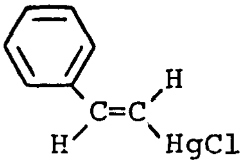
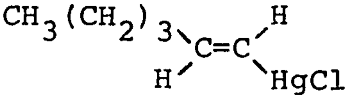
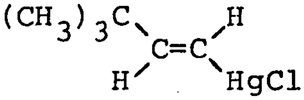
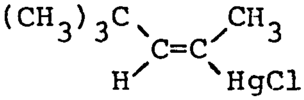
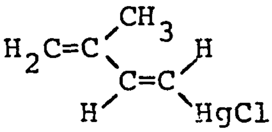
0.0949 Grams (0.1 mmoles) $Rh[CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$ was weighed into a 10 ml round bottom flask equipped with a septum inlet, a condensor with a gas inlet tube attached and a magnetic stirring bar. If appropriate, at least 0.0424 grams (1.0 mmole) lithium chloride or 0.2 ml (excess) methyl iodide was added. After flushing with nitrogen, 0.0170 grams (0.1 mmoles) *n*-dodecane and 1 ml of the appropriate solvent was added by syringe. While backflushing with nitrogen, 0.0339 grams (0.1 mmoles) trans-styrylmercuric chloride was added all at once. After allowing the reactions to proceed the appropriate time at the appropriate temperature, the reactions were directly GLPC analyzed.

8. Reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$ with vinyl-, alkynyl- and alkylmercurials

The following procedure for the formation of propenyl benzene from trans-styrylmercuric chloride is representative. 0.0473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0170 grams (0.05 mmoles) trans-styrylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 0.0085 grams (0.05 mmoles) n-dodecane and 0.5 ml HMPA were added by syringe. The reaction was allowed to stir in a 70°C oil bath. After 24 hours 0.5 ml ether was added rinsing down the interior of the condenser and the reaction mixture was analyzed by GLPC.

Other methyl-substituted olefins and alkynes were synthesized accordingly using other organomercurials, internal standards and GLPC analysis conditions as outlined in Table X. Since the conditions employed for the GLPC analysis did not allow separation of E and Z isomers of these methyl olefins, and the reactions were not carried out on a scale

Table X. Analysis conditions for the syntheses of methyl-substituted olefins, acetylenes and alkanes

Organomercurial	Methyl-substituted product
	$C_6H_5CH{=}CH(CH_3)$
	$CH_3(CH_2)_3CH{=}CH(CH_3)$
	$(CH_3)_3CCH{=}CH(CH_3)$
	$(CH_3)_3CCH{=}C(CH_3)_2$
	$H_2C{=}C(CH_3)\text{-}CH{=}CH(CH_3)$
$[(CH_3)_3CC{\equiv}C]_2Hg$	$(CH_3)_3CC{\equiv}CCH_3$
$CH_3(CH_2)_9HgCl$	$CH_3(CH_2)_9CH_3$

[a] A 1/4" x 10' 10% SE-30 column was utilized for all analyses.

[b] The GC-MS of a quenched sample indicated 2 peaks with a $M^+=98$, it was not determined whether this corresponds to cis,trans isomers or isomeric heptenes.

[c] The lowest constant temperature possible.

[d] Corresponds to the observed products, decene(s) and decane.

Hydrocarbon internal standard	GLPC analysis[a] temperature °C	GC-MS M^+
Dodecane	120	118
Octane	70	98[b]
	65	98
Heptane	55[c]	--
		--
		96
Dodecane	120	140,142[d]

enough for isolation, the stereochemistry was assumed to be trans, but this was not verified.

The effect of reaction time and work-up conditions prior to GLPC analysis was investigated for the coupling of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and trans-1-hexenylmercuric chloride. After the appropriate reaction time, either 0.5 ml ether, 0.5 ml ether plus 0.5 ml water, or 0.5 ml pentane plus 0.5 ml water was added to the reaction mixture. Either the whole solution (ether added) or the organic layer (ether plus water, or pentane plus water added) was analyzed by GLPC. Similarly, the effect of work-up conditions prior to GLPC analysis on the coupling reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and trans-1-hexenylmercuric chloride with the addition of 0.1 ml (excess) methyl iodide, and with or without added 0.213 grams (0.5 mmoles)lithium chloride was also investigated.

The effect of reaction temperatures of 100°C to 200°C (oil bath) was also investigated for the reaction of trans-1-hexenylmercuric chloride and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ with 0.0213 grams (0.5 mmoles) lithium chloride and/or 0.1 ml (excess) methyl iodide. Prior to GLPC analysis 0.5 ml pentane and 0.5 ml to 1.0 ml water was added to the reaction mixture.

9. <u>The reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride with $RhCl[P(C_6H_5)_3]_3$</u>

0.83 Grams (1 mmole) $RhCl[P(C_6H_5)_3]_3$ was weighed into a 25 ml round bottom flask equipped with a septum inlet, a gas inlet tube and a magnetic stirring bar. After flushing the system with nitrogen, 10 ml dichloromethane, THF, or benzene was added. The dichloromethane and THF solutions were cooled to -78°C, while the benzene solution was cooled in an ice bath. After cooling, 0.32 grams (1.0 mmole) *trans*-3,3-dimethyl-1-butenylmercuric chloride was added all at once while backflushing with nitrogen. The benzene solution reacted immediately at 0°C, while the dichloromethane and THF reactions did not react at -78°C, but reacted rapidly somewhere between -78°C and 25°C. Although various purification procedures were tried, the following procedure seemed to work best. Ether was added producing a reddish solid and a yellow solution. The filtrate was discarded and the solid dissolved in dichloromethane, washed with saturated ammonium chloride, dried over anhydrous sodium sulfate and concentrated to give a red solution. Pentane was then added producing a red orange powdery solid. Although further attempts were made to recrystallize these solids, multiple washings with ether after the pentane treatment seemed preferable. The yields of solid products were typically 0.7 grams crude to 0.4 grams purified, 71% yield crude to 41% yield purified if the product is Rh[CH=CHC(CH$_3$)$_3$]Cl(HgCl([P(C$_6$H$_5$)$_3$]$_2$. All compounds decomposed before melting at 165 to 170°C. The nmr spectra of the consistent peaks for the compounds formed in dichloromethane or THF are presented in Table XI. (The compound formed in benzene was more complex: ^{1}H nmr(CDCl$_3$) (δ6.8-7.8(m), δ5.83(d of m), δ5.10(d of m), δ1.13(s), δ1.03(s), δ0.85(s) and consequently was not purified further).

The IR (KBr pellet) absorptions occur at 3060 s, 2960 vs, 2910 w, 1580 m, 1565 w, 1480 s, 1440 vs, 1395 w, 1360 w, 1315 w, 1250 m. 1185 m, 1115 m, 1195 vs, 1130 m, 1000 m, 950 w, 845 w, 745 vs, 690 vs, and 520 vs cm^{-1}.

In the mass spectrum, m/e = 262 is the base peak [P(C$_6$H$_5$)$_3$]. The following m/e indicates mercury: 198, 10%: 199, 17%; 200, 23%; 201, 13%: 202, 30%; and 204, 7%.

The elemental analysis data and possible formulae are presented below:

	% C	% H	%Hg
Observed (dichloromethane preparation)	61.89	5.51	14.37
Calculated for			
Rh[CH=CHC(CH$_3$)$_3$][HgCH=CHC(CH$_3$)$_3$]Cl [P(C$_6$H$_5$)$_3$]$_3$	61.26	5.22	15.50
Rh[HgCH=CHC(CH$_3$)$_3$][P(C$_6$H$_5$)$_3$]$_3$	61.41	4.81	17.09
85% Rh[HgCH=CHC(CH$_3$)$_3$][P(C$_6$H$_5$)$_3$]$_3$ + 15% RhCl [P(C$_6$H$_5$)$_3$]$_3$	61.97	4.78	14.53
Rh[CH=CHC(CH$_3$)$_3$](HgCl)Cl[P(C$_6$H$_5$)$_3$]$_3$	57.91	4 54	16.12
90% Rh[CH=CHC(CH$_3$)$_3$](HgCl)Cl[P(C$_6$H$_5$)$_3$]$_3$ + 10% Rh[CH=CHC(CH$_3$)$_3$][P(C$_6$H$_5$)$_3$]$_3$	59.52	4.67	14.51

Table XI. Raw nmr data for the product(s) of the reaction of trans-3,3-dimethyl-1-butenylmercuric chloride and $RhCl[P(C_6H_5)_3]_3$

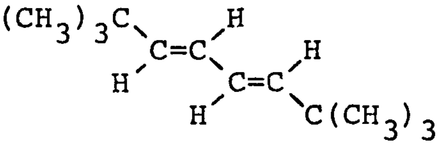
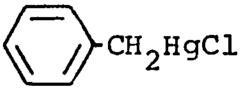
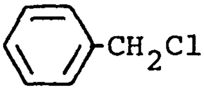
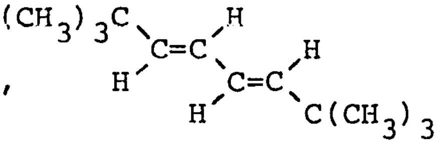
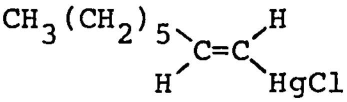
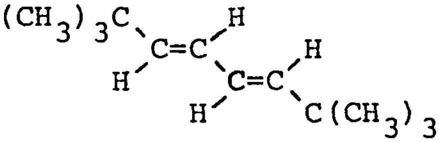
	Multiplet δ6.8-7.8	Two Multiplets δ5.05	Singlet δ1.23	Singlet δ0.85
Dichloromethane preparation:				
crude product integration[a]	62	2	6	11
purified product integration	97	2.5	21	10
THF Preparation:				
crude product integration	67	2	3.5	11.5
purified product integration	118	4	9	28

[a] Reported in the arbitrary vertical units of the nmr paper.

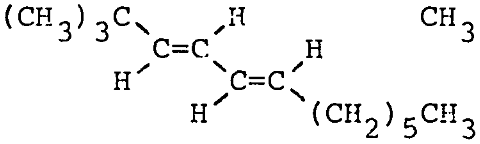
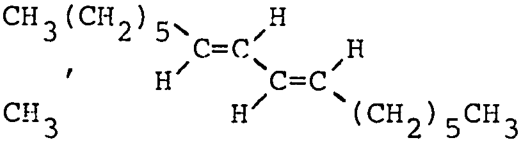
10. The reaction of other organomercurials and the compound isolated from the reaction of trans-3,3-dimethyl-1-butenylmercuric chloride and Wilkinson's catalyst

The reaction with trans-1-octenylmercuric chloride is representative. 0.0622 Grams [(0.05 mmoles) based upon $Rh[CH=CHC(CH_3)_3]Cl(HgCl)[P(C_6H_5)_3]_3]$ or [(0.063 mmoles) based upon $Rh[CH=CHC(CH_3)_3]Cl(HgCl)[P(C_6H_5)_3]_2]$, 0.0174 grams (0.05 mmoles) trans-1-octenylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen, 0.5 ml freshly distilled HMPA was added by syringe. After stirring 24 hours under nitrogen at 70°C, 0.5 ml benzene and 0.5 to 1.0 ml water was added and the benzene layer GLPC analyzed. The composition of the major peaks was verified by GC-MS to be trans,trans-2,2,7-7-tetramethyl-3,5-octadiene, trans,trans-2,2-dimethyl-3,5-dodecadiene, and trans,trans-7,9-hexadecadiene. In Table XII the GC-MS observed organic coupling products are summarized for the reactions of the compound formed from trans-3,3-dimethyl-1-butenylmercuric chloride with methylmercuric chloride, benzylmercuric chloride, and trans-1-octenylmercuric chloride, as well as the reaction containing no additional organomercurial.

Table XII. GS-MS observed organic coupling products from the reaction of different organomercurials and the compound formed from *trans*-3,3-dimethyl-1-butenylmercuric chloride and Wilkinson's catalyst

Organomercurials	GC-MS Products in order of appearance
CH_3HgCl	
	, 
	,
no added mercurial	none formed

[a] $M^+ + 2$ peak = 128 = 29% M^+.

	Observed M^+
	166
	$126,^{a}166$
 , 	166,194,222
	--

11. The reaction of $RhH[P(C_6H_5)_3]_4$ and 3,3-dimethyl-1-butyne

0.45 Grams (0.4 mmoles) $RhH[P(C_6H_5)_3]_4$ was weighed into a 250 ml heavy walled round bottom flask equipped with a stirring bar and a long stem. After flushing with nitrogen, 20 ml of ether and 0.051 grams (0.5 mmoles) phenylacetylene or 0.041 grams (0.5 mmoles) 3,3-dimethyl-1-butyne was added and the reaction vessel sealed. After stirring at room temperature 24 hours, the phenylacetylene reaction was worked up and chromatographed as described by Booth and Lloyd.[269] Since rhodium containing products were not isolated following chromatography, the 3,3-dimethyl-1-butyne reaction remained sealed for 4 months. The reaction mixture gradually darkened during this time from bright yellow to a dark red orange. Therefore it was opened, filtered and washed with ether under nitrogen. The solid was not chromatographed. The nmr indicated a multiplet at $\delta 6.8-8.2$ for the phenyl hydrogens of the triphenylphosphine ligands and a singlet at $\delta 1.08$ for the *tert*-butyl group. No vinyl hydrogens were apparent and the integration of the two peaks was too poor to allow a formula to be proposed. The IR spectrum indicated that the rhodium hydride (2100 cm^{-1}) was absent. Ir absorptions at 3040 s, 2940 w, 2840 vw, 2290 vw, 2085 vw, 1470 m, 1425 vs, 1300 w, 1175 vs, 1105 vs, 1080 s, 730 s, 705 vs, 680 vs, and 520 vs cm^{-1} indicate the presence of triphenylphosphine and a *tert*-

butyl group. An elemental analysis was obtained, but it also does not agree with any of the obvious simple mononuclear rhodium products:

	% C	% H
Observed	68.79	5.08
Calculated for $Rh[C{\equiv}C{-}C(CH_3)][P(C_6H_5)_3]_4$	76.06	5.65
$Rh[C{\equiv}C{-}C(CH_3)][P(C_6H_5)_3]_3$	74.22	5.61
$Rh[C{\equiv}C{-}C(CH_3)][P(C_6H_5)_3]_2$	71.19	5.55

The reaction of this material with methyl iodide provides the most valuable information concerning its composition.

12. The reaction of methyl iodide with the $RhH[P(C_6H_5)_3]_4$ and 3,3-dimethyl-1-butyne product

0.0487 Grams (0.05 mmoles) $Rh[HC{=}CHC(CH_3)_3][P(C_6H_5)_3]_3$ as initially assumed, but more correctly $Rh[C{\equiv}C{-}C(CH_3)_3][P(C_6H_5)_3]_3$ was weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing the system with nitrogen, 0.5 ml freshly distilled HMPA, 0.1 ml (excess) methyl iodide and 0.0057 grams (0.05 mmoles) *n*-octane was added by syringe. After stirring 6 hours at 70°C, 0.5 ml pentane and 0.5 ml water was added and the pentane layer GLPC analyzed (1/4" x 10' 10% SE-30, 50°C). Although only 1 new peak was evident, its retention time did not match that of the expected *trans*-4,4-dimethyl-2-pentene. GC-MS indicated that 4,4-dimethyl-2-pentyne

(M^+ = 96) was the product from peak matching with an authentic sample. The yield could not be obtained since the purity and composition of the rhodium compound are unknown. None-the-less the area of the product peak is small compared to the internal standard, suggesting a low yield of product.

The same product may be obtained if dichloromethane is the solvent at room temperature. However, the facility with which this reaction occurs, especially that it does not occur on the gas chromatograph injector port or the heated columns, is best demonstrated by the reaction in $CDCl_3$ at room temperature in an nmr tube.

13. The reaction of methyl iodide with the $RhH[P(C_6H_5)_3]_4$ and 3,3-dimethyl-1-butyne product at room temperature in $CDCl_3$

Methyl iodide was added to a $CDCl_3$ nmr tube containing the $RhH[P(C_6H_5)_3]_4$ and 3,3-dimethyl-1-butyne derived product. In addition to the methyl iodide singlet at δ2.15, the *tert*-butyl singlet at δ1.08 disappeared completely and moved to δ1.20, and a new singlet appeared at δ1.75. These two new peaks correspond exactly to the nmr spectrum of 4,4-dimethyl-2-pentyne in $CDCl_3$. The phenyl hydrogen multiplet also changed appearance and became narrower (δ7.1 to 7.8).

14. The reaction of trans-styrylmercuric chloride with 2 mole percent Rh(CH$_3$)I$_2$[P(C$_6$H$_5$)$_3$]$_2$ and excess methyl iodide

0.0170 Grams (0.05 mmoles) trans-styrylmercuric chloride and 0.0010 grams (0.001 mmoles) Rh(CH$_3$)I$_2$[P(C$_6$H$_5$)$_3$]$_2$·ClCH$_3$ were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser attached to a gas inlet tube and a magnetic stirring bar. At least 0.0213 grams (0.5 mmoles) lithium chloride was added in some reactions. 0.0085 Grams (0.05 mmoles) n-dodecane, 0.5 ml HMPA and 0.1 ml (excess) methyl iodide was added by syringe. 1.0 ml HMPA was required if lithium chloride was added to prevent the solution from becoming too viscous and impeding stirring. The solution was stirred under nitrogen in a 70°C oil bath. After the appropriate reaction time, 0.5 to 1.0 ml water and 0.5 ml pentane, ether or benzene was added and the organic layer subjected to GLPC analysis.

15. The reaction of bis(3,3-dimethyl-1-butynyl)mercury with 2 mole percent Rh(CH$_3$)I$_2$[P(C$_6$H$_5$)$_3$]$_2$ and excess methyl iodide

0.0091 Grams (0.025 mmoles) bis(3,3-dimethyl-1-butynyl)-mercury and 0.0010 grams (0.001 mmoles) Rh(CH$_3$)I$_2$[P(C$_6$H$_5$)$_3$]$_2$·ClCH$_3$ were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser attached to a gas inlet tube and a magnetic stirring bar. At least 0.0213 grams (0.5 mmoles) lithium chloride was added in some reactions.

0.005 Grams (0.05 mmoles) n-heptane and 0.5 ml HMPA was added by syringe. 1.0 Ml HMPA was required if lithium chloride was added. 0.1 Ml (excess) methyl iodide was also added by syringe. The solution was stirred under nitrogen in a 70°C oil bath. After the appropriate reaction time, 0.5 to 1.0 ml water and 0.5 ml pentane was added and the pentane layer subjected to GLPC analysis.

16. Attempted coupling of methyl iodide and trans-styrylmercuric chloride mediated by 50 mole percent $[Rh(H_2C=CH_2)_2Cl]_2$

0.0097 Grams (0.025 mmoles) $[Rh(H_2C=CH_2)_2Cl]_2$ and 0.0170 grams (0.05 mmoles) trans-styrylmercuric chloride was weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. At least 0.0213 grams (0.5 mmoles) lithium chloride was also added to some reactions. After flushing thoroughly with ethylene, 0.0085 grams (0.05 mmoles) n-dodecane, 0.5 ml either benzene or HMPA and 0.1 ml (excess) methyl iodide was added by syringe. After stirring 24 hours at room temperature (benzene) or 70°C (HMPA) under an ethylene atmosphere, 0.5 ml water (benzene), or 0.5 ml benzene and 0.5 to 1.0 ml water (HMPA) was added to the reaction mixtures. GLPC analysis of the benzene layers indicated propenylbenzene was not produced.

17. The attempted formation of $Pd(CH_3)I[P(C_6H_5)_3]_2$ from methyl iodide and $Pd[P(C_6H_5)_3]_4$ and the attempted coupling of $Pd(CH_3)I[P(C_6H_5)_3]_2$ with *trans*-styrylmercuric chloride

Following the sketchy procedure of Fitton, Johnson and McKeon,[270] 1.1556 grams (1.0 mmoles) $Pd[P(C_6H_5)_3]_4$ was weighed into a 250 ml round bottom flask equipped with a septum inlet, a gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 10 ml benzene and 1.419 grams (10 mmoles) methyl iodide was added by syringe. The solution immediately turned dark upon the addition of methyl iodide. After allowing the mixture to stir at room temperature for 1 hour, the excess methyl iodide and benzene were removed in vacuo and the remaining dark solid washed with ether. After several ether rinses, the ether rinse was clear but the solid was still dark brown. The solid was filtered and dried under nitrogen. In spite of a questionable melting point of 174-179°C (decomp) [the reported melting point is 151-154°C (decomp)] 0.0387 grams (0.05 mmoles) of the presumed $Pd(CH_3)I[P(C_6H_5)_3]_2$, 0.0170 grams (0.05 mmoles) *trans*-styrylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, condenser with a gas inlet tube attached and a magnetic stirring bar. 0.0085 Grams (0.05 mmoles) *n*-dodecane and 0.5 ml HMPA were added by syringe. After stirring 24 hours at 70°C under nitrogen, 0.5 ml benzene and 0.5 ml water were added. GLPC analysis of the benzene layer indicated propenylbenzene was not produced. Other attempts to produce or purify $Pd(CH_3)I[P(C_6H_5)_3]_2$ and couple it with trans-styrylmercuric chloride were similarly unsuccessful.

18. Attempted coupling of methyl iodide and *trans*-1-hexenylmercuric chloride mediated by 10 mole percent $Pd(P(C_6H_5)_3]_4$

0.0058 Grams (0.005 mmoles) $Pd[P(C_6H_5)_3]_4$ and 0.0160 grams (0.05 mmoles) trans-1-hexenylmercuric chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. 0.0057 Grams (0.05 mmoles) *n*-octane, 0.5 ml HMPA and 0.1 ml methyl iodide added by syringe. At least 0.0213 grams (0.5 mmoles) lithium chloride was also added to one reaction which also required an additional 0.5 ml HMPA. After stirring 24 hours at 70°C under nitrogen, 0.5 ml pentane and 0.5 to 1.0 ml water was added and the pentane layer GLPC analyzed. No 2-heptene was observed in the GLPC trace.

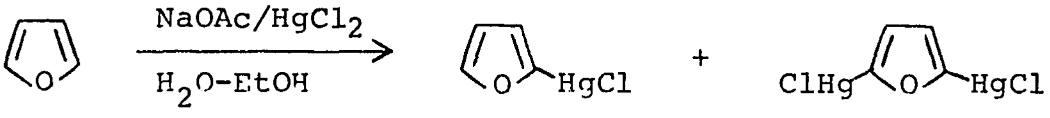
19. Coupling reaction of methyl iodide and *trans*-styrylmercuric chloride mediated by 10 mole percent $PdCl_2[P(C_6H_5)_3]_2$

0.0035 Grams (0.005 mmoles) $PdCl_2[P(C_6H_5)_3]_2$ was weighed into a 5 ml round bottom flask equipped with a round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. At least 0.0213 grams (0.5 mmoles) lithium chloride was added in some reactions. After flushing with nitrogen, 0.0085 grams (0.05 mmoles) *n*-dodecane, 0.5 ml (1.0 ml if lithium chloride was added) benzene or HMPA and 0.1 ml (excess) methyl iodide was added by syringe. Lastly, 0.0170 grams (0.05 mmoles) *trans*-styrylmercuric chloride was added all at once while backflushing with nitrogen. After stirring 24 hours at 70°C, the reactions with benzene as the solvent were GLPC analyzed directly while the benzene layer was GLPC analyzed after 0.5 ml benzene and 1.0 ml water were added to the reaction with HMPA as the solvent.

III. METHYLATION OF ARYLMERCURIALS: SYNTHESIS OF METHYL-SUBSTITUTED ARENES

A. Introduction

Following the initially successful coupling of vinylmercurials and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$, the analogous coupling with arylmercurials forming methyl-substituted arenes deserved investigation. The direct mercuration of arenes an electrophilic substitution reaction has been extensively studied and demonstrated to be quite general.[272,277] The mercuration of arenes too activated for typical Friedel-Crafts alkylations like furan (Eq. 45),[278] thiophene (Eq. 46),[279] phenols (Eq. 47)[280] or aromatic amines (Eq. 48)[281] is known. The mercuration of arenes too deactivated for



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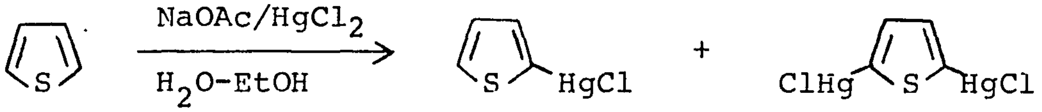

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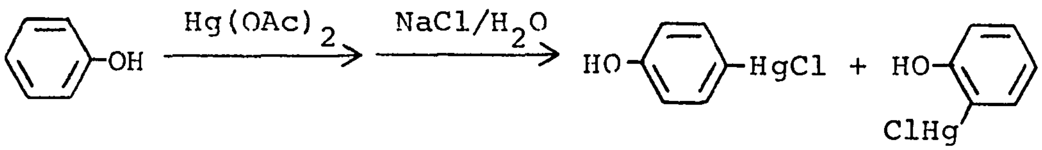

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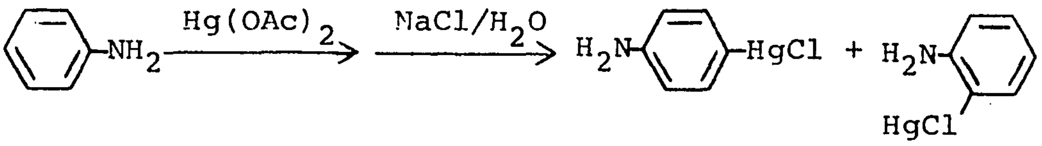

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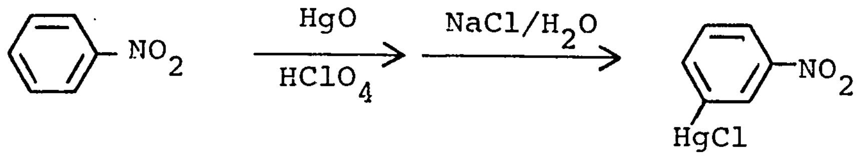
typical Friedel Crafts alkylations like nitrobenzene (Eq. 49) or benzoic acid (Eq. 50) is also known.[217] Since arenes



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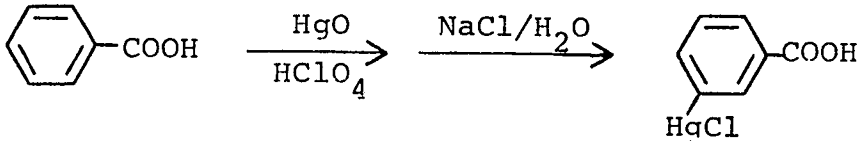
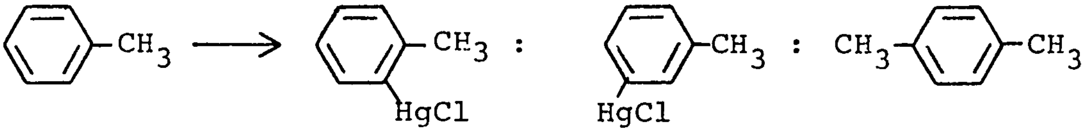


(50)

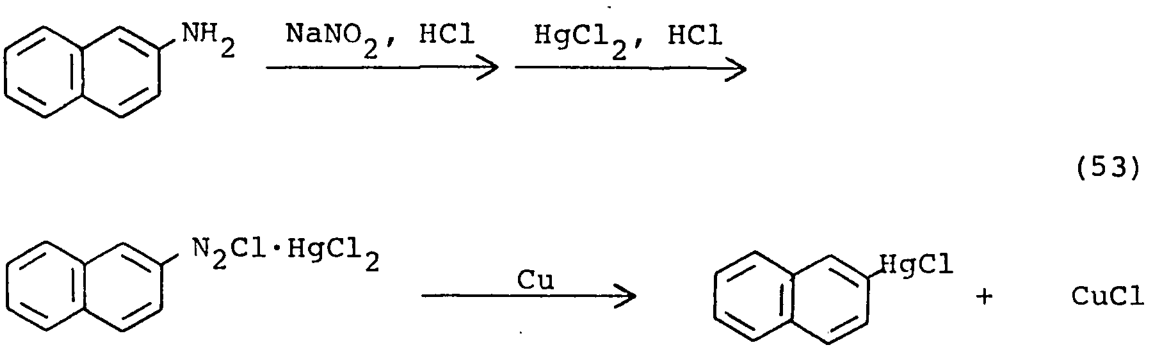
containing substituents sensitive to Grignard reagents or alkyl lithium compound may be directly mercurated, an alkylation reaction of arylmercurials would be valuable synthetically. One possible disadvantage of the direct mercuration is the possible formation of mixtures of ortho, meta and para isomers, yet conditions yielding predominantly one isomer are often known and isomerically pure compounds can usually be obtained by simple recrystallization procedures (Eqs. 51 and 52).[282,283] Complimentary to direct mercuration is the diazo



$$\xrightarrow{Hg(OAc)_2}\xrightarrow{NaCl} 43 \quad : \quad 13 \quad : \quad 43 \qquad (51)$$

$$\xrightarrow[\substack{HClO_4 \\ 25°C}]{Hg(OAc)_2}\longrightarrow 19 \quad : \quad 7 \quad\quad 74 \qquad (52)$$

method which also tolerates functionality sensitive to Grignard reagents and organolithium compounds and produces the desired mercurial free of other undesired isomers.[272,279] In this procedure a double salt of an aryldiazonium halide and a mercuric halide is decomposed by copper (Eq. 53).[284]



(53)

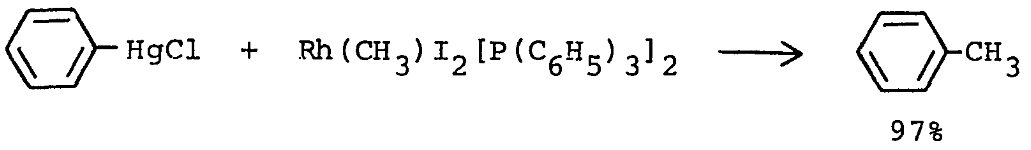
In addition to other syntheses of arylmercurials, most notably the Grignard or organolithium syntheses, the ease and versatility of direct mercuration and the specificity and versatility of the diazo synthesis of mercurials suggest the alkylation of arylmercurials might be useful in the synthesis of some arenes not easily obtained by other routes.

B. Results and Discussion

1. Initial Studies

Phenylmercuric chloride and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ were allowed to react under the previously established coupling conditions, excess lithium chloride in HMPA at 70°C for

24 hours. An essentially quantitative yield of toluene was detected by GLPC analysis (Eq. 54). Although 24 hours



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reaction time is apparently required for the highest yields, the extent of reaction after just one hour is substantial (Table XIII). THF and ether as well as the effect of one equivalent of triphenylphosphine were investigated for the reaction of phenylmercuric chloride coupling with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ in the presence of excess lithium chloride (Table XIV). HMPA however promotes the reaction to the greatest extent.

The coupling reactions of di-p-tolylmercury (Eq. 55), p-anisylmercuric chloride (Eq. 56) and 2-chloromercurithiophene (Eq. 57) with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ were also tried.

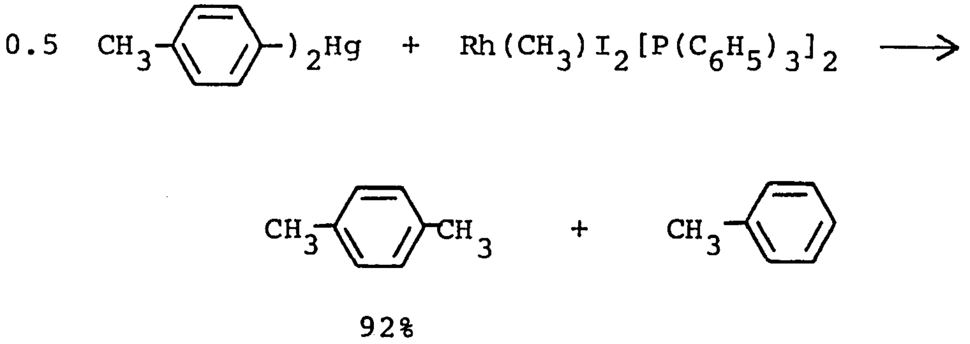

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Table XIII. Effect of time on the reaction of phenylmercuric chloride with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

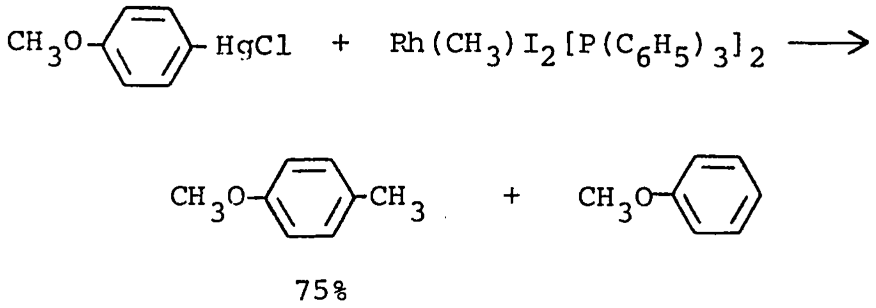
$$Rh(CH_3)I_2[P(C_6H_5)_3]_2 \quad + \quad C_6H_5HgCl \xrightarrow[\substack{LiCl \\ 70°C}]{HMPA} C_6H_5CH_3$$

Time h	Toluene GLPC Yield,%
1	68,72
3	83
6	91
12	93
24	97,92,100

Table XIV. The effect of solvent, temperature, and added triphenylphosphine on the methylation of phenylmercuric chloride

$$Rh(CH_3)I_2[P(C_6H_5)_3]_2 + C_6H_5HgCl \longrightarrow C_6H_5CH_3$$

Solvent	Added reagents	Temperature °C	Time h	Toluene GLPC Yield,%
HMPA	LiCl	70	24	97,92,100
Et_2O		25		9
THF		65	3	26
	1 eq $P(C_6H_5)_3$		24	29
				18



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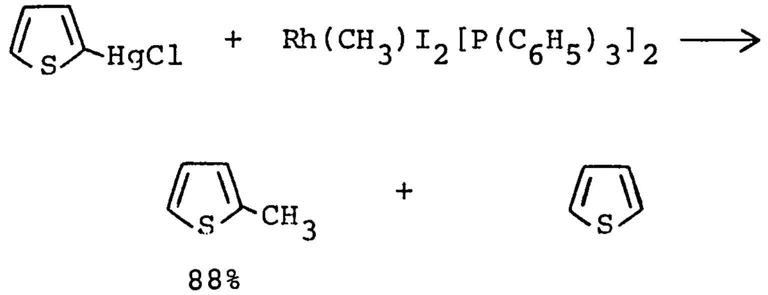
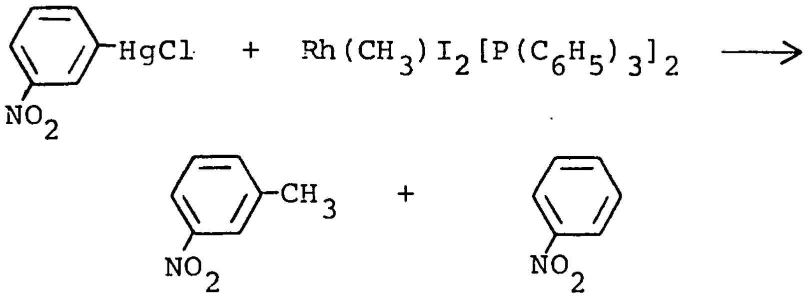


(57)

The observed yields, determined by GLPC analysis were a little lower than usual: 92%, 75%, and 88% for p-xylene, p-methylanisole and 2-methylthiophene respectively. The yield for p-xylene is based upon transfer of both organic groups of the mercurial. Upon closer examination, the GLPC traces showed a smaller peak prior to the peaks corresponding to p-xylene, p-methylanisole and 2-methylthiophene which corresponds to toluene, anisole and thiophene respectively.

This side reaction was more pronounced in the reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and m-nitrophenylmercuric chloride (Eq. 58), m-carbomethoxyphenylmercuric chloride (Eq. 59), 3-chloromercuripyridine (Eq. 60), and 2-chloromercurinaphthalene (Eq. 61) under the standard reaction conditions.



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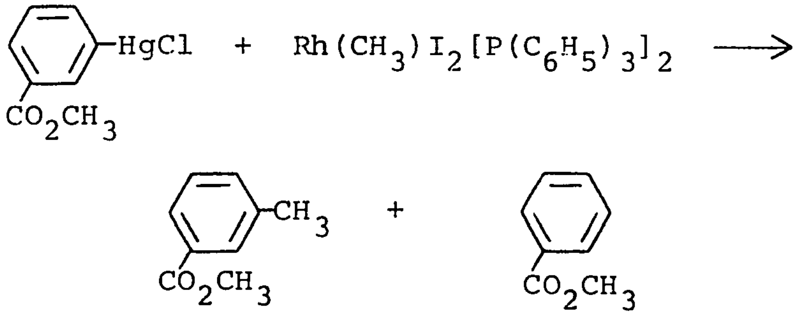

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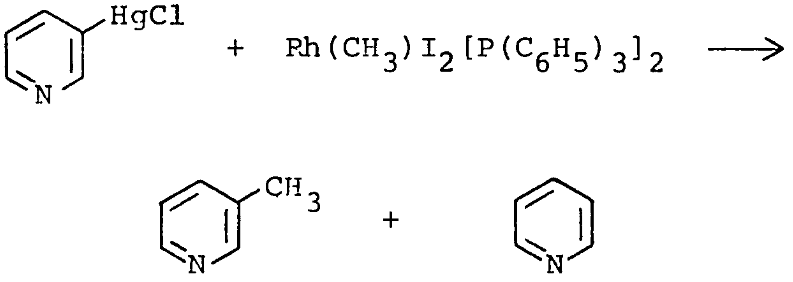

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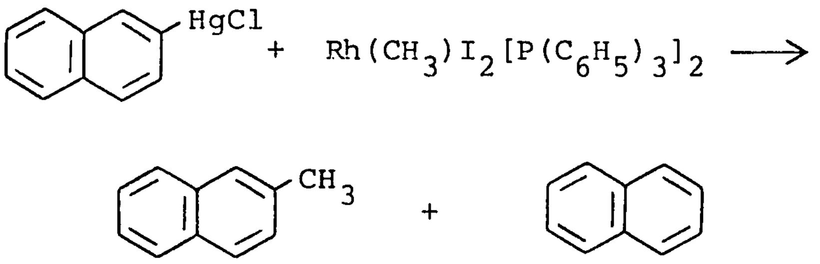


(61)

The GLPC traces consistently showed an approximately 4:1 ratio of methylated arene to arene. In these initial studies only the ratios of these two products are reported due to the fact that the corrected yields obtained using an internal standard are impossible. For a yet undetermined reason, the use of functionalized GLPC liquid phases such as carbowax, UCON, FFAP, or DC-550 with these arenes and normal alkanes as internal standards resulted in unusually high and extremely variable correction factors (response ratios) with a thermal conductivity detector which consequently gave impossibly high yields. Much later in this study it was noticed that by employing only SE-30 columns (separated predominantly by boiling point differences) reasonable and fairly consistent correction factors were obtained. The SE-30 column and addition of benzene (to extract the arene and hydrocarbon standard) and water (to dissolve HMPA) prior to analysis gave yields which were believable.

Initially it was hoped that systematic changes in the experimental conditions would reduce the side reaction. Supposing a radical abstraction of hydrogen atom from the solvent was responsible for the hydrogen substituted product, we carried out the reaction at lower temperatures and in the dark with m-nitrophenylmercuric chloride (Table XV). These changes, however, did not appreciably change the outcome of the reaction. The reaction was also carried out with other inorganic salts in place of lithium chloride (Table XVI), but these other salts generally produced a greater proportion of the hydrogen substituted product. The most encouraging

Table XV. Effect of temperature and light on the ratio of nitrotoluene to nitrobenzene in the methylation of m-nitrophenylmercuric chloride with $Rh(\bar{C}H_3)I_2[P(C_6H_5)_3]_2$

Temperature °C	Conditions	Ratio: $\underline{m}$-NO_2-$C_6H_4CH_3/C_6H_5NO_2$ [a,b]
100	lab light	8.7
70		4.1,2.1
	dark	5.4
50	lab light	1.6
	dark	4.0
35		2.5
5	lab light	∞ (3.7)[c]
	dark	∞ (4.0)[c]

[a] Ratio is from yields determined by GLPC analysis.

[b] Ether was added prior to analysis.

[c] 24 Hours after the ether was added, the reaction was analyzed again. Therefore, the reaction continues at room temperature after the addition of ether.

Table XVI. The effect of added salts on the ratio of nitrotoluene to nitrobenzene in the methylation of m-nitrophenylmercuric chloride with $\overline{Rh}(CH_3)I_2[P(C_6H_5)_3]_2$

Added Salt	Temperature °C	Ratio: m-$NO_2C_6H_4CH_3/C_6H_5NO_2$[a,b]
LiCl	70	4.1,2.1
NaI		1.5,1.2
	125	3.1[c]
LiI	70	1.4
	18	2.2
NaI		1.6
NaOAc		-[d]
$NaOCH_3$		-[d]
LiCl plus CH_3I		4.0,4.7

[a] Ratio is from yields determined by GLPC analysis.

[b] Ether was added prior to analysis.

[c] This reaction was allowed to run in the dark.

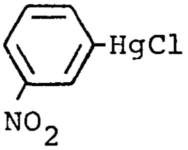
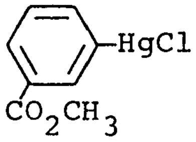
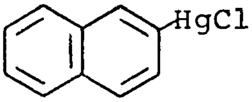
[d] No nitrotoluene was formed.

results were seen when the reaction was carried out at reduced temperatures (Table XV). The hydrogen substituted product was effectively eliminated at 5°C as evidenced by the very high ratio of nitrotoluene to nitrobenzene. However, an analysis 24 hours later after stirring at room temperature with ether shows that the reaction continues at room temperature in the manner observed previously to produce the usual 4 to 1 ratio of nitrotoluene to nitrobenzene. The yields at 5°C are only approximately 20-30% of the maximum yields observed after 24 hours at 70°C with excess lithium chloride. Table XVII also illustrates that the methylated products are formed nearly exclusively at 18°C, but the yields (determined using the SE-30 column for the analysis) are substantially reduced for *m*-nitrophenylmercuric chloride, *m*-carbomethoxyphenylmercuric chloride and 2-chloromercurinaphthalene.

In addition to selectivity, the most reasonable success this methylation might achieve is that it be catalytic with respect to the methylrhodium species. Therefore the effect of excess methyl iodide was of interest. In Table XVI, a reaction with both excess lithium chloride and excess methyl iodide displayed the usual selectivity at 70°C, an approximate 4 to 1 ratio of nitrotoluene to nitrobenzene. In Table XVII, a reaction with excess methyl iodide reacted nearly analogously with respect to yield and selectivity to a reaction

Table XVII. Product distribution for the methylation of m-nitrophenylmercuric chloride, m-carbomethoxyphenylmercuric chloride and 2-chloromercurinaphthalene at 18°C

$$Rh(CH_3)I_2[P(C_6H_5)_3]_2 \; + \; ArHgCl \; \xrightarrow[\text{LiCl} \; 18°C]{\text{HMPA}} \; ArCH_3$$

Mercurial	Time h	Methyl-substituted product GLPC Yield,%	Hydrogen-substituted product GLPC Yield,%
	1	18	5
		24[a]	0
	3	25	1
	6	31,36	1,1
	12	27	2
	24	30	3
	1	31	trace
	12	34	trace
	24	26	trace
	1	38	trace
	12	43	trace
	24	52	trace

[a] No LiCl was added; excess CH_3I was added instead.

with excess lithium chloride. These results suggest that excess lithium chloride or excess methyl iodide might be interchangeable. Tables XVIII and XIX illustrate this further. Table XVIII lists the yields for the reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and p-anisylmercuric chloride at 70°C with excess lithium chloride or excess methyl iodide. The yields and selectivities after 24 hours are quite similar, but the yield after 1 hour is substantially improved with excess methyl iodide. The addition of both excess lithium chloride and methyl iodide reflects the reactivity pattern of excess lithium chloride alone more than excess methyl iodide alone. The yields for the reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and m-nitrophenylmercuric chloride under similar conditions are listed in Table XIX.[13] Most surprisingly the yields and selectivities with respect to time are quite similar for p-anisylmercuric chloride and m-nitrophenylmercuric chloride. A greater difference in the ratio of reactions for p-anisylmercuric chloride and m-nitrophenylmercuric chloride might have suggested a reason for the appearance of the hydrogen substituted product and/or the slower rate of reaction of the arylmercurials (relative to the vinylmercurials) with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$, excess lithium chloride and HMPA at 70°C.

Supposing that acidic species might be responsible for the hydrogen substituted product, we carried out the

Table XVIII. Effect of time and added reagents on the methylation of p-anisylmercuric chloride with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

$$Rh(CH_3)I_2[P(C_6H_5)_3]_2 + \underline{p}\text{-}CH_3O\text{-}C_6H_4\text{-}HgCl \xrightarrow[70°C]{HMPA} \underline{p}\text{-}CH_3O\text{-}C_6H_4\text{-}CH_3$$

Added reagents	Time h	$\underline{p}$-CH_3O-$C_6H_4CH_3$ GLPC Yield,%	CH_3O-C_6H_5 GLPC Yield,%
Excess LiCl	1	20(43)[a]	26(57)[a]
	6	42(56)	33(44)
	12	60(83)	12(17)
	24	86(88)	12(12)
Excess CH_3I	1	91(92)	8(8)
	6	95(92)	8(8)
	12	83(91)	8(9)
	24	100(91)	10(9)
Excess LiCl and CH_3I	12	13(16)	67(84)

[a] Yields in parentheses are normalized for 100% conversion

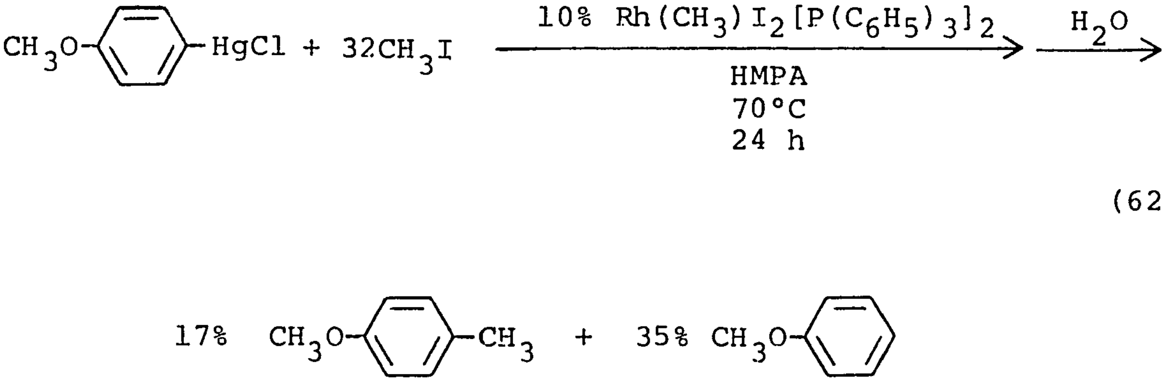
Table XIX. Effect of time and added reagents on the methylation of m-nitrophenylmercuric chloride with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

$$Rh(CH_3)I_2[P(C_6H_5)_3]_2 + \underline{m}\text{-}NO_2\text{-}C_6H_4\text{-}HgCl \xrightarrow[70\,^\circ C]{HMPA} \underline{m}\text{-}NO_2\text{-}C_6H_4CH_3$$

Added reagents	Time h	m-NO_2-$C_6H_4CH_3$ GLPC Yield,%	m-NO_2-C_6H_5 GLPC Yield,%
Excess LiCl	1	50(74)[a]	18(26)[a]
	6	53(77)	16(23)
	12	71(87)	11(13)
	24	68(87)	10(13)
Excess CH_3I	1	70(83)	14(17)
	6	88(86)	14(14)
	12	75(95)	4(5)
	24	110(97)	3(3)
Excess LiCl and CH_3I	1	59(75)	20(25)
	6	61(76)	19(24)
	12	73(86)	12(14)
	24	58(89)	7(11)

[a] Yields in parentheses are normalized for 100% conversion to methyl- and hydrogen-substituted products.

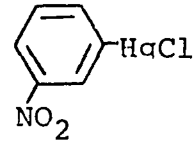
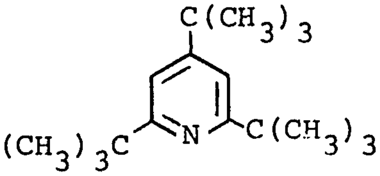
aryl-methyl coupling in the presence of various organic and inorganic bases (Table XX). Since it had already been established that excess methyl iodide did not hinder the coupling reaction and that the coupling reaction was partially catalytic, 2 mole/percent $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ was utilized for these reactions. While employing lithium carbonate with or without lithium chloride gave the highest yield of methyl-substituted product relative to the hydrogen substituted product, the addition of bases does not promote exclusive formation of the methyl-substituted product. Quenching a reaction between p-anisylmercuric chloride and excess methyl iodide catalyzed by $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ with 10% sodium hydroxide had no effect on the yield of the methyl substituted product, but did decrease the amount of hydrogen substituted product (Eqs. 62 and 63).

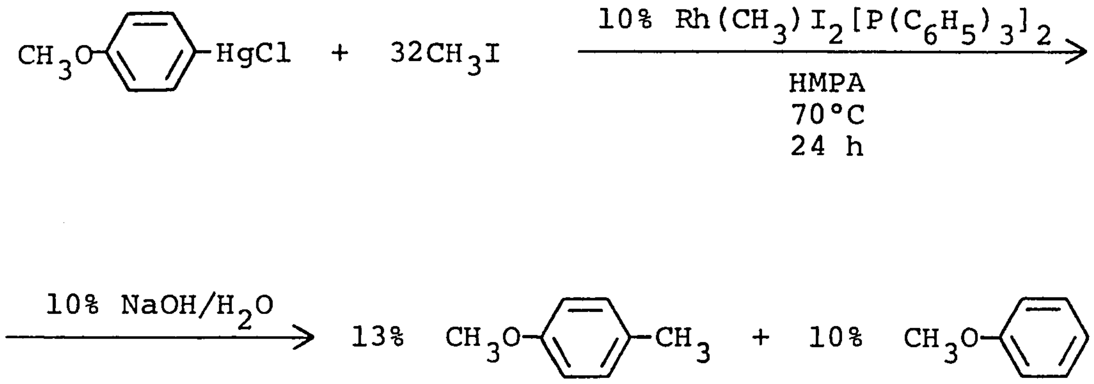


(62)

Table XX. Effect of added salts and bases on the methylation of arylmercurials with excess methyl iodide catalyzed by 2 percent $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

$$ArHgCl + 32CH_3I \xrightarrow[\text{HMPA} \quad 70\,°\text{C} \quad 24\ \text{h}]{2\%\ Rh(CH_3)I_2[P(C_6H_5)_3]_2} ArCH_3 + ArH$$

Mercurial	Added Reagents	Base	$ArCH_3$ GLPC Yield,%	ArH GLPC Yield,%
	--	Et_3N	trace,0	trace,37
	LiCl		0,3	trace,83
	$(CH_3)_4N^+I^-$	--	2,5	16,10
	--	Li_2CO_3	6	3
	LiCl		10	9
	--	$NaHCO_3$	7	12
	LiCl		5	22
	--	$NaH_2PO_4 \cdot H_2O$	1	31
	LiCl	MgO	6	29
			5	43
	LiCl		0	17
	--	--	7	41
		Li_2CO_3	17	7
		Na_2HPO_4		50



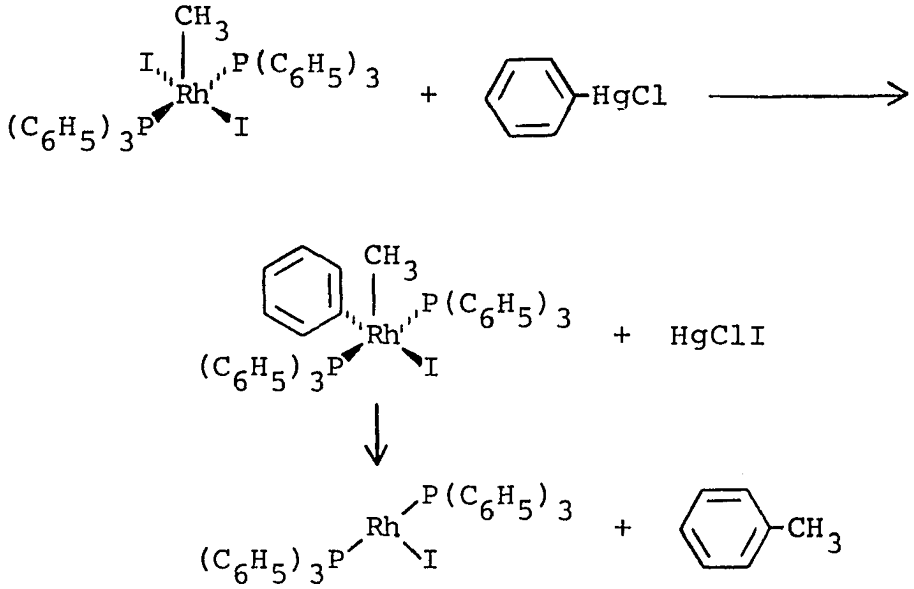
(63)

The futility of these efforts to promote methylation exclusively suggested that perhaps understanding the source of this side reaction might lead to its diminution or elimination. Some mechanistic aspects of this reaction therefore follow.

2. Mechanistic considerations

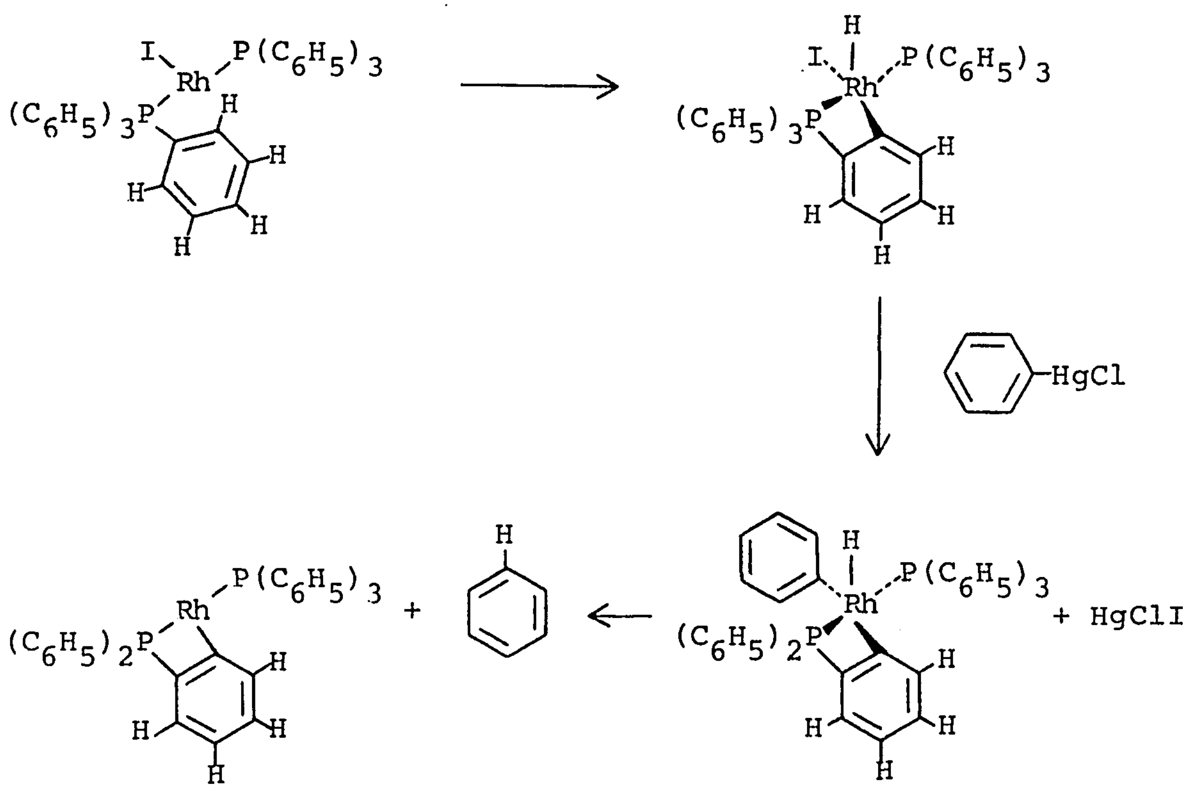
A scheme similar to that accounting for the methylation of vinylmercurials may be drawn for the methylation of arylmercurials. Transmetalation of the arylmercurials with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ forms a diorganorhodium compound which reductively eliminates forming the methyl arene and a rhodium(I) halide (Scheme 36). A similar reductive elimination has been reported by Semmelhack and Ryono.[16] However, in the methylation of vinylmercurials or alkynylmercurials the side reaction producing the hydrogen substituted product was not noticed. It may have been present in the attempted methylation of alkylmercurials since one of the products of the attempted methylation of decylmercuric chloride was decane. Initially it seemed reasonable

Scheme 36



that the source of the hydrogen was related to the methylating rhodium species. A rhodium hydride might be formed from a rhodium(I) species via the oxidative addition of an ortho hydrogen of a coordinating triphenylphosphine ligand (Scheme 37). The rhodium(I) species may be formed from the elimination of methyl iodide from $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ or a transmetalation, reductive elimination sequence. As presented in Scheme 37,[18] transmetalation and subsequent reductive elimination form the hydrogen-substituted product analogous to the methyl-substituted product. This suggested scheme is similar to the established formation of methane from methyltris(triphenylphosphine)rhodium(I) upon heating (Chapter I, Scheme 8).[44] However, when an attempted catalytic reaction produced more than one equivalent of hydrogen substituted

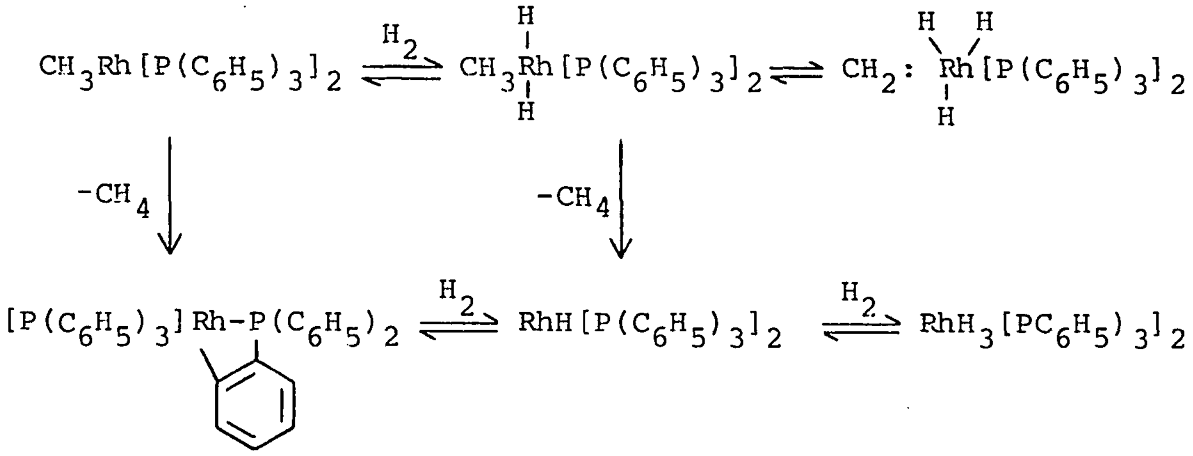
Scheme 37



product per equivalent of rhodium reactant the "reduction" of the arylmercurial via a rhodium hydride derived from an ortho hydrogen of a coordinated triphenylphosphine was plausible no longer.

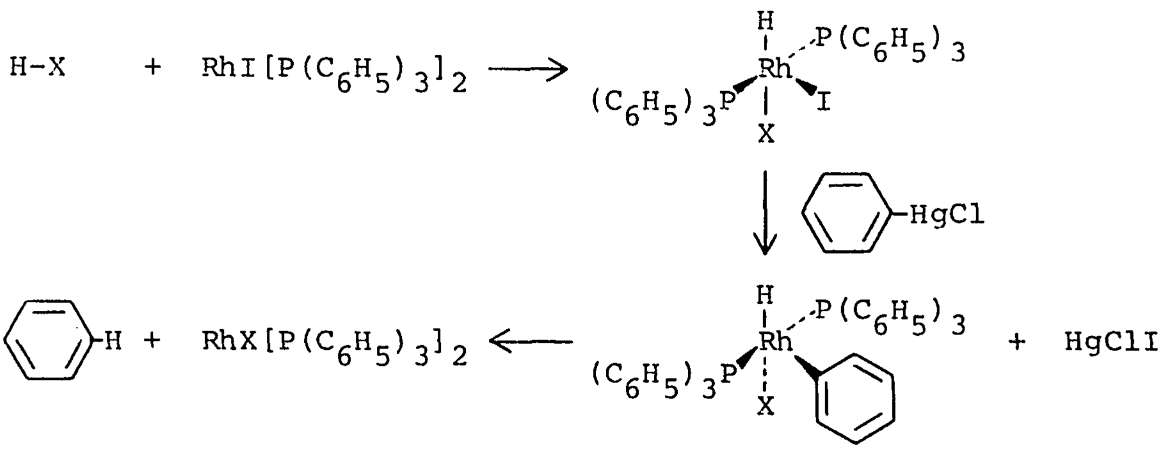
Other routes to a rhodium hydride might be considered. A methylrhodium species has been proposed to form a rhodium-hydride via a metal-carbene species (Scheme 38).[285] However, since the initial communication suggested this process, no additional evidence has been provided to support it.

Scheme 38

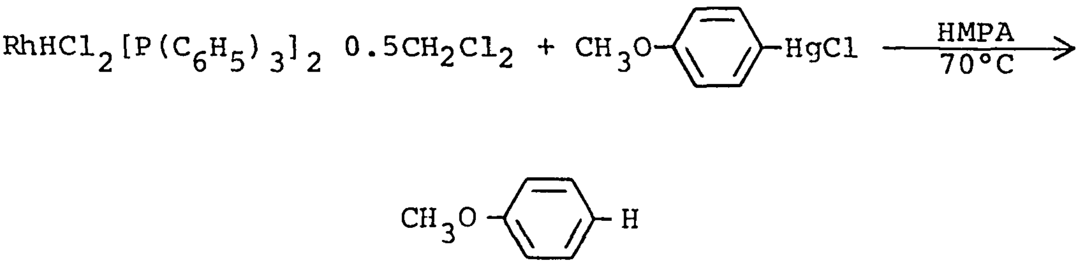


If acid were generated in the reaction mixture a rhodium-hydride might be formed via the oxidative addition of the acid to a rhodium(I) species, analogous to the reaction of Wilkinson's catalyst and hydrogen halides. If followed by transmetalation and reductive elimination, this sequence could also produce the hydrogen substituted product (Scheme 39).

Scheme 39

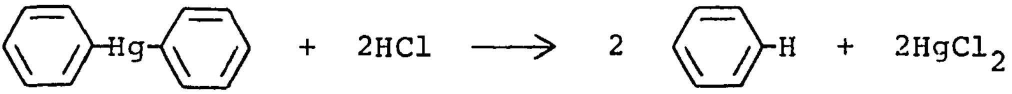


The reaction of $RhHCl_2[P(C_6H_5)_3]_2$ $0.5CH_2Cl_2$ and p-anisylmercuric chloride in HMPA at 70°C which does produce anisole also further substantiates this possibility (Eq. 64). The



(64)

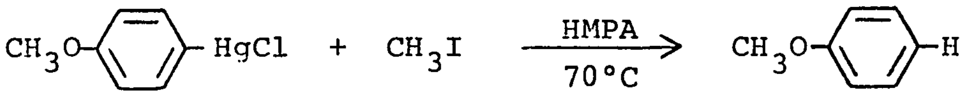
latter proposal for obtaining the rhodium hydride involves the oxidative addition of an acid to the rhodium(I) species. However, the acidolysis of mercurials also occurs and has been extensively studied (Eq. 65).[272,277]



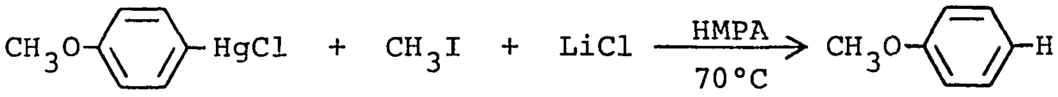
(65)

In spite of the numerous attempts to maximize the methyl-substituted product and minimize the hydrogen substituted product, the reaction yielding the hydrogen substituted product persisted. Changing conditions showed that the hydrogen substituted product might be eliminated at lower reaction temperatures, but the methylation reaction rate was also severely reduced. Some added inorganic or organic bases seemed to reduce the amount of hydrogen substituted product, but did not completely eliminate it. The fact that *p*-anisylmercuric chloride and *m*-nitrophenylmercuric chloride seemed to react similarly with respect to rates and distributions of the hydrogen and methyl-substituted products was also bewildering.

In the midst of this confusion, *p*-anisylmercuric chloride, was reacted with HMPA and excess methyl iodide. The methylrhodium species was not added. However, with or without added lithium chloride, anisole was formed (Eqs. 66 and 67).

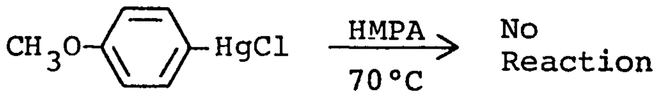


(66)



(67)

In related experiments, anisole was also formed in the reaction of *p*-anisylmercuric chloride, HMPA and ethyl or n-butyl iodide, but the reaction of *p*-anisylmercuric chloride, HMPA and phenyl iodide formed only a trace of anisole. The other possibilities, the reaction of the mercurial and HMPA or the mercurial, HMPA and excess lithium chloride did not produce anisole (Eqs. 68 and 69). These experiments established that while a



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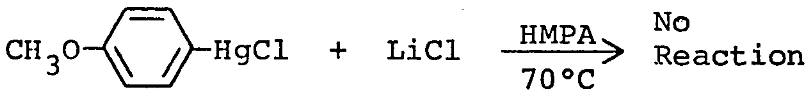
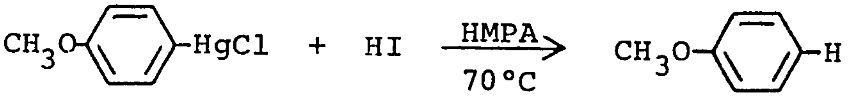


(69)

rhodium hydride might produce the hydrogen substituted product as established by the formation of anisole in the reaction of $RhHCl_2[P(C_6H_5)_3]_2$ $0.5CH_2Cl_2$ and p-anisylmercuric chloride, formation of the hydrogen-substituted product does not require the rhodium hydride intermediate.

Previously, it was mentioned that acids may react with organomercurials. However, the ease of acidolysis in a basic solvent like HMPA, and the source of an acid from HMPA and an alkyl iodide was not known. If anhydrous hydrogen iodide generated from hot decalin and iodine is allowed to react with p-anisylmercuric chloride in HMPA, anisole is formed both before and after quenching with benzene and water as indicated by GLPC analysis (Eqs. 70 and 71). The production



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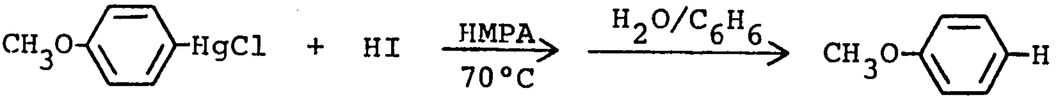
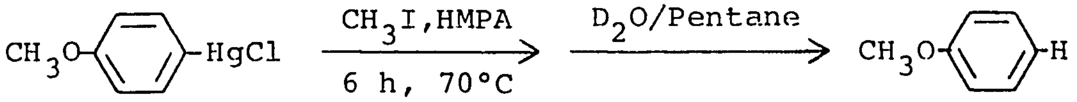


(71)

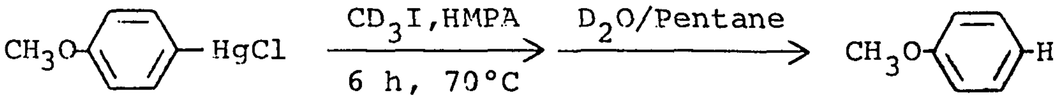
of acid and the reaction of warm HMPA and an alkyl iodide may be approached two ways: either investigation of the acid production with an arylmercurial present as a trap or investigation of HMPA and the alkyl iodide by itself.

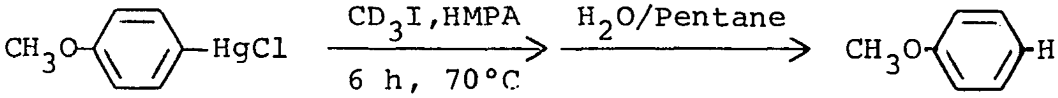
Isolation of the hydrogen-substituted arene formed in reactions containing various deuterium labeled reactants may identify the source of the hydrogen, allow a reasonable mechanism to be proposed and suggest ways to minimize this side reaction. HMPA and methyl iodide were mixed with p-anisylmercuric chloride and allowed to react at 70°C for 6 hours. The reaction was then quenched with deuterium oxide, extracted with pentane, concentrated and GLPC prepped for purification. Mass spectrometric analysis indicated that no deuterium was present in the anisole produced in this reaction (Eq. 72). HMPA, deuterated methyl iodide and



(72)

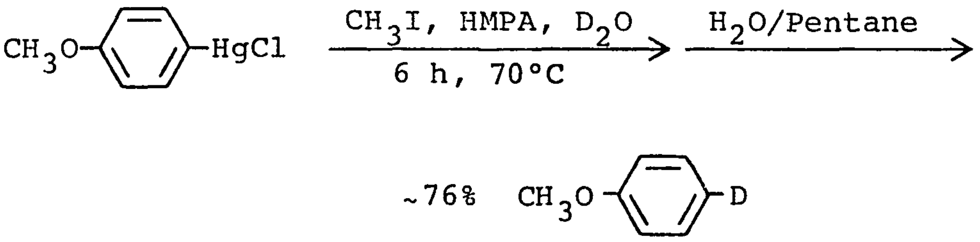
p-anisylmercuric chloride was then allowed to react under similar conditions and quenched with either water or deuterium oxide. After the usual workup and purification, mass spectrometric analysis again indicated none of the anisole formed contained deuterium (Eqs. 73 and 74). Apparently the only remaining source of hydrogen was the solvent, HMPA. Yet the


(73)


(74)

formation of tetramethylammonium iodide from the reaction of methyl iodide and HMPA in the absence of the arylmercurial suggested that partially the methyl groups of methyl iodide and the methyl groups of the N,N-dimethylamino moiety of HMPA become equivalent. Hence it was suspected that the hydrogen source was probably not HMPA and that employing deuterated HMPA might not produce the mono-deuterated anisole.

If the hydrogen source was not water employed in quenching the reaction, not the added methyl iodide and probably not HMPA, exhausting the systematic hydrogen sources forces consideration of spurious sources. HMPA deserved the first look. The HMPA utilized in most of this work was usually distilled from calcium hydride or alternatively triphenylmethyl sodium and stored under nitrogen, occasionally for periods up to four months. Perhaps the distilled and presumably dry HMPA was not dry enough. A typical methyl coupling reaction employs 0.05 millimole arylmercurial in 0.5 ml HMPA. One equivalent of water amounts to 0.0009 g which is roughly 1 microliter. To investigate whether residual water in the HMPA was the hydrogen source, HMPA, methyl iodide, p-chloromercurianisole and excess (50 microliters) deuterium oxide were allowed to react at 70°C for 6 hours. After quenching with water, and the usual workup, mass spectrometric analysis indicated that monodeuterated anisole was obtained (Eq. 75).



(75)

Therefore, the hydrogen source is identified as residual water present in HMPA or the excess lithium chloride sometimes added to promote the reaction. Investigation of the reaction of HMPA and methyl iodide alone suggests this residual water forms an acid. As previously demonstrated, the acid which is produced may react with the mercurial directly or reduce it via the rhodium hydride formed from oxidative addition of the acid to a rhodium(I) species.

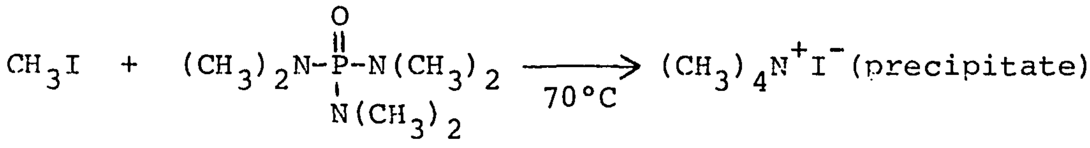
Although the propensity of the acid to oxidatively add to rhodium(I) species in HMPA was not determined, exclusive formation of the hydrogen substituted arene via either the direct protonolysis of the mercurial or the rhodium hydride mediated pathway may not be easily distinguished in this system. This side reaction was first noticed and most prominent with arylmercurials containing electron withdrawing groups especially: m-nitrophenylmercuric chloride, m-carbomethoxyphenylmercuric chloride, 3-chloromercuripyridine and 2-chloromercurinaphthalene. Since the kinetics of acidolysis have been extensively studied and the relative ease of cleavage by acid determined for many mercurials, a comparison of the rates of mercurial acidolysis with the mercurials which were most prone toward forming the hydrogen-substituted product in this coupling reaction might be interesting. Considering the rates of reaction for R_2Hg and hydrochloric acid in 90% aqueous dioxane, the following series is reported: 1,3,5-$(CH_3)_3C_6H_5$ > trans-$CH_3CH{=}CH$ > p-$C_2H_5OC_6H_4$ > cis-$CH_3CH{=}CH$ > p-$CH_3OC_6H_4$ > $C_6H_5CH{=}CH$ > trans-$CH_3OCOC(CH_3){=}C(CH_3)$ > cis-$CH_3OCOC(CH_3){=}C(CH_3)$ > α-thienyl > o-$CH_3C_6H_4$ > p-$C_2H_5C_6H_4$ > p-$CH_3C_6H_4$ > cis-$C_6H_5CH{=}C(C_6H_5)$ > o-$CH_3C_6H_4$ > α-$C_{10}H_7$ > m-$CH_3C_6H_4$ > $CH_2{=}CH$ > C_6H_5 > p-FC_6H_4 > m-$CH_3OC_6H_4$ > trans-$C_6H_5CH{=}C(C_6H_5)$ > p-ClC_6H_4 > p-BrC_6H_5 > m-FC_6H_4 > m-ClC_6H_4 > $CH_3OCOC(C_6H_5){=}C(C_6H_5)$ > o-$CH_3OCOC_6H_4$ > trans-$ClCH{=}CH$ > C_2H_5 > p-$CH_3OOCC_6H_4$ > cis-$ClCH{=}CH$ > o-$CH_3OOCC_6H_4$ > n-C_4H_9 > o-ClC_6H_4 > $C_6H_5CH_2$.[277] A series containing m-chloromercuri-nitrobenzene is also reported: p-$CH_3OC_6H_4$ > p-$C_6H_5C_6H_4$ > C_6H_5 > p-FC_6H_4 > p-ClC_6H_4 >

m-$NO_2C_6H_4$.[286] As before, the reaction studied was R_2Hg and hydrochloric acid but the solvent system was a mixture of DMSO and dioxane instead of aqueous dioxane. The mercurials for which the protonolysis was especially visible, the m-nitrophenylmercuric chloride and m-carbomethoxyphenyl mercuric chloride are the mercurials which are slow to undergo protonolysis relative to other mercurials. If the electronic factors affecting methylation of the mercurial via $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ are similar to those affecting protonolysis, the methylation rates for m-nitrophenylmercuric chloride and m-carbomethoxyphenylmercuric chloride would be expected to be slower relative to those of the vinylmercurials or p-anisylmercuric chloride and 2-chloromercurithiophene. Since the methylation rates are slower, the yield of side product formed via protonolysis might be correspondingly higher.

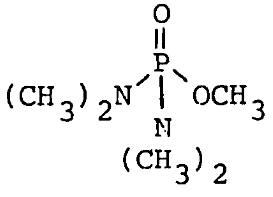
Although the hydrogen source has been identified as either residual water present in HMPA or the added lithium chloride, and minimizing the water present from these sources improves the yield of methylated product, the evidence for the formation of acid from this residual water has not been presented. A study of the reaction of HMPA and alkyl iodides suggests the hydrolysis of intermediates formed in this reaction produces acid in this system.

3. Alkylation of HMPA with alkyl iodides

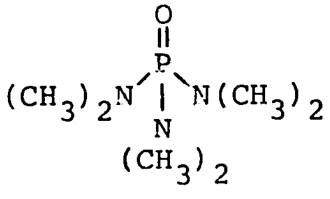
Although several alkyl iodides and HMPA react with *p*-chloromercurianisole forming anisole, only the reaction of HMPA and methyl iodide was investigated in some detail. When methyl iodide was mixed with HMPA at 70°C under nitrogen, the colorless solution gradually yellowed and simultaneously a white solid which varies from plate-like crystals to a powdery precipitate settled out. This solid was identified as tetramethylammonium iodide by the usual techniques, especially the superimposability of the IR with the IR of an authentic sample (Eq. 76). The residue left after unreacted HMPA was distilled off was dissolved in methanol to facilitate syringe handling and subjected to gas chromatography-mass spectroscopy. Analysis showed three major peaks. From the mass spectrum the three peaks in order of increasing retention times are assigned as: 13, HMPA and 14. The first and third



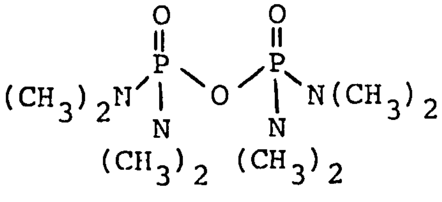
$$CH_3I \quad + \quad (CH_3)_2N-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle N(CH_3)_2}{|}}{P}}-N(CH_3)_2 \xrightarrow[70°C]{} (CH_3)_4N^+I^-\text{(precipitate)} \qquad (76)$$



13

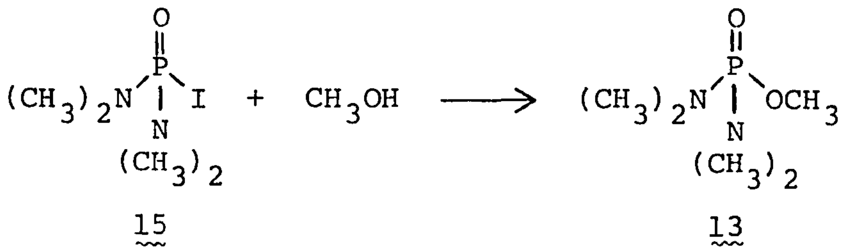


HMPA

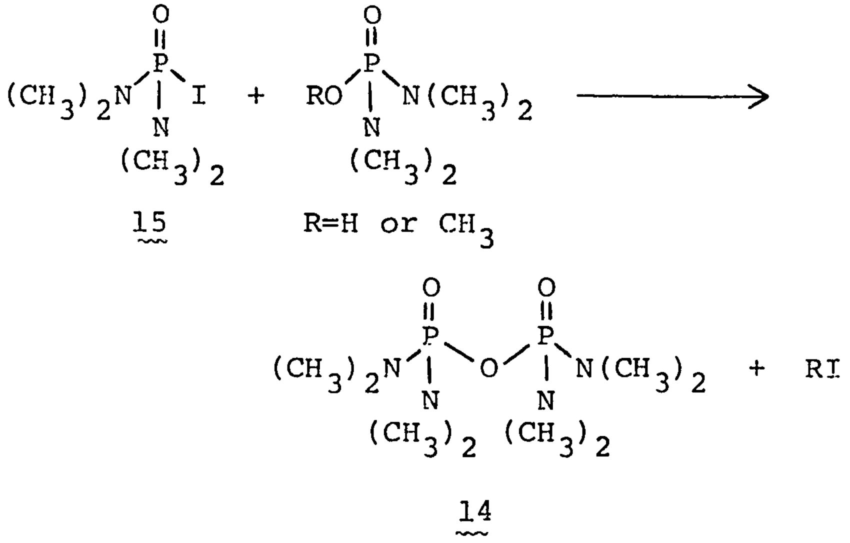


14

components might be formed in the reaction of a common intermediate, the mono-iodinated derivative 15 with methanol (Eqs. 77 and 78). Weak nmr evidence also implicates the

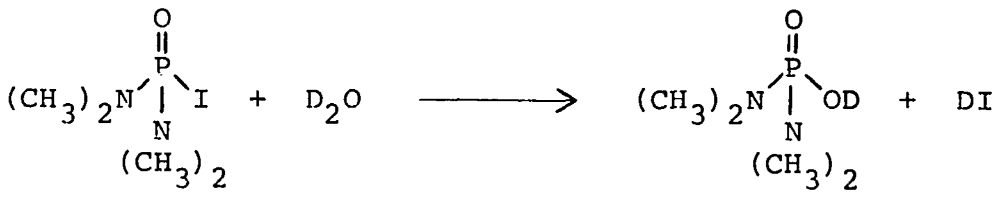


(77)



(78)

mono-iodinated derivative as an intermediate. GC prepping of the neat residue produced two major components whose nmr spectra were measured in D_2O. 16 and unreacted HMPA are consistent with the ^1H nmr spectra in D_2O. The first species might arise from hydrolysis of the mono-iodinated derivative 15 (Eq. 79). Admittedly, other similar compounds including

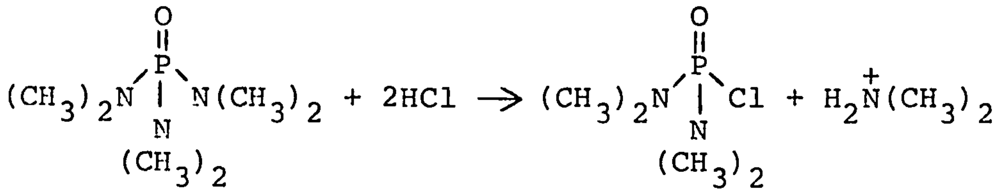


$$(CH_3)_2N-\underset{\underset{(CH_3)_2}{N}}{\overset{\overset{O}{\|}}{P}}-I + D_2O \longrightarrow (CH_3)_2N-\underset{\underset{(CH_3)_2}{N}}{\overset{\overset{O}{\|}}{P}}-OD + DI \qquad (79)$$

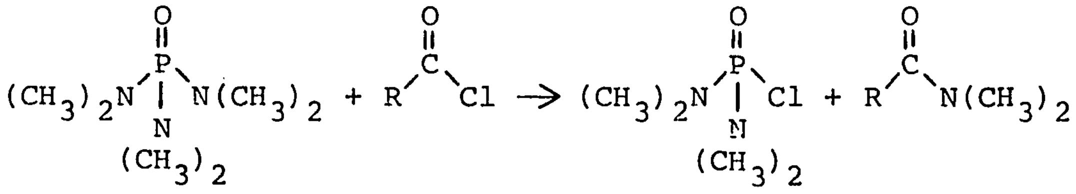
15 16

15 would also fit the observed spectra since the ^1H nmr shows only the methyl doublet due to coupling with phosphorous.

It has been reported that both hydrogen chloride[287-289] and acyl chlorides[287,288] react with HMPA to form the monochlorinated derivative (Eqs. 80 and 81). The formation of



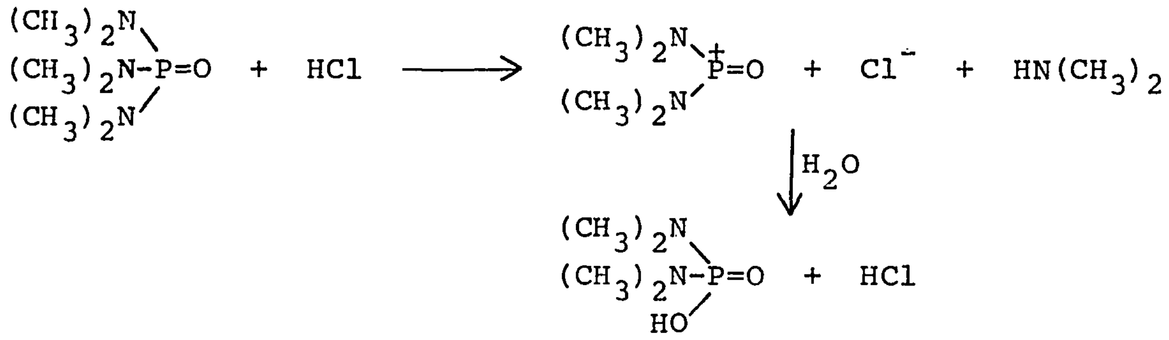
$$(CH_3)_2N-\underset{\underset{(CH_3)_2}{N}}{\overset{\overset{O}{\|}}{P}}-N(CH_3)_2 + 2HCl \rightarrow (CH_3)_2N-\underset{\underset{(CH_3)_2}{N}}{\overset{\overset{O}{\|}}{P}}-Cl + H_2\overset{+}{N}(CH_3)_2 \quad Cl^- \qquad (80)$$



$$(CH_3)_2N-\underset{\underset{(CH_3)_2}{N}}{\overset{\overset{O}{\|}}{P}}-N(CH_3)_2 + R-\overset{\overset{O}{\|}}{C}-Cl \rightarrow (CH_3)_2N-\underset{\underset{(CH_3)_2}{N}}{\overset{\overset{O}{\|}}{P}}-Cl + R-\overset{\overset{O}{\|}}{C}-N(CH_3)_2 \qquad (81)$$

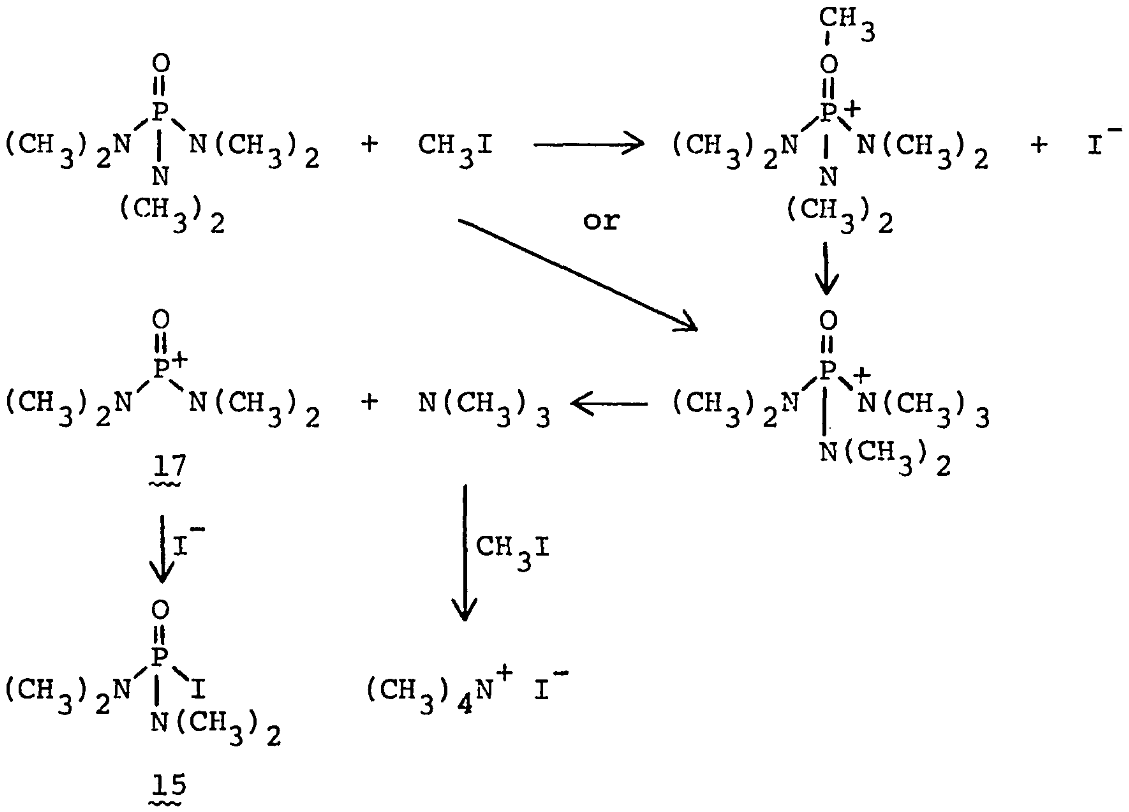
the hydroxyl derivative has been reported for the reaction of HMPA and hydrogen chloride in aqueous media (Scheme 40).[287-289] It should be noted that in the description of the HMPA-HCl adduct as a chlorinating reagent strictly anhydrous conditions were required.[289]

Scheme 40

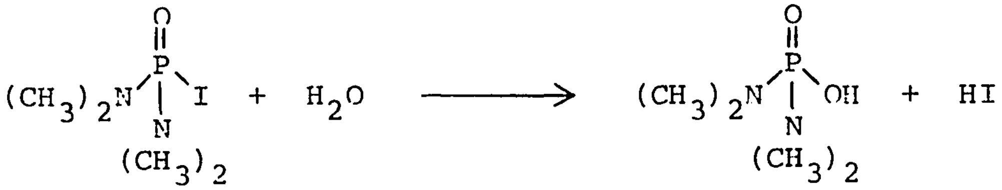


A mechanism for the alkylation of HMPA with methyl iodide analogous to either the protonation or acylation of HMPA may be proposed (Scheme 41). The end products of the alkylation

Scheme 41

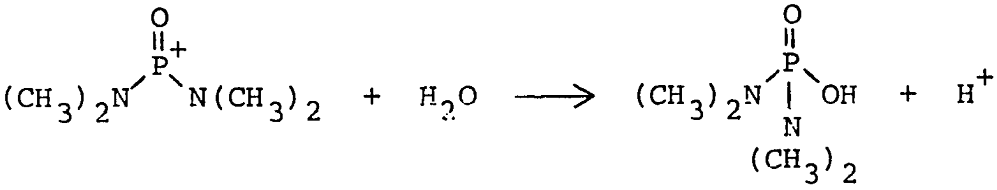


in dry HMPA are tetramethylammonium iodide and the iodinated species 15. However traces of water would be expected to react with the iodo-derivative 15 or its precursor 17 forming the hydroxyl derivative 18 and hydrogen iodide (Eqs. 82 and 83). In addition to the hydrogen iodide produced, the



$$(CH_3)_2N-\overset{O}{\overset{\|}{\underset{\underset{(CH_3)_2}{N}}{P}}}-I + H_2O \longrightarrow (CH_3)_2N-\overset{O}{\overset{\|}{\underset{\underset{(CH_3)_2}{N}}{P}}}-OH + HI \qquad (82)$$

15 18



$$(CH_3)_2N-\overset{O}{\overset{\|+}{P}}-N(CH_3)_2 + H_2O \longrightarrow (CH_3)_2N-\overset{O}{\overset{\|}{\underset{\underset{(CH_3)_2}{N}}{P}}}-OH + H^+ \qquad (83)$$

17 18

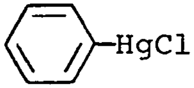
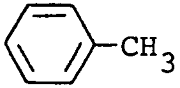
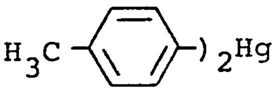
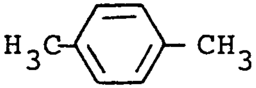
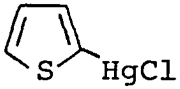
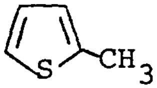
hydroxyl derivative 18 may also be a proton donor. The formation of acid was also verified in a crude manner using a pH meter (or also pH paper). A 1:1 mixture of water and HMPA registers a pH of 8.17 whereas a 1:1 mixture of water and the HMPA-methyl iodide mixture (tested after precipitation and filtration of tetramethylammonium iodide) registers a pH of 2.18.

Although the proposed iodo-derivative was not isolated, other experimental evidence and strong literature precedent imply its formation from HMPA and methyl iodide. The hydrolysis of the iodo-derivative by residual water in HMPA or lithium chloride produces acid which has been proposed to account for the formation of the hydrogen substituted arene present in the methylation of arylmercurials via $Rh(CH_3)I_2$-$[P(C_6H_5)_3]_2$. This type of reaction may not be limited to HMPA. While investigating the reaction of Rh(CO)Cl-$[P(C_6H_5)_3]_2$ and methyl iodide, Douek and Wilkinson reported that conductivity measurements indicated a reaction between methyl iodide and dimethylformamide (DMF).[90]

4. Synthesis of methyl-substituted arenes

After discovering the hydrogen source for protonolysis in the rhodium(III) methylation system is residual water present in the solvent, HMPA or the added lithium chloride, minimizing the water from these sources should noticeably increase the yield of methyl substituted arene. It was also noted that nearly equal results were obtained from the addition of excess lithium chloride or excess methyl iodide (Tables XVIII and XIX). Therefore, by omitting the lithium chloride and substituting instead excess methyl iodide and distilling the HMPA from calcium hydride immediately before each reaction, excellent yields of the methylated arene are observed with stoichiometric amounts of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and the arylmercurial (Table XXI). The protonolysis product was either eliminated or greatly reduced. Of the entries in

Table XXI. Syntheses of methyl-substituted arenes from the reaction of arylmercurials and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

Mercurial	Product	$ArCH_3$ GLPC Yield,%[a]	ArH GLPC Yield,%[a]
		97	-[b]
		95[c]	4
		97	3
		99	<2

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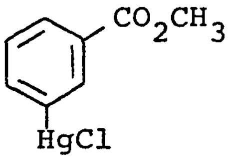
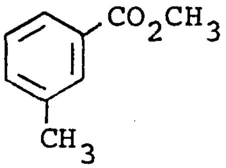
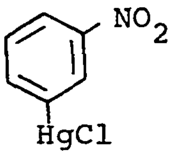
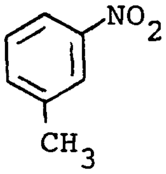
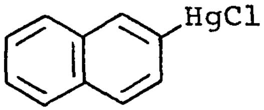
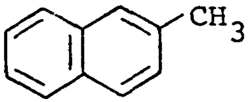
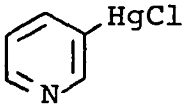
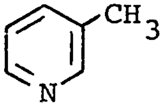
[a] Benzene and water added prior to GLPC analysis.

[b] The yield of the hydrogen substituted product, benzene was not determined.

[c] Yield is based upon alkylation of both aryl groups of the mercurial.

Table XXI. (continued)

Mercurial	Product	ArCH$_3$ GLPC Yield,%^{a}	ArH GLPC Yield,%^{a}
		91	2
		82,75,69,66	6,4,2,3
		51	<2
		--[d]	-[d]

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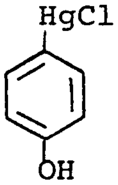
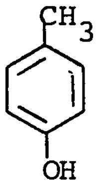
[d] Pyridine products are not observed by GLPC analysis with excess methyl iodide.

Table XXI. (continued)

Mercurial	Product	$ArCH_3$ GLPC Yield,%	ArH GLPC Yield,%[a]
		0	–[e]

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[e] Phenol is formed but the yield was not determined.

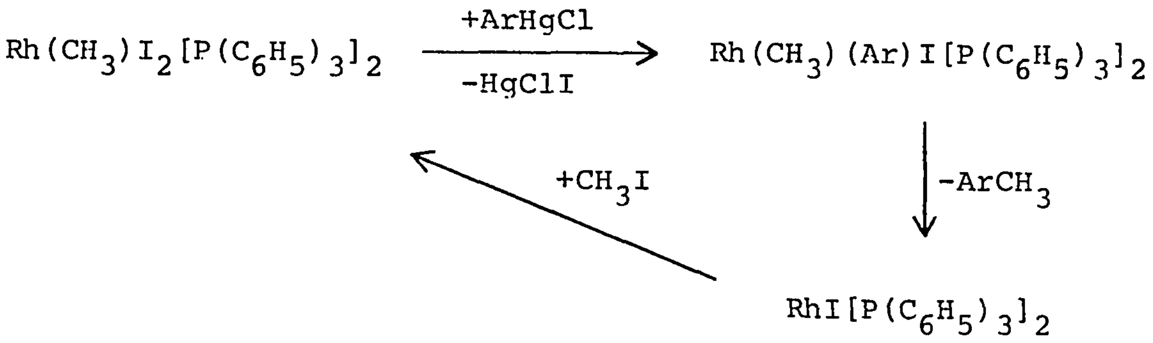
Table XXI, the yield of 2-methylnaphthalene is noticeably lower. However, this was demonstrated to be due to extraction difficulties rather than failure of the coupling reaction.

Several arylmercurials were not successfully methylated with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ under the revised conditions. With excess methyl iodide instead of lithium chloride presumably the nitrogen of pyridine is also methylated and no 3-methylpyridine is observed by GLPC. Since benzoic acid reacts with HMPA forming N,N-dimethylbenzamide, 3-methylbenzoic acid cannot be formed from 3-chloromercuri-benzoic acid and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ in HMPA. HMPA also forms complexes with phenols which may account for the absence of p-cresol in the GLPC trace for the reaction of p-chloromercuri-phenol and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$. However, a hydroxyl group per se does not cause the reaction to fail since the coupling of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and phenylmercuric chloride takes place in the presence of ethylene glycol. Alternatively the acidity of the phenol may interfere with the methyl-aryl coupling. It appears that the functionality which this coupling scheme tolerates is more dependent upon the conditions used to promote this reaction: solvent, added salts or excess methyl iodide and temperature. The interference does not appear to stem from the interaction of other functional groups with the coupling reaction itself.

5. Catalytic attempts

Although the stoichiometric reaction was finally improved by employing dry HMPA and substituting excess methyl iodide for lithium chloride, this modification did not dramatically improve the methylation of arylmercurials utilizing only a catalytic amount of $Rh(CH_3)$- of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$. Since the proposed mechanism for the coupling of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and arylmercurials is identical to that proposed for the coupling of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and vinylmercurials. The methylation of arylmercurials is also expected to be catalytic with respect to rhodium (Scheme 42).

Scheme 42



Some of the catalytic aspects of this methylation scheme have previously been mentioned in Table XX. However, the $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ mediated methylation of arylmercurials is further complicated by the competing protonolysis of the arylmercurial in the HMPA-methyl iodide solution if water is not rigorously excluded. Acidolysis interferes with the coupling reaction when only catalytic amounts of $Rh(CH_3)I_2$-

$[P(C_6H_5)_3]_2$ were employed under conditions in which the stoichiometric reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and arylmercurials produces almost exclusively the methyl-substituted arene (Table XXII). The reaction is catalytic; however, comparison of the amount of catalyst and the yield of p-xylene shows that the turnover number for methylation is low, approximately 2. Although the acidolysis of arylmercurials competes with the rhodium mediated methylation of arylmercurials, the turnover number is still unexpectedly low. The methylation of vinylmercurials also suffers catalytically because the competing dimerization of vinylmercurials which is also mediated by a rhodium(I) catalyst consumes the vinylmercurial. The related formation of biaryls from arylmercurials is also known (Eq. 84).[80] The difference in

$$\mathrm{ArHgCl} \xrightarrow[\substack{\mathrm{HMPA,\ LiCl} \\ 70\,^\circ\mathrm{C}}]{\mathrm{cat}\ [\mathrm{Rh(CO)_2Cl}]_2} \mathrm{Ar{-}Ar} \tag{84}$$

experimental conditions between diene formation (excess lithium chloride at 25°C in THF) versus biaryl formation (excess lithium chloride at 70°C in HMPA) hints that the catalytic formation of methylated arenes should be more successful. However, the facile reaction of the supposed alkynylrhodium(I) compound and methyl iodide (page 67) which presumably proceeds through oxidative addition and subsequent reductive

Table XXII. The effect of catalyst concentration on $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ catalyzed methylation of di-*p*-tolylmercury

$$(p\text{-}CH_3\text{-}C_6H_4)_2Hg \quad + \quad \text{excess } CH_3I \quad \xrightarrow[\text{HMPA} \\ 70°C]{\text{cat } Rh(CH_3)I_2[P(C_6H_5)_3]_2} \quad p\text{-}CH_3C_6H_4CH_3$$

mole % $Rh(CH_3)I_2[P(C_6H_5)_3]_2$	Time h	GLPC Yield % *p*-xylene	GLPC Yield % Toluene
10	24	18,19,22	8,8,5
	48	31	8
20	24	39	11
50		107[a]	6

[a] Actual GLPC yields obtained are reported, 107% is within experimental error.

elimination of the methyl-substituted acetylene at room temperature suggested that transfer of the organic group from the organomercurial to the organorhodium halide is the step requiring the more vigorous reaction conditions--excess lithium chloride, HMPA and 70°C. The mononuclear rhodium intermediates, 19 and 20 proposed in the transmetalation steps leading to dienes (Eq. 85) and biaryls (Eq. 86) are

$$\underset{\mathbf{19}}{[\mathrm{Rh(CH{=}CHR)Cl(HgCl)L_2}]} + \mathrm{RHC{=}CHHgCl} \longrightarrow [\mathrm{Rh(CH{=}CHR)_2(HgCl)L_2}] + \mathrm{HgCl_2} \tag{85}$$

$$\underset{\mathbf{20}}{[\mathrm{Rh(Ar)Cl(HgCl)L_2}]} + \mathrm{ArHgCl} \longrightarrow [\mathrm{Rh(Ar)_2(HgCl)L_2}] + \mathrm{HgCl_2} \tag{86}$$

different, whereas the rhodium precursor, 21 in the transmetalation step for methylation of vinyl- and arylmercurials is the same (Eqs. 87 and 88). In both cases the oxidative

$$\underset{\mathbf{21}}{\mathrm{Rh(CH_3)I_2[P(C_6H_5)_3]_2}} + \mathrm{RHC{=}CHHgCl} \longrightarrow \left[\mathrm{Rh(CH_3)(CH{=}CHR)I_2[P(C_6H_5)_3]_2}\right] \tag{87}$$

$$\underset{\mathbf{21}}{\mathrm{Rh(CH_3)I_2[P(C_6H_5)_3]_2}} + \mathrm{ArHgCl} \longrightarrow \left[\mathrm{Rh(CH_3)(Ar)I[P(C_6H_5)_3]_2}\right] \tag{88}$$

addition of either the vinyl or arylmercurial competes with the oxidative addition of methyl iodide which limits the effective methylations of the catalyst similarly for both vinyl- and arylmercurials. The oxidative addition of an organomercurial renders the rhodium inactive for the methylation reaction because the mercurial is apparently not reversibly reductively eliminated (the adduct isolated from Wilkinson's catalyst and a vinylmercurial did not produce diene under the usual coupling reaction conditions).

C. Conclusion

The reaction of arylmercurials with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ in dry HMPA and excess methyl iodide forms methyl arenes. Unfortunately, the solvent (HMPA), added reagents such as lithium chloride or methyl iodide, and the temperature (70°C) used to promote this reaction introduce competing acidolysis of the organomercurial via the alkylation of HMPA--followed by hydrolysis if water is not rigorously excluded. These conditions also somewhat limit the functional groups the reaction tolerates. Although catalytic with respect to rhodium, catalytic amounts of rhodium produce relatively low yields of methylated product probably because oxidative addition of the mercurial competes with oxidative addition of methyl iodide. Despite these limitations, the sequential transmetalation of an organo-transition metal species with either vinyl- or arylmercurials, followed by the reductive elimination of the methyl olefin or methyl arene respectively demonstrates the feasibility of carbon-carbon bond formations utilizing organomercurials and this general sequence.

D. Experimental Section

1. General

The description of the instruments used as well as routine reagents and solvent purification have been described previously.

The following commercially available mercurials were used directly, phenylmercuric chloride from Aldrich and di-*p*-tolylmercury and *p*-chloromercuriphenol from Eastman. *p*-Anisylmercuric chloride,[290] 2-chloromercurithiophene,[279,291] *m*-carbomethoxyphenylmercuric chloride,[217] *m*-nitrophenylmercuric chloride,[217], 2-chloromercurinaphthalene[284] and 3-chloromercuripyridine[277] or [292] were prepared using literature procedures.

2,4,6-Tri(*tert*-butyl)pyridine was prepared according to the literature.[292] $RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$ was prepared from Wilkinson's catalyst according to the literature.[11]

2. The reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and arylmercurials

The following procedure for the formation of toluene from phenylmercuric chloride is representative. 0.0473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0156 grams (0.05 mmoles) phenylmercuric chloride and at least 0.0213 grams

(0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen, 0.0064 grams (0.05 mmoles) n-nonane and 0.5 ml HMPA were added by syringe. After stirring 24 hours at 70°C, 0.5 ml ether was added and the reaction mixture analyzed by GLPC.

Reactions of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and phenylmercuric chloride for which the time was varied were performed and analyzed analogously after the appropriate reaction times.

$Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and other arylmercurials were reacted similarly utilizing appropriate internal standards and GLPC analysis conditions as outlined in Table XXIII.

3. The reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and phenylmercuric chloride in other solvents

0.0473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0156 grams (0.05 mmoles) phenylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. 0.0131 Grams (0.05 mmoles) triphenylphosphine was also added to one reaction. After flushing with nitrogen, 0.0064 grams (0.05 mmoles) n-nonane and 0.5 ml ether or THF were added by syringe. After stirring 24 hours at the appro-

Table XXIII. Initial analysis conditions for the synthesis of methyl-substituted arenes

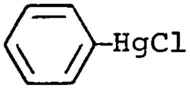
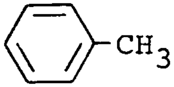
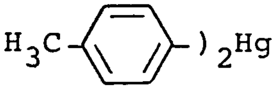
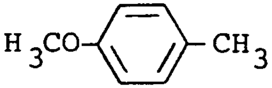
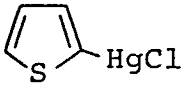
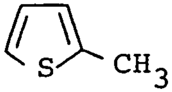
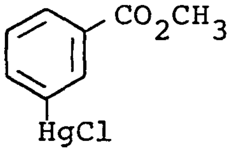
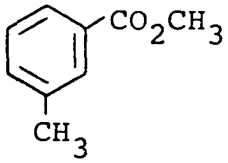
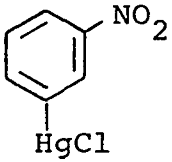
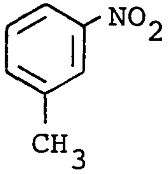
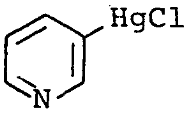
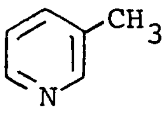
Organomercurial	Methyl-substituted arene	Internal standard	GLPC Conditions	
			Column	Temperature °C
		Nonane	1/4" x 5' 3% SE-30	70
		Decane	1/4" x 5' 10% DC 550	80
		Dodecane		120
		Decane		80

Table XXIII. (continued)

Organomercurial	Methyl-substituted arene	Internal standard	GLPC Conditions	
			Column	Temperature °C
		*p*-Di-*tert*-butylbenzene	1/4" x 5' 10% C20M	145
		Tridecane	1/4" x 5' 10% UCON	150
		Tetradecane	1/4" x 5' 10% C20M	110

priate temperature, the reaction mixture was directly GLPC analyzed. The results are summarized in Table XIV.

4. The reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and m-nitrophenylmercuric chloride in the dark or ordinary room light at different temperatures

0.473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0179 grams (0.05 mmoles) m-nitrophenylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen, the entire assembly was wrapped in aluminum foil for the dark reactions. 0.0092 Grams (0.05 mmoles) n-tridecane and 0.5 ml HMPA were added by syringe. The flask was immersed in an appropriate temperature bath (heated oil or cooled water). After 24 hours, 0.5 ml ether was added and the reaction mixture GLPC analyzed. 0.5 Mmoles of other inorganic salts such as: 0.0749 grams sodium iodide, 0.0669 grams lithium iodide, 0.0410 grams sodium acetate or 0.0270 grams sodium methoxide were added in place of lithium chloride for the investigation of the effect of different salts on aryl-methyl coupling between $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and m-nitrophenylmercuric chloride. The results are summarized in Table XV.

5. The coupling of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ with m-nitrophenylmercuric chloride, m-carbomethoxyphenylmercuric chloride and 2-chloromercurinaphthalene at 18°C

The following procedure for the reaction of m-nitrophenylmercuric chloride and $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ is representative. 0.0473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0179 grams (0.05 mmoles) m-nitrophenylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, gas inlet tube and a stirring bar. After flushing with nitrogen, 0.0092 (0.05 mmoles) n-tridecane and 0.5 ml HMPA were added by syringe. After stirring the appropriate time in an 18°C water bath, 0.5 ml benzene and 0.5 ml water were added and the benzene layer GLPC analyzed. The results are summarized in Table XVII.

6. The effect of time and excess lithium chloride and/or excess methyl iodide on the coupling of p-anisylmercuric chloride or m-nitrophenylmercuric chloride with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

The procedure for p-anisylmercuric chloride is representative. 0.0473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$ and 0.0172 grams p-chloromercuri-anisole were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. At least 0.0213 grams (0.05 mmoles) lithium chloride was added for certain reactions. After flushing with nitrogen, 0.0078 grams (0.05 mmoles) *n*-undecane and 0.5 ml HMPA were added by syringe. 0.1 Ml (excess) methyl iodide was also added to certain reactions. If lithium chloride was added as well as methyl iodide, the volume of HMPA added was increased to 1.0 ml. After stirring under nitrogen in a 70°C oil bath for the appropriate time 0.5 to 1.0 ml water and 0.5 ml benzene were added and the benzene layer GLPC analyzed. The results are summarized in Tables XXVIII and XXIX.

7. The reaction of arylmercurials and methyl iodide mediated by 2 mole % $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ in the presence of inorganic and organic bases

The reaction with *m*-nitrophenylmercuric chloride in the presence of lithium carbonate and lithium chloride is representative. 0.0010 Grams (0.0001 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0179 grams (0.05 mmoles) *m*-nitrophenylmercuric chloride, 0.0369 grams (0.5 mmoles) lithium carbonate and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen, 0.0092 grams (0.05 mmoles) *n*-tridecane, 1.0 ml HMPA and 0.1 ml (excess) methyl iodide were added by syringe. After stirring at 70°C for 24 hours, 0.5 ml benzene and 1.0 ml water were added and the benzene layer GLPC analyzed.

Other reactions were carried out using 0.5 mmoles of other bases such as magnesium oxide, sodium bicarbonate, sodium phosphate monobasic, sodium phosphate dibasic, triethylamine and 2,4,6-tri(*tert*-butyl)pyridine in place of lithium carbonate and both with and without lithium chloride. The results are summarized in Table XX.

8. The reaction of *p*-anisylmercuric chloride and methyl iodide mediated by 10% $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and quenched with 10% aqueous sodium hydroxide

0.0047 Grams (0.005 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$ and 0.0172 grams (0.05 mmoles) *p*-anisylmercuric chloride were weighed into a 5 ml round bottom flask equipped with septum inlet, condenser with a gas inlet tube attached and a magnetic stirring bar. 0.0078 Grams (0.05 mmoles) *n*-undecane, 0.5 ml HMPA and 0.1 ml (excess) methyl iodide were added by syringe. After stirring at 70°C for 24 hours, 0.5 ml benzene and 0.5 ml aqueous 10% sodium hydroxide were added and the benzene layer GLPC analyzed.

9. The reaction of $RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$ and *p*-anisylmercuric chloride

0.0371 Grams (0.05 mmoles) $RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$ and 0.0172 grams (0.05 mmoles) *p*-anisylmercuric chloride were weighed into a 5 ml round bottom flask equipped with septum inlet, condenser with a gas inlet tube attached and a magnetic stirring bar. 0.0078 Grams (0.05 mmoles) *n*-undecane and 0.5

ml HMPA were added by syringe. After stirring at 70°C for 24 hours, 0.5 ml benzene and 0.5 ml water were added and the benzene layer GLPC analyzed. Anisole was produced, the yield may be estimated at greater than 50%.

10. The reaction of *p*-anisylmercuric chloride with anhydrous hydrogen iodide

0.0172 Grams (0.05 mmoles) *p*-anisylmercuric chloride was weighed into a 5 ml round bottom flask equipped with a septum inlet, a magnetic stirring bar and a gas inlet tube connected to either a nitrogen filled balloon or a mercury bubbler during the addition of hydrogen iodide. 0.5 Ml HMPA and 0.0086 grams (0.055 mmoles) *n*-undecane was added by syringe. The solution was stirred in a 70°C oil bath and hydrogen iodide was added for 1 hour. Hydrogen iodide was generated in a 3 neck flask of boiling tetralin equipped with a nitrogen inlet, an air cooled condenser and an addition funnel of iodine dissolved in tetralin. Hydrogen iodide was generated by dropping the iodine solution into the boiling tetralin and sweeping it with nitrogen into the HMPA solution. GLPC analysis of the unquenched reaction mixture after 4 hours indicated anisole was formed. GLPC analysis of the unquenched reaction mixture after 24 hours showed more anisole was present, the yield may be estimated to be approximately 80%.

11. The reaction of p-anisylmercuric chloride with methyl iodide and HMPA

0.0172 Grams (0.05 mmoles) p-anisylmercuric chloride was weighed into a 5 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. At least 0.0213 grams (0.5 mmoles) lithium chloride was added to some reactions. 0.0078 Grams (0.05 mmoles) n-undecane, 0.5 ml HMPA and 0.1 ml (excess) methyl iodide were added by syringe. After stirring 6 hours at 70°C, 0.5 ml pentane and 0.5 ml water were added and the pentane layer GLPC analyzed. Anisole was produced in 60-80% yield. Anisole was also produced if an alkyl iodide such as ethyl iodide or n-butyl iodide was used in place of methyl iodide. However, only a trace of anisole was formed if phenyl iodide was used in place of methyl iodide. Similar reactions containing either 0.0172 grams (0.05 mmoles) p-anisylmercuric chloride, 0.0078 grams (0.05 mmoles) n-undecane and 0.5 ml HMPA or 0.0172 grams p-anisylmercuric chloride, at least 0.0213 grams (0.5 mmoles) lithium chloride, 0.0078 grams n-undecane and 0.5 ml HMPA did not produce anisole.

12. Reaction of p-anisylmercuric chloride, methyl iodide and HMPA with deuterium oxide quench, hydrogen oxide quench utilizing deuterated methyl iodide or after initial deuterium oxide addition

0.1716 Grams (0.5 mmoles) p-anisylmercuric chloride was weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. 5 Ml HMPA and 1 ml methyl iodide were added by syringe. After stirring 6 hours at 70°C, the reaction mixture was poured into pentane and deuterium oxide. The pentane layer was separated and the deuterium oxide layer re-extracted with pentane. The pentane layers were combined, dried (Na_2SO_4), concentrated, GLPC prepped and submitted for MS analysis. The mass spectral data for the anisole obtained are reported in Table XXIV. The reaction with deuterated methyl iodide was performed analogously except hydrogen oxide (ordinary water) was employed for quenching the reaction. The reaction was also attempted with methyl iodide, HMPA and the addition of 0.1 ml deuterium oxide at the start of the reaction. Hydrogen oxide (ordinary water) was employed for quenching this reaction. The same reaction was also tried with 5 ml deuterated DMSO as the solvent in place of HMPA. Deuterium incorporation was observed, but not further investigated. The reaction of greatest interest is that with methyl iodide and the immediate addition of 0.1 ml D_2O followed by a H_2O quench later. Since the observed M + 1 peak is too high for the calculated value for C_7H_7OD, the percents C_7H_7OD and C_7H_8O were estimated in the following manner. M - 1 is typically 2% of M, therefore, (36% - 2% = 34%), the adjusted intensity of M^+ = 108 = 34%. M + 1 is approximately 8% of M. Therefore, of the 109 peak, 3% (0.08 x 34% = 3%), may be attributed to the M + 1 peak for

Table XXIV. Mass spectral data for anisole formed from the reaction of p-anisylmercuric chloride, methyl iodide and HMPA with various deuterated reactants

	CH_3I H_2O Quench	CH_3I D_2O Quench	CD_3I H_2O Quench	CH_3I +.1 ml D_2O H_2O Quench	CD_3SOCD_3 CH_3I H_2O Quench
m/e: Intensities[a]	--	--	--	9.61	4.21
110	--	--	7.90	100.00	70.78
109	100.00	100.00[b]	100.00	35.67	100.00
108	2.55	2.17	2.29	.90	1.96
107					
ppm Error for Exact Mass					
C_7H_8O	-2.7	+0.15	-3.1	-8.2	+5.5
C_7H_7OD	--	-15.5	-13.5	-6.0	+4.1
Interpretation	C_7H_8O	C_7H_8O	C_7H_8O	~74% C_7H_7OD + ~26% C_7H_8O	~38% C_7H_7OD + ~62% C_7H_8O

[a] Actual intensities.

[b] Normalized, in this run M^+ did not happen to be the base peak.

M = 108. After these adjustments, 97% of the 109 peak = M for 108. The percent C_7H_7OD = 74% (97/131), and the percent C_7H_8O = 26% (34/131).

13. The production of acid from the reaction of methyl iodide and HMPA

2 Ml (33 mmoles) methyl iodide and 5 ml (41 mmoles) HMPA were mixed under nitrogen in a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. After the initial mixing, the stirrer was turned off and the flask remained undisturbed in a 70°C oil bath for 4 hours. A pH = 7 buffer tablet was dissolved in de-ionized water as directed and a pH meter standardized. 0.5 Ml distilled HMPA and 0.5 ml de-ionized water were mixed and the pH measured 8.17. 0.5 Ml of the solution from the reaction of methyl iodide and HMPA and 0.5 ml de-ionized water were also mixed and the pH measured 2.18. The approximate pH of the solutions measured were also visible using pH paper.

14. The reaction of methyl iodide and HMPA

2 Ml (33 mmoles) methyl iodide and 5 ml (41 mmoles) HMPA were mixed under nitrogen in a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. After the initial mixing, the stirrer was turned off and the flask reminaed undisturbed in a 70°C oil bath. The methyl iodide did not boil or distill off. After 4 hours plate-like crystals were visible in the bottom of the

flask. The crystals were then filtered off, washed with acetone and dried. 0.2546 Grams of $(CH_3)_4N^+I^-$ (1.3 mmoles 4%) were obtained. Higher yields up to 1.2 grams (18%) may be obtained from longer reaction times and a flask with an etched surface. After recrystallization from water, the nmr and IR spectra indicated the product to be $(CH_3)_4N^+I^-$. ^1H nmr: δ3.20(t (1:1:1) J=0.6 Hz) ^{31}P: No peaks are present. IR: 3100 w, 3020 ms, 2960 w, 2940 (sh), 2920 w, 2880 (sh), 2840 w, 2790 w, 2740 w, 2570 w, 2670 w, 1490 s, 1410 ms, 1400 (sh), 1295 w, 950 s and 920 m.$^{cm-1}$ The compound does not melt below 350°C which agrees with the reported melting point >355°C.[293] An authentic sample of $(CH_3)_4N^+I^-$ prepared from the addition of methyl iodide to trimethylamine, recrystallized from water and dried gave a superimposable IR spectrum.

The unreacted HMPA of the organic solution remaining after the isolation of tetramethylammonium iodide was distilled off at reduced pressure. Since the resulting residue was too viscous to be handled by syringe, methanol was added. GLPC analysis gave three longer retention time peaks. GC-MS results indicated $[(CH_3)_2N]_2PO(OCH_3)$ $M^+ = 166$, HMPA $M^+ = 179$ and $[(CH_3)_2N]_2POOPO[N(CH_3)_2]_2$ $M^+ = 286$ were formed. Another sample of the residue was dissolved in acetone and subjected to GC-MS analysis also, but HMPA was the only peak observed.

Although the first and third peaks were GC prepped and their ^{31}P and ^1H nmr spectra measured in D_2O, the two samples were nearly identical: ^{31}P +29.9 PPM (H_3PO_4) (t, J=2.2) and ^1H δ2.65 (d, J = 9.8 Hz). Another sample of the crude residue was dissolved in D_2O and its ^1H nmr spectrum measured. Surprisingly this showed three sets of doublets at δ2.60 (d, J = 9.5 Hz), δ2.75 (d, J = 10.75 Hz) and δ2.83 (d, J = 11.0 Hz). The ^{31}P and ^1H nmr spectra of HMPA in D_2O were also measured, ^{31}P +29.4(s) and ^1H δ2.6 (J = 9.5 Hz). Thus the doublet of the crude residue at δ2.6 may be attributed to residual HMPA which leaves the remaining two sets for $[(CH_3)_2N]_2PO(OD)$ and $[(CH_3)_2N]$ $POOPO[N(CH_3)_2]_2$. However, since $[(CH_3)_2N]_2POOPO[N(CH_3)_2]_2$ should possess the same ^1H nmr spectra whether it was prepped after a methanol or just dissolved in D_2O and $[(CH_3)_2N]_2PO(OCH_3)$ should exhibit a singlet corresponding to the methoxy hydrogen, further study is mandatory for confirmation of $[(CH_3)_2N]_2POI$ as an intermediate and full characterization of the HMPA residue products.

15. The revised coupling of an arylmercurial with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

The reaction with p-anisylmercuric chloride is representative. 0.0473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$ and 0.0172 grams p-anisylmercuric chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen, 0.0078 grams (0.05 mmoles) n-undecane, 0.1 ml (excess) methyl iodide and

0.5 ml HMPA were added by syringe. After stirring for 24 hours at 70°C, 0.5 ml benzene and 0.5 ml water were added and the benzene layer GLPC analyzed. Other arylmercurials were also reacted with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ using the appropriate internal standards and GLPC analysis conditions outlined in Table XXV. The results are summarized in Table XXI. The success of this reaction depends greatly upon rigorously excluding water. Consequently the glassware was flame dried and cooled under a nitrogen stream. The HMPA employed must be dried and freshly distilled before each reaction for best results.

16. The reaction of di-p-tolylmercury and methyl iodide catalyzed by 10 mole % $Rh(CH_3)I_2[P(C_6H_5)_3]_2$.

These reactions were performed with the previously described measures to exclude moisture. 0.0047 Grams (0.005 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot CH_3Cl$ and 0.0073 grams (0.025 mmoles) di-p-tolylmercury were weighed into a 5 ml round bottom flask equipped with a septum inlet, condenser with a gas inlet tube attached and a magnetic stirring bar. After flushing with nitrogen 0.0064 grams (0.05 mmoles) n-nonane, 0.1 ml excess methyl iodide and 0.5 ml HMPA were added by syringe. After stirring at 70°C for the appropriate time, 0.5 ml benzene and 0.5 ml water were added and the benzene layer GLPC analyzed. The results are summarized in Table XXII.

Table XXV. Revised analysis conditions for the syntheses of methyl-substituted arenes

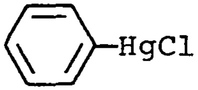
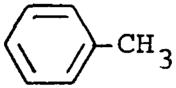
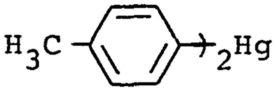
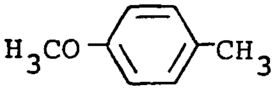
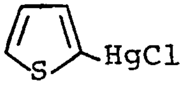
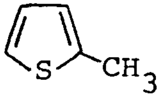
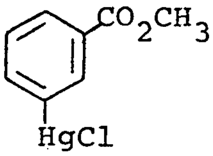
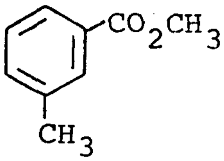
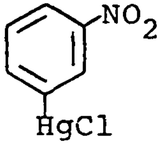
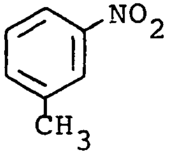
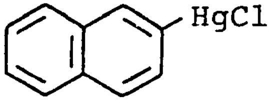
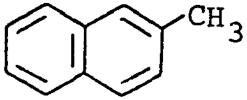
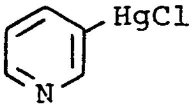
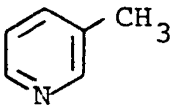
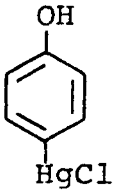
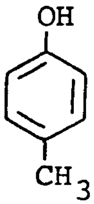
Organomercurial	Methyl-substituted arene	Internal standard	GLPC Conditions		GC-MS M^+
			Column	Temperature °C	
		Nonane	1/4% x 10' 10% SE-30	80	92
				90	106
		Undecane		120	122
		Nonane		80	--
		Tetradecane or Tridecane		130-150	150

Table XXV. (continued)

Organomercurial	Methyl-substituted arene	Internal standard	GLPC Conditions		GC-MS M^+
			Column	Temperature °C	
					137
		Tetradecane		155	142
		Decane		95	--
		Octadecane	1/4" x 5' 10% SE-30	200	--

IV. VINYL AND ARYL SUBSTITUTION OF ORGANOMERCURIALS

A. Introduction

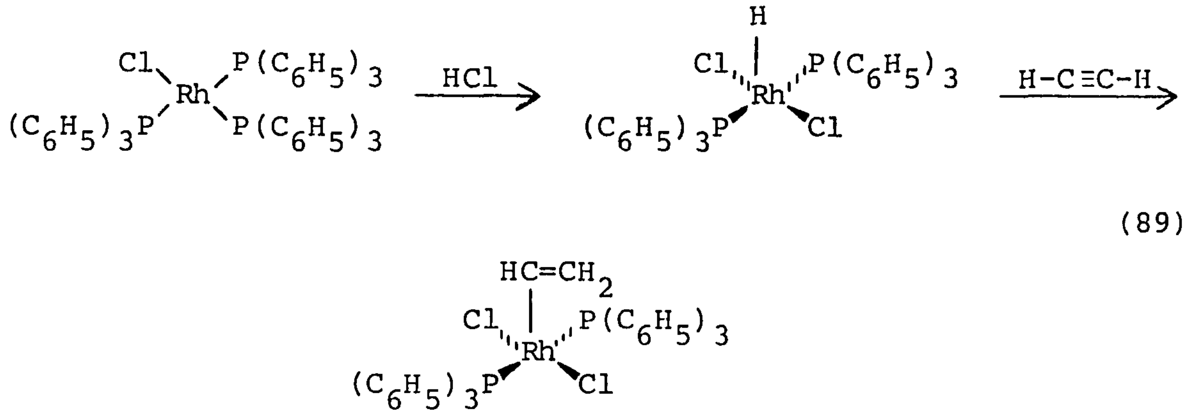
While the methylation of vinyl- and arylmercurials with methyl iodide mediated by catalytic amounts of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ is not valuable synthetically due to the competing reactions, dimerization or dimerization and protonolysis, the successful stoichiometric methylation of vinyl- and arylmercurials with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ illustrates the feasibility of a sequence involving transmetalation between an organorhodium halide and an organomercurial followed by reductive elimination as a method of forming carbon-carbon bonds. The use of other organorhodium species suggests other coupling reactions.

Other organorhodium(III) compounds of the type $Rh(R)X_2L_2$ derived from Wilkinson's catalyst include, allylic rhodium compounds which have been reported to exist as both the sigma-allyl and pi-allyl isomers,[13] a vinylrhodium compound,[11] an ethylrhodium compound,[11] and various acyl rhodium compounds.[90] A phenylrhodium compound is also known. However, one triphenylphosphine ligand has been replaced by a carbon monoxide ligand.[22] Although numerous other organometallic methods are known for vinyl, phenyl, or allylic couplings, the handling ease, the functionality tolerated by organomercury compounds, and the relatively mild reaction conditions utilized in the previous rhodium mediated methylation of organomercurials encouraged us to investigate the related vinyl- and phenylrhodium couplings with organomercurials.

B. Results and Discussion

1. Vinylrhodium(III) approach

a. The reaction of $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ and phenylmercuric chloride Wilkinson's catalyst may be treated with hydrogen chloride forming a hydridorhodium(III) compound which reacts with acetylene forming a vinylrhodium(III) compound (Eq. 89).[11] The coupling of the vinylrhodium(III)



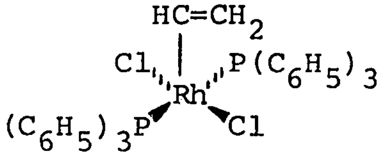
(89)

compound with organomercurials was previously investigated in K. M. Beatty's master's thesis.[294] A re-investigation was demanded since her results were variable and the coupling yields were never excellent or quantitative (Eq. 90). Although other reactions conditions were investigated, it was determined that the originally selected reaction conditions: HMPA solvent, added lithium chloride and 70°C promoted the coupling

Table XXVI. Beatty's experimental conditions for the reaction of phenylmercuric chloride and $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$[a]

Equivalents LiCl	Atmosphere	Temperature °C	Solvent	GLPC Yield Styrene %
10	HC≡CH	25	THF	42
			HMPA	45
	N_2			60
	HC≡CH	70		64
	Ar			63
	N_2			60

[a] Reaction time is 24 hours.

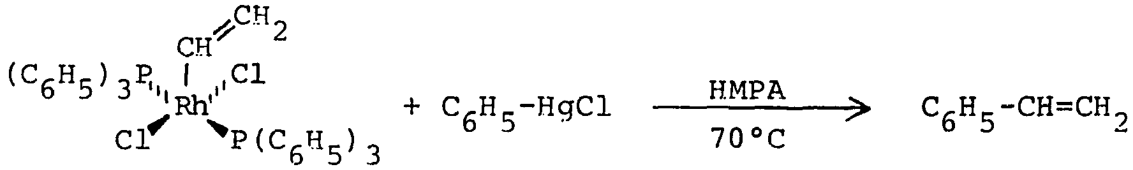


$$+ \quad C_6H_5\text{-HgCl} \longrightarrow RhCl[P(C_6H_5)_3]_2 \quad + \quad C_6H_5\text{-CH=CH}_2 \quad + \quad HgCl_2 \qquad (90)$$

reaction to the greatest extent. However, Beatty suggested an acetylene atmosphere was equal to or superior to a nitrogen atmosphere (Table XXVI).[294]

A re-investigation of this reaction has established its scope and limitations. The results obtained from the reaction of phenylmercuric chloride and $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ (prepared via acetylene insertion into $RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$ under different reaction conditions) are presented in Table XXVII. Although at first glance the results in Table XXVII appear variable, the necessary information concerning this coupling reaction is provided. Most importantly, the yields in the coupling reaction of phenylmercuric chloride and $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ are reproducible. The yields of styrene under identical conditions after either six or twenty-four hours are exactly the same (within experimental error). Entries 3 and 5 are very comparable with 46% and 48%, as are entries 4 and 6 with 59% for both cases. For entries 15 and 16, a slightly different experimental procedure was used for manipulating the HMPA and lithium chloride under anhydrous conditions. (See experimental section for details). However,

Table XXVII. Effect of vinylrhodium species, added reagents, time and atmosphere on the reaction of phenylmercuric chloride and $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$



Entry	Vinylrhodium sample	Added Reagents	Time h	Atmosphere	GLPC Yield %
1	1	$H_2C{=}CHBr$	1	H-C≡C-H	30[a]
2			24	N_2	12
3		LiCl		H-C≡C-H	46[b]
4				N_2	59
5			6	H-C≡C-H	48
6				N_2	59
7	2			H-C≡C-H	8
8				N_2	29
9	3				10
10	3[c]				37
11	4				9
12				H-C≡C-H	18
13				N_2	28
14	6				38

---

[a] Also contains ethylbenzene as evidenced in GC-MS.

[b] Estimated.

[c] Recrystallized from CH_2Cl_2 at -78°C.

Table XXVII. (continued)

Entry	Vinylrhodium sample	Added Reagents	Time h	Atmosphere	GLPC Yield %
15	5				25[d]
16	6				37[d]
17	5	$(CH_3)_4N^+I^-$			8[d]
18	7			H-C≡C-H	49
19				N_2	42

[d] Alternate experimental technique utilized (see text and/o and/or experimental section).

the yield of styrene for entries 13 and 15 compares very favorably with 28% and 25%, as do entries 14 and 16 with 38% and 37%. Secondly, entries 3 through 6 indicate the optimal reaction conditions which are: HMPA as the solvent, plus excess lithium chloride, at a temperature of 70°C, under a nitrogen atmosphere. The product yield after six hours is comparable to that after 24 hours. Entries 12 and 18 are the only definitive examples for which the yield of styrene was greater with an acetylene atmosphere. Entry 1 cannot be compared because both styrene and ethylbenzene are present and both possess similar GLPC retention times with the column conditions most convenient for the analyses. Entries 1 and 2 illustrate that excess vinyl bromide does not function as advantageously as excess methyl iodide does in the syntheses of methyl substituted arenes. Further, entry 17 shows tetramethylammonium iodide as an added salt is inferior to lithium chloride.

The greatest variable in this synthesis of styrene, however is the vinylrhodium compound itself. In Table XXVII, this styrene synthesis was attempted with seven different preparations of the vinylrhodium complex. Additionally, one of the vinylrhodium preparations was recrystallized (entries 9 and 10). The preparation of these eight different vinylrhodium samples are detailed in the experimental section.

Similar reaction conditions and a consistent vinylrhodium compound were strived for but could not be easily achieved.

The difficulty observed in obtaining consistent and high purity vinylrhodium compounds is not without literature precedent. The original investigators report that accurate analyses of the rhodium hydride, $RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5\ CH_2Cl_2$ were difficult to obtain due to the instability of the rhodium hydride towards loss of both hydrogen chloride and co-ordinated dichloromethane. Analysis difficulties were also reported for the vinylrhodium compound prepared from the rhodium hydride. The chlorine content was high, even after vacuum drying at 80°C overnight. This was rationalized as residual solvent, chloroform, in spite of their statement that the rhodium hydride contains one molecule of CH_2Cl_2 per two molecules of $RhHCl_2[P(C_6H_5)_3]_2$, while the vinylrhodium does not contain a coordinated solvent molecule.[11]

The carbon and hydrogen elemental analysis obtained for vinylrhodium sample No. 1 agrees better with a compound containing one molecule CH_2Cl_2 per two molecules $Rh(CH{=}CH_2)Cl_2$-$[P(C_6H_5)_3]_2$. Alternatively the presence of some of the phosphonium salt derived from triphenylphosphine and hydrogen chloride would also support the observed elemental analysis. Considering the statement that dichloromethane is co-ordinated to the rhodium hydride but not co-ordinated to the vinylrhodium compound and recalling that vinylrhodium sample No. 1

produces only 60% of the vinyl-aryl coupling product suggest that vinylrhodium sample No. 1 as produced is nonhomogeneous.

A side reaction in the addition of hydrogen halides to rhodium(I) compounds may also be suspected. Other workers have reported RhX_3L_n products from the addition of hydrogen halides to similar rhodium(I) compounds (Eqs. 91 and 92).[8,86] In one attempted synthesis of $RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$

$$RhCl(CO)[PC_6H_5(C_2H_5)_2]_2 + HCl \xrightarrow[CH_3CH_2OH]{} RhCl_3(CO)[PC_6H_5(C_2H_5)_2]_2 \tag{91}$$

$$\{Rh(H)Cl[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl + HCl \xrightarrow[CH_2Cl_2]{} cis\{RhCl_2[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2\}Cl \tag{92}$$

it was observed that during the addition of hydrogen chloride, the dark red dichloromethane solution of Wilkinson's catalyst gradually lightened and turned yellow. The solution did not remain yellow upon further addition of hydrogen chloride, but instead darkened to an orange solution. This species was not fully characterized but after addition of acetylene and product isolation a gold colored solid was formed which coupled with phenylmercuric chloride to a lesser extent.

b. *The reaction of phenylmercuric chloride and $\mathrm{Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2}$ formed in situ from $\mathrm{RhHCl_2[P(C_6H_5)_3]_2}$ and acetylene* It was suggested that some of the difficulty in obtaining the pure vinylrhodium compound might be alleviated by starting with the isolated rhodium hydride forming the vinylrhodium compound *in situ* and performing the vinyl-aryl coupling reaction under an acetylene atmosphere. Although it is reported that isolated $\mathrm{RhHCl_2[P(C_6H_5)_3]_2\cdot 0.5CH_2Cl_2}$ loses both hydrogen chloride and dichloromethane in air and in vacuo[11] and it has also been demonstrated (page 122) that $\mathrm{RhHCl_2[P(C_6H_5)_3]_2\cdot 0.5CH_2Cl_2}$ reacts with arylmercurials forming the protonated aryl compound, this approach was reinvestigated. While Beatty reported a 64% yield of styrene starting with $\mathrm{RhHCl_2[P(C_6H_5)_3]_2\cdot 0.5CH_2Cl_2}$ and acetylene, followed by the addition of phenylmercuric iodide (Eq. 93),[294] re-investigation of this reaction demonstrates that it is less productive (Eqs. 94 and 95). Both

$$\mathrm{RhHCl_2[P(C_6H_5)_3]_2\cdot 0.5CH_2Cl_2} \xrightarrow[\substack{\mathrm{LiCl}\\ \mathrm{HMPA}\\ \mathrm{RT}\\ \mathrm{15\ min}}]{\mathrm{HC{\equiv}CH}} \xrightarrow[\substack{70^\circ\mathrm{C}\\ \mathrm{24\ hours}}]{\mathrm{C_6H_5HgI}} \tag{93}$$

$$64\%\ \mathrm{C_6H_5CH{=}CH_2}$$

$$RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2 \xrightarrow[\substack{25°C \\ HMPA/LiCl \\ 15\ min}]{HC\equiv CH} \xrightarrow[\substack{70°C \\ 6\ hours}]{C_6H_5HgCl} \quad (94)$$

$$23\%\ C_6H_5CH{=}CH_2$$

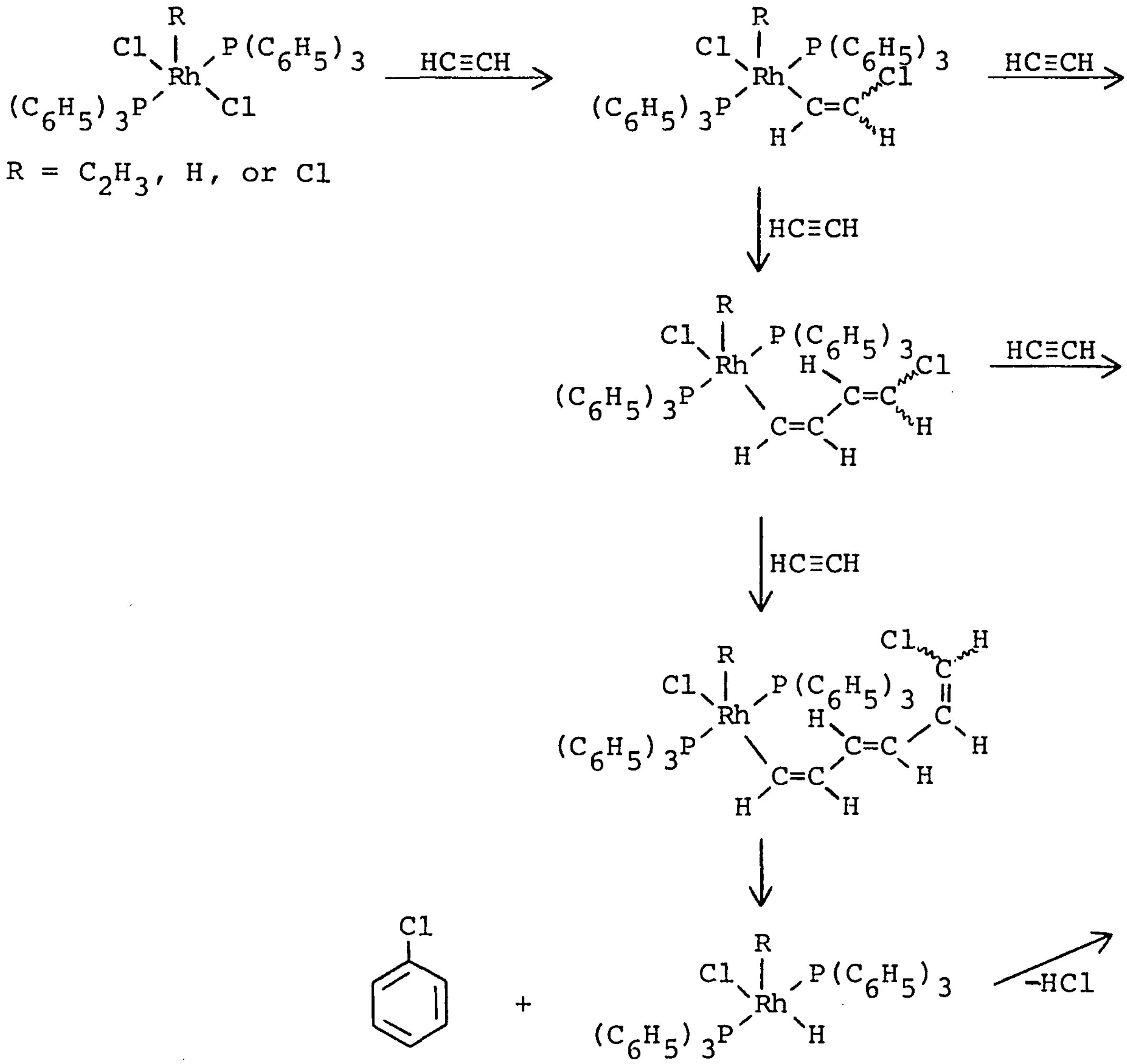
$$RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2 \xrightarrow[\substack{25°C \\ HMPA/LiCl \\ 15\ min}]{HC\equiv CH} \xrightarrow[\substack{70°C \\ 6\ hours}]{C_6H_5HgI} \quad (95)$$

$$29\%\ C_6H_5CH{=}CH_2$$

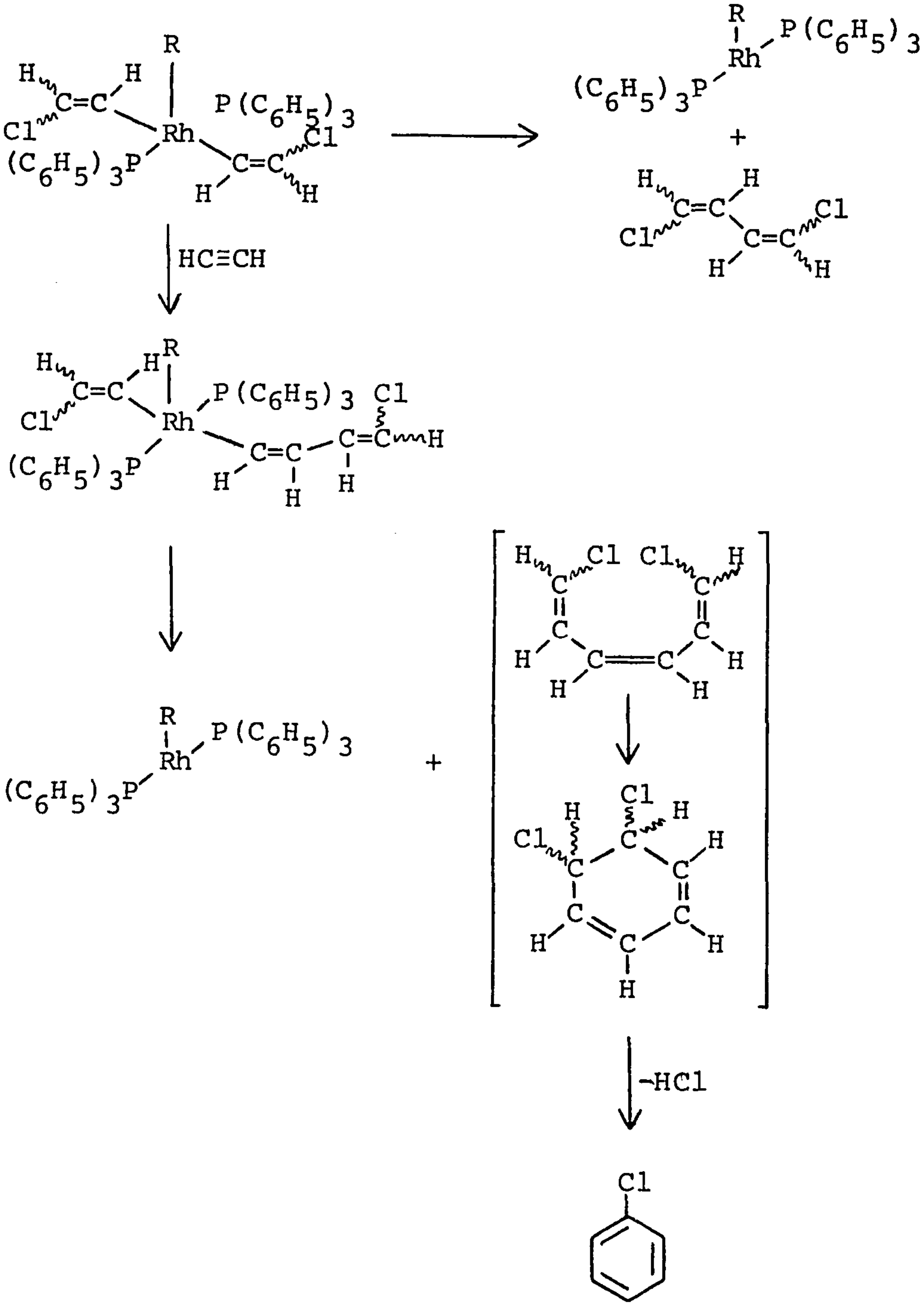
phenylmercuric chloride and phenylmercuric iodide were studied due to the fact that previously only the reaction of the iodide was reported. The yields, 23% and 29%, although similar may or may not imply a real difference due to the fact that a new GLPC peak present in both reactions has a slightly greater area with phenylmercuric chloride compared to phenylmercuric iodide.

As previously stated, the isolation of pure rhodium hydride is difficult. However, other factors may influence the low yields. Table XXVII and Table XXVIII (presented later) compare various vinylrhodium species under either nitrogen or acetylene atmospheres. Generally, the yields in an acetylene atmosphere are lower. An acetylene atmosphere also introduces a new peak in the GLPC trace of reactions utilizing either the rhodium hydride or a vinylrhodium compound. The retention time of the new peak is 15 to 30 seconds shorter than that of styrene. (The former use of old GLPC columns with poor resolution may have resulted in the merger of styrene and this new peak. This is a possible explanation for the 64% yield reported previously). From the GC-MS the new peak apparently contains two components. From the mass spectrum and comparison of retention times with a commercial sample, chlorobenzene is one component. The other component as determined solely from the mass spectrum is a dichlorobutadiene. Since chlorobenzene and dichlorobutadiene are formed only in the presence of acetylene, it is reasonable for acetylene to appear in a scheme accounting for their formation. Scheme 43 is one possible scheme. If $RhCl_3[P(C_6H_5)_3]_2$ were present it might possibly react similarly. It was not established which of several possible rhodium species are responsible for chlorobenzene and dichlorobutadiene formation. It is also possible that acetylene may induce the formation of chlorobenzene from phenylmercuric chloride. Performing the vinyl-aryl coupling reaction with di-p-tolylmercury instead of phenylmercuric chloride in an acetylene atmosphere distinguishes between these two possibilities. Di-p-tolylmercury formed predominantly chlorobenzene and a smaller amount of dichlorobutadiene while

Scheme 43



R = C_2H_3, H, or Cl


HC≡CH
-HCl

p-chlorotoluene was not detected. Hence, chlorobenzene is most probably not produced from the organomercurial. Although other similar rhodium(I) and iridium(I) compounds are established acetylene trimerization catalysts,[153-161] the formation of chlorobenzene is obviously not simply an acetylene cyclotrimerization. Scheme 43 is only one possible scheme which may account for the formation of chlorobenzene and this proposed scheme was not fully substantiated. Emphasis on the vinyl-aryl coupling reaction precluded further investigation of the formation of chlorobenzene.

The coupling of a vinylrhodium(III) species and an arylmercurial in an acetylene atmosphere with either an isolated vinylrhodium(III) species or a vinylrhodium(III) species generated *in situ* from the corresponding rhodium hydride usually results in decreased vinyl-aryl coupling yields and the formation of chlorobenzene and dichlorobutadiene. Only occasionally are higher vinyl-aryl coupling yields seen with an isolated vinylrhodium(III) species in an acetylene atmosphere and this may be attributed to an impure vinylrhodium(III) sample partially containing the rhodium hydride precursor. Acetylene then converts some of the rhodium hydride to the corresponding vinylrhodium species which improves the vinyl-aryl coupling yield slightly.

c. The reaction of phenylmercuric chloride and $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ Since the possibility is remote that formation of $RhHCl_2[P(C_6H_5)_3]_2\cdot 0.5CH_2Cl_2$ and/or $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ at lower temperatures, in other solvents, or under different reaction conditions might yield compounds of consistently high purity, other approaches to vinylrhodium(III) compounds were briefly investigated. The results of the coupling of vinylrhodium compounds obtained via other routes with phenylmercuric chloride are presented in Table XXVIII.

A minor adjustment in our earlier approach involved treating Wilkinson's catalyst with hydrogen bromide instead of hydrogen chloride followed by the insertion of acetylene and product isolation. Organorhodium sample No. 1 was formed in this manner. The coupling reaction with phenylmercuric chloride produced low yields of styrene. Perhaps not all the rhodium hydride was converted to the vinylrhodium species since the yield in an acetylene atmosphere was slightly higher than the yield in a nitrogen atmosphere.

The formation of a vinylrhodium compound via the oxidative addition of vinyl bromide to Wilkinson's catalyst was also investigated. Varied reaction times and purification procedures were employed as detailed in the experimental section. At first glance the attempted preparation of $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ appears as variable as $Rh(CH{=}CH_2)$-

Table XXVIII. Effect of vinylrhodium species, temperature and atmosphere on the reaction of phenylmercuric chloride and $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$

$$Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2 + C_6H_5HgCl \xrightarrow[\text{6 hours}]{\text{HMPA}\atop\text{Excess LiCl}} C_6H_5CH{=}CH_2$$

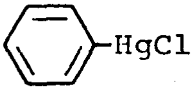
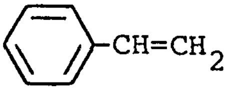
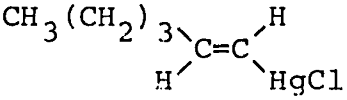
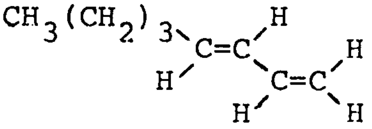
Organorhodium sample	Atmosphere	Temperature °C	GLPC Yield %[a]
1	N_2	70	15
	H-C≡C-H		19
2	N_2		6
	H-C≡C-H		10
	N_2	25	0
	H-C≡C-H		5
	N_2	70	57
	H-C≡C-H		47
4	N_2		76
	H-C≡C-H		58
5	N_2		45
	H-C≡C-H		27
6	N_2		73
7			0
	H-C≡C-H		0

[a] The yield of styrene is based on the rhodium compound composition being $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$.

$Cl_2[P(C_6H_5)_3]_2$. However, the results of coupling reactions with organorhodium sample No. 4 and organorhodium sample No. 6 are encouraging. Styrene yields of 76% and 73% respectively represent the highest yields observed so far. Since organorhodium sample No. 4 and organorhodium sample No. 6 were also prepared by similar procedures, the formation and purification of $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ via vinyl bromide is apparently more reproducible than $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ via acetylene. The elemental analysis, however, suggests nonhomogeneity may also be a problem with $Rh(CH{=}CH_2)BrCl$-$[P(C_6H_5)_3]_2$. For organorhodium sample No. 6 the carbon and hydrogen analysis does not fit for $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$. (No doubt fortuitously, the elemental analysis for carbon and hydrogen fits for a 75:25 mixture of $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ and $RhBr_2Cl[P(C_6H_5)_3]_2$ respectively). $RhBr_2Cl[P(C_6H_5)_3]_2$ is a possible side product which might be formed if bromine were generated or if the vinylrhodium species reacted further with vinyl bromide. Although an olefin trap might be used in the vinylrhodium synthesis to scavenge bromine, Wilkinson's catalyst is probably as or more reactive towards bromine than an olefin would be. Hence, a very short reaction time was employed in the preparation of organorhodium sample No. 7. However, the compound formed does not form styrene when reacted with phenylmercuric chloride under the usual conditions.

Table XXIX. Coupling of organomercurials and $Rh(CH=CH_2)ClBr[P(C_6H_5)_3]_n$ formed <u>in situ</u> from $RhCl[P(C_6H_5)_3]_3$ and vinyl bromide

$$RhCl[P(C_6H_5)_3]_3 \quad + \quad RHgCl \quad \xrightarrow{\substack{\text{Excess } H_2C=CHBr \\ \text{Excess LiCl} \\ \text{HMPA } 70^\circ C}} \quad RCH=CH_2$$

Organomercurial	Time h	Atmosphere	Product	GLPC Yield %
	1	N_2		55
	6			81,72
		HC≡CH		71
		N_2		23^a
$CH_3(CH_2)_5HgCl$			$CH_3(CH_2)_5CH=CH_2$	0

[a] A correction factor was not determined. Since correction factors for similar compounds are approximately 1, the yield is based on a correction factor of 1.

d. The reaction of organomercurials and $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ formed *in situ* from $RhCl[P(C_6H_5)_3]_2$ and vinyl bromide The reaction of Wilkinson's catalyst, excess vinyl bromide and phenylmercuric chloride in HMPA with excess lithium chloride at 70°C produced yields of styrene slightly higher or comparable to those observed with isolated $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ (Table XXIX). As observed previously, the yield of styrene in an acetylene atmosphere is decreased. Although a color change was immediately observed when Wilkinson's catalyst and vinyl bromide were mixed, the highest vinyl-aryl coupling yields were obtained from the isolated complex which was allowed to react for six hours or more. This may indicate either the oxidative addition of vinyl bromide is not exceedingly facile under the optimum vinyl-aryl coupling conditions or the vinyl-aryl reductive coupling is slower than the previously investigated methyl-vinyl and methyl-aryl couplings.

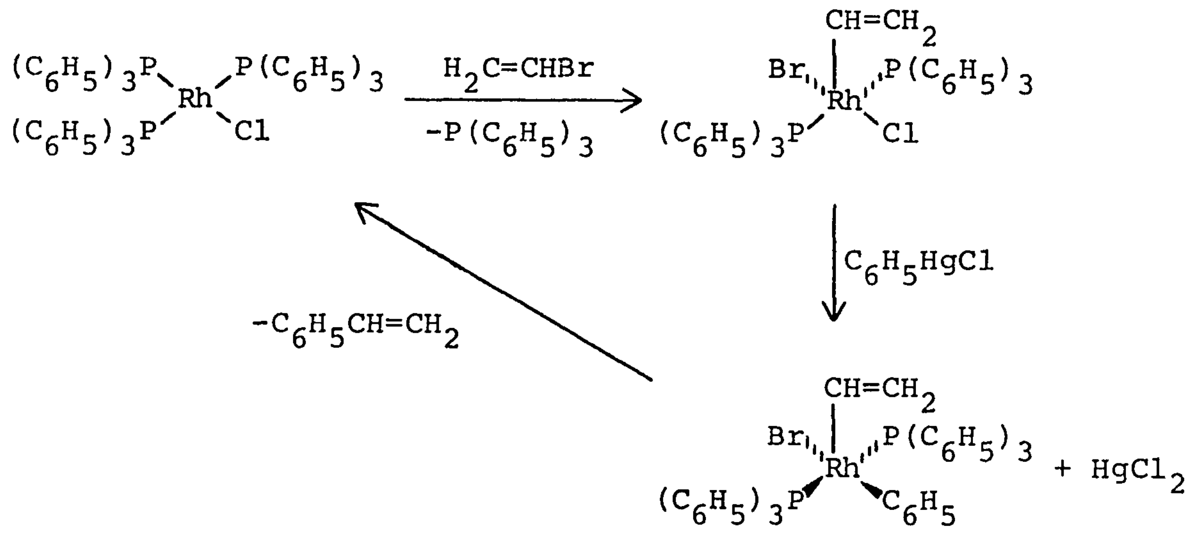
Beatty previously reported coupling the isolated vinylrhodium compound $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ with the vinylmercurials *trans*-1-hexenylmercuric chloride and *trans*-3,3-dimethyl-1-butenylmercuric chloride in 27 and 30% yield respectively.[294] The same vinylrhodium species apparently coupled with phenylmercuric chloride in approximately 60% yield. This vinyl-vinyl coupling was briefly re-investigated. Although the optimum vinyl-aryl coupling reaction conditions were employed (Wilkinson's catalyst, excess vinyl bromide, trans-1-hexenylmercuric chloride in HMPA with excess lithium chloride at 70°C for 6 hours) (Table XXIX), the yield of 1,3-octadiene (assumed to be trans) was disappointingly low--approximately 25%. However, considering the mild reaction conditions for the formation of dienes from vinylmercurials and rhodium(I) or -(III) catalysts[80] (room temperature in THF or ether for 6 hours) and that an oxidative addition of the vinylmercurials themselves is facile under those conditions, the low vinylation of vinylmercurials may be understandable. The low unsymmetrical vinyl-vinyl coupling in HMPA at 70°C with added lithium chloride may be due to the vinylmercurial competing effectively with vinyl bromide in the oxidative addition to Wilkinson's catalyst resulting in diene formation (also a vinyl-vinyl reductive coupling) at the expense of simple vinylation of the vinylmercurial.

Beatty also reported 33 and 15 percent yields of 1-octene from the reaction of the isolated vinylrhodium compound $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ and 1-hexylmercuric chloride with 1 and 2 equivalents of alkylmercurial respectively.[295] This result deserved re-investigation since the reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ with decylmercuric chloride yielded only decane, 1-decene, and probably other decenes but no undecane under reaction conditions which usually produced quantitative methylations of vinyl- or arylmercurials. Under the optimum vinyl-aryl coupling conditions, using Wilkinson's catalyst, excess vinyl bromide, and 1-hexylmercuric chloride in HMPA with excess lithium chloride at 70°C for 6 hours no 1-octene was observed (Table XXIX). The other products, presumably hexane and hexenes, could not be separated well-enough from the solvent pentane to be positively identified. Although alkyl-vinyl coupling has been observed with $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and vinylmercurials, the failure of this vinyl-alkyl coupling, as in the attempted methyl-alkyl coupling may be attributed to facile beta hydride elimination forming a rhodium hydride and a corresponding alkene of the alkyl fragment.

Although an ethylrhodium compound has been reported,[11] all attempts so far to couple it with either vinyl- or arylmercurials failed, presumably due to the formation of ethylene and the rhodium hydride. Despite the limited success of the vinylation of vinylmercurials, the facile vinyl-aryl coupling of a vinylrhodium species prepared _in situ_ from Wilkinson's catalyst and vinyl bromide with arylmercurials suggested investigation of a catalytic process.

e. _Catalytic attempts_ Similar to the methylation of aryl- and vinylmercurials the reaction of Wilkinson's catalyst, excess vinyl bromide and arylmercurials is potentially catalytic (Scheme 44). The reaction of 10 percent Wilkinson's

Scheme 44



catalyst, excess vinyl bromide and 1 equivalent phenylmercuric chloride formed an 82% GLPC yield of styrene after six hours at 70°C in HMPA with excess lithium chloride (Eq. 96).

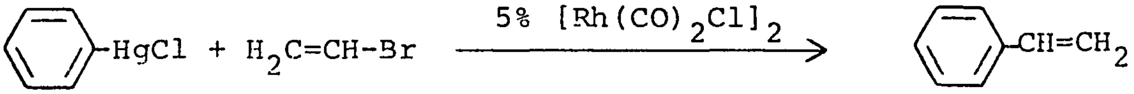
$$C_6H_5HgCl \quad + \quad \text{excess } H_2C{=}CHBr \xrightarrow[\substack{\text{HMPA/LiCl} \\ 70°\text{C} \\ \text{6 hours}}]{10\%\ RhCl[P(C_6H_5)_3]_3} 82\%\ C_6H_5CH{=}CH_2 \qquad (96)$$

Although not quantitative, this yield is comparable to that observed with 1 equivalent of Wilkinson's catalyst. The yield of styrene after 1 hour with 10 percent Wilkinson's catalyst is 43%, compared to 55% after 1 hour with 1 equivalent of Wilkinson's catalyst. It should be emphasized that this vinylation of arylmercurials is catalytic in more than a definitional sense, it is also functionally catalytic.

During a previous study of the formation of dienes and biaryls via the rhodium catalyzed transmetalation and reductive coupling of vinyl- and arylmercurials, Wilkinson's catalyst was inferior to other rhodium(I) or -(III) compounds, especially $[Rh(CO)_2Cl]_2$.[80] Due to the fact that reaction mixtures without triphenylphosphine or HMPA afford easier isolation of organic products, reactions involving excess vinyl bromide, phenylmercuric chloride and catalytic amounts of $[Rh(CO)_2Cl]_2$ were investigated (Table XXX). $[Rh(CO)_2Cl]_2$ however is inferior to $RhCl[P(C_6H_5)_3]_2$ as a catalyst for the vinylation of arylmercurials. This failure might be attributed to the oxidative addition of phenylmercuric chloride competing with the oxidative addition of vinyl bromide. Alternatively, the reaction conditions may not promote the transmetalation of phenylmercuric chloride with a vinylrhodium(III) halide. Recall that in the methylation of vinyl- and arylmercurials with isolated $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ the step requiring HMPA at 70°C and excess lithium chloride is apparently the transmetalation step.

Supposing that the unsymmetrical vinyl-vinyl coupling in the reaction of $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ formed _in situ_ from vinyl bromide and Wilkinson's catalyst was low due to the formation of the symmetrical diene via the facile oxidative

Table XXX. Effect of different reaction conditions on the formation of styrene from phenylmercuric chloride and vinyl bromide catalyzed by 5 mole percent $[Rh(CO)_2Cl]_2$



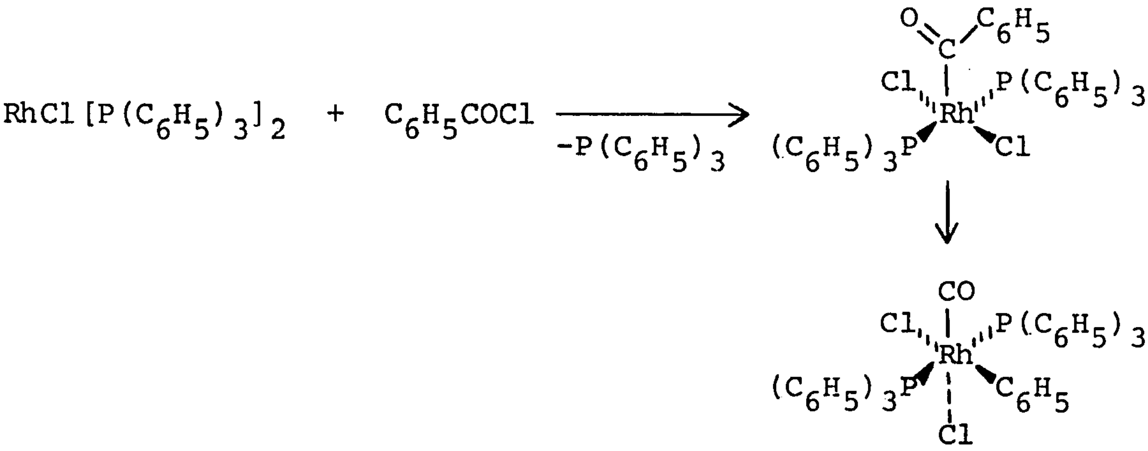
Solvent	Added Reagents	Temperature °C	Time h	GLPC Yield %
THF	2LiCl	25	1	11
			16	11
	--		1	17
			16	35
		65		31
Ether		25	1	19
			16	19
CH_2Cl_2			1	19
C_6H_6			16	16
			1	0
			16	trace

addition of the vinylmercurial, perhaps reducing the reaction temperature might reduce the extent of vinylmercurial oxidative addition. Therefore, the excess vinyl bromide, trans-1-hexenylmercuric chloride and 10 percent $RhCl[P(C_6H_5)_3]_3$ were stirred in THF with excess lithium chloride at room temperature for 16 hours. GLPC analysis showed 1,3-octadiene was not formed although some of the symmetrical diene from the vinylmercurial was present.

2. Phenylrhodium(III) approach

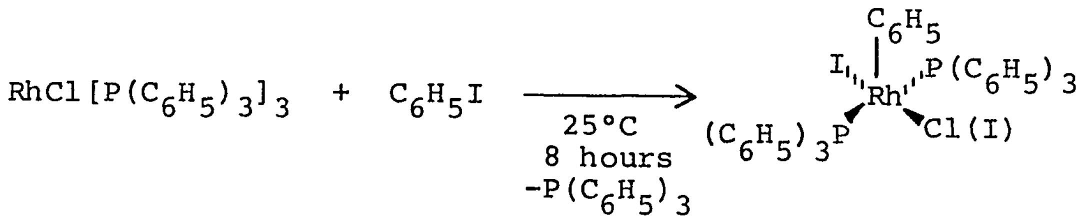
The coupling reaction of a phenylrhodium compound with organomercurials was also investigated by Beatty. The phenylrhodium compound, $Rh(CO)Cl_2(C_6H_5)[P(C_6H_5)_3]_2$ (prepared via the oxidative addition of benzoyl chloride to Wilkinson's catalyst followed by facile phenyl migration) (Scheme 45)[22]

Scheme 45



coupled in low yield with methylmercuric chloride (30%) and 4-chloromercuribiphenyl (30%). No coupling products were reported for the reactions of $Rh(CO)Cl_2(C_6H_5)[P(C_6H_5)_3]_2$ and either vinyl or styrylmercuric chloride.[294] In addition to these low coupling yields, the coupling reactions of organomercurials and $Rh(CO)Cl_2(C_6H_5)[P(C_6H_5)_3]_2$ were not reinvestigated due to the possible interference of the carbonyl ligand. Vinyl and aryl ketones have been isolated from the reactions of organomercurials and rhodium compounds with carbonyl ligands (Chapter V). The successful vinyl-aryl coupling observed with a vinylrhodium compound generated in situ from the reaction of Wilkinson's catalyst and vinyl bromide suggested a phenylrhodium compound prepared from the reaction of Wilkinson's catalyst and phenyl iodide might also couple with organomercurials.

a. The reaction of $RhClI(C_6H_5)[P(C_6H_5)_3]_2$ and methyl- or vinylmercuric chloride Similar to the isolation of a vinylrhodium(III) species presumed to be $Rh(CH=CH_2)BrCl[P(C_6H_5)_3]_2$ from the oxidative addition of vinyl bromide to Wilkinson's catalyst, a phenylrhodium(III) species from the oxidative addition of phenyl iodide to Wilkinson's catalyst was isolated (Eq. 97). Since the elemental analysis of compounds previously prepared and purified in this manner were rarely acceptable, the reaction of this compound with vinyl- and methylmercuric chloride was used to partially



(97)

characterize it. Reacting the presumed $Rh(C_6H_5)ClI[P(C_6H_5)_3]_2$ with vinyl- and methylmercuric chloride in HMPA with excess lithium chloride at 70°C for 6 hours produces styrene (Eq. 98) in 52% yield and toluene (Eq. 99) in 23% yield respectively.

$$Rh(C_6H_5)ClI[P(C_6H_5)_3]_2 \; + \; H_2C{=}CHHgCl \xrightarrow[70°C]{HMPA/LiCl} 52\% \; C_6H_5CH{=}CH_2 \qquad (98)$$

$$Rh(C_6H_5)ClI[P(C_6H_5)_3]_2 \; + \; H_3CHgCl \xrightarrow[70°C]{HMPA/LiCl} 23\% \; C_6H_5CH_3 \qquad (99)$$

The mediocre nature of these rhodium mediated phenylations may be attributed to impure $Rh(C_6H_5)ClI[P(C_6H_5)_3]_2$; however, the discrepancy between the successful phenyl-vinyl and phenyl-methyl couplings suggests other factors may contribute. The reduced phenyl-vinyl coupling may be explained by competing symmetrical vinyl-vinyl coupling, although in this particular case, the formation of butadiene was not verified.

b. *The reaction of organomercurials with Rh(C_6H_5)ClI-[P(C_6H_5)$_3$]$_2$ formed in situ from RhCl[P(C_6H_5)$_3$]$_2$ and phenyl iodide* Because the vinyl-aryl coupling was successful for the vinylrhodium(III) halide formed *in situ* between vinyl bromide and Wilkinson's catalyst, the phenyl-vinyl and phenyl-methyl coupling was attempted with the phenylrhodium(III) halide formed *in situ* from phenyl iodide and Wilkinson's catalyst. However, in this case the reaction of stoichiometric Wilkinson's catalyst and excess phenyl iodide with vinyl- or methylmercuric chloride in HMPA with excess lithium chloride at 70°C for 24 hours produced styrene (Eq. 100) in 17% yield and toluene (Eq. 101) in 43% yield, respectively.

$$\mathrm{RhCl[P(C_6H_5)_3]_3} \xrightarrow[\substack{\text{HMPA/LiCl} \\ 70^\circ\text{C} \\ \text{15 min}}]{\mathrm{C_6H_5I}} \xrightarrow[\substack{\text{HMPA/LiCl} \\ 70^\circ\text{C} \\ \text{24 h}}]{\mathrm{H_2C{=}CHHgCl}} 17\%\ \mathrm{C_6H_5CH{=}CH_2} \tag{100}$$

$$\mathrm{RhCl[P(C_6H_5)_3]_3} \xrightarrow[\substack{\text{HMPA/LiCl} \\ 70^\circ\text{C} \\ \text{15 min}}]{\mathrm{C_6H_5I}} \xrightarrow[\substack{\text{HMPA/LiCl} \\ 70^\circ\text{C} \\ \text{24 h}}]{\mathrm{H_3CHgCl}} 43\%\ \mathrm{C_6H_5CH_3} \tag{101}$$

These phenyl-vinyl and phenyl-methyl coupling yields are not similar to those observed with the isolated phenylrhodium(III) compound. The phenyl-vinyl coupling was lower than previously observed presumably due to the competing symmetrical vinyl-

vinyl coupling. Also the observed phenyl-methyl coupling is probably limited to alkylmercurials not containing beta hydrogens. Since the phenyl-vinyl coupling yields were low and the phenyl-methyl coupling a special case, the catalytic aspects of this reaction were not investigated further.

C. Conclusion

The coupling of other organorhodium(III) halides with organomercurials has been reinvestigated. Successful coupling of a vinylrhodium(III) halide with arylmercurials is most dependent upon the method of formation and the purity of the vinylrhodium species. The oxidative addition of a vinyl halide such as vinyl bromide is superior to the formation of a rhodium hydride followed by the insertion of acetylene into the rhodium hydride. Although analytically pure $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ is not isolated from the reaction of Wilkinson's catalyst and vinyl bromide, good vinylation yields are observed from *in situ* formation of a vinylrhodium compound in the presence of the arylmercurial. The vinylation of arylmercurials is also functionally catalytic with comparable yields observed with either stoichiometric or 10% Wilkinson's catalyst. This is the most successful catalytic unsymmetrical carbon-carbon bond formation observed using organomercurials and rhodium catalysts so far. While stoichiometric conversions establish that the transmetalation, reductive elimination sequence forms carbon-carbon bonds, the catalytic vinylation of arylmercurials suggests some synthetic feasibility and importance. Unfortunately, the rhodium mediated vinylation of vinylmercurials or phenylation of vinyl- or methylmercurials similar to the methylation of vinyl- or arylmercurials is not as successful.

D. Experimental Section

1. General

The description of the instruments used as well as routine reagents and solvent purification have been described previously. Phenylmercuric chloride was obtained from Aldrich, methylmercuric chloride from Alfa-Ventron and *trans*-1-hexenylmercuric chloride[253,254] was prepared according to the literature procedure. $RhCl[P(C_6H_5)_3]_3$[273] and $[Rh(CO)_2Cl]_2$[295] were prepared from $RhCl_3 \cdot 3H_2O$ according to literature procedures. The $RhCl_3 \cdot 3H_2O$ was generously loaned by Matthey Bishop.

2. Preparation of $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$

The following procedure is representative of those used to prepare $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$. 0.70 Grams (0.75 mmoles) or 0.35 grams (0.375 mmoles) $RhCl[P(C_6H_5)_3]_3$ was placed in a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 20 or 10 ml dichloromethane was added by syringe and the system flushed with nitrogen again. Hydrogen chloride produced from sodium chloride and concentrated sulfuric acid was added via a needle inserted into the septum inlet until the color of the solution changed from dark red to yellow. After flushing out excess hydrogen chloride with nitrogen, acetylene was bubbled in until the color of the solution became a dark orange. Approximately 1 ml Skelly B was added and the mixture flushed with acetylene until crystals formed or until dry. Under acetylene the resulting solid was washed and shaken with ether, filtered and dried. The solids obtained all melt with extensive decomposition around 150°C.

Elemental analysis for vinylrhodium sample No. 1:

	C	H
Found	60.51	4.65
Calculated for		
$Rh(CH=CH_2)Cl_2[P(C_6H_5)_3]_2$	62.92	4.59
$Rh(CH=CH_2)Cl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$	60.22	4.46
60% $Rh(CH=CH_2)Cl_2[P(C_6H_5)_3]_2$ plus 40% $RhCl_2[P(C_6H_5)_3]_2$	61.31	4.40

Vinylrhodium sample No. 1 was prepared according to the above procedure in dichloromethane with a slow acetylene stream. Sample No. 2 was produced in what was assumed to be the same manner, but upon addition of Skelly B a yellow solid and a red gum formed. More dichloromethane was then added to obtain a homogeneous solution and the synthesis carried out as before. The vinylrhodium compound obtained, however, produced substantially less styrene in the coupling reaction. Similar problems occurred in the synthesis of sample No. 3 and Sample No. 4. sample No. 3 was darker orange and recrystallization of it (dichloromethane at -78°C) improved it moderately. Sample No. 4 ended up a dark gold color vaguely similar to the rhodium hydride. (This also agrees with the modestly increased styrene yield observed under an acetylene atmosphere). After this series of poor preparations, sample No. 5 and sample No. 6 were prepared as quickly as possible using decreased amounts of both dichloromethane and Skelly B. Although both sample No. 5 and sample No. 6 were very similar in color to sample No. 1, the yield of styrene using them was disappointingly low. Sample No. 7 was prepared in benzene, another possible solvent other than the chlorinated hydrocarbons dichloromethane and chloroform previously employed, yet the coupling yield using sample No. 7 is similar to the other yields. All the vinylrhodium compounds obtained were not crystalline, but are instead solid, powdery precipitates.

3. Representative procedure for the formation of styrene from $Rh(CH{=}CH_2)Cl_2[P(C_6H_5)_3]_2$ and phenylmercuric chloride

Approximately 0.05 grams (excess) lithium chloride was placed in a 5 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. The lithium chloride was heated in a 120°C oil bath overnight under vacuum. 0.0363 Grams (0.05 mmoles) $Rh(CH=CH_2)Cl_2[P(C_6H_5)_3]_2$ and 0.0157 grams (0.05 mmoles) phenylmercuric chloride were added while backflushing with nitrogen. A condenser was placed on the flask and the gas inlet tube replaced. A balloon of acetylene was added to some reactions. 0.0071 Grams (0.05 mmoles) n-decane and 0.5 ml dried and freshly distilled HMPA were added by syringe. The mixture was allowed to stir 24 or 6 hours in a 70°C oil bath. To quench the reaction, 0.5 ml benzene and 1.0 ml water were added and the benzene layer analyzed by GLPC. The GLPC conditions used were 1/4" x 10' 10% SE-30 on Chromosorb W 60/80 mesh at 115°C. The retention time of styrene is about 4 minutes while n-decane is about 7 minutes. Styrene was also confirmed by a M^+ of 104 in the GC-MS. The results are summarized in Table XXVII.

4. Modified procedure for the formation of styrene from $Rh(CH=CH_2)Cl_2[P(C_6H_5)_3]_2$ and phenylmercuric chloride

Approximately 0.5 grams lithium chloride was weighed into a 10 ml round bottom flask and dried in the previously described manner. Using a transfer needle approximately 5 ml dried and freshly distilled HMPA was transferred under nitrogen to the flask containing lithium chloride. 0.5 Ml of this solution was subsequently added by syringe to a typically equipped reaction flask flushed with nitrogen and containing the vinylrhodium compound and phenylmercuric chloride. After the addition of 0.0071 grams (0.05 mmoles) n-decane also via syringe, the reaction was then continued in the usual manner.

5. Procedure for the formation of styrene via $RhHCl_2[P(C_6H_5)_3]_2$, acetylene and phenylmercuric chloride

$RhHCl_2[P(C_6H_5)_3]_3 \cdot 0.5CH_2Cl_2$ was prepared by bubbling hydrogen chloride through a dichloromethane solution of $RhCl[P(C_6H_5)_3]_2$ as described in the preparation of $Rh(CH=CH_2)Cl_2[P(C_6H_5)_3]_2$. After the yellow color developed throughout, 1 ml Skelly B was added and the solution flushed with nitrogen. The yellow precipitate which formed was filtered under nitrogen and used immediately.

Approximately 0.05 grams (excess) lithium chloride was weighed into a 5 ml round bottom flask equipped with septum inlet, gas inlet tube and magnetic stirring bar. The lithium chloride was dried overnight in a 120°C oil bath under vacuum. 0.0371 Grams (0.05 mmoles) freshly prepared $RhHCl_2[P(C_6H_5)_3]_2 \cdot 0.5CH_2Cl_2$ was added while backflushing with nitrogen. A condenser was added and the gas inlet tube replaced. The system was flushed with acetylene. After 15 minutes the color of the solution changed to dark red, and 0.0157 grams (0.05 mmoles) phenylmercuric chloride or 0.0202 grams (0.05 mmoles) phenylmercuric iodide was added all at once while backflushing with acetylene. An acetylene balloon was attached to the gas inlet tube. 0.0071 Grams (0.05 mmoles) n-decane was added by syringe and the reaction mixture stirred 6 hours in a 70°C oil bath. 0.5 Ml benzene and 1.0 ml water were added and the benzene layer analyzed by GLPC.

6. The reaction of $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ and di-p-tolylmercury in an acetylene atmosphere

Approximately 0.05 grams (excess) lithium chloride was weighed into a 5 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. The lithium chloride was dried overnight in a 120°C oil bath under vacuum. 0.0385 Grams (0.05 mmoles) $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ organorhodium sample No. 4 and 0.0096 grams (0.025 mmoles) di-p-tolylmercury were added while backflushing with nitrogen. A condenser was placed on the flask and the gas inlet tube replaced. The system was flushed with acetylene from a balloon both before and after 0.5 ml dried and freshly distilled HMPA was added by syringe. After the mixture stirred 6 hours at 70°C, 0.5 ml benzene and 1.0 ml water were added and the benzene layer analyzed by GLPC. p-Methylstyrene (M^+ = 118 from the GC-MS) was observed wtih a retention time of 6.5 minutes, approximately 2.5 minutes longer then stryene. The impurity peak present at approximately 3.25 minutes was still present and contained both chlorobenzene and dichlorobutadiene. The presence of both chlorobenzene and dichlorobutadiene was determined from the GC-MS. The mass peaks at 51, 77, and 112 fit with chlorobenzene (M^+ = 112, 114 is about 30% of 112), while the peaks at 87 and 122 fit with a dichlorobutadiene (M^+ = 122, 124 is about 65% of 192, and 126 is about 10% of 122). The ratios of 51, 77 and 112 versus 87 and 122 vary as the mass spectrum is measured at different times during the GLPC analysis. No peak corresponding to p-chlorotoluene was observed by either GLPC or GC-MS analysis.

7. Attempted preparation of $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$ via acetylene

0.35 Grams (0.375 mmoles) $RhCl[P(C_6H_5)_3]_3$ was weighed into a 250 ml round bottom flask equipped with septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 10 ml dichloromethane was added by syringe. Hydrogen bromide was then bubbled in until a color change was observed. The mixture turned from dark red to dull green. After sweeping the system with nitrogen, acetylene was then bubbled in until the solution changed colors again from dull green to lighter yellow green. 1 Ml Skelly B was added and the acetylene bubbled through the solution until it was nearly dry. Under acetylene the resulting solid was washed and shaken with ether, filtered and dried, producing a dull yellow-green solid. The identity of this and subsequent rhodium compounds as containing a vinylrhodium species, presumably impure $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$, was established primarily by subsequent reaction with phenylmercuric chloride.

8. Attempted preparation of $Rh(CH{=}CH_2)BrCl[P(C_6H_5)_3]_2$

0.35 Grams (0.375 mmoles) $RhCl[P(C_6H_5)_3]_2$ was weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, the flask was placed in an ice/water bath and 10 ml (excess) vinyl bromide added all at once. After stirring a variable time at 0°C the vinyl bromide was removed (water aspirator) leaving a dark red brown solid. The gas inlet tube was replaced with a filter frit also attached to another 250 ml round bottom flask with a septum inlet. Under nitrogen the solid was washed and agitated with appropriate solvents, filtered and dried. Various dull pink-orange solids were obtained.

Organorhodium sample No. 2 was prepared from a very short (~5 minutes) reaction time of Wilkinson's catalyst plus vinyl bromide followed by an ether rinse. Sample No. 3 was prepared from a longer (6 to 8 hours) reaction time of Wilkinson's catalyst and vinyl bromide followed by one acetone rinse. sample No. 4 was prepared as sample No. 3 however four acetone rinses were employed. Sample No. 5 was prepared similar to sample No. 3 and sample No. 4, except the acetone was added before the excess vinyl bromide was removed. sample No. 6 was prepared like sample No. 4. Three minutes reaction time, followed by several acetone rinses, was employed in the preparation of sample No. 7.

Unfortunately, the carbon and hydrogen analysis for sample No. 6 does not agree with any of the rhodium compounds which might be expected to be formed.

Elemental analysis for organorhodium sample No. 6:

	C	H
Found	57.88	4.31
Calculated for		
$Rh(CH=CH_2)BrCl[P(C_6H_5)_3]_2$	59.28	4.32
$Rh(CH=CH_2)BrCl[P(C_6H_5)_3]_3$	65.16	4.69
$Rh(CH=CH_2)Br_2[P(C_6H_5)_3]_2$	56.06	4.08
$Rh(CH=CH_2)Br_2[P(C_6H_5)_3]_3$	63.31	4.49
75% $Rh(CH=CH_2)BrCl[P(C_6H_5)_3]_2$ plus 25% $RhBr_2Cl[P(C_6H_5)_3]_2$	57.52	4.15

9. Representative procedure for the formation of styrene from $Rh(CH=CH_2)BrCl[P(C_6H_5)_3]_2$ and phenylmercuric chloride

Approximately 0.05 grams (excess) lithium chloride was weighed into a 5 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. The lithium chloride was dried overnight in a 120°C oil bath under vacuum. 0.0385 Grams (0.05 mmoles) $Rh(CH=CH_2)BrCl[P(C_6H_5)_3]_2$ and 0.0157 grams (0.05 mmoles) phenylmercuric chloride was added while backflushing with nitrogen. A condenser was placed on the flask and the gas inlet tube replaced. A balloon of acetylene was added to some reactions. 0.0071 Grams (0.05

mmoles) n-decane and 0.5 ml dried and freshly distilled HMPA were added by syringe. After the mixture stirred 6 hours at 70°C, 0.5 ml benzene and 1.0 ml water were added and the benzene layer analyzed by GLPC. The results are summarized in Table XXVIII.

10. Vinylation of organomercurials with $Rh(CH=CH_2)BrCl[P(C_6H_5)_3]_2$ formed in situ from Wilkinson's catalyst and excess vinyl bromide

Approximately 0.05 grams (excess) lithium chloride was placed in a 5 ml round bottom flask equipped with septum inlet, gas inlet tube and magnetic stirring bar. The lithium chloride was dried overnight in a 120°C oil bath under vacuum. 0.0463 Grams (0.05 mmoles) $RhCl[P(C_6H_5)_3]_2$ and 0.0157 grams (0.05 mmoles) phenylmercuric chloride were added while backflushing with nitrogen. A condenser was placed on the flask, approximately 0.3 ml (excess) vinyl bromide was added and the gas inlet tube replaced. 0.0071 Grams (0.05 mmoles) n-decane and 0.5 ml dried and freshly distilled HMPA were added by syringe. After the mixture stirred the appropriate time at 70°C, 0.5 ml benzene and 1.0 ml water were added and the benzene layer analyzed by GLPC.

The reactions with 0.0160 or 0-0161 grams (0.05 mmoles) trans-1-hexenylmercuric chloride or 1-hexylmercuric chloride respectively were quenched with 0.5 ml pentane and 1.0 ml water instead of benzene and water. The GLPC analysis conditions and internal standard were changed also to 1/4 x 10' 10% SE-30 on Chromosorb W 60/80 mesh at 75°C with nonane as an internal standard. The reaction with *trans*-1-hexenylmercuric chloride produces 1,3-octadiene, but the reaction with 1-hexylmercuric chloride does not produce 1-octene as indicated by GLPC. The stereochemistry of 1,3-octadiene was not determined.

11. *Vinylation of phenylmercuric chloride with vinyl bromide catalyzed by 10 mole % RhCl[P(C_6H_5)$_3$]$_3$*

Approximately 0.05 grams (excess) lithium chloride was placed in a 5 ml round bottom flask equipped with septum inlet, gas inlet tube and magnetic stirring bar. The lithium chloride was dried overnight in a 120°C oil bath under vacuum 0.0046 grams (0.005 mmoles) RhCl[P(C_6H_5)$_3$]$_3$ and 0.0157 grams (0.05 mmoles) phenylmercuric chloride were added while backflushing with nitrogen. A condenser was placed on the flask, approximately 0.3 ml (excess) vinyl bromide was added and the gas inlet tube replaced. 0.0071 Grams (0.05 mmoles) *n*-decane and 0.5 ml dried and freshly distilled HMPA were added by syringe. After the mixture stirred the appropriate time at 70°C, 0.5 ml benzene and 1.0 ml water were added and the benzene layer GLPC analyzed.

12. Attempted vinylation of phenylmercuric chloride with vinyl bromide catalyzed by 5 mole % $[Rh(CO)_2Cl]_2$

0.0010 Grams (0.0025 mmoles) $[Rh(CO)_2Cl]_2$ and 0.0157 grams (0.05 mmoles) phenylmercuric chloride were weighed into a 5 ml round bottom flask equipped with septum inlet, gas inlet tube and magnetic stirring bar. At least 0.0213 grams (0.5 mmoles) lithium chloride was added in some reactions. After flushing with nitrogen, approximately 0.3 ml (excess) vinyl bromide was added. Finally 0.0071 grams (0.05 mmoles) *n*-decane and 0.5 ml THF or other appropriate solvent were added by syringe. After stirring at room temperature, the reaction mixtures were directly analyzed by GLPC after 1, 6 and 24 hours. The results are summarized in Table XXX.

13. Attempted vinylation of *trans*-1-hexenylmercuric chloride with vinyl bromide catalyzed by 10 mole percent $RhCl[P(C_6H_5)_3]_3$

0.0046 Grams (0.005 mmoles) $RhCl[P(C_6H_5)_3]_3$ and 0.0160 grams (0.05 mmoles) *trans*-1-hexenylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with septum inlet and magnetic stirring bar. 0.3 Ml (excess) vinyl bromide was added and a gas inlet tube added to the flask. After sweeping the reaction flask with nitrogen, 0.0057 grams (0.05 mmoles) *n*-nonane and 0.5 ml THF were added by syringe. After stirring at room temperature 16 hours, the mixture was analyzed directly by GLPC. GLPC analysis indicated 1,3-octadiene was not formed, although a small amount of trans,trans-5,7-dodecadiene was formed as established by comparison of the GLPC retention times with those of an authentic sample.

14. Attempted preparation of $Rh(C_6H_5)ClI[P(C_6H_5)_3]_2$

0.35 Grams (0.375 mmoles) $RhCl[P(C_6H_5)_3]_3$ was weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 10 ml iodobenzene was added all at once. Since a striking color change did not occur immediately, the mixture was stirred for 6 hours at room temperature. The excess iodobenzene was removed in vacuo (oil pump with slight warming of the flask) and the resulting solid washed and shaken four times with acetone, filtered and dried under nitrogen. Previous limited success at preparing these types of compounds in this manner suggests that the reaction with organomercurials may be just as enlightening as other methods of characterization.

15. Phenylation of organomercurials with $Rh(C_6H_5)ClI-P(C_6H_5)_3]_2$

Approximately 0.05 grams lithium chloride was weighed into a 5 ml round bottom flask equipped with septum inlet, gas inlet tube and magnetic stirring bar. The lithium chloride was dried overnight in a 120°C oil bath under vacuum. 0.0434 Grams (0.05 mmoles) $Rh(C_6H_5)ClI[P(C_6H_5)_3]_2$

and 0.0126 or 0.0132 grams (0.05 mmoles) methyl- or vinylmercuric chloride respectively were added while backflushing with nitrogen. A condenser was placed on the flask and the gas inlet tube replaced. 0.0064 or 0.0071 Grams (0.05 mmoles) n-nonane or n-decane and 0.5 ml dried and freshly distilled HMPA were added by syringe depending on the organomercurial employed. After the mixture stirred 6 hours at 70°C, 0.5 ml benzene and 1.0 ml water were added and the benzene layer analyzed by GLPC.

The GLPC conditions for toluene were 1/4" x 10' 10% SE-30 on Chromosorb W 60/80 mesh at 90°C. Toluene ($M^+ = 92$) and styrene ($M^+ = 104$) were also verified by GC-MS.

16. Phenylation of organomercurials with $Rh(C_6H_5)ClI[P(C_6H_5)_3]_2$ formed in situ from $RhCl[P(C_6H_5)_3]_3$ and excess iodobenzene

Approximately 0.05 grams (excess) lithium chloride was placed in a 5 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar and dried overnight at 120°C under vacuum. 0.0463 Grams (0.05 mmoles) $RhCl[P(C_6H_5)_3]_3$ and 0.0126 or 0.0132 grams (0.05 mmoles) methyl- or vinylmercuric chloride, respectively, were added while backflushing with nitrogen. A condenser was added and the gas inlet tube replaced. 0.0064 or 0.0071 Grams (0.05 mmoles) n-nonane or n-decane, 0.2 ml (excess) iodobenzene and 0.5 ml dried and freshly distilled HMPA were added by syringe. After the reaction mixtures stirred 16 hours at 70°C, 0.5 ml benzene and 1.0 ml water were added and the benzene layer GLPC analyzed.

V. THE SYNTHESIS OF DIVINYL AND DIARYL KETONES

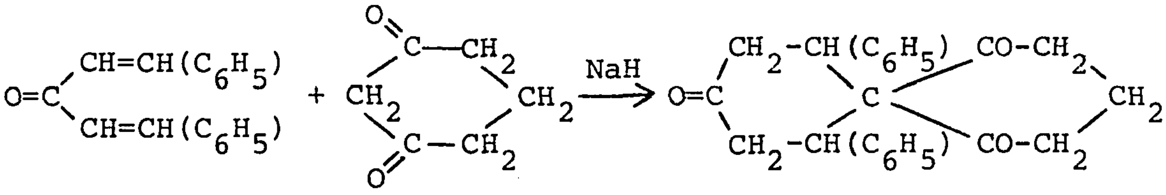
A. Introduction

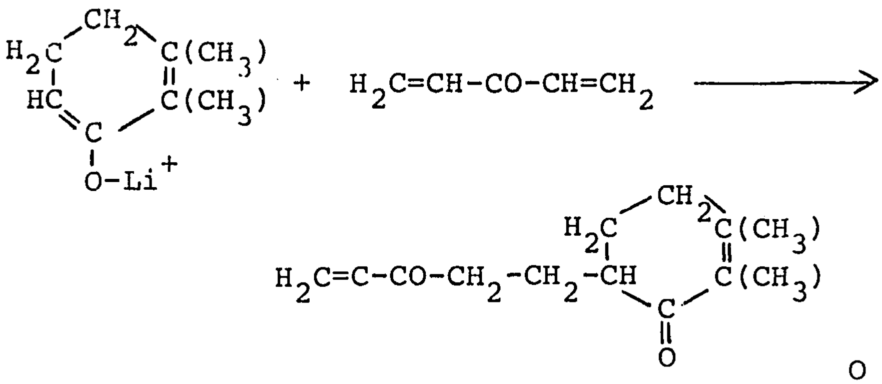
During studies on the acylation of vinylmercurials with acyl halides and Lewis acids, the acylation of vinylmercurials with acyl halides and transition metal compounds was briefly investigated and determined to be unpromising.[265,266] Unfortunately, none of the investigated reactions were performed in a carbon monoxide atmosphere. Despite numerous reports of the formation of aryl ketones from arylmercurials and transition metal compounds, the carbonylation of vinylrhodium species prepared via the transmetalation of vinylmercurials with rhodium(I) or -(III) compounds was not established. Analogous to the reported formation of benzophenone from phenylmercuric chloride and $Rh(CO)Cl[P(C_2H_5)_3]_2$ under a carbon monoxide atmosphere,[78] vinylmercurials would be expected to form divinyl ketones. Before beginning this discussion of the carbonylation of vinyl- and arylrhodium species, other methods of forming divinyl ketones and the reaction of arylmercurials and other transition metal carbonyl compounds should be considered.

1. Synthetic Utility and Synthesis of Divinyl Ketones

Divinyl ketones have been demonstrated to react as double (Eq. 102)[296-303] and less frequently single[304] (Eq. 103) Michael acceptors. Danishefsky has developed divinyl ketone equivalents to be employed as symmetrical or unsymmetrical double Michael acceptors in order to avoid the handling difficulties of divinyl ketone itself.[305-307] In the Nazarov cyclization (Eq. 104),[308] divinyl ketones are

(102)





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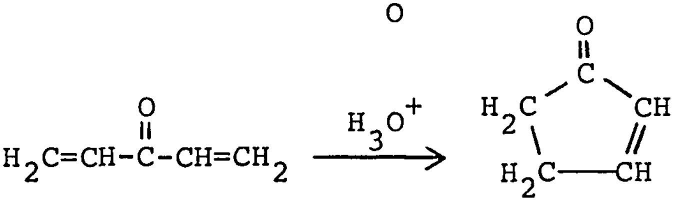


(104)

treated with acid generating pentadienyl cations which cylize to cyclopentenones, in some cases stereospecifically.[309] Unfortunately, a direct stereospecific synthesis of divinyl ketones is lacking. Nazarov's divinyl ketone synthesis involves reaction of the Grignard reagent derived from 1-bromobut-3-en-1-yne with paraformaldehyde, and subsequent treatment with mercuric sulfate and methanol generating 1,5-dimethoxy-3-pentanone which eliminates methanol twice forming 1,4-pentadien-3-one.[310,311] 1,4-Pentadien-3-one has more recently been prepared from the reaction of β-chloropropionyl chloride and ethylene with aluminum chloride, followed by distillation from sodium carbonate to dehydrohalogenate completely.[312] Higher olefins are less reactive in the acylation step. 1,5-Diphenyl-3-pentadienone is easily prepared from the condensation of benzaldehyde and acetone with sodium hydroxide,[313] however this reaction cannot be extended to aldehydes with β-methine or β-methylene hydrogens.

2. The reaction of organomercurials with transition metal carbonyl compounds

The formation of ketones from organomercurials, transition metal compounds and carbon monoxide or transition metal carbonyl compounds is well-established for aryl- and alkylmercurials with various transition metal salts and compounds. In a patent, Henry reported the formation of diaryl ketones as well as acids, anhydrides, and esters from organomercury, -tin, or -lead compounds, a Group VIII metal salt and carbon monoxide.[314] Heck published the reaction of arylmercuric chlorides and catalytic amounts of palladium or rhodium compounds with carbon monoxide in methanol, acetonitrile, or toluene.[78] The products were often mixtures composed of methyl esters (if methanol was the solvent), acid chlorides, diaryl ketones and biaryls. Yields of diaryl ketones up to 50% were reported for the reaction of 10 mole percent

$Rh(CO)Cl[P(C_2H_5)_3]_2$ and phenylmercuric chloride in toluene under one atmosphere of carbon monoxide.

Seyferth and Spohn reported the formation of symmetrical diaryl or dialkyl ketones from the reaction of aryl- or alkylmercuric chlorides or diaryl- or dialkylmercury compounds with dicobalt octacarbonyl in THF.[315,316] Since a product of this reaction, $Hg[Co(CO)_4]_2$ forms dicobalt octacarbonyl and mercury(0) upon photolysis, diaryl- or dialkylmercury compounds, carbon monoxide and a catalytic amount of $Hg[Co(CO)_4]_2$ or $Co_2(CO)_8$ forms ketones upon photolysis.[317] Nickel carbonyl also reacts with aryl- or alkylmercuric halides and carbon monoxide forming diaryl or dialkyl ketones.[318] Unsymmetrical ketones such as p-tolyl phenyl ketone could be obtained from the reaction of iodobenzene, nickel carbonyl and p-tolylmercuric chloride in THF.

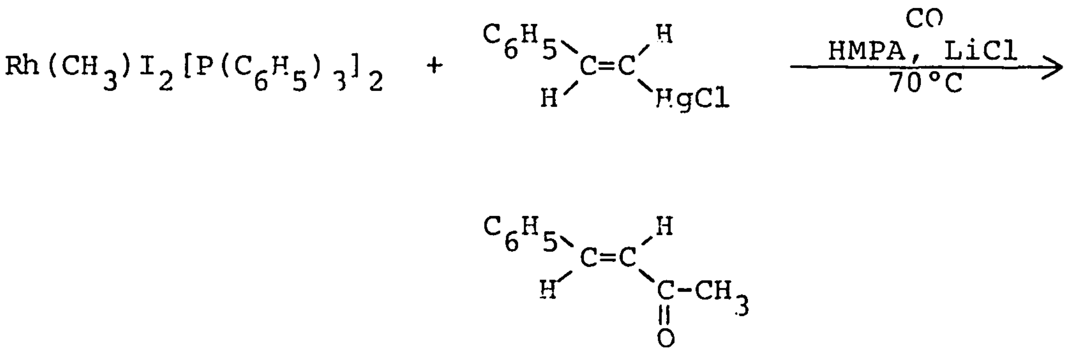
Also, as previously mentioned (Chapter II), unsymmetrical ketones are also formed from acyl halides and diorganomercury compounds catalyzed by tetrakis(triphenylphosphine)palladium(0).[264] The carbonylation of vinylmercurials is an attractive route to divinyl ketones because both transmetalation[319] and carbonylation[320] proceed with retention of stereochemistry with respect to carbon, the vinylmercurials are available stereospecifically from acetylenes,[253,254] and both reaction and work-up conditions are mild and neutral, enabling excellent yields of acid and base sensitive molecules to be obtained.

B. Results and Discussion

1. Divinyl ketone synthesis

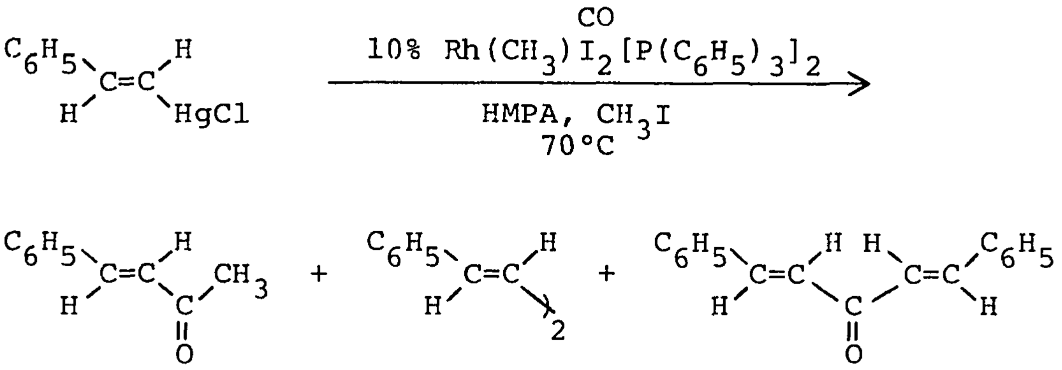
a. Initial studies Since the methylation of vinylmercurials mediated by catalytic amounts of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ was not successful due to the competing formation of dienes, other possible rhodium catalysts were also investigated for the methylation of vinylmercurials. In addition to the results discussed in Chapter II, the results with rhodium catalysts containing carbon monoxide ligands or in a carbon monoxide atmosphere were especially interesting.

The reaction of a stoichiometric quantity of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and styrylmercuric chloride in HMPA at 70°C with added lithium chloride under an atmosphere of carbon monoxide formed 4-phenyl-3-buten-2-one as the major product in ~60% yield (Eq. 105). Employing a catalytic amount of $Rh(CH_3)I_2$-



(105)

$[P(C_6H_5)_3]_2$ with excess methyl iodide produced a mixture of 4-phenyl-3-buten-2-one, 1,4-diphenylbutadiene and 1,5-diphenyl-3-pentadienone (Eq. 106). Using $Rh(CO)Cl[P(C_6H_5)_3]_2$



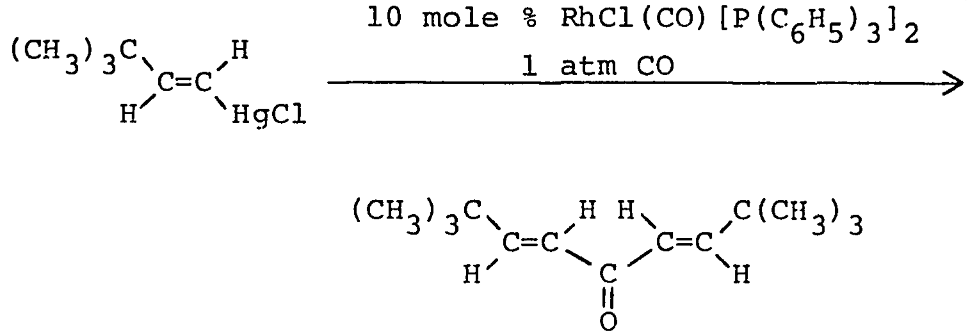
(106)

as the catalyst under the same conditions but at room temperature produced less 4-phenyl-3-buten-2-one and 1,4-diphenylbutadiene but more 1,5-diphenyl-3-pentadienone.

Efforts toward maximizing the yield of divinyl ketone involved omitting methyl iodide and investigating the effect of various rhodium(I) or rhodium(III) compounds as catalysts. The effect of solvent and added reagents, such as lithium chloride upon the formation of divinyl ketones was also considered. Since the styrylmercurial possesses unusually low solubility properties, a typical vinylmercurial <u>trans</u>-3,3-dimethyl-1-butenylmercuric chloride was selected for these studies.

Table XXXI indicates the effect of solvent and temperature upon reactions catalyzed by 10 mole percent Rh(CO)Cl-

Table XXXI. Effect of solvent and temperature on the formation of divinyl ketones from vinylmercurials

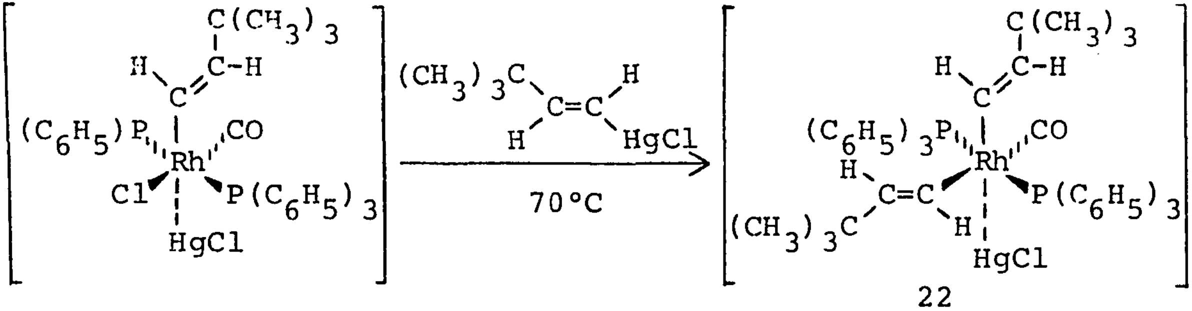


Solvent	Temperature °C	Time h	GLPC Yield %
THF	25	24	85,94
	65	1	19
		24	19
$(C_2H_5)_2O$	25		68
CH_2Cl_2			58
HMPA			60
	70	1	~21[a]
		24	~25[a]

[a] % Corrected yield determined from peak heights and not peak areas since HMPA interferes with the peak area measurement.

$[P(C_6H_5)_3]_2$. THF at room temperature produces the highest yield of divinyl ketone. Refluxing the THF solution substantially reduces the yield of divinyl ketone due to the preferential formation of the symmetrical diene, trans,trans-2,2,7,7-tetramethyl-3,5-octadiene. Apparently transmetalation of the vinylrhodium(III) halide with the vinylmercurial and subsequent reductive elimination of the diene (Eq. 107) is faster (above room temperature) than carbon monoxide insertion (vinyl migration) (Eq. 108) forming the acyl species.

(107)



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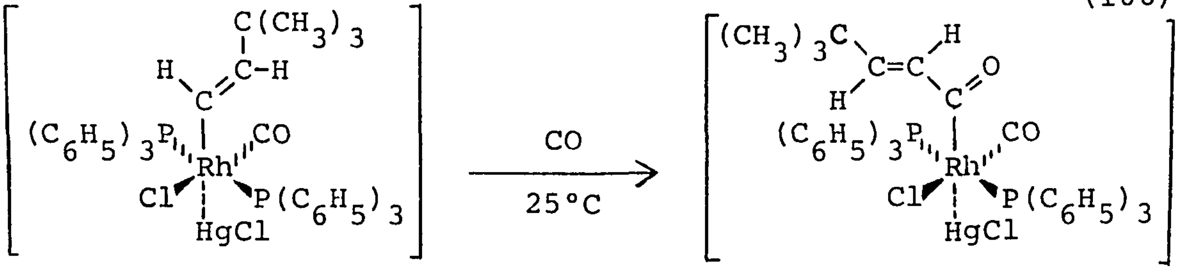
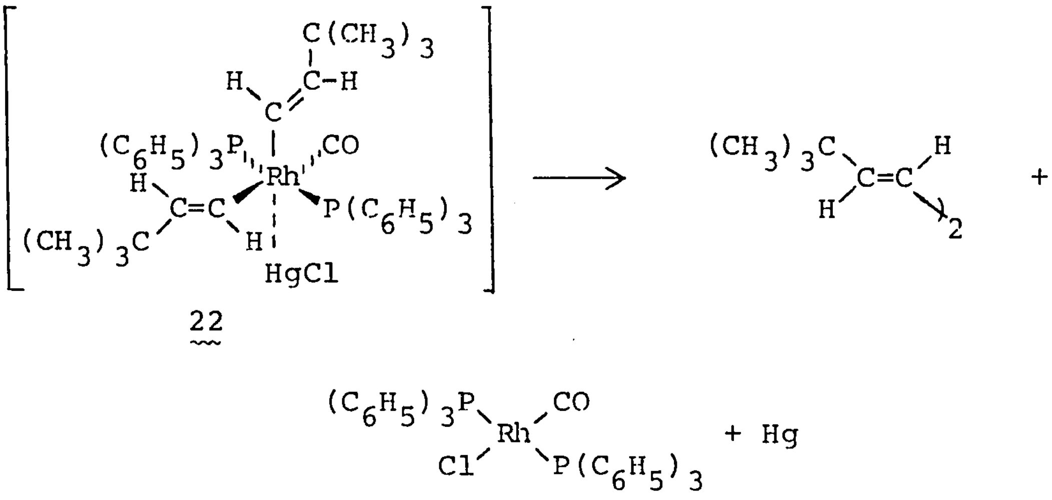
(108)



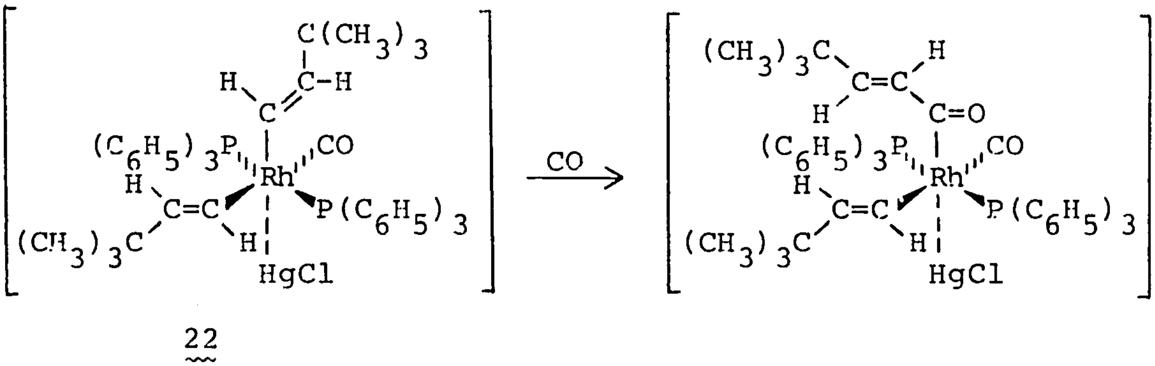
It is also possible but less likely for the competing processes of reductive elimination (Eq. 109) and carbon monoxide insertion followed by reductive elimination (Eq. 110) to involve a single, common intermediate **22**. Later in a discus-



22

(109)

(110)

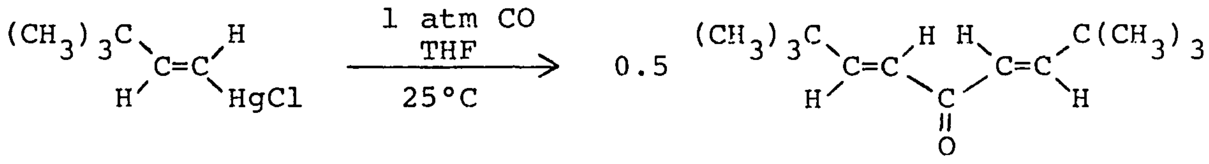


22

sion of the possible mechanistic pathways the order of the mechanistic steps is again considered. The effect of temperature on the reaction in HMPA is similar. Although the yield in HMPA is only slightly less, it is not the solvent of choice due to its carcinogenic properties. The yield in either ether or dichloromethane at room temperature is also a little less than THF. Despite the lower yield, the reaction in dichloromethane was quite clean.

The effect of various rhodium catalysts on the formation of divinyl ketones is indicated in Table XXXII. Most striking

Table XXXII. Effect of catalyst on the formation of divinyl ketones from vinylmercurials



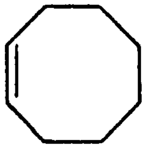
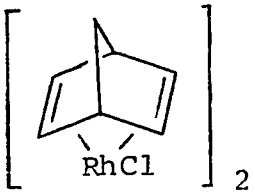
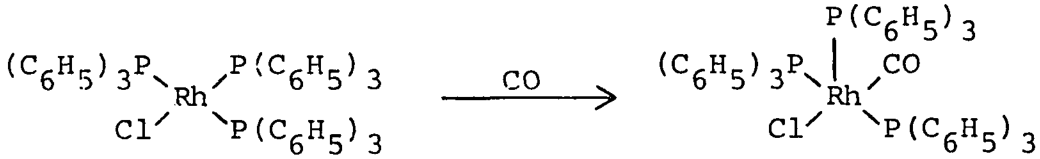
Catalyst	Mole % Metal	Added Reagents	Time h	GLPC Yield %
$RhCl(CO)[P(C_6H_5)_3]_2$	10	--	24	85,94
	1			69
			84	82
	.1		24	42
			84	67
			132	64
		>2LiCl	24	80
$RhCl_3 \cdot 3H_2O$		--		60
			48	68
$RhCl[P(C_6H_5)_3]_3$			24	20
			48	21
$[Rh(H_2C{=}CH_2)_2Cl]_2$			24	69
$[Rh(CO)_2Cl]_2$				77
		>2LiCl		99
[Rh()$_2$Cl]$_2$		--		52

Table XXXII. (continued)

Catalyst	Mole % Metal	Added Reagents	Time h	GLPC Yield %
		--		64
Li_2PdCl_4	100	--	6	10
			24	7
Li_2PdCl_4	100		4	33[a]
			24	18[a]
Li_2PdCl_4	10	$CuCl_2$	6	0
			24	0

[a] Reaction temperature began at -78°C and warmed to room temperature.

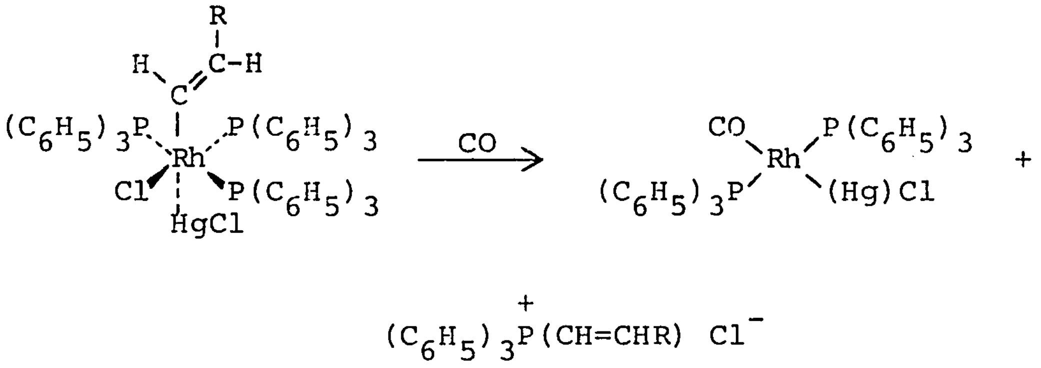
perhaps is the extensive number of rhodium compounds which catalyze this reaction. Wilkinson's catalyst with three triphenylphosphine ligands is the least catalytic with respect to the formation of divinyl ketones. The initial dark red solution immediately turned yellow upon flushing the solution with carbon monoxide. Although the color of the reaction then resembled that of $Rh(CO)Cl[P(C_6H_5)_3]_2$ catalyzed reactions, the yield of divinylketone was significantly lower. Perhaps carbon monoxide is coordinated to rhodium, but a triphenylphosphine ligand is not completely displaced from the coordination sphere (Eq. 111), thus decreasing reactivity. A



(111)

EAN Rule	Rh	9e	Rh	9e
	Cl	1e	Cl	1e
	$(C_6H_5)_3P$	6e	$(C_6H_5)_3P$	6e
			CO	2e
		16e		18e

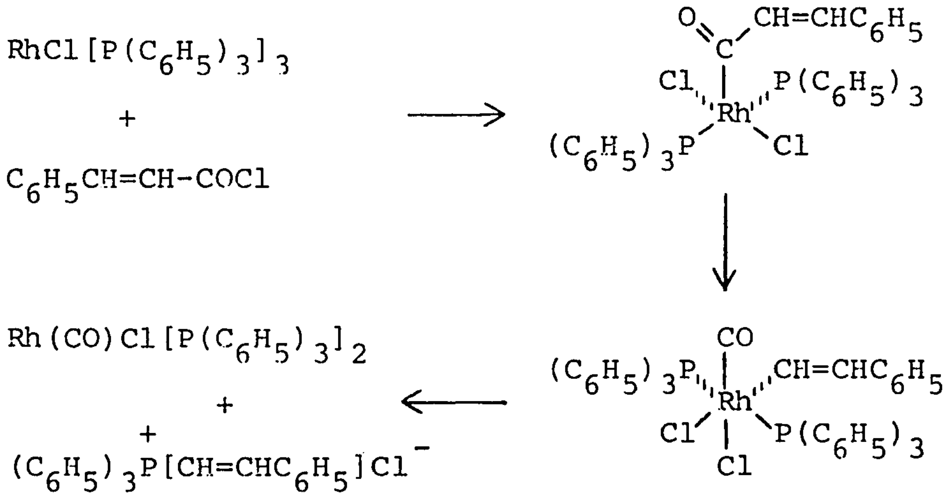
more satisfying explanation for the poor yield observed with Wilkinson's catalyst may be the competing formation of a vinylphosphonium salt (Eq. 112). Kampmeier has very recently reported the formation of β-styryltriphenylphosphonium chloride from cinnamoyl chloride and Wilkinson's catalyst



(112)

(Scheme 46).[321] The sequential formation of the rhodium(III) acyl compound and the rhodium(III) sytryl compound were

Scheme 46

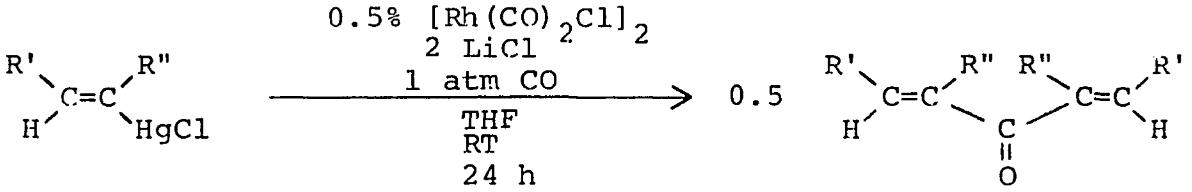


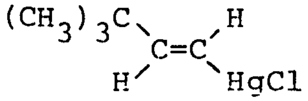
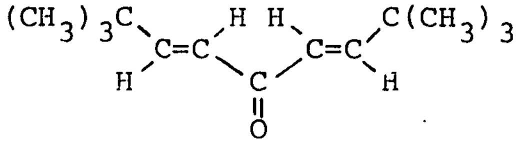
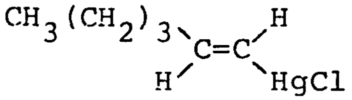
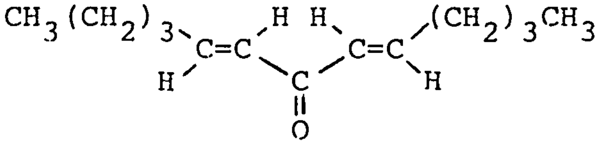
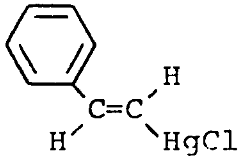
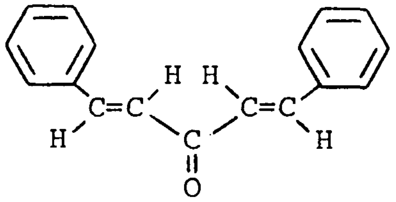
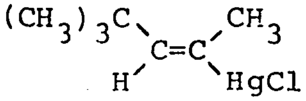
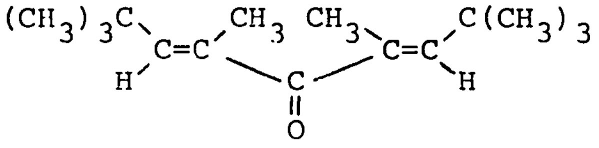
followed spectroscopically. The other rhodium catalysts which were almost as effective as $Rh(CO)Cl[P(C_6H_5)_3]_2$ contained two coordinating ligands of the olefin or carbon monoxide type. Their success may depend upon the facile displacement of the olefin ligand by carbon monoxide. The success of the rhodium(III) species, $RhCl_3 \cdot 3H_2O$ suggests that it is possible for two successive transmetalations to occur followed by the reductive elimination of the divinyl ketone which also forms a catalytically active rhodium(I) species. $Rh(CO)Cl[P(C_6H_5)_3]_2$ is the superior catalyst (producing yields of approximately 90%) for reactions in THF which employ only the vinylmercurials, carbon monoxide and the catalyst. Although more than 24 hours are required, good yields of the divinyl ketone may be obtained with as low as one mole percent or 0.1 mole percent rhodium. However, the addition of lithium chloride to the reaction mixture changes the catalyst choice to $[Rh(CO)_2Cl]_2$. Not only is the yield quantitative, the reaction is cleaner and easier to work up since the triphenylphosphine ligand is not present to interfere in the isolation of the divinyl ketone. Incidentally, $[Rh(CO)_2Cl]_2$ with added lithium chloride and THF as solvent, but under a nitrogen atmosphere, was the preferred catalyst for the formation of the symmetrical dienes from vinylmercurials.[80]

Since palladium(0)/palladium(II) compounds often react similarly to rhodium(I)/rhodium(III) compounds and palladium chloride is employed in the carbonylation of vinylmercurials to form unsaturated acids and esters,[213] whether divinyl ketone formation might also be catalyzed by palladium chloride was also investigated. Dilithium tetrachloropalladate promotes the formation of divinyl ketones but apparently reacts further once the divinyl ketone is formed. The reaction containing one equivalent of dilithium tetrachloropalladate turned black immediately at room temperature forming 10% divinyl ketone after 6 hours which decreased to 7% after 24 hours. Starting the reaction at -78°C formed 33% of the divinyl ketone which decreased to 18% after 24 hours. Since a palladium zero complex of 1,5-diphenyl-3-pentadienone is known,[322,323] the formation and subsequent reactions of an analogous compound might account for the decreased yields although this was not investigated further. Attempting to employ cupric chloride as a re-oxidant for palladium(0) with 10 mole percent palladium chloride was unsuccessful. No divinyl ketone was observed by GLPC analysis.

b. The synthesis of divinyl ketones Under the optimum reaction conditions for divinyl ketone formation (1 equivalent of the vinylmercurial, 2 equivalents lithium chloride, 0.5 percent $[Rh(CO)_2Cl]_2$ and one atmosphere of carbon monoxide in THF at room temperature), other vinylmercurials also produce excellent yields of divinyl ketones (Table XXXIII). In all cases the stereochemistry of the trans-vinylmercurial is preserved as exclusively trans,trans-divinyl ketones are formed. Vinylmercurials derived from terminal alkynes produce nearly quantitative yields of

Table XXXIII. The synthesis of symmetrical divinyl ketones



Vinylmercurial	Divinyl Ketone	Isolated Yield %[a]
		96(78)[b]
		94(78)[c]
		99(88)[d]
		64(47)[c]

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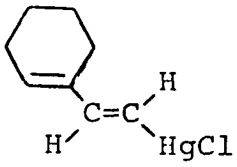
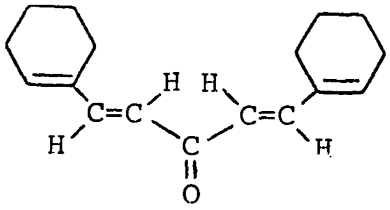
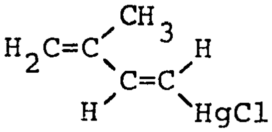
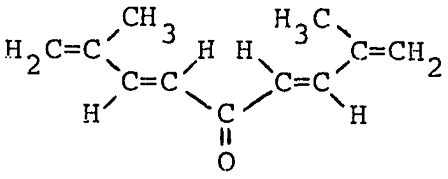
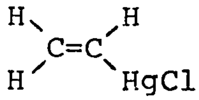
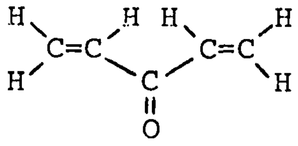
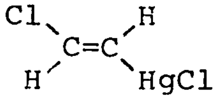
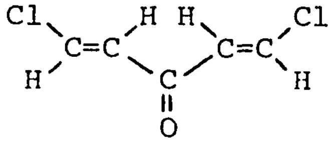
[a] Crude isolated yield, spectra identical with further purified product.

[b] Sublimed.

[c] Bulb-to-bulb distilled.

[d] Recrystallized.

Table XXXIII. (continued)

Vinylmercurial	Divinyl Ketone	Isolated Yield %
		100[e]
		41
		89[f]
		--[g]

[e] Attempted purification caused decomposition.

[f] GLPC yield due to high volatility of product.

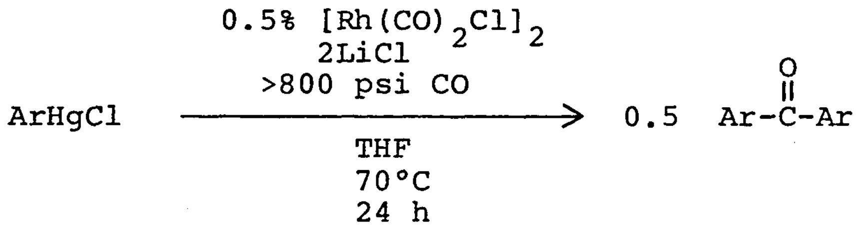
[g] Yield could not be determined due to the unknown purity of the vinylmercurial.

divinyl ketones after 24 hours. Although 3-pentadienone is available by this route, it is not easily isolated due to its low boiling point and difficulties in separating it from THF. Changing the solvent from THF to ether resulted in formation of a white precipitate during the reaction and significantly slower and lower production of 3-pentadienone. Vinylmercurials derived from internal alkynes require increased reaction times and produce decreased yields of divinyl ketones. Mercurials derived from enynes are also transformed into symmetrical polyenones. However, the yield of symmetrical tetraenone derived from 2-methyl-1-buten-3-yne might be unusually low due to the questionable purity of the mercurial. Although difficulties have been encountered reproducing the reported synthesis of the *trans*-β-chlorovinylmercuric chloride,[277] thus preventing the yield of *trans*,*trans*-1,5-dichloro-3-pentadienone from being determined, a small scale reaction beginning with a mixture of *trans*-β-chlorovinylmercuric chloride, *trans*,*trans*-bis-β-chlorovinylmercury and mercuric chloride indicates that *trans*,*trans*-1,5-dichloro-3-pentadienone is also formed by this synthetic route.

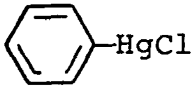
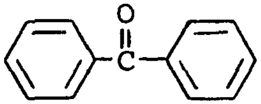
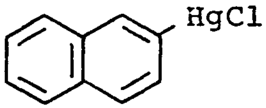
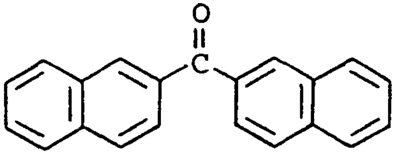
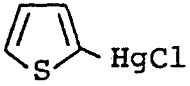
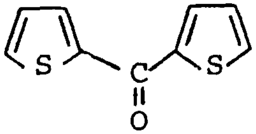
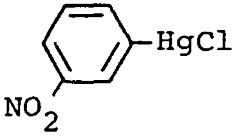
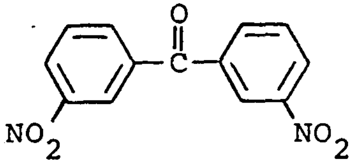
2. The synthesis of diaryl ketones

Although the formation of diaryl ketones via carbonylation of arylmercurials mediated by transition metal compounds has been well-established, the yields of diaryl ketones via similar rhodium(I) and -(III) compounds were not high. The highest yield reported by Heck is approximately 50%. Therefore, the carbonylation of arylmercurials under the catalytic conditions producing quantitative carbonylation of vinylmercurials deserved investigation. The reaction of phenylmercuric chloride with 2 equivalents lithium chloride and 5 mole percent $[Rh(CO)_2Cl]_2$ with one atmosphere of carbon monoxide in THF at room temperature did not produce benzophenone, but yields biphenyl instead. Diaryl ketones, however, are formed if more vigorous reaction conditions are employed. Increasing both the reaction temperature to 70°C and the carbon monoxide pressure from 1 atmosphere to 1000--1525 psi (68-104 atmospheres) while decreasing the catalyst concentration to one mole percent rhodium (0.5% dimer) allows good to excellent yields of diaryl ketones to be obtained in THF (Table XXXIV). While all these yields are not quantitative, they are significantly higher than those previously observed with other rhodium(I) or -(III) catalysts. $[Rh(CO)_2Cl]_2$ has previously been observed to catalyze the formation of biaryls from arylmercurials. The optimum conditions previously established for that reaction (HMPA at 70°C) are also more vigorous than the optimum reaction conditions for diene formation from vinylmercurials. While HMPA is carcinogenic and therefore not the solvent of choice, the use of THF at higher temperatures and pressures sometimes gives THF

Table XXXIV. The synthesis of symmetrical diaryl ketones



$$\mathrm{ArHgCl}\ \xrightarrow[\substack{\mathrm{THF}\\ 70\,^{\circ}\mathrm{C}\\ 24\ \mathrm{h}}]{\substack{0.5\%\ [\mathrm{Rh(CO)_2Cl}]_2\\ 2\mathrm{LiCl}\\ >800\ \mathrm{psi\ CO}}}\ 0.5\ \ \mathrm{Ar{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Ar}$$

Arylmercurial	Diaryl Ketone	Isolated Yield %[a]	mp(°C) (lit mp)	Ref.
		80(66)	23-25 (26 or 48)	324
		100(95)	159-161 (164.5)	325
		89(78)	89-90 (90.5)	326
		60(38)	152-153 (155-155.5)	314

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[a] Crude isolated yield (recrystallized yield).

derived carbonylation products. Of the arylmercurials investigated here, this was noticed only with phenylmercuric chloride.

3. Mechanistic considerations

Although a mechanistic investigation of this reaction is lacking, a reasonable mechanism can be proposed based upon analogous reactions. Certainly, the rhodium(I) or -(III) catalyzed formation of divinyl ketones from vinylmercurials would be expected to be similar to the rhodium(I) or -(III) catalyzed formation of dienes from vinylmercurials. The proposed mechanism[80] for the formation of dienes involved the transmetalation of the rhodium(I) or -(III) halide with one or two vinylmercurials respectively. Under rhodium(I) catalysis, oxidative addition of the vinylmercurial to the rhodium(I) species may then occur. Reductive elimination from the diorganorhodium(III) species forms the diene and reforms a catalytically active rhodium(I) species (Scheme 47).

Scheme 47

$$\mathrm{RHC{=}CHHgCl} + \mathrm{RhClL_2} \longrightarrow \mathrm{Rh(CH{=}CHR)L_2} + \mathrm{HgCl_2}$$

$$\mathrm{Rh(CH{=}CHR)L_2} + \mathrm{RHC{=}CHHgCl} \longrightarrow \mathrm{Rh(CH{=}CHR)_2(HgCl)ClL_2}$$

$$\mathrm{Rh(CH{=}CHR)_2(HgCl)ClL_2} \longrightarrow \mathrm{RHC{=}CH{-}CH{=}CHR} + \mathrm{RhClL_2} + \mathrm{Hg}$$

However, the reactivity of the adduct from a vinylmercurial and Wilkinson's catalyst at low temperature (Chapter II), and the facile oxidative addition of methyl iodide to $Rh[C{\equiv}C\text{-}C(CH_3)_3][P(C_6H_5)_3]_3$ and the subsequent facile reductive elimination of 4,4-dimethyl-2-pentyne (Chapter II) may suggest for rhodium(I) catalysis the previously proposed order of transmetalation, oxidative addition and reductive elimination might be more correctly sequenced: oxidative addition, transmetalation and reductive elimination (Scheme 48). It is also possible that the intermediate formed after the initial oxidative addition may reductively eliminate mercuric chloride forming the rhodium(I) species analogous to an initial transmetalation intermediate (Eq. 113).

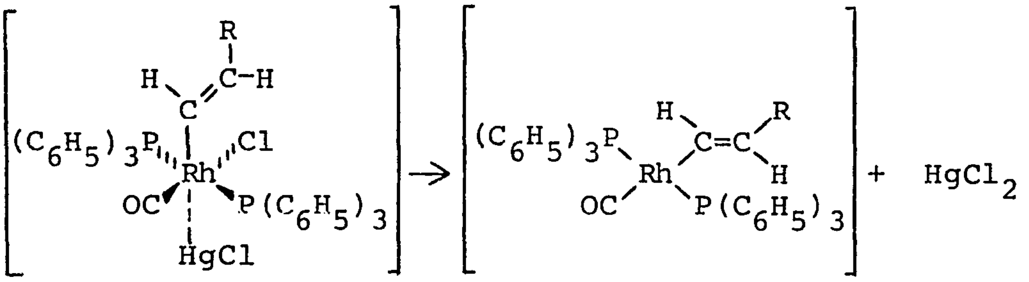
Scheme 48

$$RHC{=}CHHgCl \quad + \quad RhClL_2 \longrightarrow Rh(CH{=}CHR)(HgCl)ClL_2$$

$$Rh(CH{=}CHR)(HgCl)ClL_2 \quad + \quad RHC{=}CHHgCl \longrightarrow$$
$$Rh(CH{=}CHR)_2(HgCl)L_2 \quad + \quad HgCl_2$$

$$Rh(CH{=}CHR)_2(HgCl)L_2 \longrightarrow RHC{=}CH\text{-}CH{=}CHR \quad + \quad RhClL_2 \quad + \quad Hg$$

A scheme proposed to account for the formation of the divinyl ketone is comprized of precisely the same steps with the addition of another step, the insertion of carbon monoxide into a rhodium-carbon bond (actually a vinyl migration). It

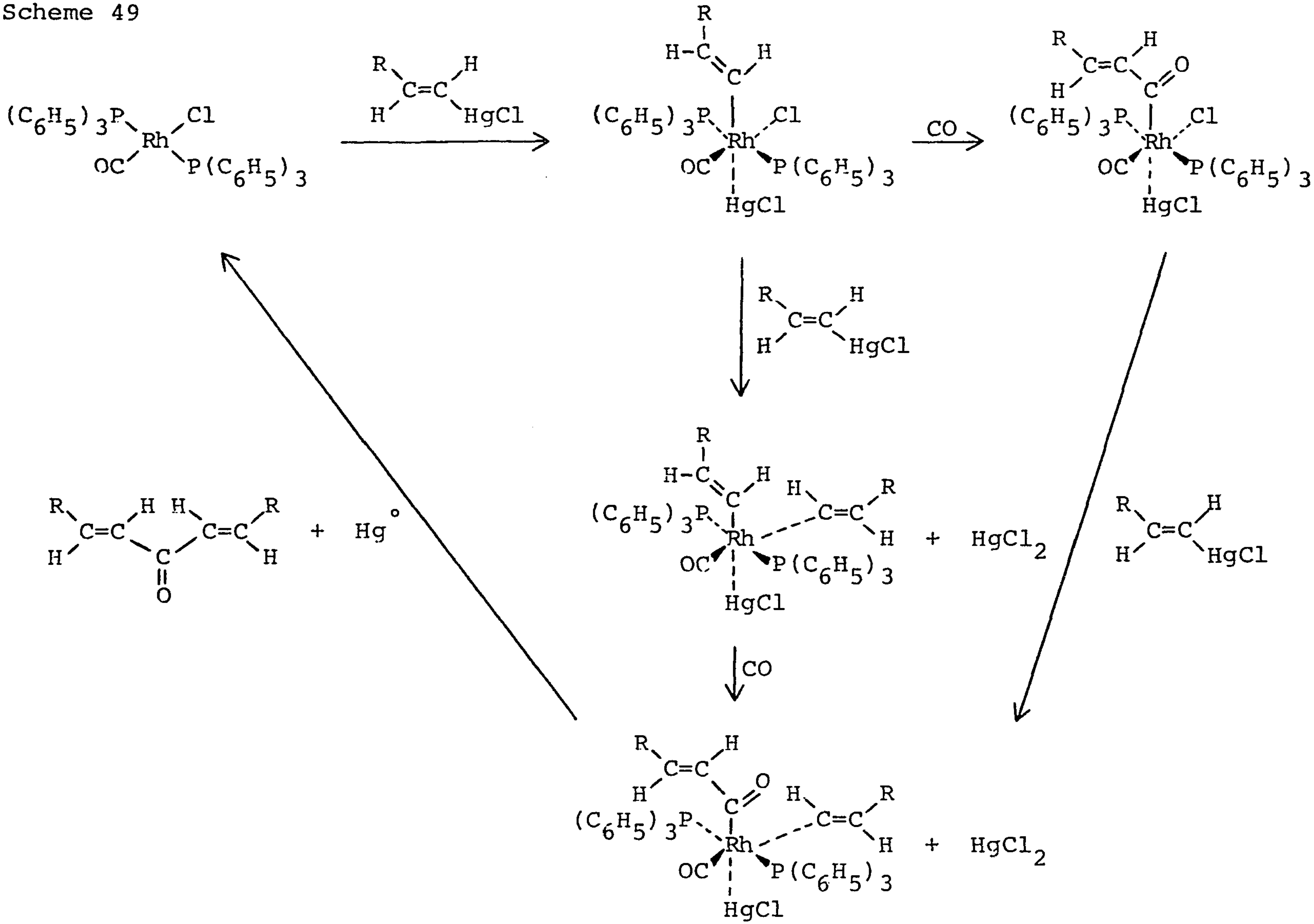


(113)

is not at all clear, however, which of several possible intermediates participate in this step. The acyl species may be formed immediately after the oxidative addition step, or after the transmetalation step in the scheme where oxidative addition precedes the transmetalation (Scheme 49). Alternatively, the migration may occur immediately after the oxidative addition step in a scheme where transmetalation precedes the oxidative addition step (not illustrated). In each of the latter options the insertion of carbon monoxide might involve the preferential migration of one vinyl ligand over another vinyl ligand depending on the relative stereochemistry of the other ligands.

Experimental evidence which strongly supports any of these schemes is sparse. Although GLPC analysis of the reaction mixture indicates both short and long retention time peaks are initially present which decrease as the reaction progresses, the peaks are apparently due to decomposition of the vinylmercurial in the gas chromatograph and are also present in a GLPC trace of a solution of the vinyl-

Scheme 49



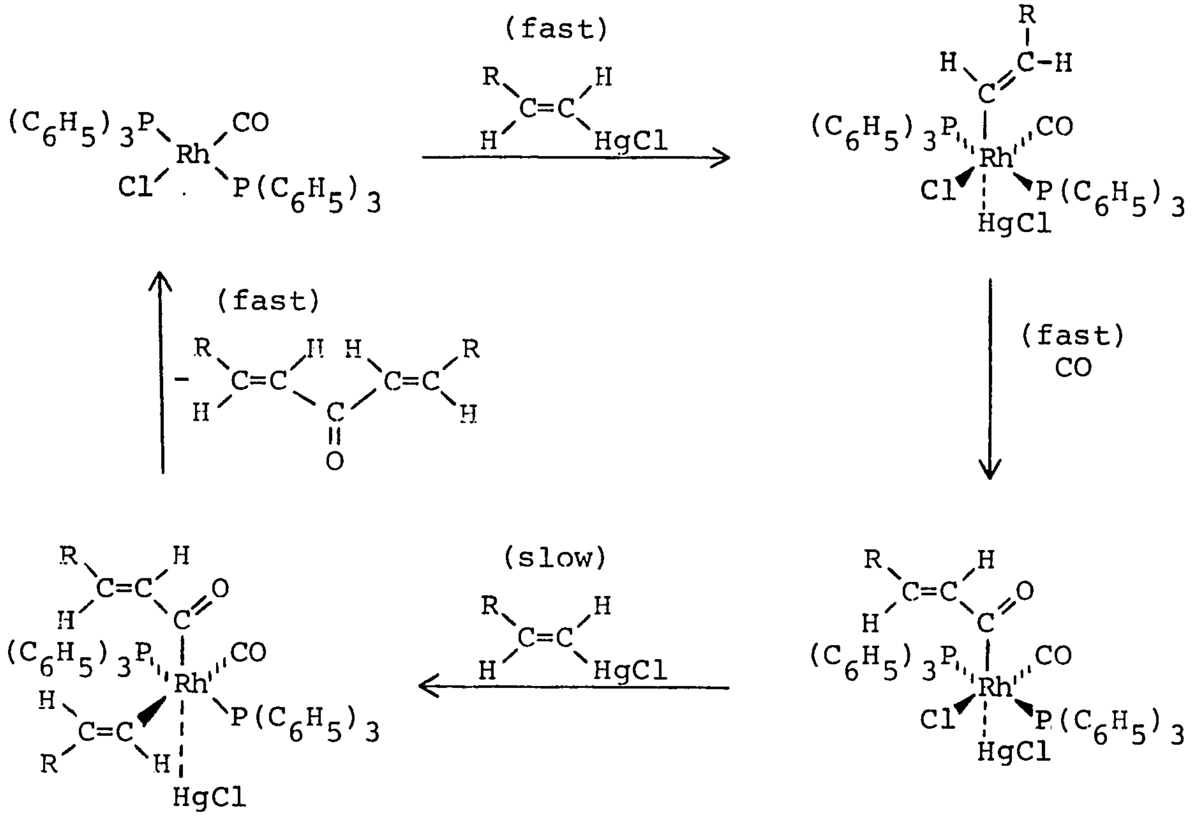
mercurial in THF. The α,β-unsaturated acid chloride, RCH=CHCOCl, a possible intermediate, is also not formed. Quenching an incomplete reaction with methanol does not form the unsaturated methyl ester. Only the divinyl ketone and the symmetrical diene were observed. Although the oxidative addition of a mercurial to $Rh(CO)_2[P(C_6H_5)_3]_2^-$ is reported to form the mercury-rhodium bonded species,[327] the interaction of Wilkinson's catalyst and a vinylmercurial as indicated in Chapter II suggests both the formation of the rhodium carbon bonded species and the occurrence of oxidative addition prior to transmetalation. Even less can be said concerning the vinyl migration to a carbon monoxide ligand. However, since divinyl diketones are not observed, the carbon monoxide insertion probably does not occur after the divinylrhodium(III) species is formed. Alternatively, carbon monoxide insertion may promote rapid reductive elimination of the ketone. However, the facility with which carbon monoxide inserts into both platinum-carbon bonds of $Pt(CH_3)_2[P(C_2H_5)_3]_2$ to form biacetyl (Eq. 114)[328] further suggests the insertion

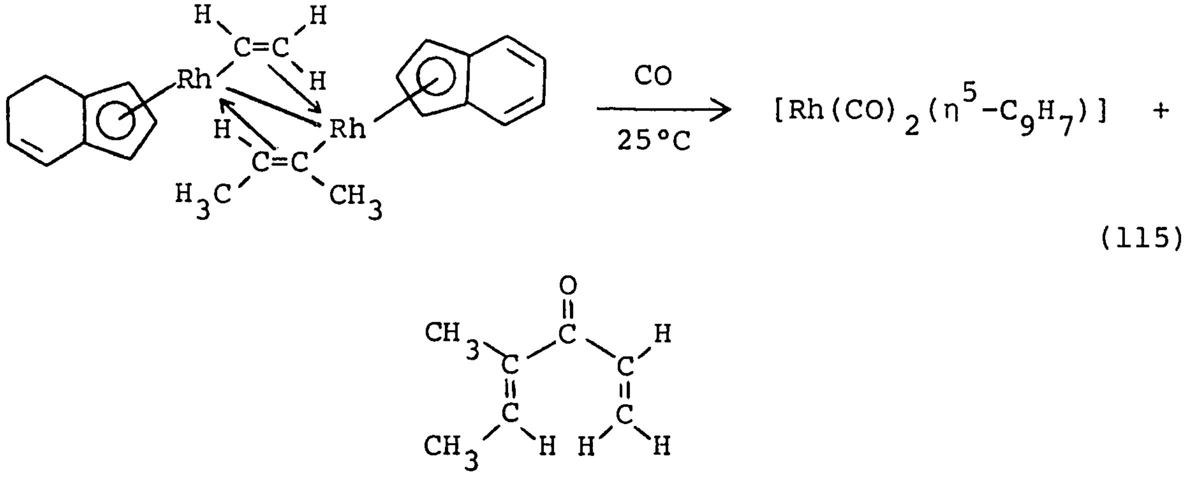
$$Pt(CH_3)_2[P(C_2H_5)_3]_2 \xrightarrow[90\,°C]{1\ atm\ CO} CH_3COCOCH_3 + Pt(CO)_{3\ or\ 4}[P(C_2H_5)_3]_4 \qquad (114)$$

of carbon monoxide is perhaps most likely to occur after the initial oxidative addition. The formation of high yields of divinyl ketones is also consistent with the insertion of carbon monoxide after the initial oxidative addition of the vinylmercurial. In addition, the rates of oxidative addition of the vinylmercurial to the rhodium(I) species, the carbon monoxide insertion, and the reductive elimination of the divinyl ketone are proposed to be relatively fast while the rate of the transmetalation of the acylrhodium(III) species with the vinylmercurial is proposed to be relatively slow. Similar rate relationships were proposed in the methylation of vinylmercurials. These considerations are summarized in Scheme 50.

Although it is always possible and largely ridiculous to propose a complicated model when a simple one suffices, a report of divinyl ketone formation from a dirhodium species,[268] and the reactivity of organomercurials and the rhodium species isolated from Wilkinson's catalyst and a vinylmercurial (Chapter II) hints dirhodium species might alternatively be involved. Scheme 51 is one of many possibilities and involves the oxidative addition of a rhodium(III) species to a rhodium(I) species. The similarity of intermediate 23 in Scheme 51 to an isolated diorganodirhodium compound which also produces a divinyl ketone[268] is notable (Eq. 115).

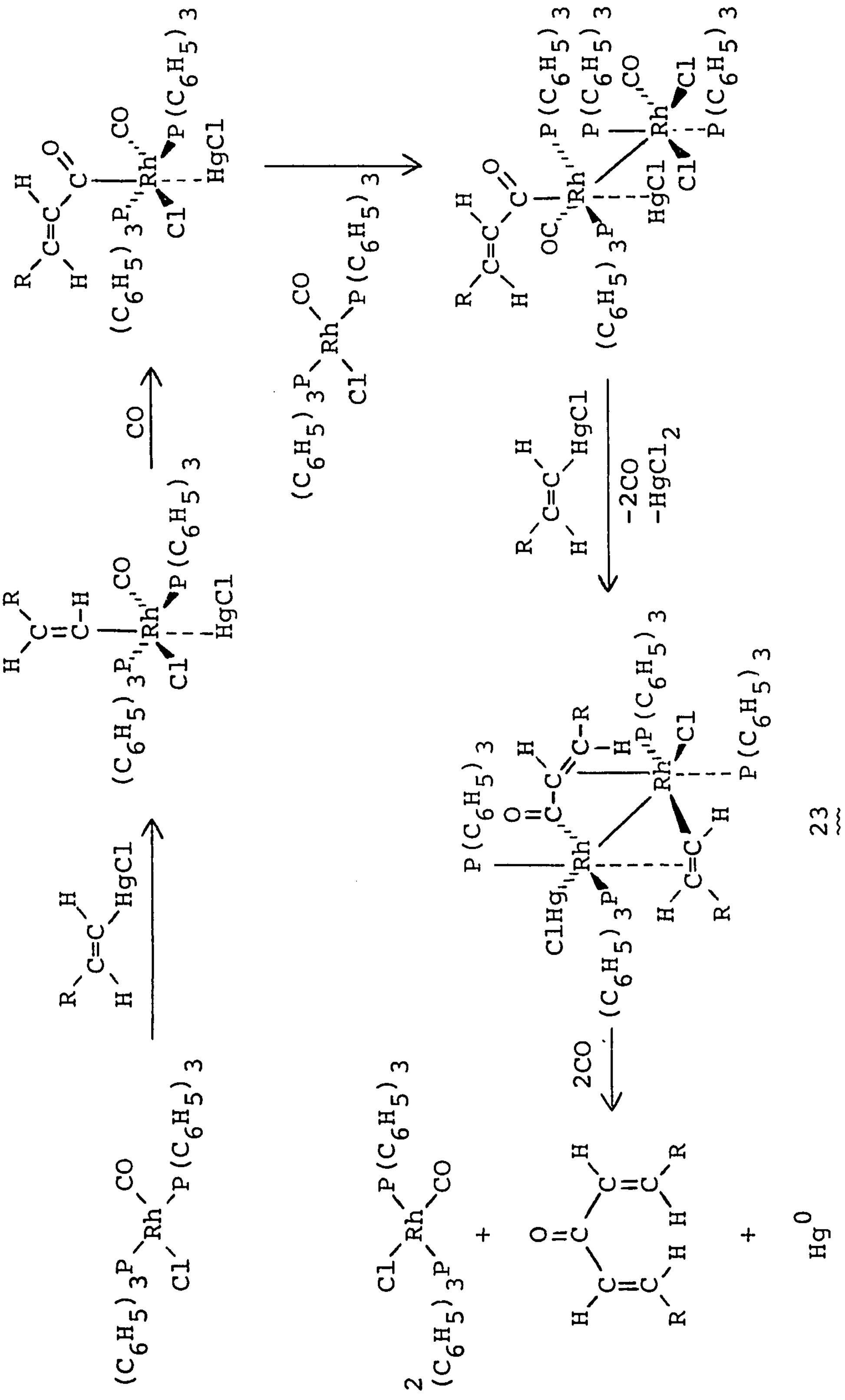
Scheme 50





(115)

Scheme 51



It should be emphasized, however, that the present data for divinyl ketone formation does not require this more complicated model. It is proposed merely from the presumed analogy with rhodium(I) and -(III) catalyzed diene and biaryl formaion from organomercurials where mechanistic evidence is also sparse.

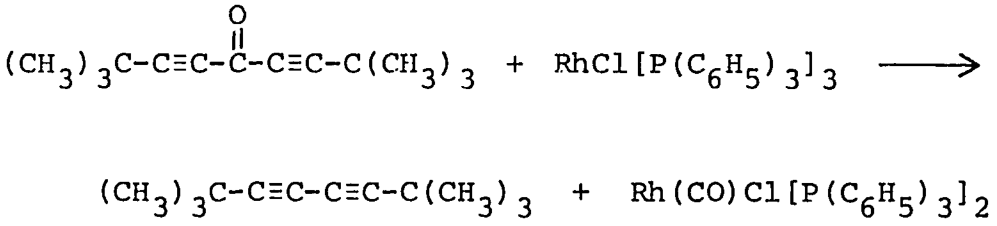
4. Unsuccessful extensions

Whether this insertion of carbon monoxide and subsequent reductive coupling may be extended to other small unsaturated molecules was considered in addition to extending ketone formation to other organomercurials. The studies involving bis(alkynyl)mercury and alkylmercurials are described first.

Attempts to utilize bis(alkynyl)mercury compounds in place of either vinyl- or arylmercurials results in the formation of the diyne and did not produce the dialkynyl ketone. 2,2,7,7-Tetramethyl-3,5-octadiyne is isolated from the reaction of bis(3,3-dimethyl-1-butynyl)mercury, 2 equivalents lithium chloride, 0.005 equivalents $[Rh(CO)_2Cl]_2$ and one atmosphere carbon monoxide in THF at room temperature (Eq. 116). If the carbon monoxide pressure is increased to 1200

$$[(CH_3)_3C\text{-}C{\equiv}C]_2Hg \xrightarrow[\text{THF}]{\substack{\text{CO} \\ 0.5\%\ [Rh(CO)_2Cl]_2 \\ 2LiCl}} (CH_3)_3C\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C(CH_3)_3 \qquad (116)$$

psi, bis(3,3-dimethyl-1-butynyl)mercury again yields 2,2,7,7-tetramethyl-3,5-octadiyne as the only product. However bis-(phenylethynyl)mercury, under the same conditions forms an intractable red oil. The major component of the oil is apparently bis(phenylethynyl)mercury. This difference between alkynylmercurials is unexplained. The formation of the diyne may not be too surprising considering the reported formation of a diyne from the reaction of a dialkynyl ketone with $RhCl[P(C_6H_5)_3]_3$ (Eq. 117).[40] However, it is also possible the



$$(CH_3)_3C\text{-}C\equiv C\text{-}\overset{O}{\overset{\|}{C}}\text{-}C\equiv C\text{-}C(CH_3)_3 + RhCl[P(C_6H_5)_3]_3 \longrightarrow (CH_3)_3C\text{-}C\equiv C\text{-}C\equiv C\text{-}C(CH_3)_3 + Rh(CO)Cl[P(C_6H_5)_3]_2 \tag{117}$$

organomercurial itself may account for the difference. This attempted dialkynyl ketone synthesis began with a diorganomercury compound whereas the previous divinyl and diaryl ketone syntheses began with organomercuric chlorides.

The reaction of n-butylmercuric chloride, 2 equivalents lithium chloride, 0.005 equivalents $[Rh(CO)_2Cl]_2$ and one atmosphere carbon monoxide at room temperature did not form 5-nonanone. This is consistent with other observed reactions of alkylmercurials. Alkylmercurials do not couple under conditions in which rhodium(I) or -(III) mediates the formation of symmetrical dienes and biaryls,[80] and as reported previously in this thesis, alkylmercurials do not couple with a methyl- or vinylrhodium species under conditions where coupling occurs with vinyl and arylmercurials. The failure is presumably due to facile beta hydride elimination from intermediate alkylrhodium species, forming the alkene and a rhodium(III) hydride which may reform the rhodium(I) catalyst.

The insertion of more than one carbon monoxide was considered. As alluded to in the mechanistic discussion, the reaction of trans-3,3-dimethyl-1-butenylmercuric chloride and excess lithium chloride in THF with 0.5% $[Rh(CO)_2Cl]_2$ under carbon monoxide pressures up to 1525 psi affords only the divinyl ketone and no divinyl diketone.

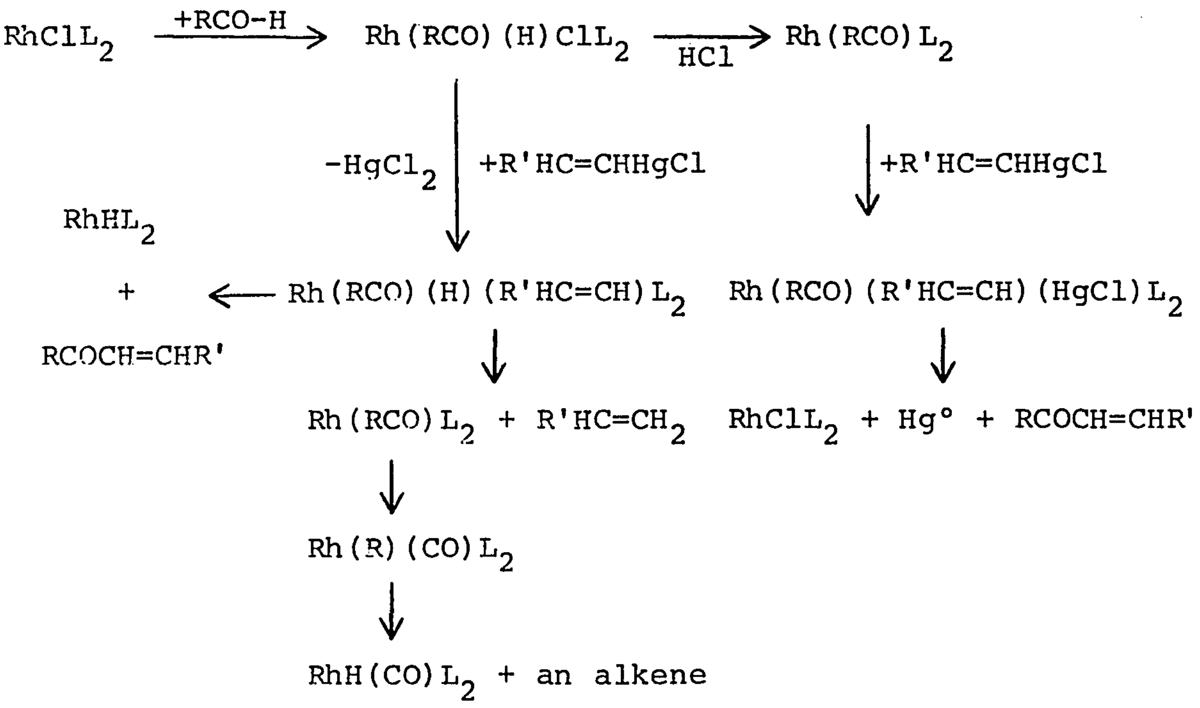
Since other unsaturated molecules may possibly coordinate to rhodium and insert into a rhodium carbon bond, the extension of this process to other unsaturated molecules has been briefly investigated. Substituting either an ethylene or acetylene atmosphere for carbon monoxide or adding a ten-fold excess of norbornene gives no evidence for the formation of an unsymmetrical 1,3-diene, a symmetrical 1,5-diene or a triene. Only the symmetrical 1,3-diene 2,2,7,7-tetramethyl-3,5-octadiene was observed. The substitution of either an ethylene or acetylene atmosphere at higher pressures was not investigated. Nor was the insertion of acetylenes containing electron withdrawing groups such as dimethyl acetylene dicarboxylate investigated. In retrospect such acetylenes should be most likely to insert.[269]

Because rhodium(I) catalysts are active in aldehyde decarbonylation reactions, the reaction of excess propanal, 1 equivalent trans-3,3-dimethyl-1-butenylmercuric chloride, 2 equivalents lithium chloride and 0.5% $[Rh(CO)_2Cl]_2$ in THF with a carbon monoxide atmosphere was investigated (Scheme 52). The ^1H nmr spectrum of the reaction products indicated the formation of some symmetrical divinyl ketone among other unidentified products. Whether trans-2,2-dimethylhept-3-en-5-one (the RCOCH=CHR' product of Scheme 52) was among them was difficult to discern. Since acid may be produced in the decarbonylation of aldehydes the addition of an inorganic base may reduce side reactions. Also employing an α,β-unsaturated aldehyde may increase the reactivity of the aldehyde and reduce the symmetrical carbonylation and coupling. The reaction of a vinylmercurial, lithium chloride, carbon monoxide, and α,β-unsaturated aldehydes mediated by rhodium(I) catalysts might afford the unsymmetrical divinyl ketones, although the evidence presented so far is poor.

C. Conclusion

The reaction of vinylmercurials, 2 equivalents lithium chloride in THF with one atmosphere carbon monoxide catalyzed by one mole percent rhodium (added as $[Rh(CO)_2Cl]_2$) produces excellent yields of divinyl ketones. The neutral, mild con-

Scheme 52



ditions under which the reaction occurs permit this acid and base sensitive class of compounds to be isolated in high yield. The reaction is stereospecific with trans-vinylmercurials forming exclusively trans,trans-divinyl ketones. This reaction may be extended to diaryl ketones if arylmercurials, increased carbon monoxide pressure and a 70°C reaction temperature is employed instead. The yields of diaryl ketones are good to excellent. This carbonylation and coupling may be considered an extension of the previously observed Rh(I) and -(III) catalyzed coupling of vinyl- and arylmercurials which forms dienes and biaryls.[80] Carbonylation and coupling was not successfully extended to alkylmercurials and bis(alkynyl)-mercury compounds. A preliminary investigation of the insertion of olefins and acetylenes was also unsuccessful, but possibly not extensive enough to be discarded as an area of further research.

D. Experimental Section

1. General

The description of the instruments used as well as routine reagents and solvent purification have been described previously. Phenylmercuric chloride was obtained from Aldrich, vinylmercuric-chloride from Orgmet and the vinyl-,[253,254] aryl-[217,279,284] and alkynylmercurials[272] were prepared according to literature procedures. $[Rh(C_7H_8)Cl]_2$ was obtained from Research Organic/Inorganic Chemical. Although commercially available, $RhCl[P(C_6H_5)_3]_3$,[273] $[Rh(H_2C{=}CH_2)Cl]_2$,[275] $[Rh(CO)_2Cl]_2$[295] and $Rh(CO)Cl[P(C_6H_5)_3]_2$[329] were prepared according to literature procedures from $RhCl_3 \cdot 3H_2O$ generously loaned by Matthey Bishop. Palladium chloride was also loaned by Matthey Bishop.

2. The reaction of $Rh(CH_3)I_2[P(C_6H_5)_3]_2$ and *trans*-styrylmercuric chloride under a carbon monoxide atmosphere

0.0473 Grams (0.05 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0170 grams (0.05 mmoles) *trans*-styrylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube and a magnetic stirring bar. A balloon of carbon monoxide placed on the gas inlet tube was used to flush the system and to supply a carbon monoxide atmosphere. After flushing with carbon monoxide, 0.0085 grams (0.05 mmoles) *n*-dodecane and 0.5 ml HMPA were added by syringe. After stirring for 24 hours at 70°C, 0.5 ml benzene and 0.5 ml water were added and the benzene layer GLPC analyzed on a 10' x 1/4" 10% SE-30 column at 120°C. Although a correction factor for the observed product, benzalacetone was not determined, the relative peak areas indicate that benzalacetone is the major product and might be estimated as being formed in greater than 60% yield.

3. The attempted formation of benzalacetone from methyl iodide, *trans*-styrylmercuric chloride and carbon monoxide catalyzed by 10 mole % $Rh(CH_3)I_2[P(C_6H_5)_3]_2$

0.0047 Grams (0.005 mmoles) $Rh(CH_3)I_2[P(C_6H_5)_3]_2 \cdot ClCH_3$, 0.0170 grams (0.05 mmoles) *trans*-styrylmercuric chloride and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube and a magnetic stirring bar. A balloon of carbon monoxide placed on the gas inlet tube was used to flush the system and provided a carbon monoxide atmosphere. After flushing with carbon monoxide, 0.1 ml (excess) methyl iodide, 0.0085 grams (0.05 mmoles) n-dodecane and 0.5 ml HMPA were added by syringe. After stirring for 24 hours at 70°C, 0.5 ml benzene and 0.5 ml water were added and the benzene layer GLPC analyzed as described previously. The peak corresponding to benzalacetone was less the 10% of the standard peak. However, increasing the column temperature to 180°C and 210°C showed the presence of 1,4-diphenylbutadiene (major peak) and 1,5-diphenyl-3-pentadienone (minor peak) respectively. The side products were identified by comparison and co-injection of authentic samples on both the SE-30 column and a 5' x 1/4" 10% DC-550 column.

4. The attempted formation of benzalacetone from methyl iodide, trans-styrylmercuric chloride and carbon monoxide catalyzed by 10 mole % $Rh(CO)Cl[P(C_6H_5)_3]_2$

0.0035 Grams (0.005 mmoles) $Rh(CO)Cl[P(C_6H_5)_3]_2$ and at least 0.0213 grams (0.5 mmoles) lithium chloride were weighed into a 5 ml round bottom flask equipped with a septum inlet, a condenser with a gas inlet tube and a magnetic stirring bar. A balloon of carbon monoxide placed on the gas inlet tube was used to flush the system and supplied a carbon monoxide atmosphere. After flushing with carbon monoxide, 0.1 ml (excess) methyl iodide, 0.0085 grams (0.05 mmoles) n-dodecane and 0.5 ml HMPA were added by syringe. After stirring at room temperature 15 minutes, 0.0170 grams (0.05 mmoles) trans-styrylmercuric chloride was added all at once while backflushing with carbon monoxide. After flushing again with carbon monoxide, the reaction was stirred for 24 hours either at room temperature or in a 70°C oil bath. 0.5 Ml benzene and 0.5 ml water were added and the benzene layer GLPC analyzed. In both reactions the yield of benzalacetone was low, less than 10%. However, the relative amount of 1,5-diphenyl-3-pentadienone in the reaction at room temperature was substantially greater than that observed at 70°C or in the previous reaction with 10 mole % $Rh(CH)_3I_2[P(C_6H_5)_3]_2$.

5. The effect of solvent and temperature on the formation of trans,trans-2,2,8,8-tetramethylnona-3,6-dien-5-one from trans-3,3-dimethyl-1-butenylmercuric chloride and carbon monoxide catalyzed by 10 mole % $Rh(CO)Cl[P(C_6H_5)_3]_2$

0.0691 Grams (0.1 mmole) $Rh(CO)Cl[P(C_6H_5)_3]_2$ and 0.3192 grams (1.0 mmole) trans-3,3-dimethyl-1-butenylmercuric chloride were weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with a balloon of carbon monoxide, 0.1132 grams hexadecane and 10 ml THF, ether, dichloromethane or HMPA were added by syringe. The reaction mixture was flushed twice with carbon monoxide and the carbon monoxide balloon refilled on the gas inlet tube The reaction proceeded at room temperature or in a heated oil bath at 70°C. After stirring an appropriate time the reaction mixture was GLPC analyzed: 1/4" x 5' 10% DC-550 on Chromosorb W at 160°C. The retention time of trans,trans-2,2,8,8-tetramethylnona-3,6-dien-5-one is approximately 4 minutes while the retention time of hexadecane is approximately 7 minutes. The results are summarized in Table XXXI.

6. The effect of different rhodium catalysts on the formation of trans,trans-2,2,8,8-tetramethylnona-3,6-dien-5-one from trans-3,3-dimethyl-1-butenylmercuric chloride and carbon monxide

The reaction with $Rh(CO)Cl[P(C_6H_5)_3]_2$ is representative. 0.0691 Grams (0.1 mmoles) $Rh(CO)Cl[P(C_6H_5)_3]_2$ and 0.3192 grams (1.0 mmoles) trans-3,3-dimethyl-1-butenylmercuric chloride were weighed into a 25 ml round bottom flask equipped with septum inlet, gas inlet tube and magnetic stirring bar. After flushing with a balloon of carbon monoxide, 0.1132 grams hexadecane and 10 ml THF were added by syringe. After flushing twice with carbon monoxide, the balloon of carbon monoxide was refilled on the gas inlet tube. The reaction mixture was analyzed directly by GLPC after stirring an appropriate time at room temperature. The reaction was also attempted with 0.0069 grams (0.01 mmoles) and 0.0007 grams (0.001 mmoles) $Rh(CO)Cl[P(C_6H_5)_3]_2$. The following catalysts were also employed in place of $Rh(CO)Cl[P(C_6H_5)_3]_2$: $RhCl_3 \cdot 3H_2O$, $RhCl[P(C_6H_5)_3]_3$, $[Rh(H_2C{=}CH_2)_2Cl]_2$, $[Rh(CO)_2Cl]_2$, $[RH(C_8H_{14})_2Cl]_2$ and $[Rh(C_7H_8)Cl]_2$. At least 0.0828 grams (2.0 mmoles) lithium chloride was also added to reactions catalyzed by $[Rh(CO)_2Cl]_2$ and $Rh(CO)Cl[P(C_6H_5)_3]_2$. The effect of dilithium tetrachloropalladate on this transformation was investigated with the addition of 0.1773 grams (1.0 mmoles) palladium chloride plus 0.0828 grams (2.0 mmoles) lithium chloride in place of 10 mole percent $Rh(CO)Cl[P(C_6H_5)_3]_2$ either at room temperature or from -78°C to room temperature. Lastly, 0.0177 grams (0.1 mmoles) palladium chloride, 0.0082 grams (0.2 mmoles) lithium chloride and 0.1344 grams (1.0 mmoles) cupric chloride was added in place of 10 mole percent $Rh(CO)Cl[P(C_6H_5)_3]_2$ to a room temperature reaction. The results are summarized in Table XXXII.

7. The synthesis of divinyl ketones

The synthesis of trans,trans-trideca-5,8-dien-7-one is representative. 1.60 Grams (5.0 mmoles) trans-1-hexenylmercuric chloride and at least 0.42 grams (10.0 mmoles) lithium chloride were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. After flushing with a balloon of carbon monoxide, 40 ml THF was added by syringe. 0.0097 Grams (0.025 mmoles) $[Rh(CO)_2Cl]_2$ (1.0 mole percent rhodium) dissolved in 10 ml THF was added under a carbon monoxide atmosphere using a double ended needle. (This method of catalyst addition reduces initial unwanted side reactions which occur if the rhodium catalyst and the organomercurial are both present in a very concentrated solution). The reaction was flushed twice with carbon monoxide from a balloon and placed under a carbon monoxide atmosphere with a balloon of carbon monoxide on the gas inlet tube. After stirring at room temperature 24 hours, the reaction mixture was filtered into a separatory funnel (to remove elemental mercury which formed). 70 Ml Skelly A (pentane) was added and the organic layer washed three times with saturated sodium thiosulfate and saturated sodium chloride solutions, dried (anhydrous Na_2SO_4) and concentrated to give 0.46 grams (94% yield) of a nearly colorless oil. The oil bulb-to-bulb distilled from 75 to 80°C at 0.35 mm Hg. The yield after distillation is 0.38 grams (78% yield). The spectra were identical before and after distillation: ^1H nmr ($CDCl_3$) δ0.7-1.1 (6H, m, $-CH_3$), 1.1-1.8 (8H, m, $-CH_2-CH_2-$), 2.0-2.5 (4H, m, $-C{=}C-CH_2-$), 6.32 (2H, dt, _J_ = 15.5 Hz, _J_ = 1.0 Hz, $-CO-CH{=}C-$), 6.96 (2H, dt, _J_ = 15.5 Hz, _J_ = 6.5 Hz, $-CO-C{=}CH-$); IR (CCl_4) 3040 w, 3010 vw, 2970 vs, 2950 vs, 2890 s, 2870 s, 1690 s, 1675 vs, 1645 vs, 1620 vs, 1470 m, 1460 m, 1380 m, 1345 m, 1300 m, 1285 m, 1260 m, 1215 m, 1185 m, 1150 m, 1090 m, 1010 m, and 980 ms cm^{-1}; m/e 194.16692 (calculated for $C_{13}H_{22}O$: 194.16707).

The following compounds were prepared similarly. _trans_, _trans_-2,2,8,8-tetramethylnona-3,6-dien-5-one: obtained as off-white needles after solvent removal, 0.47 grams (96% yield); white needles after sublimation, 0.38 grams (78% yield), mp 69-72°C; ^1H nmr (CCl_4) δ1.12 (18H, s, $-C(CH_3)_3$), 6.13 (2H, d, J = 15.5 Hz, -CO-CH=C-), 6.73 (2H, d, J = 15.5 Hz, -CO-C=CH-); IR (CCl_4) 3060 w, 3010 w, 2980 s, 2940 m, 2915 m, 2880 m, 1690 ms, 1673 s, 1643 s, 1620 s, 1480 m, 1470 m, 1450 w, 1395 m, 1370 mw, 1325 s, 1310 m, 1270 mw, 1210 mw, 1170 m, 1103 m, 1070 w, 1027 w, 986 m, 948 w, 940 w, 927 m, 915 mw, 880 w, 685 mw, 645 mw, 420 mw cm^{-1}; m/e 194.16707 (calculated for $C_{13}H_{22}O$: 194.16713).

trans,trans-1,5-Diphenyl-penta-1,4-dien-3-one obtained as a yellow solid after solvent removal, 0.58 grams (99% yield); fine yellow plates after recrystallization from benzene, 0.52 grams (88% yield); mp 107-110°C (lit.[313] mp 110-111°C); ^1H nmr ($CDCl_3$) δ7.07 (2H, d, J = 16 Hz, -CO-CH=C-), 7.1-7.6 (10H, m, $-C_6H_5$), 7.67 (2H, d, J = 16 Hz, -CO-C=CH-); IR (CCl_4) 3120 w, 3100 w, 3080 w, 3040 w, 2940 m, 2860 w, 1960 vw, 1890 vw, 1810 vw, 1750 vw, 1685 ms, 1665 s, 1630 s, 1610 s, 1580 m, 1500 m, 1455 ms, 1345 s, 1315 vw, 1300 vw, 1290 mw, 1260 w, 1200 m, 1180 ms, 1060 w, 1095 ms, 1075 m, 1030 w, 990 m, 980 m, 880 mw, 695 s and 550 ms cm^{-1}.

trans,trans-2,2,4,6,8,8-Hexamethylnona-3,6-dien-5-one: obtained as a colorless oil after solvent removal, 0.35 grams (64% yield); bulb-to-bulb distillation from 105 to 110°C at 0.35 mm Hg; 0.26 grams (47% yield); ^1H nmr (CCl_4) δ1.18 (18H, s, $-C(CH_3)_3$), 1.95 (6H, d, J = 1.0 Hz, $-CH_3$), 6.08 (2H, d, J = 1.0 Hz, -CH=C-CO-); IR (CCl_4) 3045 w, 2970 s, 2950 s, 2920 ms, 2880 ms, 1718 vs, 1665 ms, 1645 m, 1485 s, 1470 ms, 1420 ms, 1370 s, 1290 s, 1240 ms, 1200 s, 1180 m, 1170 m, 1090 w, 1050 m, 1025 m, 940 mw, 915 mw cm^{-1}; m/e 222.19786 (Calculated for $C_{15}H_{26}O$: 222.19837).

trans,_trans_-1,5-Di(1-cyclohexenyl)penta-1,4-dien-3-one: obtained as a yellow solid after solvent removal, 0.61 grams (100% yield); fine yellow needles after recrystallization (pentane, -78°C) (decomposes partially during the attempted recrystallization), mp 138-142°C (decomposes); ^1H nmr ($CDCl_3$) δ1.5-2.0 (8H, m, $-CH_2-CH_2-$), 2.0-2.4 (8H, m, $-CH_2-C=C-$), 6.25 (2H, m, -CH-C-C=C-), 6.35 (2H, d, _J_ = 15.8 Hz, -C=CH-CO-), 7.38 (2H, d, _J_ = 15.8 Hz, -C=C-CH=C-CO-); IR (CCl_4) 3045 w, 3025 w, 2940 s, 2860 ms, 2840 m, 2830 mw, 1673 m, 1657 s, 1625 s, 1608 s, 1590 s, 1460 w, 1450 w, 1435 w, 1425 w, 1345 m, 1320 s, 1285 m, 1265 m, 1235 w, 1190 m, 1180 ms, 1130 w, 1095 s, 1070 m, 1040 w, 980 s, 913 w and 875 w cm^{-1}; m/e 242.16671 (calculated for $C_{17}H_{22}O$, 242.16707).

trans,_trans_-2,8-Dimethylnona-1,3,6,8-tetraen-5-one: obtained as a yellow oil after solvent removal, 0.17 grams (41% yield); decomposed prior to bulb-to-bulb distillation; ^1H nmr (CCl_4) δ1.90 (6H, s, $-CH_3$), 5.35 (4H, d, _J_ = 6 Hz, $-C=CH_2$), 6.30 (2H, d, _J_ = 15.5 Hz, -C=CH-CO-), 7.25 (2H, d, _J_ = 15.5 Hz, -CH=C-CO-); IR(CCl_4) 3080 vw, 2970 ms, 2920 s, 2850 ms, 1740 m, 1720 ms, 1670 s, 1655 s, 1620 s, 1605 s, 1590 s, 1450 m, 1435 mw, 1375 mw, 1320 mw, 1300 w, 1275 s, 1250 m, 1185 mw, 1105 mw, 1025 w, 985 ms, 905 mw, 880 mw and 720 w cm^{-1}; m/e not obtained.

1,4-Pentadien-3-one: (not isolated pure from THF due to its low boiling point and obnoxious properties); ^{1}H nmr (THF/ CCl_4) δ5.85 (2H, dd, *J* = 9.5 Hz, *J* = 3.0 Hz, *trans*-CH=C-CO-), 6.25 (2H, dd, *J* = 17.5 Hz, *J* = 3.0 Hz, *cis*-CH=C-CO-), 6.65 (2H, dd, *J* = 17.5 Hz, *J* = 9.5 Hz, C=CH-CO-). A small sample was purified by preparative gas chromatography for a correction factor and a yield determined by gas chromatography with *n*-octane as the internal standard.

trans,*trans*-1,5-Dichloropenta-1,4-dien-3-one: obtained as an oil which corresponds to a single peak in the gas chromatograph: ^{1}H nmr (CCl_4) δ6.75 (2H, d, *J* = 13.5 Hz, -CO-CH=C-), 7.45 (2H, d, *J* = 13.5 Hz, -CO-C=CHCl); IR (neat) 3040 mw, 3030 w, 1670 ms, 1660 mw, 1610 m, 1590 s, 1305 vw, 1265 vw, 1245 vw, 1220 vw, 1080 vw, 1110 m, 960 s, 870 m and 840 mw cm^{-1} (the intensities of the IR as a smear do not exactly match those previously reported[330]).

8. The syntheses of diaryl ketones

The synthesis of benzophenone is representative. 1.57 Grams (5.0 mmoles) phenylmercuric chloride and at least 0.42 grams (10.0 mmoles) lithium chloride were weighed into a glass lined Parr pressure reactor equipped with a magnetic stirring bar. 50 Ml THF was added and lastly 0.0097 grams (0.025 mmoles) $[Rh(CO)_2Cl]_2$ was added gently and without stirring.

Quickly the top of the pressure reactor was replaced, sealed and charged with carbon monoxide from 950 psi to 1250 psi (tank pressures). The reactor was then placed in a 70°C oil bath and stirred for 24 hours. The reactor was then cooled, vented and opened, and the reaction mixture rinsed into a separatory funnel through a filter funnel to remove the mercury. 80 Ml ether was added and the organic layer washed successively three times each with saturated sodium thiosulfate solution, 5% sodium bicarbonate solution and saturated ammonium chloride solution. (The sodium bicarbonate wash was added because it removes traces of acidic THF related side products). The ether layer was dried (anhydrous Na_2SO_4) and concentrated giving 0.36 grams (80% yield) crude benzophenone, 0.30 grams (66% yield) recrystallized (ether), mp 23-25°C (lit.[324] mp 26 or 48°C).

The following diaryl ketones were prepared in a similar manner. 2,2'-Dinaphthyl ketone: 100% crude yield, 95% recrystallized yield (ether, chloroform), mp 159-161°C (lit.[325] mp 164.5°C). 2,2'-Dithienyl ketone: 89% crude yield, 78% recrystallized yield (ether) mp 89-90°C (lit.[326] mp 90.5°C). 3,3'-Dinitrobenzophenone: 60% crude yield, 38% recrystallized yield (ethyl acetate), mp 150-151°C (crude), mp 152-153°C (recrystallized) (lit.[314] mp 155.0-155.5°C).

9. Attempted formation of a diacetylenic ketone

0.91 Grams (2.5 mmoles) bis(3,3-dimethyl-1-butynyl)-mercury, at least 0.42 grams (10 mmoles) lithium chloride and 0.0097 grams (0.025 mmoles) $[Rh(CO)_2Cl]_2$ were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with a balloon of carbon monoxide, 50 ml THF was added by syringe, the system flushed twice with carbon monoxide and the balloon of carbon monoxide refilled on the gas inlet tube. After stirring 24 hours at room temperature, the reaction mixture was filtered into a separatory funnel (to remove the solid mercury which formed) and 100 ml Skelly A (pentane) was added. The organic layer was washed three times each with saturated sodium thiosulfate solution and saturated ammonium chloride solution, dried (Na_2SO_4) and concentrated to give a pale yellow oil which solidified. Sublimation produced colorless needles; mp 130-130.5°C (lit.[331] mp 130-132°C). Spectral evidence indicated the diyne is formed instead of the diacetylenic ketone: ^1H nmr ($CDCl_3$) δ1.22 (18H, s, $-C(CH_3)_3$); IR (CCl_4) 2980 vs, 2940 vs, 2920 s, 2880 s, 2860 s, 2180 mw, 2140 m, 1470 s, 1450 s, 1410 w, 1390 ms, 1360 s, 1320 vw, 1275 w, 1240 s, 1195 s, 1075 m, 1020 mw, 920 m, 880 s, 650 m, 530 ms cm^{-1}.

Whether or not the diacetylenic ketone might be formed under higher carbon monoxide pressure was also investigated.

0.91 Grams (2.5 mmoles) bis(3,3-dimethyl-1-butynyl)mercury and at least 0.42 grams (10 mmoles) lithium chloride were weighed into a glass lined Parr pressure reactor with a magnetic stirring bar. 50 ml THF was added and the mixture stirred to dissolve the mercurial while carbon monoxide was bubbled into the solution. The stirring was stopped, 0.0097 grams (0.025 mmoles) $[Rh(CO)_2Cl]_2$ was added and the liner quickly inserted into the reactor which was closed, pressurized with carbon monoxide (1150 psi) and placed on the stir plate. After 48 hours at room temperature, the reactor was opened and the reaction worked up as previously described. Comparison of the spectral evidence (the IR's are superimposable) indicated the diacetylene was formed again rather than the diacetylenic ketone.

Under the same high pressure conditions, bis(phenyl)-ethyl)mercury yielded a red orange solution and a thick red orange oil after work-up. The thin layer chromatogram of the oil behaved similar to the starting mercurial, although the IR spectrum of the crude orange oil was not identical to that of the mercurial.

10. <u>Attempted formation of a dialkyl ketone</u>

0.2932 Grams (1.0 mmoles) n-butylmercuric chloride, 0.0194 grmas (0.05 mmoles) $[Rh(CO)_2Cl]_2$ and 0.0828 grams (2.0 mmoles) lithium chloride were weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing the system with a balloon of carbon monoxide, 10 ml THF was added by syringe. The reaction mixture was flushed twice with carbon monoxide and the carbon monoxide balloon refilled on the gas inlet tube. After stirring the reaction mixture at room temperature 24 hours, a gray precipitate formed on the bottom of the flask indicating a reaction occurred. However, GLPC analysis failed to detect the formation of any products with retention times longer than THF. A couple of new peaks with a retention time shorter than THF were observed, but these were not analyzed.

11. The $[Rh(CO)_2Cl]_2$ catalyzed reaction of *trans*-3,3-dimethyl-1-butenylmercuric chloride under higher carbon monoxide pressures--an unsuccessful attempt to form a divinyl diketone.

1.60 Grams (5.0 mmoles) *trans*-3,3-dimethyl-1-butenylmercuric chloride and at least 0.42 grams (10.0 mmoles) lithium chloride were weighed into a glass lined Parr pressure reactor equipped with a magnetic stirring bar. 50 ml THF was added and lastly 0.0097 grams (0.025 mmoles) $[Rh(CO)_2Cl]_2$ was added gently and without stirring. Quickly the top of the pressure reactor was replaced, closed and charged with carbon monoxide (once with 625 psi and once with 1250 psi). The reactor was placed on top of a magnetic stirring plate and stirred 24 hours at room temperature. The reactor was then vented, opened and the reaction mixture filtered (to remove mercury) into a separatory funnel. 80 ml Skelly A were added and the organic layers successively washed three times with saturated sodium thiosulfate solution and saturated ammonium chloride solutions. Following drying (anhydrous Na_2SO_4) and concentration, colorless needles with a melting point and IR spectrum identical to the divinyl ketone, _trans_,_trans_-2,2,8,8-tetramethyl-nona-3,6-dien-5-one were obtained.

12. _Unsuccessful attempts to insert either ethylene or acetylene into the vinylrhodium intermediates formed from one mole % $[Rh(CO)_2Cl]_2$ and a vinylmercurial_

1.60 Grams (5.0 mmoles) _trans_-3,3-dimethyl-1-butenylmercuric chloride, at least 0.42 grams (10.0 mmoles) lithium chloride and 0.0097 grams (0.025 mmoles) $[Rh(CO)_2Cl]_2$ were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. A balloon of ethylene (acetylene) was attached to the gas inlet tube and used to flush the system and maintain an atmosphere of ethylene (acetylene). After flushing the system with ethylene (acetylene), 50 ml THF was added by syringe. The system was again flushed with ethylene (acetylene) and allowed to stir at room temperature for 24 hours. The reaction mixture was filtered (to remove mercury) into a separatory funnel and 80 ml Skelly A added. After washing successively three times with saturated sodium thiosulfate and ammonium chloride solutions, the organic layer was dried (anhydrous Na_2SO_4) and concentrated to give an off-white solid with spectra identical to that of the symmetrical diene, 2,2,7,7-tetramethyl-3,5-octadiene. The above reaction was also attempted under a nitrogen atmosphere with a 10-fold excess of norbornene instead of ethylene or acetylene. The symmetrical diene was again produced.

13. An attempt to couple an aldehyde and a vinylmercurial forming an unsymmetrical ketone

0.80 Grams (2.5 mmoles) trans-3,3-dimethyl-1-butenylmercuric chloride, at least 0.21 grams (5 mmoles) lithium chloride and 0.0049 grams (0.0125 mmoles) $[Rh(CO)_2Cl]_2$ were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. A balloon of carbon monoxide was attached to the gas inlet tube and used to flush the system and maintain an atmosphere of carbon monoxide. After flushing the system with carbon monoxide, 10 ml (excess) propanal and 50 ml THF were added by syringe. The system was again flushed with carbon monoxide and allowed to stir at room temperature for 24 hours. After filtering the reaction mixture to remove elemental mercury, 80 ml Skelly A (pentane) was added and the organic layer washed three times each with saturated sodium thiosulfate and saturated ammonium chloride solutions. The ^1H nmr ($CDCl_3$) of the oil obtained after drying (anhydrous Na_2SO_4) and concentrating the solution indicated some divinyl ketone was formed, δ6.25 (d, J = 15.5 Hz) and δ6.90 (d, J = 15.5 Hz) but also contains a small amount of unidentified vinyl peaks near δ6.0 as well as probable THF derived products products near δ5.10.

VI. CONCLUSION

Although not presently synthetically useful, there is real value in studying these rhodium mediated carbon-carbon bond formations of organomercurials. The facile synthesis of divinyl ketones is a notable exception. Divinyl ketones are formed stereospecifically in excellent yields from vinylmercurials and a catalytic amount of $[Rh(CO)_2Cl]_2$ under 1 atmosphere of carbon monoxide at room temperature in THF. Also 10% Wilkinson's catalyst effectively catalyzed the formation of styrene from vinyl bromide and phenylmercuric chloride. Certainly the stoichiometric coupling of an organorhodium(III) halide with an organomercurial demonstrates that carbon-carbon bonds may be formed by a scheme presumably involving oxidative addition of an organic halide (or an organomercurial) to a rhodium(I) species, transmetalation of the resulting organorhodium(III) halide with an organomercurial and reductive elimination of the coupled product from a diorganorhodium(III) species. The different alkyl-, vinyl-, aryl- and alkynylmercurials and alkyl, vinyl and aryl halides which react certainly illustrate the potential generality of such a carbon-carbon bond forming sequence. Although these different couplings were investigated individually and each seemed to possess unique difficulties and to demand special conditions, an overall view of these reactions may provide a peculiar (because the approach was synthetic and not mechanistic) understanding of these couplings.

Two obviously different sets of conditions are apparently necessary for successful rhodium mediated carbon-carbon bond formations using organomercurials: excess lithium chloride at room temperature in THF and excess lithium chloride at 70°C in HMPA. The investigated couplings are catalogued beginning with the most successful catalytic couplings and concluding with the least successful reactions (Table XXXV). This Table is partially useful in evaluating the results since the bottom reactions which are unsuccessful catalytically are unsuccessful due to the ease of the top reactions. For example, diene formation was observed to compete with methyl-substituted olefin formation under catalytic conditions where methyl-vinyl coupling was desired. Consideration of this experimental guide may make the search for new carbon-carbon bond formation of organomercurials mediated by rhodium species easier. Another way of expressing this reactivity in terms of the proposed mechanism is to state that productive catalytic unsymmetrical couplings must involve an oxidative addition of a species which is faster than oxidative addition of the organomercurial. Another relatively unexplored parameter in this guide is temperature. Although neat HMPA tolerates very limited lower temperatures (melting point = 5°C), it is possible greater selectivity in these couplings may be observed at lower temperatures.

Table XXXV. A tabulation of the observed rhodium(I) and/or -(III) mediated coupling reactions of organomercurials and their conditions

Coupling Process	Product	Conditions
vinyl, vinyl	symmetrical diene	25°C, THF
vinyl acyl, vinyl	symmetrical dienone	25°C, THF, CO = 1 atm
aryl, aryl	symmetrical biaryl	70°C, HMPA
aryl acyl, aryl	symmetrical diaryl ketone	70°C, THF, CO > 1 atm
vinyl, aryl	vinyl arene	70°C, HMPA
methyl, alkynyl	methyl acetylene	
methyl, vinyl	methyl-substituted olefin	
methyl, aryl	methyl-substituted arene	
aryl, vinyl	aryl-substituted olefin	not determined

Although other conditions, especially other rhodium catalysts, may possess greater selectivity and might be investigated, the other obvious area to be pursued is further characterization of the adduct formed from one equivalent of Wilkinson's catalyst or other rhodium catalysts and one equivalent of an organomercurial. The identification and characterization of possible intermediates in these couplings would enable more reasonable mechanisms to be proposed. In turn, new carbon-carbon bond formations might be predicted with greater accuracy and hence be significantly more useful in organic synthesis.

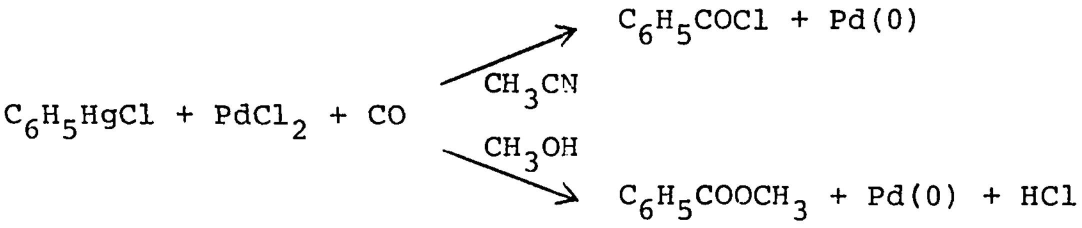
Although separate from the carbon-carbon bond forming reactions of organomercurials, an interesting transformation involving a vinylmercurial was also observed during the course of this investigation. _Trans_-1-chloro-3,3-dimethyl-1-butene was isolated from the reaction of _trans_-3,3-dimethyl-1-butenylmercuric chloride with excess cupric chloride at 70°C. Time did not permit the synthetic aspects of this reaction to be further explored. This reaction, while not previously observed with vinylmercurials, has been observed with other organomercurials such as benzylmercuric bromide and cupric bromide.[332]

PART II: STABLE ALKYLPALLADIUM COMPOUNDS FROM VINYLMERCURIALS, DILITHIUM TETRACHLOROPALLADATE AND BICYCLIC OLEFINS

I. ORGANOPALLADIUM CHEMISTRY PERSPECTIVES

The insertion of carbon monoxide, olefins, acetylenes or other unsaturated molecules into palladium carbon or palladium-hydrogen bonds has established the importance of organopalladium chemistry in synthetic organic chemistry. Although this area of palladium chemistry is well-known, extensively investigated and the subject of numerous reviews[333-339] and books,[340,341] current research interest is still high. However a comprehensive review would be lengthy and inappropriate. In Part I, the proposed transmetalation of an organomercurial with an organorhodium(III) halide was crucial to the formation of the diorganorhodium(III) intermediate proposed to reductively eliminate different carbon-carbon bonded species. The transmetalation of organomercury compounds with palladium(II) halides is also an established method of forming organopalladium compounds. A review of the transmetalation of organomercurials with palladium salts and a brief survey of the reactions of the resulting organopalladium compounds should provide some perspective for the syntheses of the stable alkylpalladium compounds which follow.

Although an extensively employed synthesis of organomercury compounds involves the transmetalation of Grignard or organolithium reagents with mercury salts, the transmetalation of organomercury compounds with transition metal salts seems not to have been reported until 1967 in a patent. P. M. Henry of Hercules, Inc. reported that carboxylic acids, anhydrides, esters, or ketones were produced from Group VIII (platinum, palladium, or rhodium) salts, organomercury, -tin, or -lead compounds, carbon monoxide and an oxidant.[314] A year later, Henry published the synthesis of carboxylic acids and their derivatives via the transmetalation of arylmercurials with palladium chloride followed by the insertion of carbon monoxide (Eq. 1).[342] In the absence of palladium chloride or other transition metal salts the carbonylation of mercurials occurs only at high temperature and pressure.[343,344]



$$C_6H_5HgCl + PdCl_2 + CO \xrightarrow{CH_3CN} C_6H_5COCl + Pd(0)$$

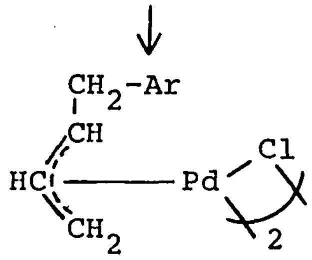
$$C_6H_5HgCl + PdCl_2 + CO \xrightarrow{CH_3OH} C_6H_5COOCH_3 + Pd(0) + HCl$$

(1)

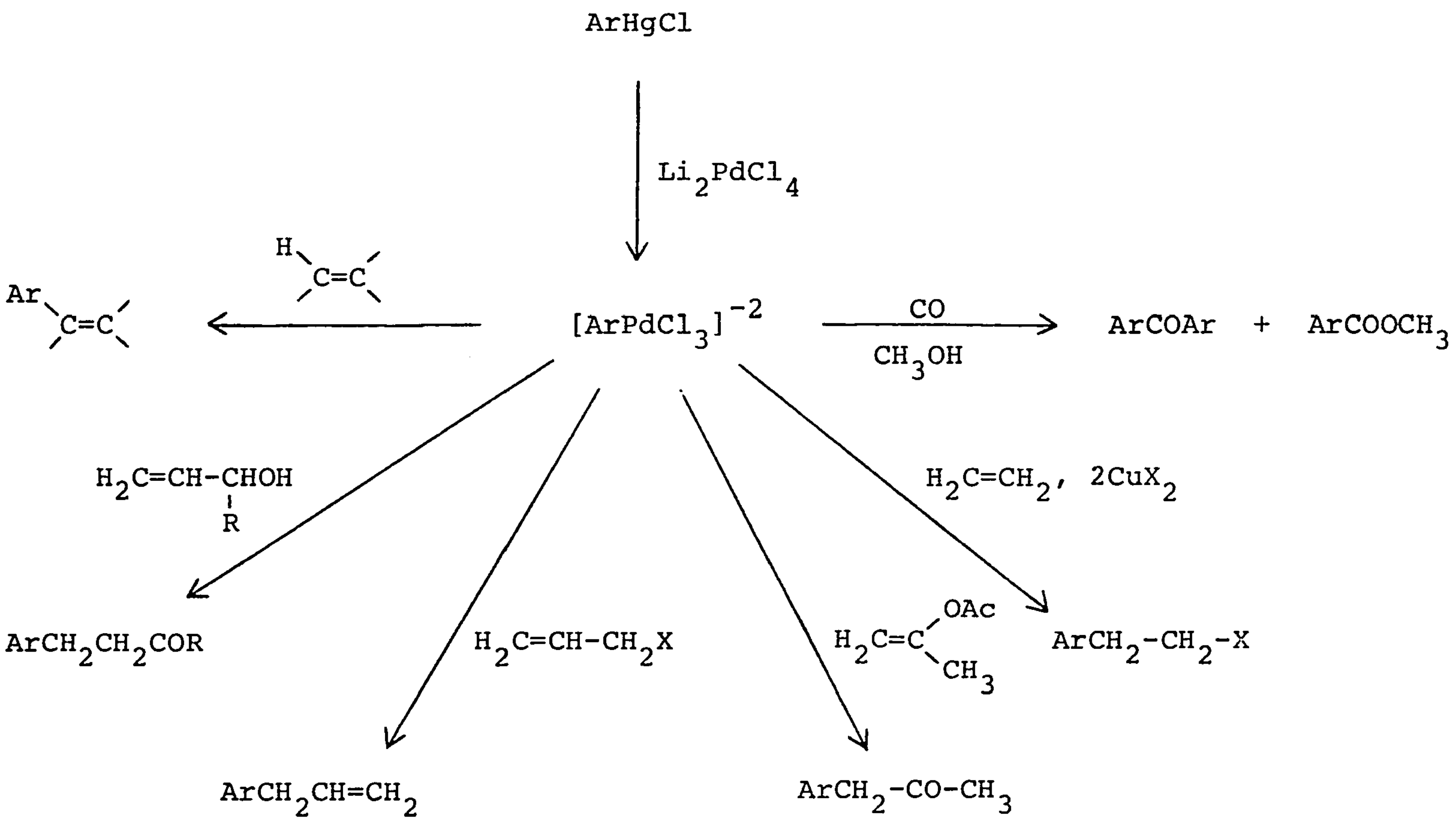
Concurrently Heck (then also of Hercules, Inc.) reported the insertion of olefins into the organotransition metal compounds formed from the transmetalation of methyl-, benzyl, and arylmercurials with Group VIII metal salts, especially Li_2PdCl_4. The facile elimination of beta hydrogens from alkylpalladium compounds prohibited the use of other alkylmercurials. Organotin and -lead compounds were also observed to transmetalate with palladium salts. The organopalladium species were not isolated but were instead characterized by the insertion products of various olefins as illustrated in Scheme 1.[78,217-221] The insertion of the olefin into the carbon-palladium bond is proposed to occur as a syn(cis) addition of carbon and palladium to the olefin, syn(cis) elimination of hydrogen palladium chloride. Perhaps due to steric effects, the organic group generally adds to the lesser substituted carbon of the double bond. The reaction of phenylmercuric acetate, palladium acetate and trans- and cis-1-phenyl-1-propene (Scheme 2) suggested the syn(cis) addition, syn(cis) elimination sequence.[345] Although the transmetalation product, $[ArPdX_3]^{-2}$, has not been fully characterized, it reacts similarly to the arylpalladium species obtained from the oxidative addition of aryl halides to palladium(0) species.[346] The formation of π-allyl-palladium compounds from the insertion of conjugated dienes is especially noteworthy because the organopalladium product is stabilized by the remaining unsaturation in the molecule (Scheme 3).[347]

Scheme 3

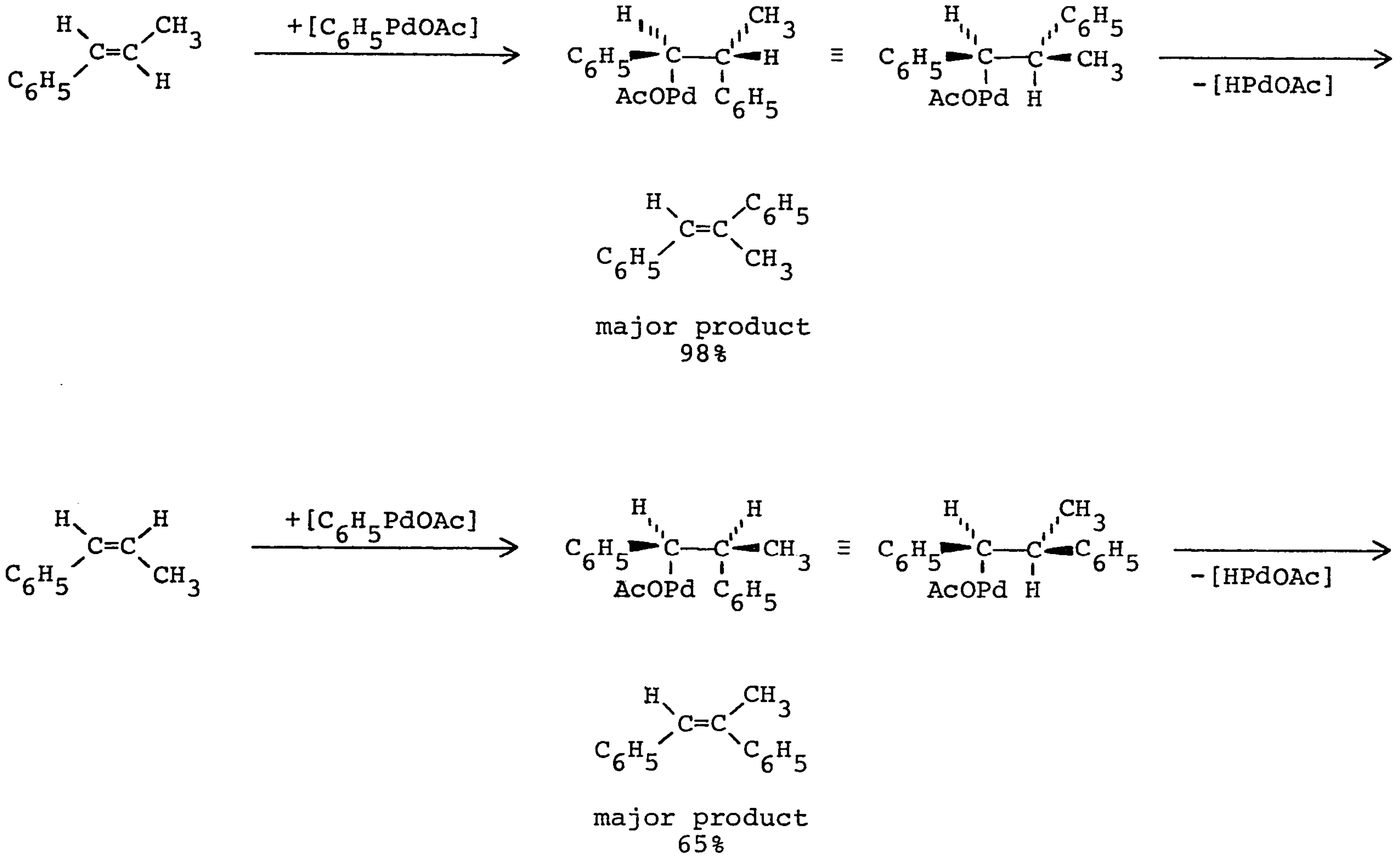
$$ArHgCl + Li_2PdCl_4 \rightarrow [ArPdCl_3]^{-2} + HgCl_2 + 2LiCl$$



Scheme 1


ArHgCl
Li2PdCl4
[ArPdCl3]-2
CO
CH3OH
ArCOAr + ArCOOCH3
H C=C
Ar C=C
H2C=CH-CHOH
R
ArCH2CH2COR
H2C=CH-CH2X
ArCH2CH=CH2
H2C=C OAc CH3
ArCH2-CO-CH3
H2C=CH2, 2CuX2
ArCH2-CH2-X

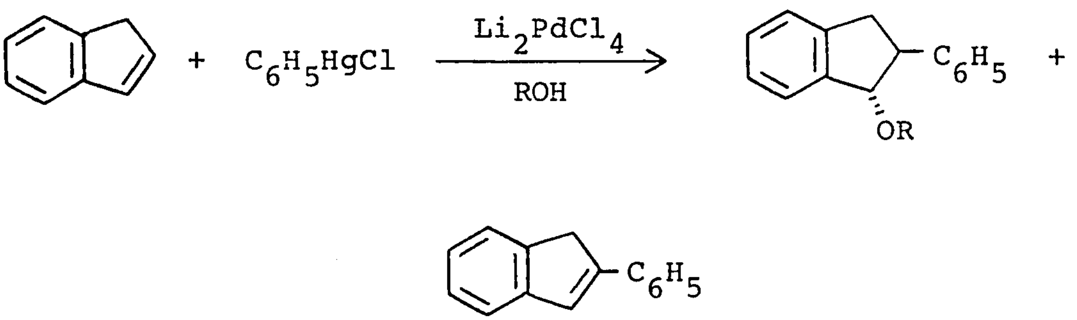
Scheme 2



major product
98%

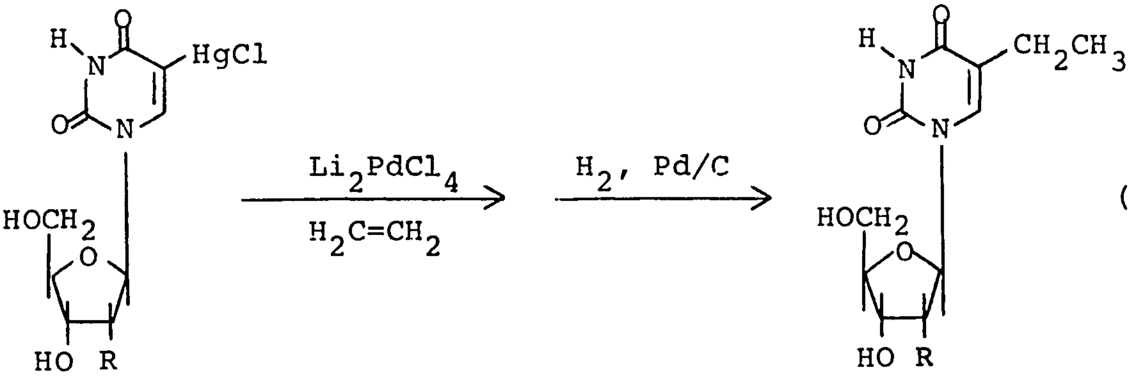
major product
65%

The organopalladium intermediate may also be trapped by oxygen nucleophiles which is formally termed "oxyphenylation of olefins". Unfortunately, hydrogen palladium chloride elimination also occurs decreasing the oxyphenylation yields (Eq. 2).[348,349]

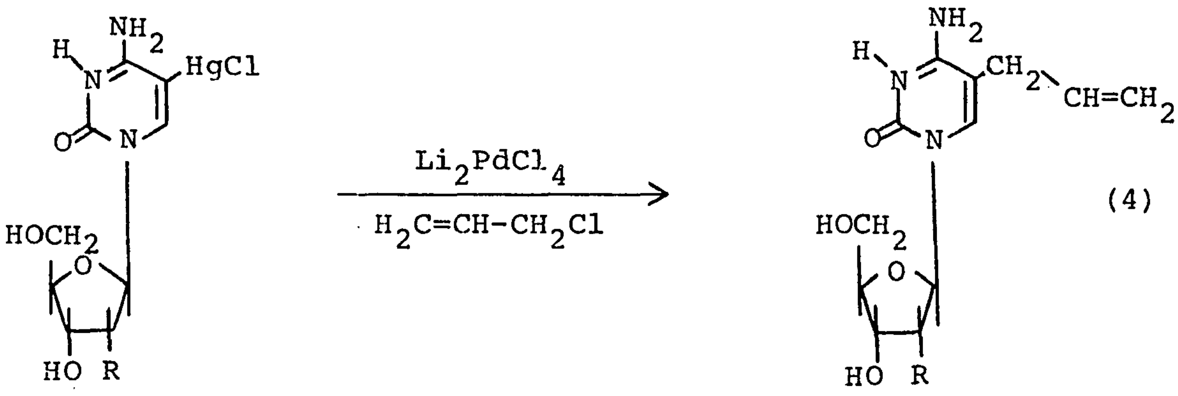


(2)

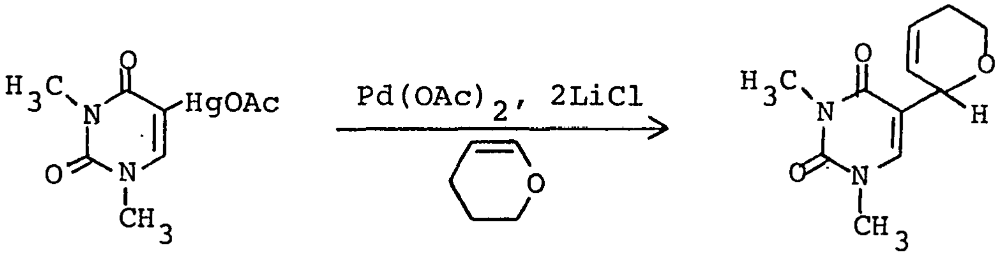
Since pyrimidines are selectively mercurated in the 5-position, pyrimidines have been alkylated in the 5-position via transmetalation and the insertion of olefins such as ethylene (Eq. 3),[350] allyl chloride (Eq. 4)[351] or enol ethers (Eq. 5).[352,353]



(3)

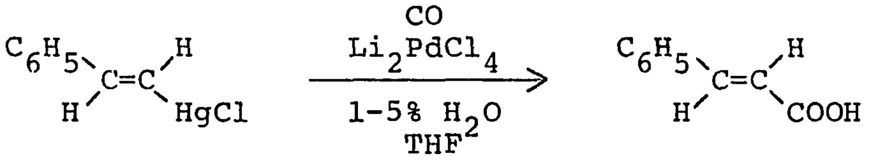


(4)

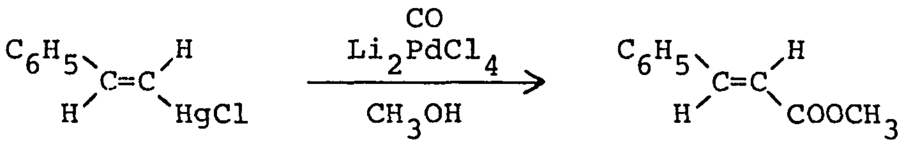


(5)

The development of a facile stereospecific vinylmercurial synthesis by Larock and Brown[253,254] prompted Larock to investigate the transmetalation of vinylmercurials. α,β-Unsaturated acids (Eq. 6) and esters (Eq. 7) are formed from



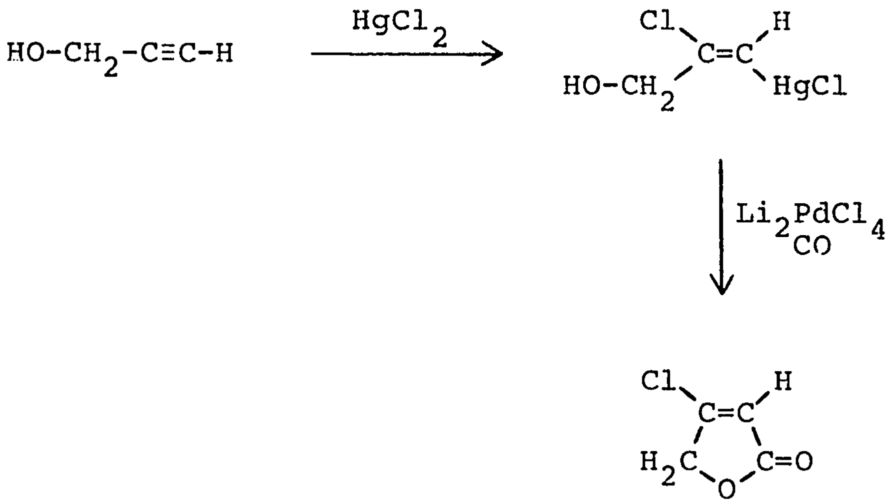
$$C_6H_5CH{=}CHHgCl \xrightarrow[\text{1-5\% } H_2O,\ THF]{CO,\ Li_2PdCl_4} C_6H_5CH{=}CHCOOH \qquad (6)$$



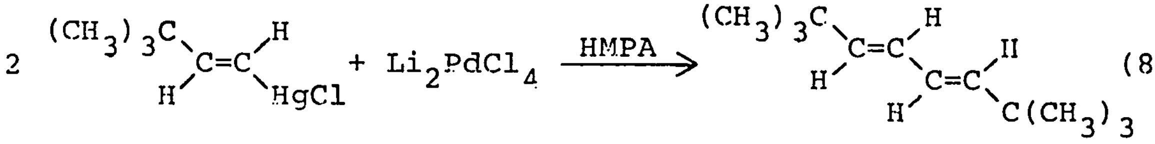
$$C_6H_5CH{=}CHHgCl \xrightarrow[CH_3OH]{CO,\ Li_2PdCl_4} C_6H_5CH{=}CHCOOCH_3 \qquad (7)$$

the transmetalation of vinylmercurials with dilithium tetrachloropalladate followed by carbonylation at one atmosphere.[213] Vinylmercurials derived from propargylic alcohols also undergo transmetalation and carbonylation to form butenolides (Scheme 4).[214,215] Vinylmercurials presumably transmetalate

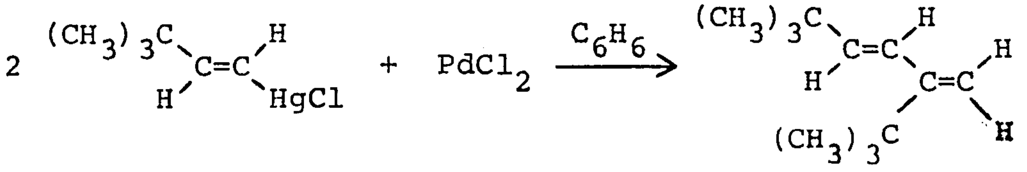
Scheme 4



twice with dilithium tetrachloropalladate in HMPA producing a dichlorodivinylpalladium dianion. After reductive elimination, symmetrical 1,3-dienes and palladium(0) are formed (Eq. 8).[354] In a less polar solvent without lithium chloride,

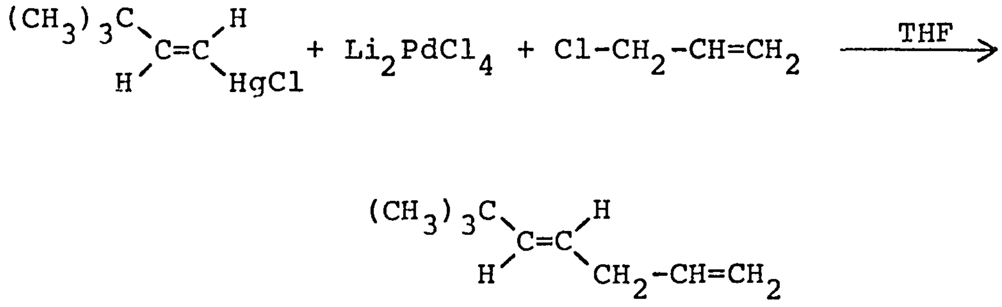
 (8)

the head-to-tail dimer is formed (Eq. 9). Although a vinylpalladium chloride derived from the transmetalation of the vinylmercurial with palladium chloride is presumed to form,



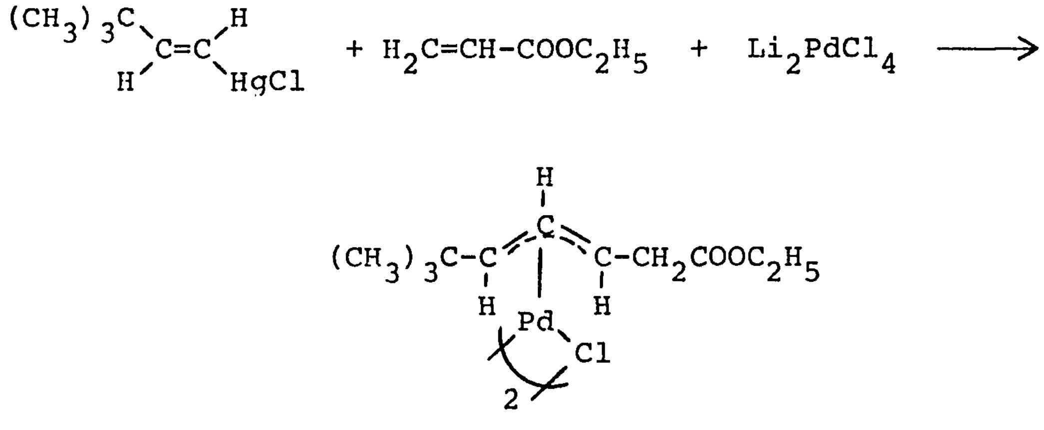
(9)

the mechanism of the head-to-tail dimer formation is not known.[354,355] After transmetalation with dilithium tetrachloropalladate, vinylmercurials also insert allyl chlorides producing 1,4-dienes (Eq. 10).[216] However, following the



(10)

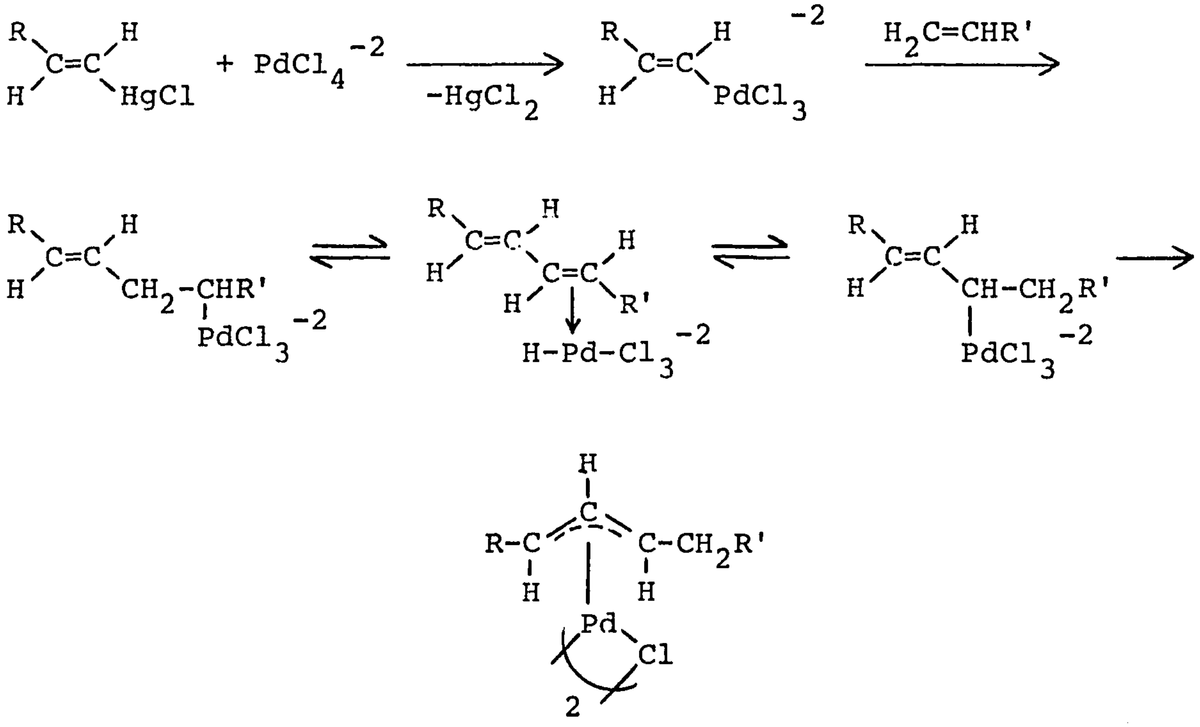
transmetalation of vinylmercurials with dilithium tetrachloropalladate the insertion of other olefins does not form unsymmetrical dienes analogous to the reactions of Heck with arylmercurials. Instead π-allyl palladium compounds are formed (Eq. 11). The mechanism proposed to account for π-allyl



(11)

formation (Scheme 5) suggests after the initial elimination, hydrogen palladium trichloride anion readds in the opposite

Scheme 5

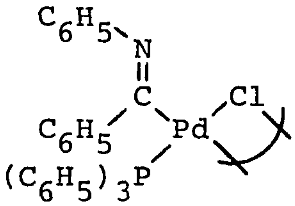


direction forming a σ-allylpalladium species which isomerizes to a π-allylpalladium compound.[355,356] Undoubtedly, the original vinylmercurial double bond influences the formation of the allyl palladium compound since changes in other ligands have induced the formation of dienes from π-allylpalladium compounds.[357] Heck suggested that a similar π-allylpalladium compound may be formed from the oxidative addition of vinyl chlorides to palladium(0) compounds followed by the insertion of olefins in a synthesis of conjugated dienes.[358]

Although aryl- or vinylpalladium species have not been isolated from the transmetalation reaction of aryl- or vinylmercurials with dilithium tetrachloropalladate or palladium chloride, the products of the reactions with carbon monoxide, olefins and other reagents strongly indicate their formation. It has also been demonstrated by Heck that the palladium intermediates formed from the oxidative addition of aryl and vinyl halides react with olefins analogously to the palladium species presumably formed from the transmetalation of aryl- and vinylmercurials.[339]

The reactions of organomercurials and palladium compounds containing isocyanide ligands are also interesting. Transmetalation presumably occurs, followed by the insertion of the isocyanide ligand, perhaps more correctly considered an alkyl or aryl migration (Eq. 12).[359] The double insertion of

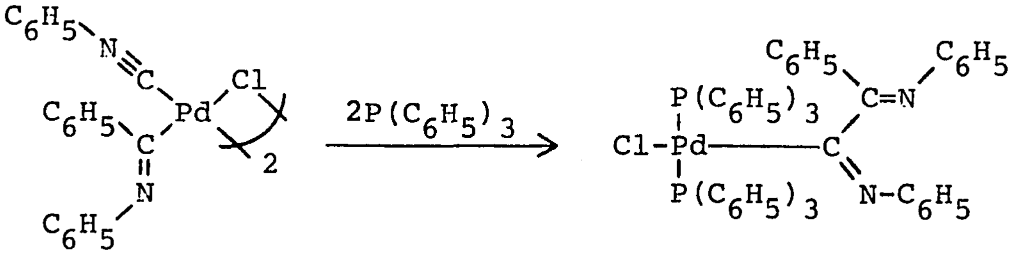
$$\text{cis }\{PdCl_2(CNC_6H_5)[P(C_6H_5)_3]_2\} \ + \ (C_6H_5)_2Hg \longrightarrow$$



(12)

the isocyanide ligand was observed with $PdX_2(CNR)_2$ after the addition of triphenylphosphine (Eq. 13).[360] A complex analo-

$$PdCl_2(CNC_6H_5)_2 + Hg(C_6H_5)_2 \xrightarrow[-(C_6H_5HgCl)]{}$$



(13)

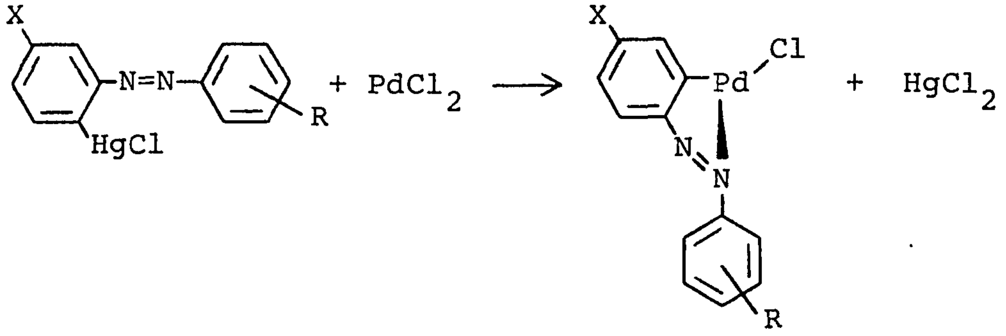
ogous to the proposed intermediate $PdX(R')(CNR)_2$ for this transmetalation reaction was isolated from the oxidative addition of methyl iodide to $Pd[CNC(CH_3)_3]_2$ in hexane and was observed to insert an isocyanide ligand in toluene solution.[361]

The organopalladium species from the transmetalation of palladium(II) with organomercurials have been isolated for special palladium(II) complexes or organomercurials. Cross initially reported the formation of phenylbis(dimethylphenylphosphine)palladium(II) chloride and phenylmercuric chloride from the reaction of bis(dimethylphenylphosphine)palladium(II) chloride and diphenylmercury (Eq. 14). The same products are obtained from diphenylbis(triphenylphosphine)palladium(II) and mercuric chloride (Eq. 15).[362] Later 2-(arylazo)arylmercury compounds were reported to react with palladium chloride or

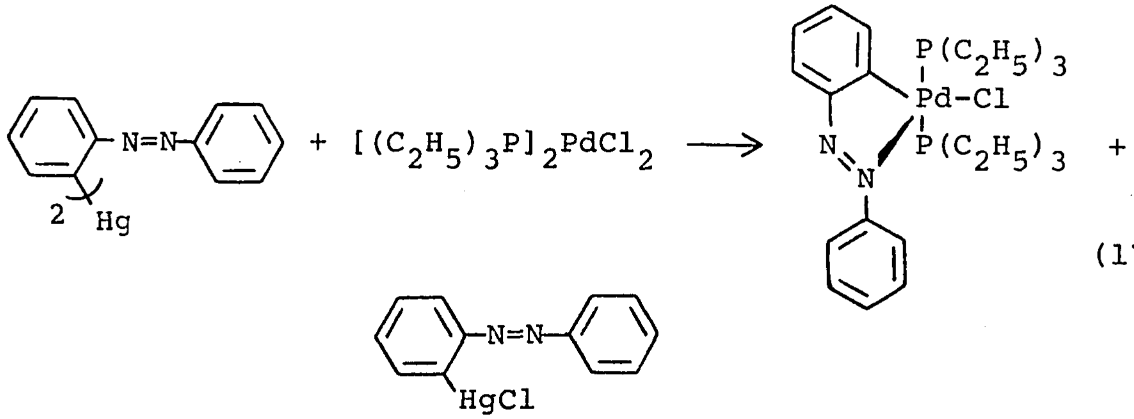
$$[(CH_3)_2PC_6H_5]_2PdCl_2 + (C_6H_5)_2Hg \longrightarrow \underline{trans}\text{-}[(CH_3)_2PC_6H_5]_2Pd(C_6H_5)Cl + C_6H_5HgCl \qquad (14)$$

$$[(CH_3)_2PC_6H_5]_2Pd(C_6H_5)_2 + HgCl_2 \longrightarrow \underline{trans}\text{-}[(CH_3)_2PC_6H_5]_2Pd(C_6H_5)Cl + C_6H_5HgCl \qquad (15)$$

palladium phosphine complexes (Eqs. 16 and 17). The transmetalation product is stabilized by coordination to nitrogen.[363] In his first paper, Cross proposed two mecha-



(16)



(17)

nisms for transmetalation. One mechanism involved the oxidative addition of the organomercurial producing a palladium(IV) intermediate which reductively eliminates organomercuric chloride (Scheme 6). The other mechanism involved a bimolecular substitution most simply pictured as a four-center reaction (Scheme 7).[362] The oxidative addition of the organomercurial to palladium(II) forming a palladium(IV) species is especially interesting in light of a very recent investigation into the mechanism of reductive elimination.[267] Palladium(IV) intermediates were proposed because the addition of benzyl bromide to dimethylbis(triphenylphosphine)palladium(II) produced predominantly ethylbenzene and only a small amount of ethane (Scheme 8). Since the dialkylpalladium com-

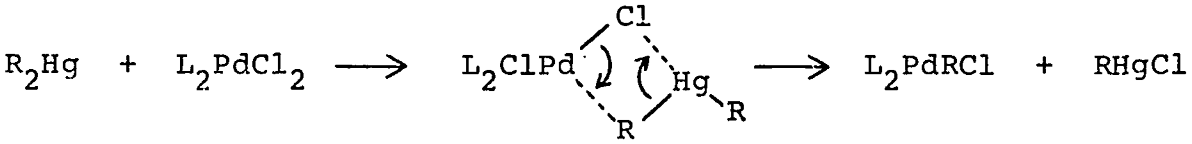
Scheme 6

$$\mathrm{R_2Hg + L_2PdCl_2 \longrightarrow [L_2PdCl_2R(HgR)]}$$

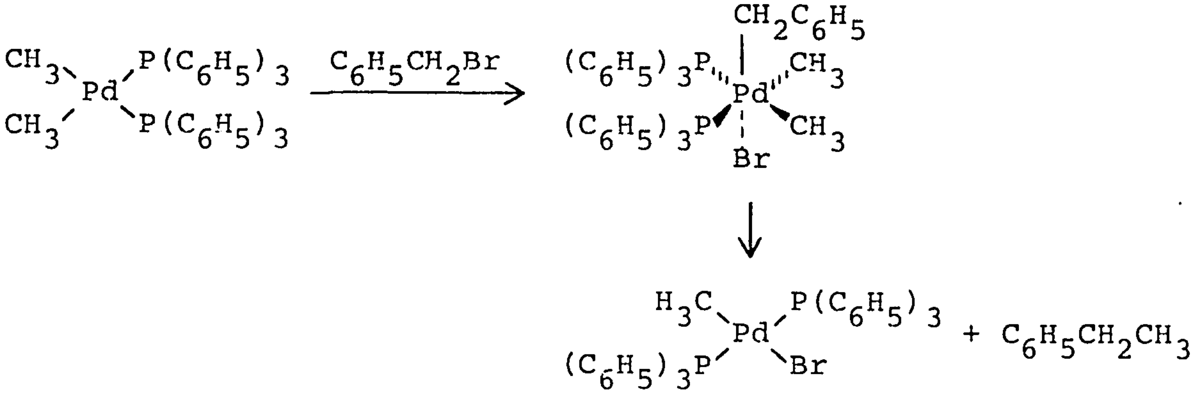
$$\downarrow$$

$$\mathrm{L_2PdRCl + RHgCl}$$

Scheme 7

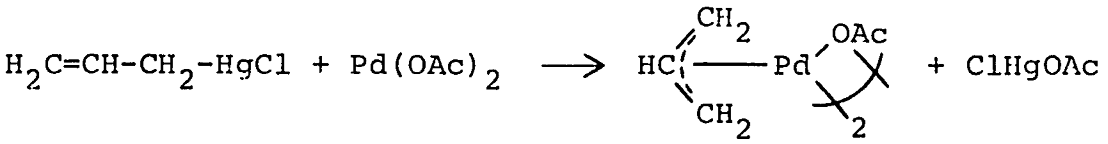


Scheme 8



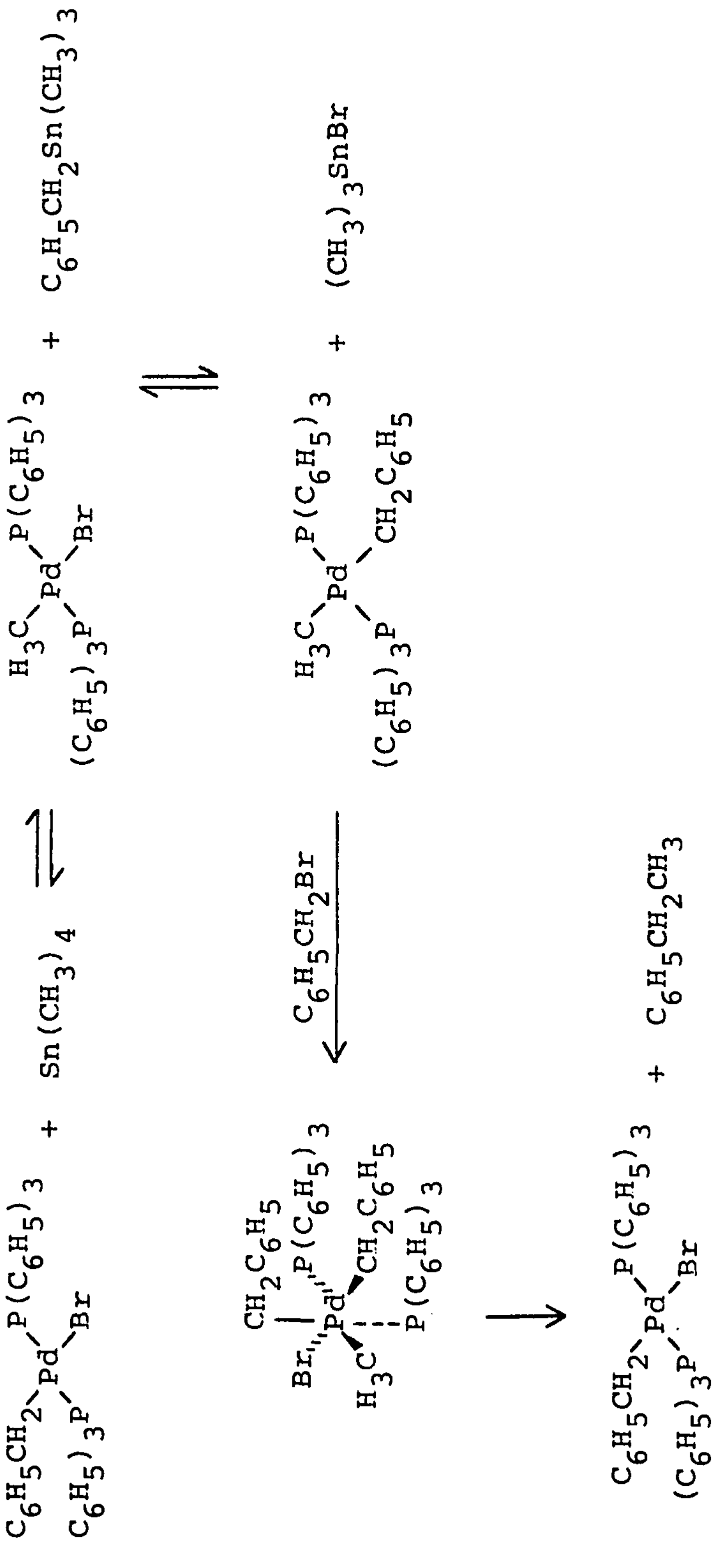
pounds are formed via the transmetalation of tetraorganotin compounds (Scheme 9), this study may also be related to the transmetalation of organomercurials with palladium compounds. Although palladium(IV) was proposed in this report, the oxidative addition of the tetralkyltin to palladium(II) was not proposed. The transmetalation steps suggested involved only exchange of two alkyl groups or exchange of an alkyl group and a halide without further mechanistic description (Scheme 9).

Allylmercury halides have also been reported to form numerous π-allyl transition metal compounds via transmetalation with numerous transition metal salts (Eq. 18). However



(18)

Scheme 9



there is no synthetic advantage to this transmetalation for palladium since the authors prepared the allylmercuric halides from allylpalladium halides and metallic mercury.[364] However, allylmercuric halides can also be prepared from allyl halides and metallic mercury.[277]

Despite an incomplete understanding of the transmetalation process with respect to either synthetic feasibility or mechanism, transmetalation of an organomercurial is established as a method of forming transition metal-carbon bonds. These transition metal-carbon bonds may be utilized for further functionalization, carbon-carbon bond formation or the synthesis of other transition metal organometallic compounds. In a reaction similar to the synthesis of π-allyl palladium compounds from arylmercurials, dilithium tetrachloropalladate and dienes, or vinylmercurials, dilithium tetrachloropalladate and olefins, the next chapter presents the synthesis of stable σ-bonded vinyl norbornylpalladium chlorides from vinylmercuric chlorides, dilithium tetrachloropalladate and norbornene or other bicyclic olefins.

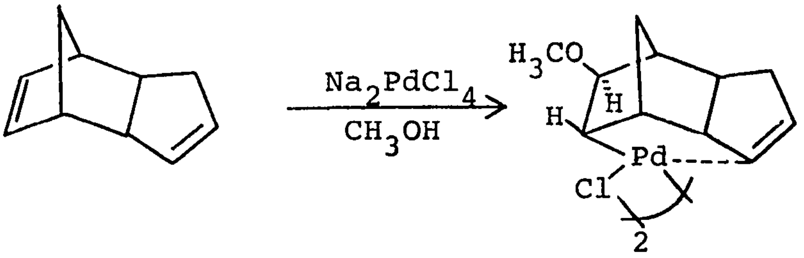
II. SYNTHESIS OF VINYL NORBORNYLPALLADIUM COMPOUNDS, RELATED VINYL ALKYLPALLADIUM COMPOUNDS AND A VINYL NORTRICYCLYLPALLADIUM COMPOUND

A. Introduction

In addition to the previously mentioned syntheses of π-allylpalladium compounds from arylmercurials, dilithium tetrachloropalladate and dienes, or vinylmercurials,[356,357] lithium tetrachloropalladate and olefins, organomercurials react with palladium chloride and bicyclic olefins or organopalladium derivatives of bicyclic olefins forming stable σ-bonded alkylpalladium compounds. Due to the facile loss of a beta hydrogen via the proposed syn(cis) elimination of hydrogen palladium chloride, the isolation of stable alkylpalladium compounds requires unique steric considerations. This introduction contains a review of the reactions of bicyclic olefin or diene palladium derivatives with organomercurials and the reactions of norbornene and other bicyclic olefins or dienes with organopalladium compounds.

1. <u>Reactions of bicyclic olefin or diene palladium derivatives with organomercurials</u>

The reactions of bicyclic olefin or cyclic diene palladium compounds with nucleophiles provide perspective for the reactions of bicyclic olefin or diene palladium derivatimes with organomercurials. In 1957 Chatt reported cyclic dienes such as dicyclopentadiene reacted in alcohol with disodium tetrachloropalladate and anhydrous sodium carbonate to yield an alkoxy organopalladium compound (Eq. 19).[365] Later the stereochemistry of the product was established by Stille who found that the same compound is also prepared by the reaction of dicyclopentadiene palladium dichloride with anhydrous sodium carbonate in alcohol (Eq. 20).[366] Norbornadiene palladium dichloride reacts analogously[367] (Eq. 21) and the acetate derivative has also been prepared (Eq. 22).[368,369]



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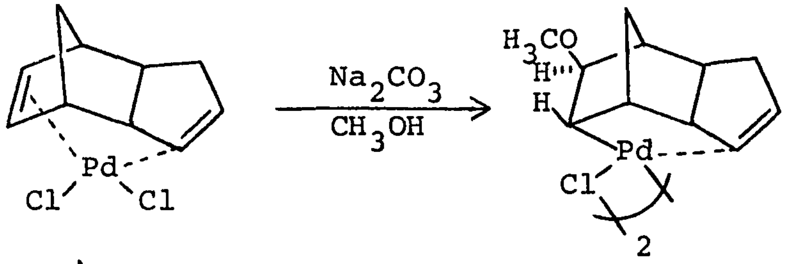

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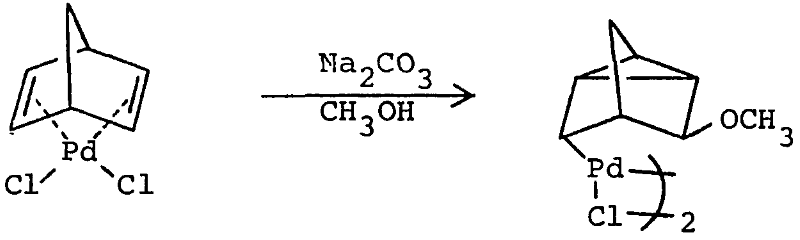

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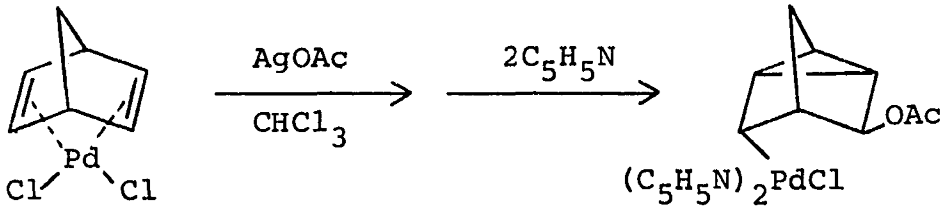

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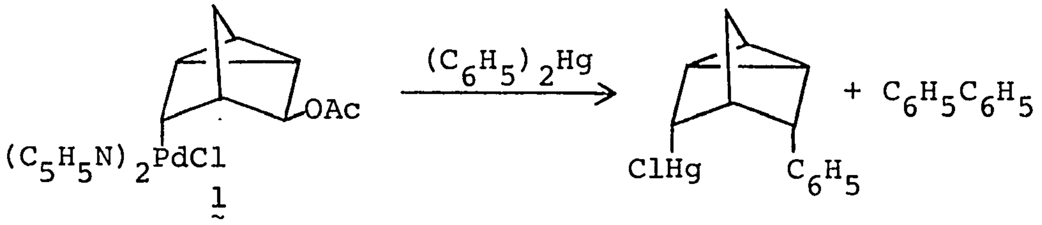
(22)

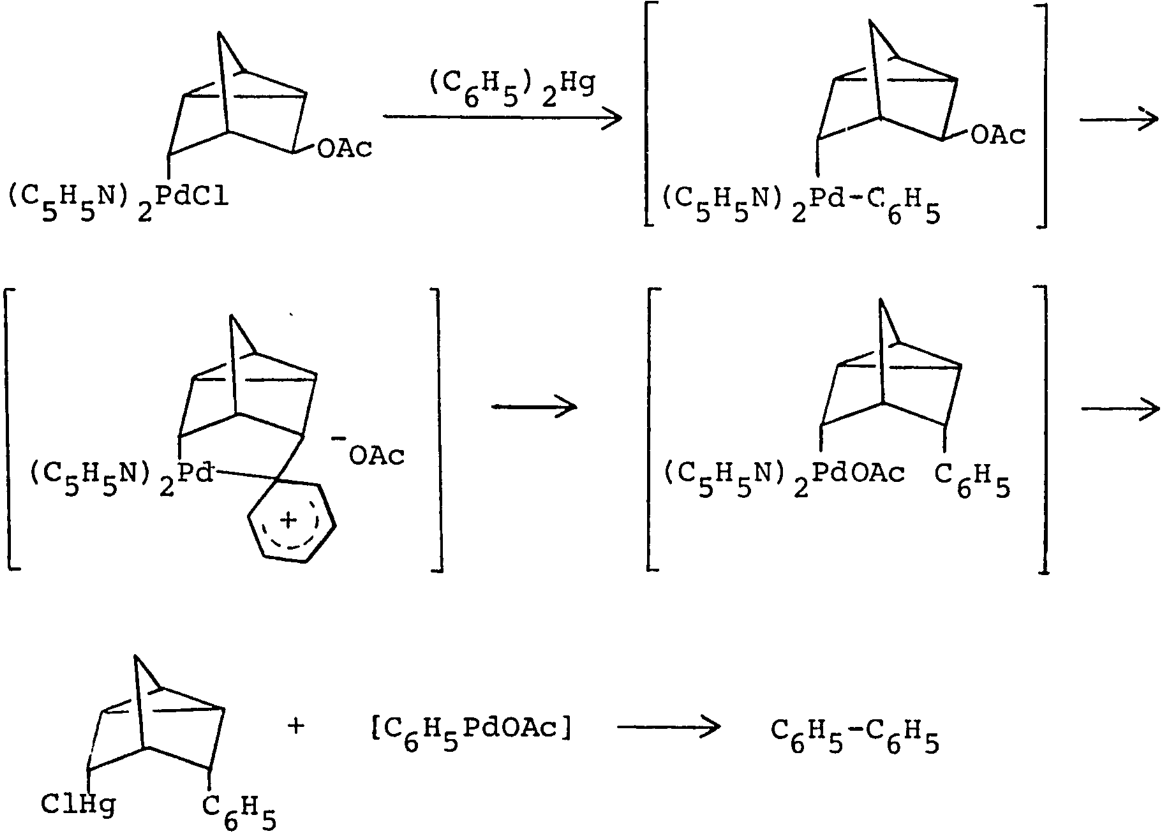
These derivatives as well as the bicyclic olefin or diene palladium compounds react with organomercurials.

The popular interest in reactions similar to the Wacker process prompted Vedejs and co-workers to investigate the association of strained bicyclic olefins and dienes with palladium chloride.[370] As part of that study, palladium compound 1 was reacted with diphenylmercury (Eq. 23). Scheme

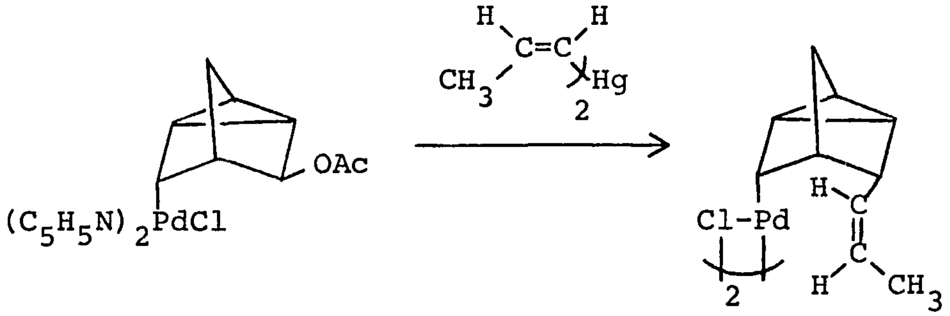


(23)

Scheme 9



9 was proposed to account for the products.[371] Later the palladium intermediate was isolated in the reaction with di(cis-propenyl)mercury (Eq. 24). Carbonylation further substantiated the structure of the palladium species (Eq. 25).[372]



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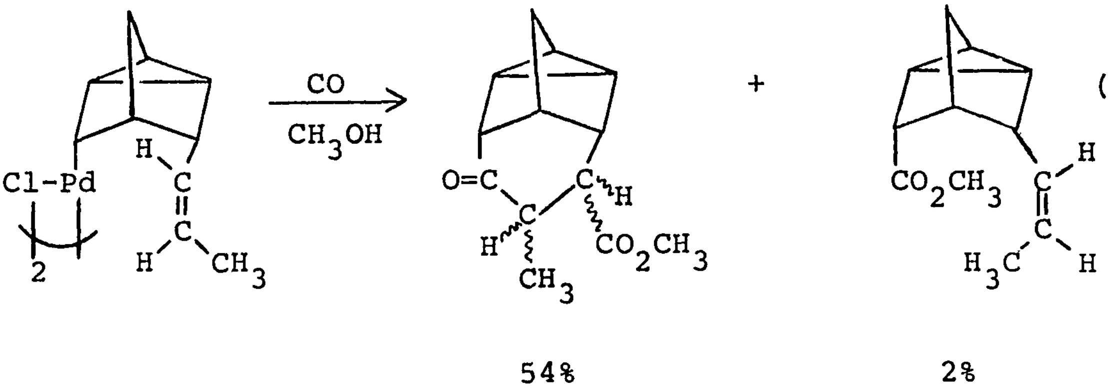
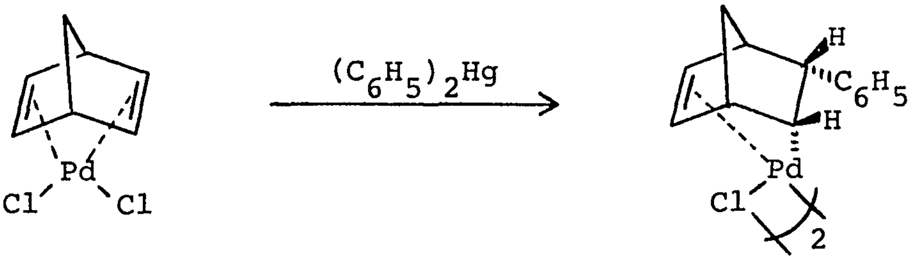


(25)

The reaction of diphenylmercury and norbornadiene palladium dichloride was first reported to yield a related organopalladium compound (Eq. 26).[373] Similar to the previously



(26)

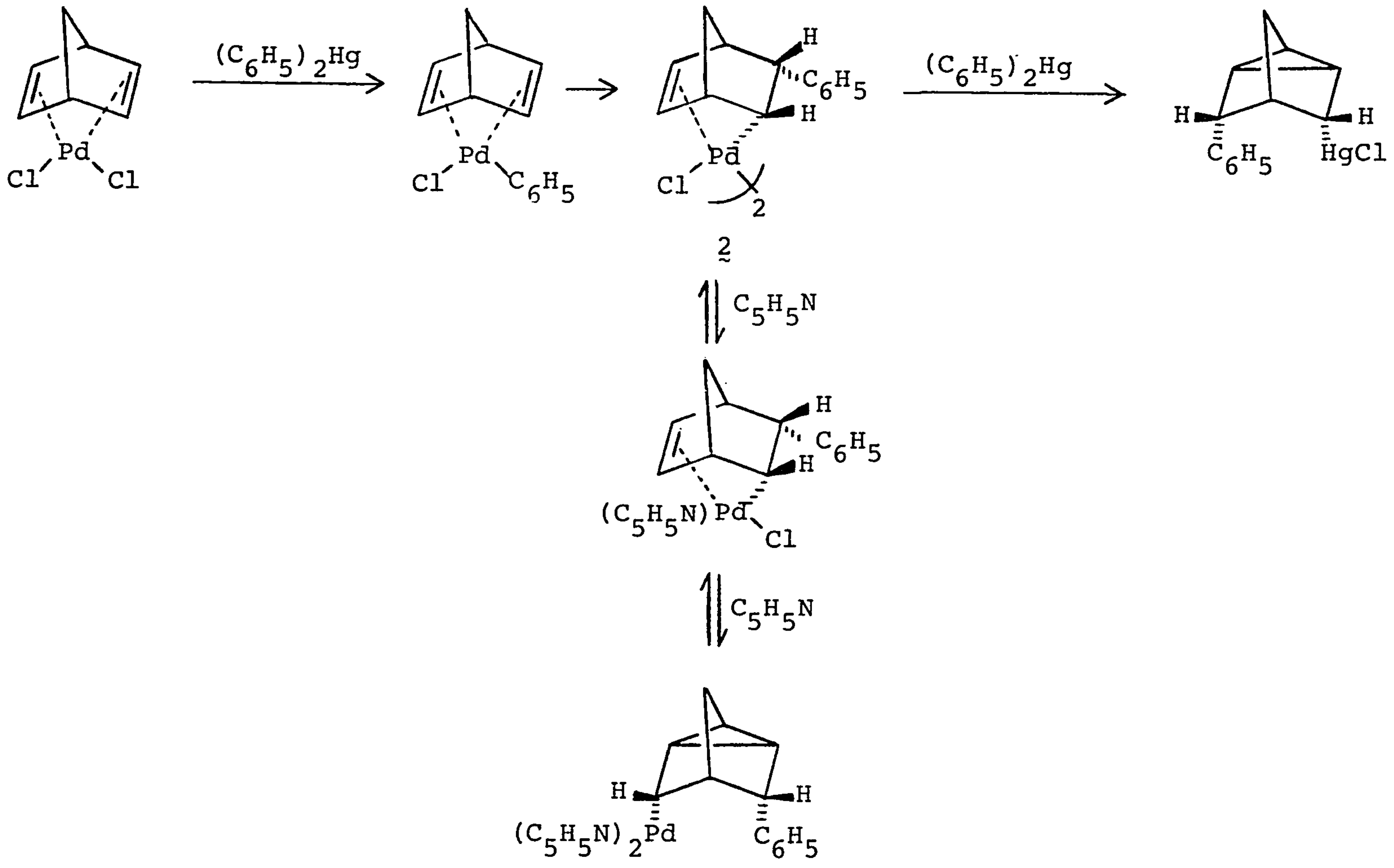
2

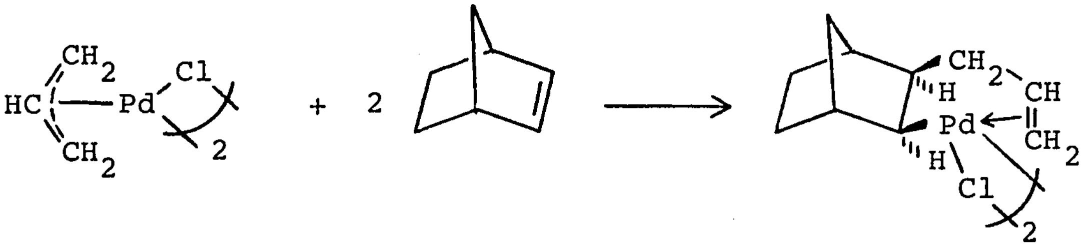
prepared derivative, the stereochemistry of both the palladium and phenyl moieties is endo. The norbornadiene portion was determined by x-ray diffraction methods to be a norbornenyl unit with an endo palladium coordinated to the double bond, compound 2.[373] Upon addition of pyridine a nortricyclyl species was formed. Further addition of diphenylmercury formed the nortricyclylmercury derivative (Scheme 10).[374]

2. Reactions of norbornene and other bicyclic olefins or dienes with π-allylpalladium compounds or other palladium species

Since π-allylpalladium compounds are isolable, norbornene was inserted into isolated π-allylpalladium compounds forming the stable σ-bonded allylnorbornylpalladium compounds (Eq. 27).[375-381] X-ray diffraction studies indicate that the addition of both the allyl unit and the palladium moiety occurs syn(cis) with the exo orientation. The x-ray diffraction studies were carried out with

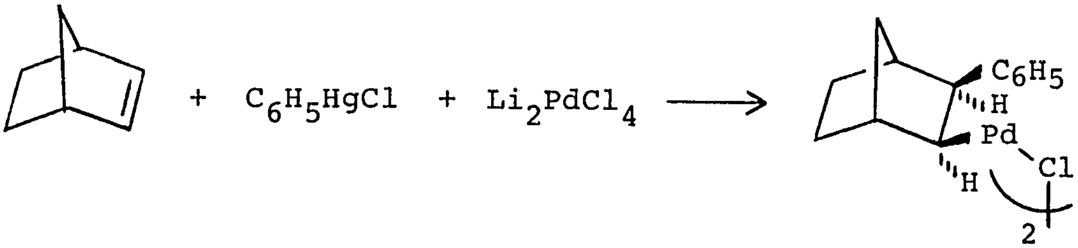
Scheme 10


Pd
Cl
Cl
(C6H5)2Hg
Pd
Cl
C6H5
H
C6H5
H
Pd
Cl
2
(C6H5)2Hg
H
C6H5
H
HgCl
2
C5H5N
H
C6H5
H
(C5H5N)Pd
Cl
C5H5N
H
(C5H5N)2Pd
H
C6H5

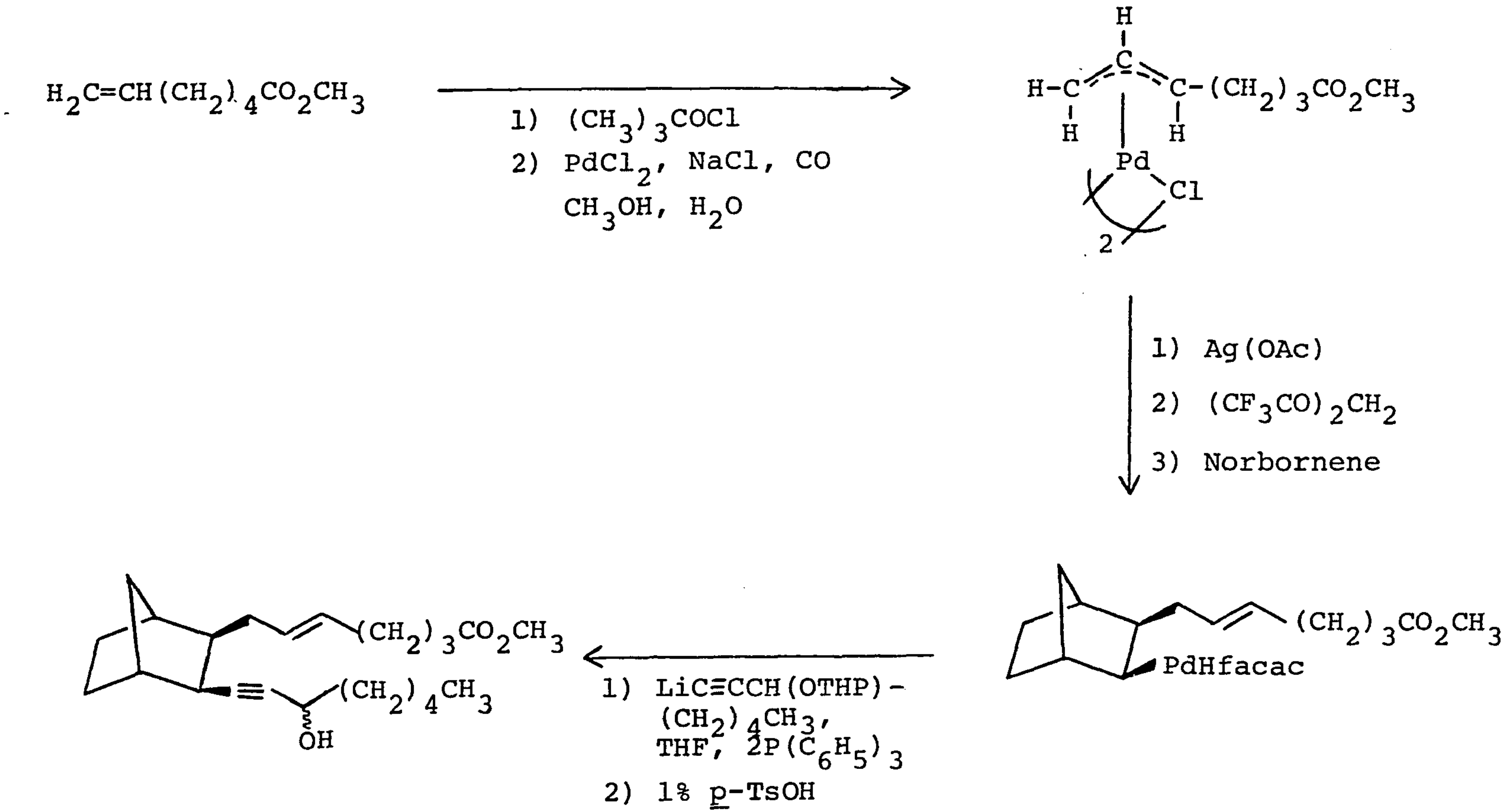

(27)

different coordinating ligands including both chloride and acetate. Nmr spectral data for these compounds has been compiled.[381] It also indicates that the two norbornene olefinic hydrogens become cis,endo hydrogens in the allyl norbornylpalladium moiety. This allylation of norbornene with a π-allylpalladium compound has been applied to the synthesis of analogs of the endo peroxide prostaglandins by R. C. Larock and J. P. Burkhart (Scheme 11).[382]

The insertion of norbornene into a phenylpalladium compound derived from phenylmercuric chloride and dilithium tetrachloropalladate produces a palladium intermediate with a σ-carbon-palladium bond (Eq. 28). The palladium inter-


(28)

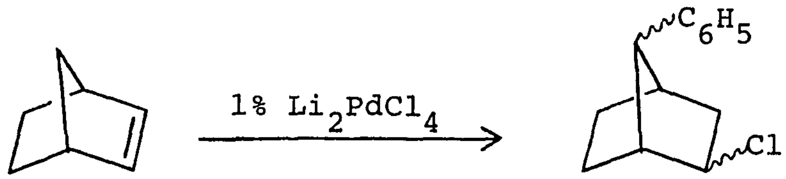
Scheme 11


H2C=CH(CH2)4CO2CH3
1) (CH3)3COCl
2) PdCl2, NaCl, CO
CH3OH, H2O
H
H-C
C
C-(CH2)3CO2CH3
H
H
Pd
Cl
2
1) Ag(OAc)
2) (CF3CO)2CH2
3) Norbornene
(CH2)3CO2CH3
PdHfacac
1) LiC≡CCH(OTHP)-
(CH2)4CH3,
THF, 2P(C6H5)3
2) 1% p-TsOH
(CH2)3CO2CH3
(CH2)4CH3
OH

mediate is isolable and stable because, following the cis insertion of norbornene into the initial palladium-phenyl bond, a cis elimination of hydrogen palladium chloride is not possible.[383] When Heck substituted norbornene for ethylene (Eq. 29) in his haloethylation reaction, the product isolated

$$C_6H_5HgCl + 2CuCl_2 + 2LiCl + \qquad (29)$$

excess



~5%

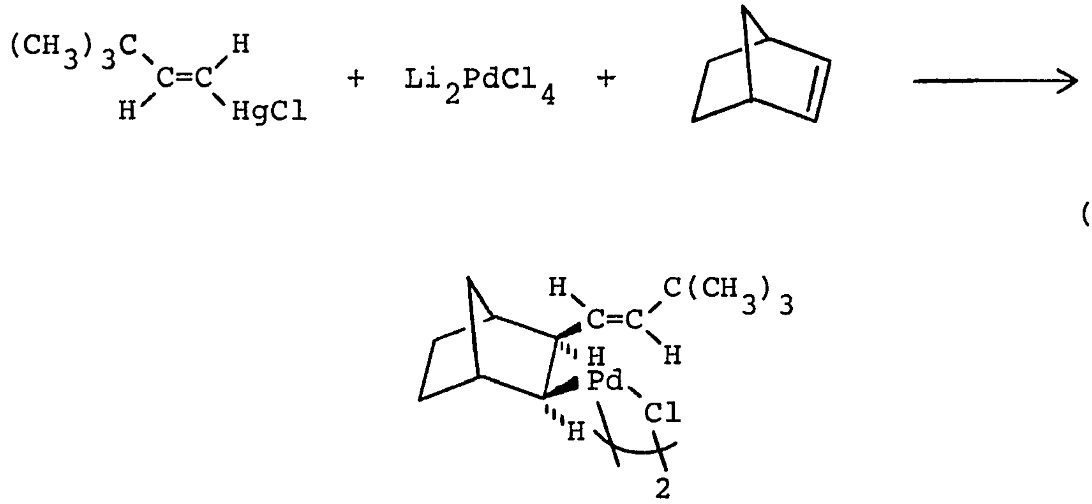
3

in only 5% yield was tentatively reported to be 2-chloro-7-phenyl bicyclo[2.2.1]heptane, 3, based solely on nmr evidence.[221]

B. Results and Discussion

1. Vinyl norbornylpalladium compounds and related vinyl alkylpalladium compounds

a. Initial studies Following an investigation of the reaction of dilithium tetrachloropalladate, vinylmercurials and olefins which forms π-allylpalladium compounds in high yield,[356,357] the reaction of dilithium tetrachloropalladate, a vinylmercurial and norbornene was of interest. Analogous to the reaction of dilithium tetrachloropalladate, phenylmercuric chloride and norbornene, the reaction of dilithium tetrachloropalladate, trans-3,3-dimethyl-1-butenylmercuric chloride and norbornene produced a stable organometallic palladium compound (Eq. 30). trans-Styrylmercuric chloride,



(30)

89%

4

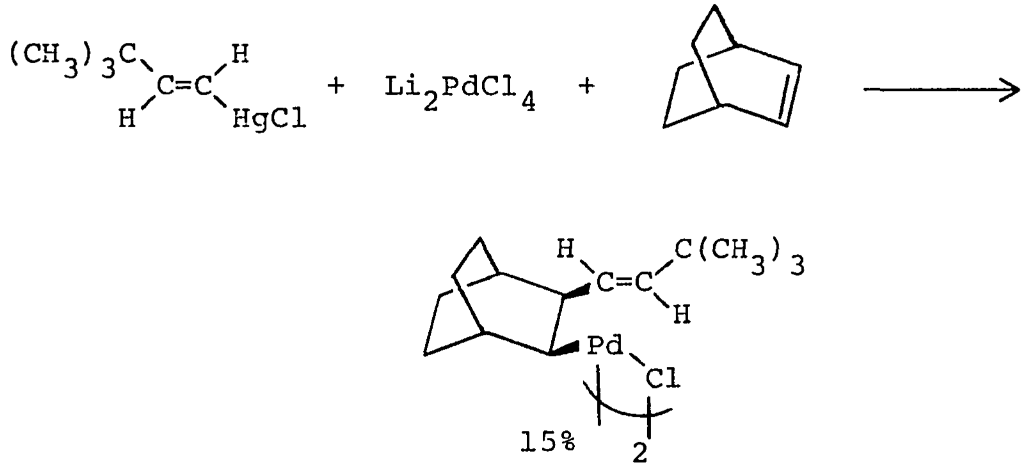
E-4,4-dimethyl-2-pentenylmercuric chloride and trans-β-chlorovinylmercuric chloride also form similar stable organopalladium compounds. **4** is the proposed structure of the product from trans-3,3-dimethyl-1-butenylmercuric chloride and it is analogous to the dilithium tetrachloropalladate, phenylmercuric chloride and norbornene product. It possesses both vinyl and palladium groups cis(syn) and exo. Since the hydrogens beta to palladium are not cis to palladium, syn elimination of hydrogen palladium chloride is not possible, enabling the alkylpalladium compound to be stable and isolable.

These reactions were initially investigated by R. C. Larock and M. A. Mitchell and later pursued by this researcher. Further investigations described in this thesis include extension of the synthetic scope of this reaction, verification of the proposed structure as containing both vinyl and palladium groups cis(syn) and exo, and some carbon-carbon bond formations or other functionalization of the organopalladium moiety.

b. Syntheses and scope of the reaction This synthesis of σ-bonded vinyl norbornylpalladium compounds has been extended by employing other bicyclic olefins as well as other organomercurials. The formation of sigma bonded vinyl norbornylpalladium compounds via transmetalation of a vinylborane has also been briefly considered.

1. Extension of the approach via transmetalation of a vinylmercurial with dilithium tetrachloropalladate The extension of this reaction to other bicyclic olefins is considered first, followed by a study of additional vinylmercurials. Substituting bicyclo[2.2.2]oct-2-ene for norbornene also results in the formation of a vinyl bicyclo[2.2.2]octylpalladium compound, but the yield is lower

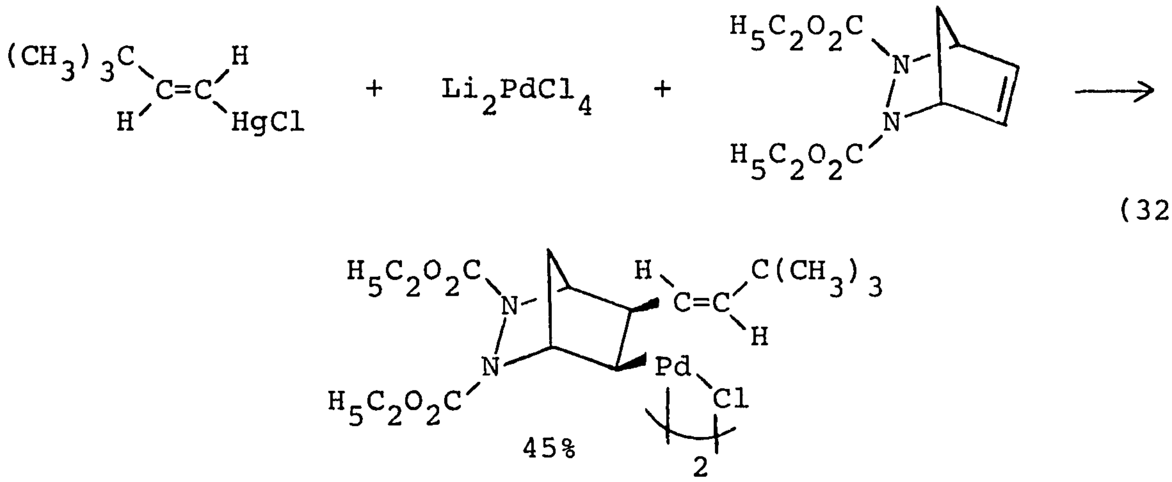
than that observed with norbornene (Eq. 31). The preceding reaction with bicyclo[2.2.2]oct-2-ene and previous reactions



(31)

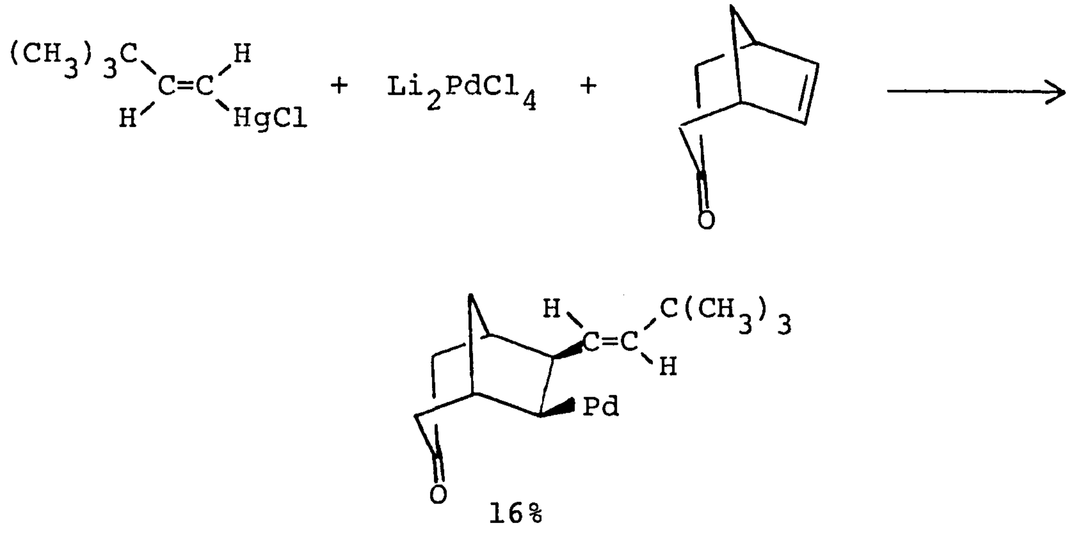
with norbornene utilized a ten-fold excess of the olefin. Since other bicyclic olefins may be more expensive and/or less volatile and consequently more difficult to separate from the alkylpalladium compound, reducing the bicyclic olefin concentration was considered.

The reaction of dilithium tetrachloropalladate, trans-3,3-dimethyl-1-butenylmercuric chloride and one equivalent of norbornene produced a lower yield of the vinyl norbornylpalladium compound. A yield of 50% was obtained compared to 89% with excess norbornene. None the less, this approach was attempted with nearly stoichiometric quantities (1.2 equivalents) of two other bicyclic olefins. Dilithium tetrachloropalladate, trans-3,3-dimethyl-1-butenylmercuric chloride and N,N-bis-carboethoxy-5,6-diazabicyclo[2.2.1]hept-2-ene form the corresponding vinyl diazabicyclo[2.2.1]heptylpalladium compound (Eq. 32). The reaction of dilithium tetrachloropalladate, trans-3,3-dimethyl-1-butenylmercuric chloride



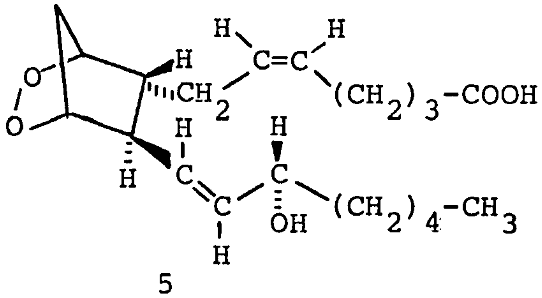
(32)

and bicyclo[3.2.1]oct-6-en-3-one also forms the corresponding vinyl bicyclo[3.2.1]octylpalladium compound (Eq. 33). Thus



(33)

this vinyl bicyclic alkylpalladium synthesis tolerates various bicyclic olefins and functionality such as ketones, esters and the N,N-bis-carboethoxydiaza group. The synthetic impetus for these syntheses stems from prostaglandin endoperoxides such as 5.



5

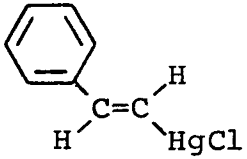
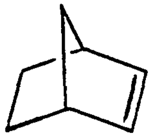
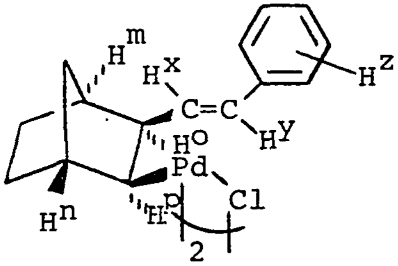
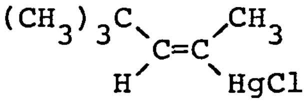
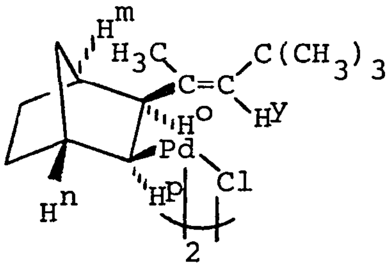
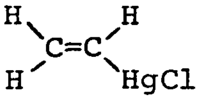
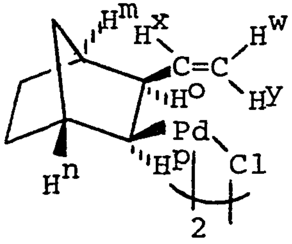
Some analogs of prostaglandin endoperoxides previously prepared contain an olefin group, an oxamethylene group, or a diaza group in place of the peroxide group.[384-390] Some of these and other prostaglandin endoperoxide analogs have been demonstrated clinically to be prostaglandin mimics, antagonists or stimulants. However, all of the analogs investigated previously contain one exo and one endo side chain. Since the exo,exo side chain derivatives have not been synthesized or clinically tested, a vinylpalladium intermediate which is a highly stereospecific method for introducing both the vinyl and palladium groups exo represents a potentially facile approach to exo,exo prostaglandin analogs if the palladium moiety is transformed into the allylic side chain. The N,N-bis-carboethoxydiaza group has been shown to be a suitable precursor for the sensitive diaza group,[390] while bicyclo-[3.2.1]oct-6-en-3-one might be a model for a potential protecting group for the cis diol reminiscent of the endoperoxide.

Since analogs are known which contain the olefin group (CH=CH) replacing the peroxide group,[384-387] lithium tetrachloropalladate and trans-3,3-dimethyl-1-butenylmercuric chloride were reacted with excess norbornadiene in the usual manner. The product obtained was neither the analogous vinyl norbornenylpalladium compound containing one unreacted olefin nor the divinyl norbornyldipalladium compound where reaction occurred with both olefins independently. Further characterization of the product obtained continues in a following section.

The synthesis of vinyl norbornylpalladium compounds was also extended to two other vinylmercurials. Both vinylmercuric chloride and trans-1-octenylmercuric chloride form the analogous vinyl norbornylpalladium compounds. The trans-1-octenyl derivative was prepared since it is the deoxy analog of the vinyl prostaglandin side chain. The vinyl alkylpalladium compounds prepared so far are summarized in Table I.

2. An alternate approach via transmetalation of a vinylborane with palladium acetate These vinyl norbornylpalladium compounds are presumably prepared via the transmetalation of the vinylmercurial with dilithium tetrachloropalladate forming a vinylpalladium species which adds to

Table I. Synthesis of vinyl alkylpalladium compounds from vinylmercurials, dilithium tetrachloropallate and bicyclic olefins

Entry	Vinylmercurial	Bicyclic Olefin	Product[a]	% Yield[b]
1				58(22)[c] -(38)
2				88(58)[c]
3				63(46)

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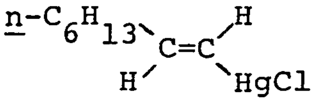
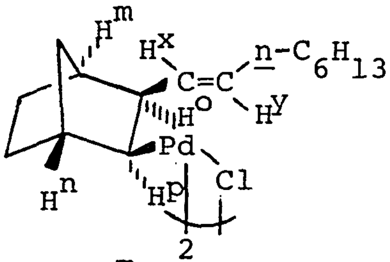
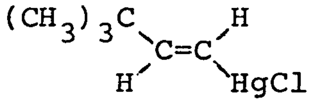
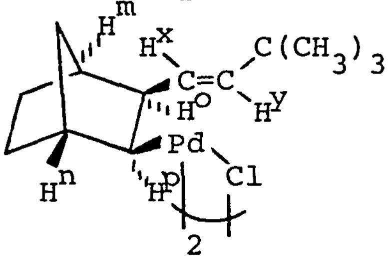
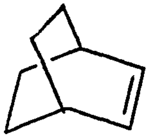
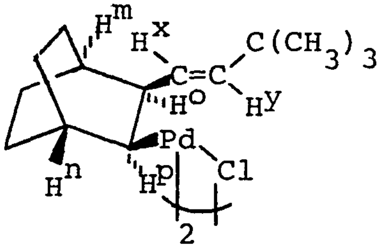
[a] Superscripts identifying hydrogens are referred to in Table II (p. 304).

[b] Crude yield (recrystallized yield).

[c] Original synthesis performed by M. A. Mitchell.

Table I. (continued)

Entry	Vinylmercurial	Bicyclic Olefin	Product	% Yield[b]
4				85(46)
5				89(39)[c] 50(29)[d]
6				15(8)

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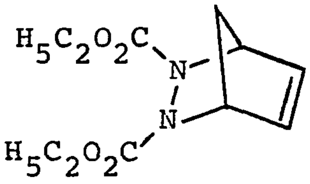
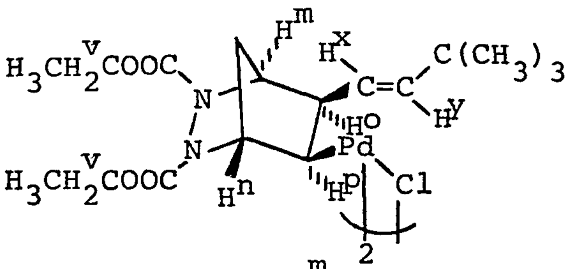
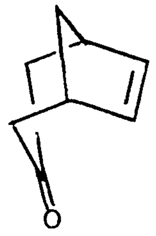
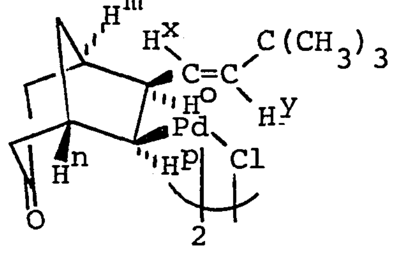
[d] 1.1 Equivalents of the bicyclic olefin is employed; other yields were obtained using 10 equivalents of the bicyclic olefin.

Table I. (continued)

Entry			
7			45(15)^{d,e}
8			16(10)^{d}

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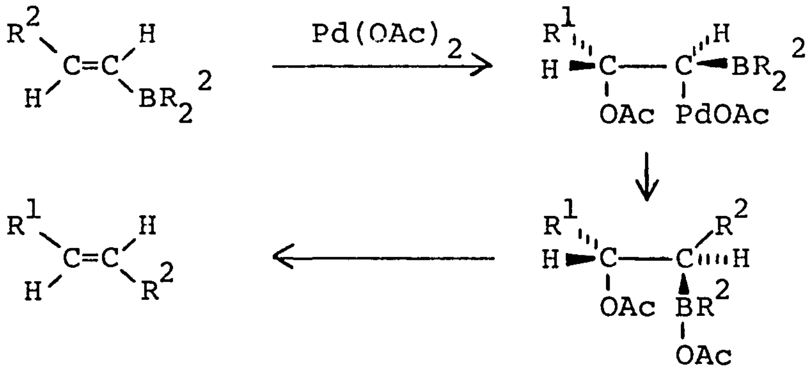
[e] Recrystallization method not found.

norbornene. Since the vinylmercurials are prepared from alkenyldialkylboranes, whether an alkenyldialkylborane might transmetalate directly with a palladium(II) salt was also of interest, since the synthesis of sigma vinyl norbornyl palladium compounds would be shortened by one step. The reaction of dicyclohexyl(trans-3,3-dimethyl-1-butenyl)borane with one equivalent of palladium acetate and a 10-fold excess of norbornene does form the appropriate vinyl norbornylpalladium derivative. However, the yield was not determined since purification of the vinyl norbornylpalladium compound from the remaining alkylboron compounds was extremely tedious.

Anhydrous trimethylamine oxide is reported to oxidize alkenyldialkylboranes both selectively and nonselectively.[391-394] Considering the selective reports, dicyclohexyl (trans-3,3-dimethyl-1-butenyl)borane was treated with two equivalents of anhydrous trimethylamine oxide at room temperature and with heating. Subsequently, palladium acetate and a 10-fold excess of norbornene was added. Both reactions were complicated by incomplete and unselective oxidation and the same isolation difficulties. After these partial failures, a report suggesting that the method used to dry trimethylamine oxide was not adequate was noticed.[395] Therefore, the success or failure of this approach may not have been established.

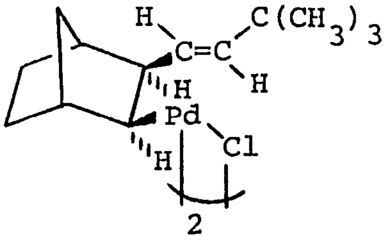
While this investigation was in progress, the formation of alkylated olefins from alkenyldialkylboranes, palladium acetate and triethylamine appeared. This reaction is proposed to occur via cis acetoxypalladation, migration with inversion and cis beta elimination (Scheme 12).[396] The

Scheme 12



partial success observed earlier with respect to transmetalation of the alkenyldialkylborane with palladium acetate followed by olefin insertion might be attributed to the retarded acetoxypalladation of a hindered alkenyl group such as <u>trans</u>-3,3-dimethyl-1-butenyl and/or the rather bulky cyclohexyl groups. Although the transmetalation of an alkenyldialkylborane with palladium acetate produces a vinylpalladium species which reacts with norbornene similar to the vinylpalladium species formed from the mercurial, further investigation of the selective oxidation of alkenyldialkylboranes and subsequent transmetalation with palladium acetate, or the transmetalation of alkenylcatecholboranes with palladium acetate is required.

c. Characterization and stereochemistry Although literature precedent from the reactions of π-allylpalladium chloride with norbornene, and phenylmercuric chloride, dilithium tetrachloropalladate and norbornene strongly suggest the analogous product structure 4 for the reaction of a



4

vinylmercurial, dilithium tetrachloropalladate and norbornene or other bicyclic olefins, these structures require confirmation. Although x-ray diffraction studies have not been done, all organopalladium compounds except the compound derived from trans-β-chlorovinylmercuric chloride gave carbon and hydrogen analyses consistent with this type of structure. In addition, spectral evidence, especially ^{1}H nmr data provides further structural detail.

The IR spectrum of the vinylnorbornyl compound derived from trans-3,3-dimethyl-1-butenylmercuric chloride is reproduced in Figure 1. Although the strong trans olefin absorp-

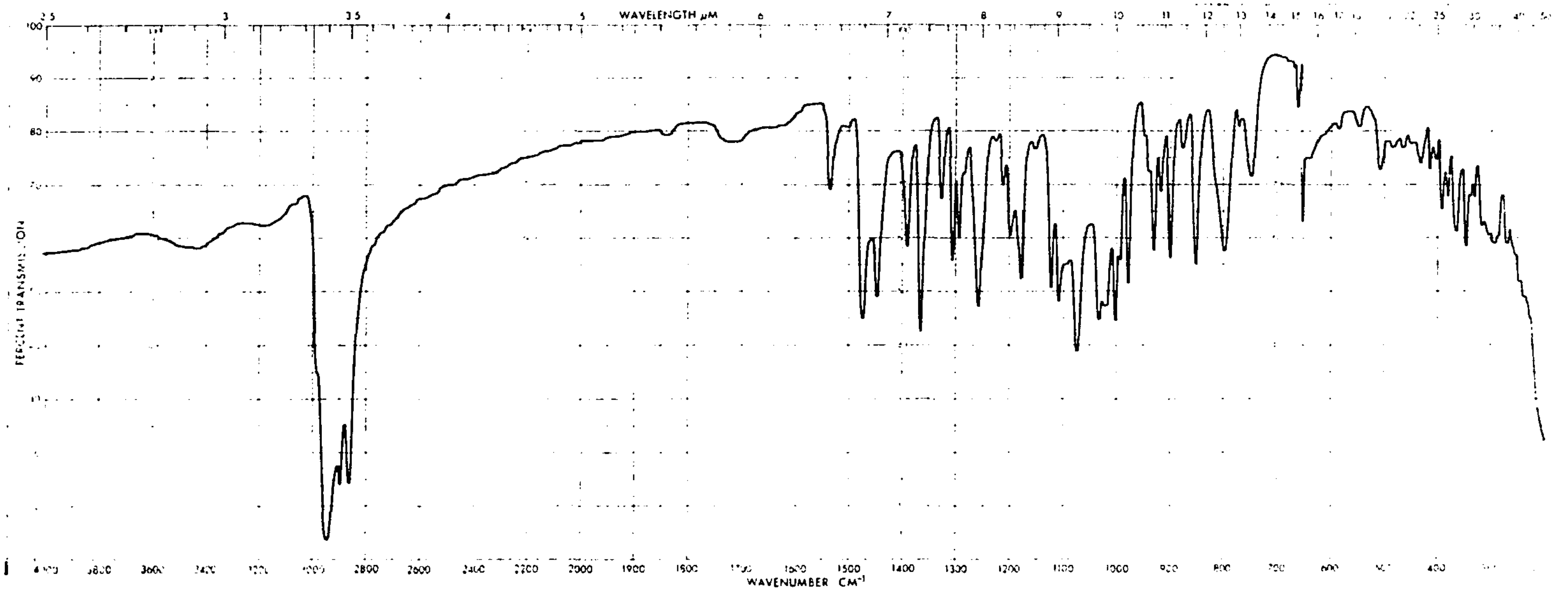


Figure 1. IR spectrum of compound 4 (Table I, Entry 5)

tion usually found between 980 and 960 cm^{-1} is quite variable in these compounds, a weak olefinic absorption consistently appears near 1540 cm^{-1} instead of 1670 cm^{-1} as expected for trans olefins. The coordination of the olefin to palladium perhaps accounts for the observed deviations. For example, the carbon-carbon absorptions in norbornadiene appear at 1640, 1535 and 1445 cm^{-1}, whereas in norbornadiene palladium dichloride the carbon-carbon absorptions occur at 1460, 1410 and 1305 cm^{-1}. Other functionalized derivatives displayed absorptions corresponding to the appropriate functionality in addition to the usual alkyl absorptions. The absorptions of the palladium chloride moiety were not determined, because previous workers have not reported IR data for the similar allyl- or phenyl norbornylpalladium compounds, apparently because such data was felt to be less informative than other spectral data, especially nmr. In addition the IR spectrum was often obscured by other ligands such as hexafluoroacetylacetonate.

The nmr data, as measured on a 100 MHz instrument are tabulated in Table II. The terminal vinyl hydrogen (the vinyl hydrogen which is farthest from the bicyclic skeleton) possesses a typical to slightly downfield chemical shift while the internal (the vinyl hydrogen closest to the bicyclic skeleton) vinyl hydrogen appears appreciably upfield. The shielding effect of an exo palladium adjacent to an exo

Table II. ^{1}H nmr spectra of the vinyl norbornylpalladium compounds[a]

Entry[b]	H_z	H_y	H_x	H_w	H_v	H_p
1[c]	7.55-7.95 m	6.97 d,J=14Hz	5.24 dd,J=14Hz, J=3Hz	-	-	3.30-3.40[d] m
2	-	5.13s	-	-	-	2.88
3	-	4.82 dd,J=14Hz, J=2Hz	4.0-4.5 m		-	2.82
4	-	5.60 m	3.97 dd,J=14Hz, J=3Hz	-	-	2.80
5	-	5.80 d,J=14Hz	3.98 dd,J=14Hz, J=3Hz	-	-	2.98 dd,J=11Hz
6	-	6.03 d,J=14Hz	4.23 dd,J=14Hz, J=3Hz	-	-	-29.5- 2H,m
7	-	5.88 d,J=14Hz	4.77 m	-	4.2 m	3.50 d,J=12Hz
8[e]	-	4.78 dd,J=14Hz, J=1.0Hz	3.97 dd,J=14Hz, J=3Hz	-	-	3.20 m

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[a] Measured on an HA-100.

[b] Entry numbers refer to the organopalladium compounds listed in Table I. Superscripted hydrogens are identified in the structures in Table I (p. 296).

[c] Measured in d_6-DMSO. All the others measured in $CDCl_3$.

[d] Partially obscured by d_6-DMSO.

[e] If coordination to the carbonyl is important, addition may occur endo, instead of exo; however, the carbonyl IR absorption which is nearly identical to bicyclo[3.2.1]octan-3-one might be interpreted in terms of negligible coordination and exo attack as usual.

H_o	H_n	H_m	Other H
2.80	2.50^d	2.26	.85-1.4 6H,m
2.80	2.64	2.38	1.84 3H,s,-CH_3 .9-1.6 15H's m + s
2.65	2.55	2.34	0.9-1.7 6H, m
2.65	-2.28- 2H,m		0.9-1.7 17H,m
2.78 d,*J*=11Hz	2.68	2.30	0.9-1.6 15H,m + s
	-2.0- 2H,m		.9-1.7 17H,m + s
3.38	-2.95 2H,m		1.10-1.30 6H,t + 2H,m + 9H,s
3.10 m	2.86 m	2.56 m	2.38,1H,d=4 2.30,2H,m 2.20,1H,d=4 .9-2.0 11H,m + s

vinyl moiety is one possible explanation for these observed chemical shifts since the exo-exo geometry may place the internal vinyl hydrogen closer to the palladium atom. The observed coupling constants between the vinyl hydrogens are approximately 14 Hz, which is consistent with the presence of trans vinyl hydrogens in the product. The stereochemistry of the olefin is as expected, if the proposed transmetalation yields a vinylpalladium species which reacts with retention of stereochemistry with respect to the olefin of the vinylmercurial. The internal vinyl hydrogen is also coupled more strongly to the adjacent allylic hydrogen (as demonstrated by coupling constants of approximately 4 Hz) than the terminal vinyl hydrogen which is only weakly coupled as demonstrated by coupling constants of 1 Hz to 0 Hz. Of the remaining protons on the bicyclic skeleton, the furthest downfield appears as a broad doublet or doublet of multiplets. Since the doublet is not visibly coupled further to the internal vinyl hydrogen ($\underline{J}$ = 4 Hz), this signal may be tentatively assigned to the hydrogen of the carbon bearing the palladium chloride. The observed coupling constant of approximately 10 to 11 Hz, is consistent with cis endo hydrogens observed in other norbornyl systems.[397-400] The cis endo hydrogen signals might not be expected to be split due to coupling with the bridgehead hydrogens due to consideration of the dihedral angle. Some long range coupling might be possible with a bridge hydrogen via "W" coupling, but this is not discernible. The suspected doublet due to the hydrogen of the carbon bearing the vinyl group is partially visible approximately 0.15 to 0.2 ppm upfield of the previously described doublet. Unfortunately, the coupling to the internal vinyl hydrogen (*J* = 4 Hz) is not clearly discernible here either, although the cis endo coupling (*J* = 10-11 Hz) is just visible. Multiplets or broad singlets which may be assigned to the bridgehead hydrogens usually appear just upfield of the cis endo hydrogens. Since the hydrogen adjacent to palladium is tentatively assigned to the furthest downfield endo doublet, the broad singlet furthest downfield is tentatively assigned to the bridgehead hydrogen nearest to palladium. The other norbornyl skeleton hydrogens were not assigned but appear as a multiplet from δ0.9 to 1.9. Superimposed on these multiplets, the singlet for the *tert*-butyl hydrogens or signals for other appropriate alkyl hydrogens appear. The functionalized examples also display the expected signals appropriate for the hydrogens of the added functionality.

Decoupling of the nmr of the sigma vinyl norbornyl palladium compound derived from *E*-4,4-dimethyl-2-pentenylmercuric chloride also supports the previous assignments. Irradiation at δ2.88 produces a singlet at δ2.80 and also sharpens the appearance of the multiplet at $\delta 2.64$, but does not change the appearance of the multiplet at $\delta 2.38$.

Since decoupling did not completely clarify the tentative nmr assignments of these compounds an nmr shift reagent was added. The effect of $Eu(fod)_3$ on the ^1H nmr spectrum of the vinyl norbornylpalladium compound derived from trans-3,3-dimethyl-1-butenylmercuric chloride is discussed in the following section. However, in addition to the tabulated nmr data found in Table II, the nmr spectrum of this compound before $Eu(fod)_3$ addition is also reproduced in Figure 2.

The lanthanide of an nmr shift reagent usually coordinates to an appropriate functional group of a molecule with the hydrogens nearest the functional group experiencing a shift induced by the metal ion. Appropriate functional groups usually contain oxygen or nitrogen. Although the vinyl norbornyl palladium compounds do not contain such functionality, perhaps a reversal of the typical coordination mode is possible. The palladium might partially coordinate to the coordinating ligand of the shift reagent. Through the ligand, the lanthanide would therefore be closer to palladium to induce a shift enabling the cis-endo stereochemistry to be verified. The effect of adding $Eu(fod)_3$ to the sigma vinyl norbornyl palladium compound derived from trans-3,3-dimethyl-1-butenylmercuric chloride is reproduced in Figure 2. With increasing additions of $Eu(fod)_3$, one of the cis endo hydrogen

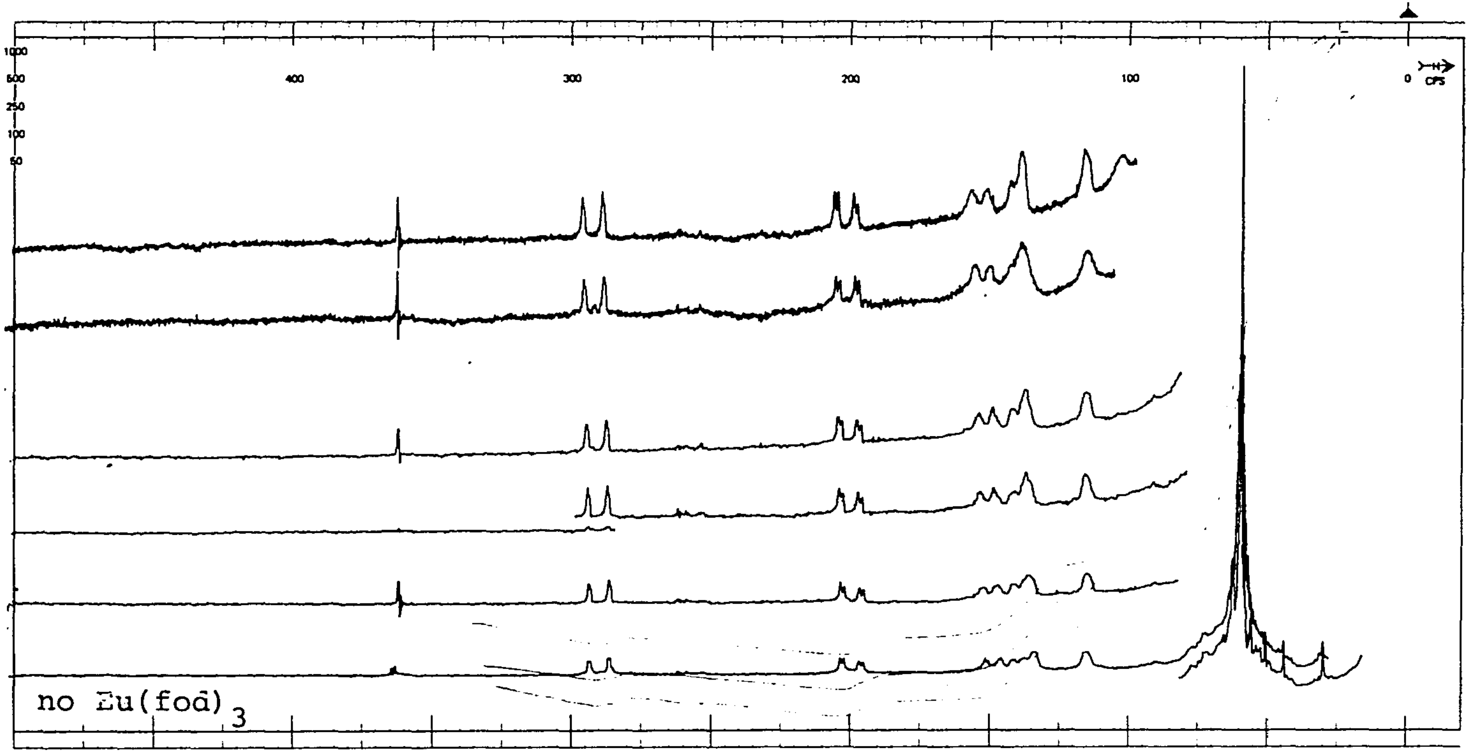
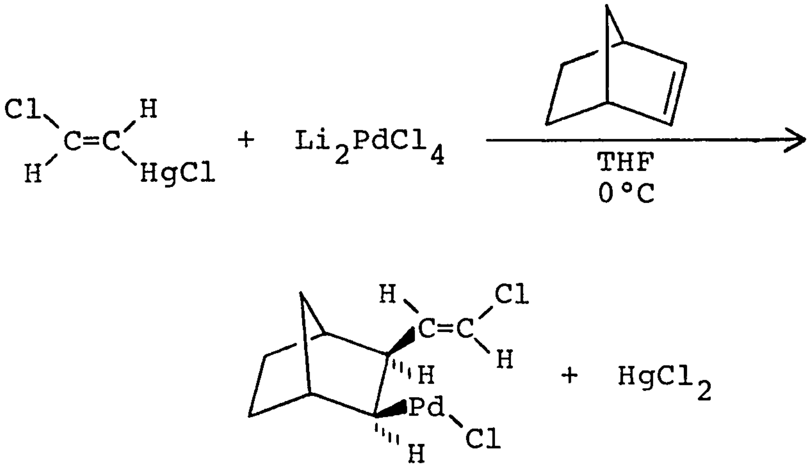


Figure 2. ^{1}H nmr spectrum of compound 4 (Table I, Entry 5) with successive additions of Eu(fod)$_3$

doublets and one bridgehead multiplet are shifted downfield more than the other endo doublet or bridgehead multiplet. Since the doublet which is shifted most appears as a doublet, rather than a doublet of doublets, where the hydrogen is also coupled to the internal vinyl hydrogen ($\underline{J}$ = 3-4 Hz), the most shifted doublet is assigned the endo hydrogen of the carbon bearing palladium. The cis endo coupling constant of 11 Hz is clearly visible after the fifth addition of Eu(fod)$_3$ confirming the presence of cis endo hydrogens, and the cis exo addition of a vinylpalladium species to norbornene. It is somewhat surprising that one of the multiplets assigned to a bridgehead hydrogen is shifted nearly the same as the endo hydrogen adjacent to palladium. This suggests the shift reagent may be coordinated sidewise rather than endwise. Alternatively, it also might suggest the shift reagent is conventionally coordinated sidewise through chlorine rather than palladium as previously suggested. The fact that the shifts of the vinyl hydrogens, especially the internal vinyl hydrogen which is shielded by palladium, are hardly effected by Eu(fod)$_3$ also might support the chlorine coordination model. Although further Eu(fod)$_3$ additions were not made due to partial decomposition of the palladium compound, the addition of Eu(fod)$_3$ establishes the presence of cis endo hydrogens, and the cis exo addition of a vinylpalladium species to norbornene. Before discussing further reactions of the palladium moiety, which also confirms this stereochemistry, the structure of the derivative formed from *trans*-β-chlorovinylmercuric chloride remains to be considered.

2. The organopalladium compound derived from *trans*-β-chlorovinylmercuric chloride

Although the reaction of dilithium tetrachloropalladate, *trans*-β-chlorovinylmercuric chloride and norbornene was first reported by M. A. Mitchell and the product assumed to be the analogous vinyl norbornylpalladium compound (Eq. 34), further



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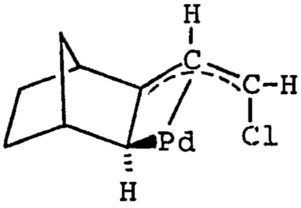
(34)

investigation suggests the reaction is not as simple as previously imagined. Similar to the reactions with other *trans*-vinylmercurials the solid product obtained is light yellow in color. In the ^1H nmr spectrum, however, the coupling constant for the olefinic hydrogens does not agree with that expected for trans hydrogens. It is only 5 Hz instead of 12 to 18 Hz.

Also the integration indicates approximately 5 hydrogens downfield of δ2.0, instead of the typical 6 hydrogens downfield of δ2.0 for the other vinyl norbornylpalladium compounds. The IR spectrum is also unusual because the olefinic carbon-carbon stretch usually occurring near 1540 cm^{-1} is absent. An acetylenic carbon-carbon absorption is also absent. Finally, the elemental analysis for carbon and hydrogen does not agree with the formula $C_9H_{12}PdCl_2$ which corresponds to structure 6. The carbon and hydrogen analyses agree better with the formula $C_9H_{11}PdCl$ which might be considered as a loss of hydrogen chloride from $C_9H_{12}PdCl_2$. One possible structure which fits this formula and possibly agrees with the ^1H nmr chemical shift information is the π-allyl organopalladium compound 7. Proposing a reasonable



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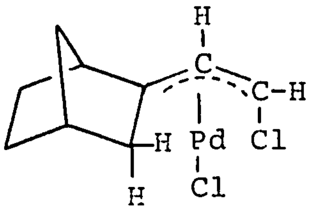
pathway for the formation of this organopalladium compound is difficult. Although no evidence for cationic intermediates exists, a rearrangement more or less similar to a 2,3 endo hydrogen shift might explain the observed product. However, it remains most perplexing that this product has only been observed in the β-chlorovinyl derivative. Despite the carbon and hydrogen analysis, a consideration of the elemental analysis for chlorine, carbon and hydrogen and palladium by difference supports neither $C_9H_{12}PdCl_2$ or $C_9H_{11}PdCl$. The actual formula suggested by the analysis is $PdCl_2C_{11.7}H_{16.5}$. However, a reasonable structure of this formula is difficult to imagine. Considering the chlorine analysis alone however argues for $C_9H_{12}PdCl_2$. Since the ^1H nmr spectrum possibly indicates evidence for a π-allyl organopalladium compound, 8 is another structure which might be considered. However, this



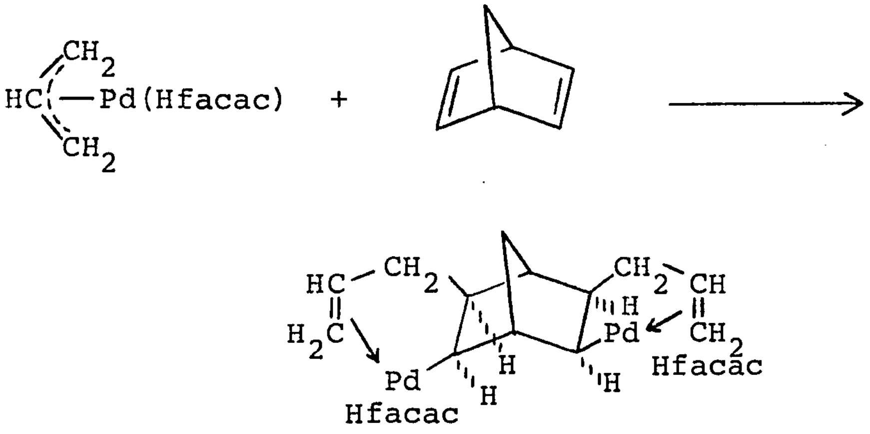
8

derivative must be further purified and/or characterized prior to publication.

3. A vinyl nortricyclylpalladium compound

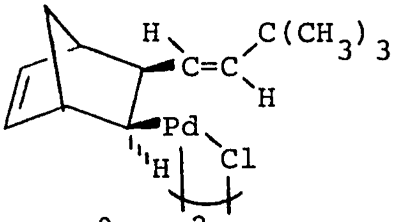
Since an endoperoxide prostaglandin analog containing an olefin in place of the peroxy function has been prepared and demonstrated to be biologically active, the reaction of a vinylpalladium species and norbornadiene was of interest.

In the reactions of allylpalladium species with norbornadiene, the formation of the di-allyl norbornyldipalladium species was reported (Eq. 35).[381] Unfortunately but perhaps



(35)

not unexpectedly, the reaction of dilithium tetrachloropalladate and trans-3,3-dimethyl-1-butenylmercuric chloride with norbornadiene does not form either a vinyl norbornenylpalladium compound 9 or a divinyl norbornyldipalladium compound 10. Instead a vinyl nortricyclylpalladium



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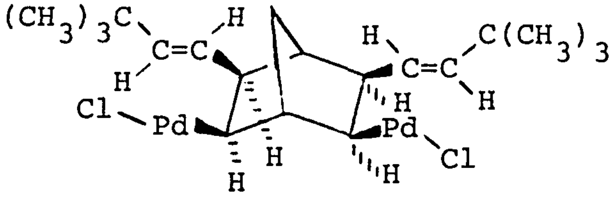

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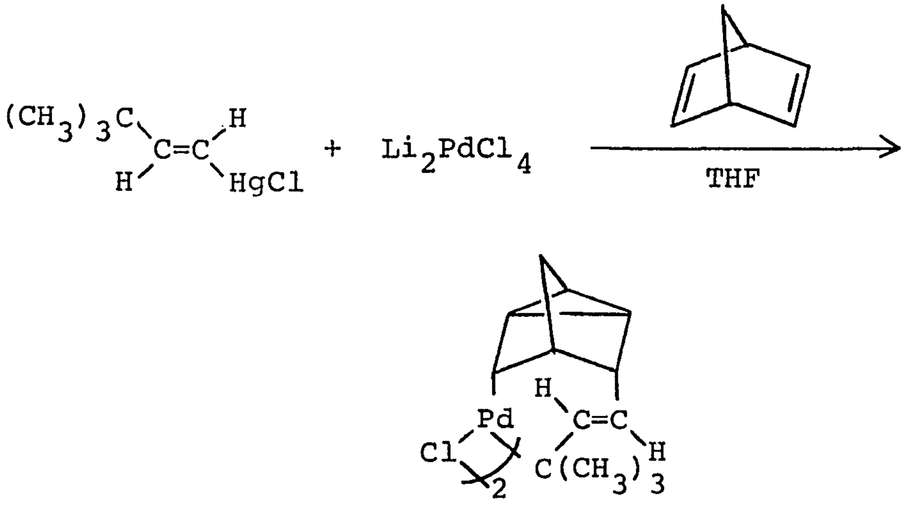
compound is formed (Eq. 36). This same organopalladium compound is also formed from reaction of norbornadiene palladium dichloride with trans-3,3-dimethyl-1-butenylmercuric chloride (Eq. 37). An analogous product has been isolated from a



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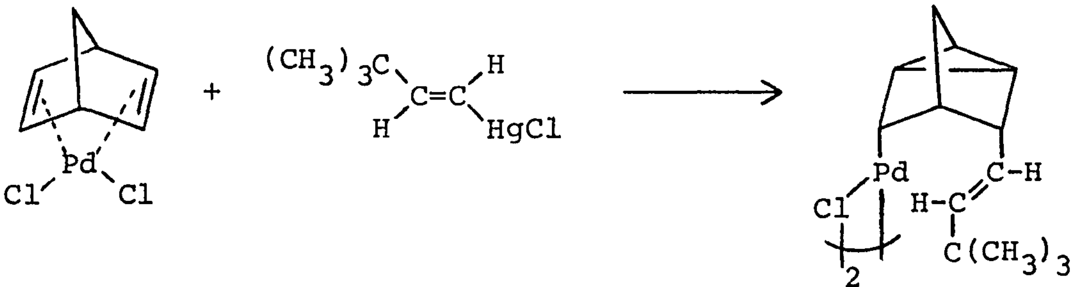
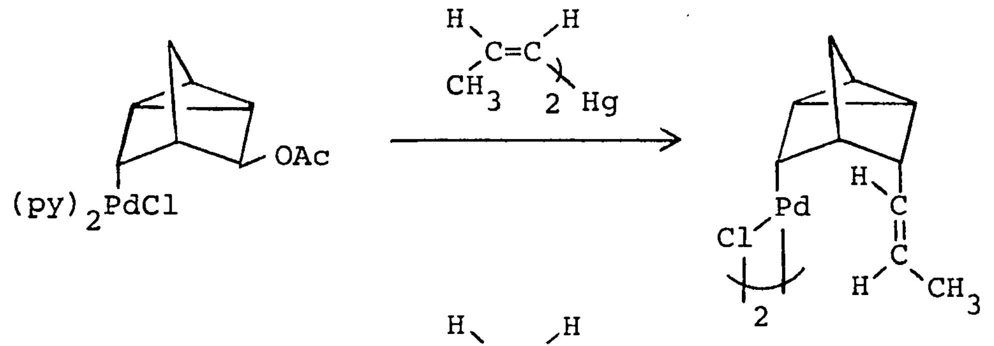


11

(37)

sigma nortricyclyl palladium[372] compound or norbornadiene palladium dichloride and di(cis-propenyl)mercury[401] (Eqs. 38 and 39) as previously reported by Vedejs. The strongest



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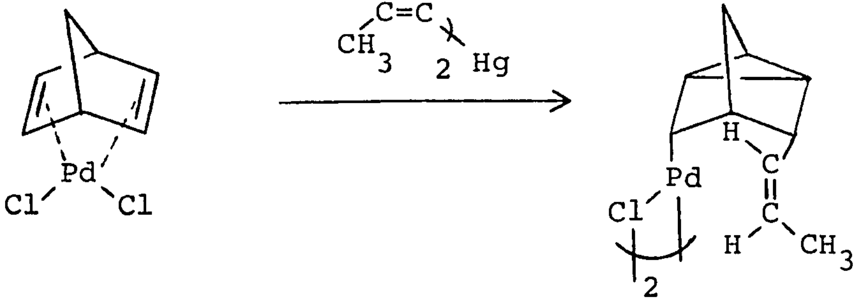
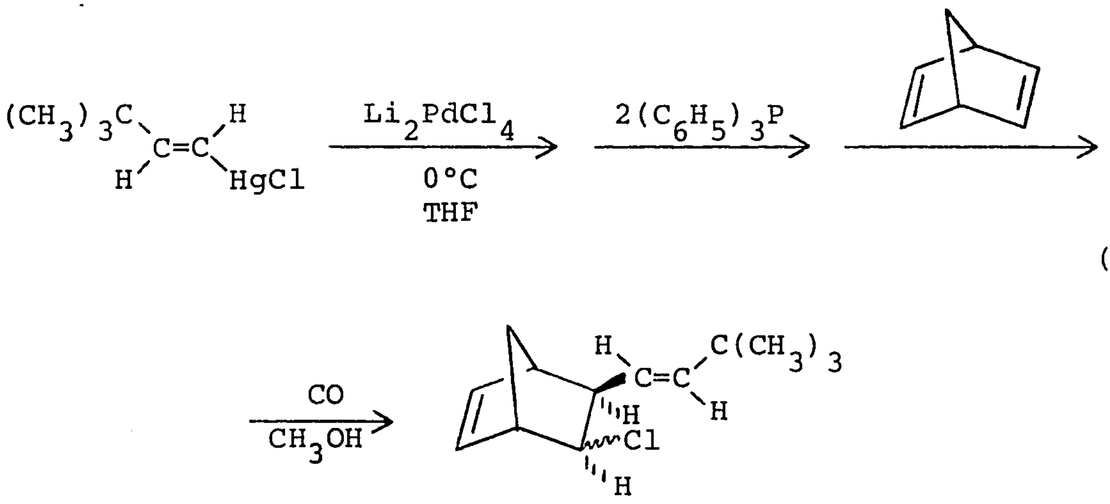


(39)

support for the nortricyclyl structure is the nmr data. The ^1H nmr contains only 2 vinyl protons at δ5.38 with a typical trans coupling constant of 14 Hz. A multiplet corresponding to the hydrogen on the carbon bearing palladium or the vinyl moiety occurs at δ2.82. The remaining nortricyclyl hydrogens appear from δ1.45 to δ2.20. Apparently the cyclopropyl hydrogens are shifted downfield by the palladium and vinyl substituents, because the ^1H nmr spectrum is very similar to a ^1H nmr spectrum supplied by Vedejs for the analogous propenyl derivative. The addition of one equivalent of triphenylphosphine changes the ^1H nmr spectrum quite significantly. The vinyl hydrogens are shifted downfield to δ6.22. The nortricyclyl hydrogens are shifted upfield. The hydrogen of the carbon bearing palladium or the vinyl moiety shifts from δ2.8 to δ2.25, and the other skeletal hydrogens shift from δ1.45-2.20 to δ0.70-2.00. The tert-butyl singlet however is shifted slightly downfield from δ1.24 to δ1.30. Although the ^1H nmr spectrum of the palladium compound after triphenylphosphine addition is perhaps more consistent with the proposed nortricyclyl structure, observing only two olefinic resonances rules out the norbornenyl structure.

One possible approach to a norbornenyl palladium compound might involve formation of a vinylpalladium species which is bulky and might prefer to approach norbornadiene exo rather than endo. trans-3,3-Dimethyl-1-butenylmercuric chloride and dilithium tetrachloropalladate were mixed in THF with an excess of triphenylphosphine presumably forming a vinylpalladium triphenylphosphine species to which norbornadiene was added after 15 minutes. Isolation of the product was difficult because attempted purification of the product from excess triphenylphosphine resulted in decomposition. However, a crude ^1H nmr spectrum indicated multiple olefinic signals at δ5.25, δ5.45 and δ5.8. (The vinyl hydrogens of norbornadiene appear at δ6.7, the vinyl hydrogens of norbornene appear at δ6.05, and the vinyl hydrogens of compound **11** appear at δ5.25 and δ5.35). Due to the difficulties encountered attempting to isolate this compound, in one attempt the crude product with excess triphenylphosphine was redissolved in methanol and carbonylated (Chapter II, Part 4a). Unfortunately, the product isolated was not enough for a definitive ^{1}H nmr spectrum. In a repeat of this one pot transmetalation, addition and carbonylation in the presence of excess triphenylphosphine the vinyl norbornenyl chloride was isolated (Eq. 40). Although the mass spectrum may also be consistent with a vinylnortricyclyl chloride, a ^{1}H nmr multiplet at δ5.40 in addition to doublets at δ5.75 (*J* = 15.5 Hz) and δ6.95 (*J* = 15.5 Hz) supports the proposed vinylnorbornenyl chloride (Eq. 40). Although tantalizing, due to limited time this reaction was not pursued further.



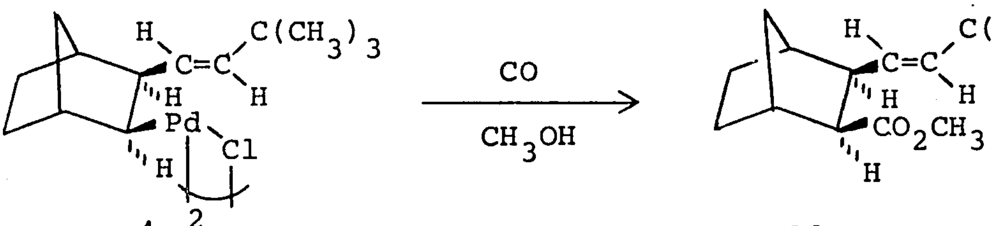
(40)

4. Functionalization of the carbon skeleton via the palladium moiety

Various functionalizations of carbon skeletons via the metal moiety of organometallic compounds have been extensively investigated from several perspectives, including characterization of the organometallic compound, investigation of organometallic compound reactivity and utilization of organometallic compounds in organic synthesis. The reactivity of these sigma vinylpalladium compounds is considered here primarily as further characterization of the organopalladium compounds, while the study of reactivity or their use as organic synthetic intermediates is considered rather peripherally. Unfortunately, due to the predominant emphasis on the first part of this thesis, this section is quite incomplete.

a. Carbonylation Since the carbonylation of organopalladium compounds is generally considered to occur with retention of configuration with respect to carbon,[320] the carbonylation of the norbornylpalladium compounds is expected to produce carbonyl derivatives of retained stereochemistry. Therefore, characterization of the carbonylation product may confirm the proposed structure of the original organopalladium compound.

Treating the vinyl norbornylpalladium compound derived from trans-3,3-dimethyl-1-butenylmercuric chloride with carbon monoxide in refluxing methanol produces the corresponding methyl ester, **12** (Eq. 41). IR and mass spectroscopy support the proposed product structure. Although the ^{1}H nmr spectrum displays both a tert-butyl singlet and a methyl ester singlet as well as norbornyl skeletal hydrogens, the signal for the



4 12 (41)

vinyl hydrogens is complex due to partial overlap of the two signals. Successive additions of Eu(fod)$_3$ eventually separates the vinyl hydrogens enabling discernment of the olefinic coupling constant, J = 15.5 Hz, and the allylic coupling constant, J = 9 Hz (Figure 3). The internal vinyl hydrogen is shifted more than the external vinyl hydrogen, in accord with cis ester and vinyl groups. The hydrogen on the carbon bearing the ester is also shifted faster and further downfield than the other norbornyl skeletal hydrogens. This hydrogen appears as a doublet of doublets with one coupling constant of 10 Hz, which agrees with other observed cis endo coupling constants.[397-400] Since this ester or its acid might be reduced to the aldehyde and subsequently developed as the allylic prostaglandin side chain, the carbonylation of vinyl norbornylpalladium compounds is also important synthetically.

Carbonylation of the vinyl nortricyclylpalladium compound also confirms its structure assignment. Treating the vinyl nortricyclylpalladium compound derived from trans-3,3-

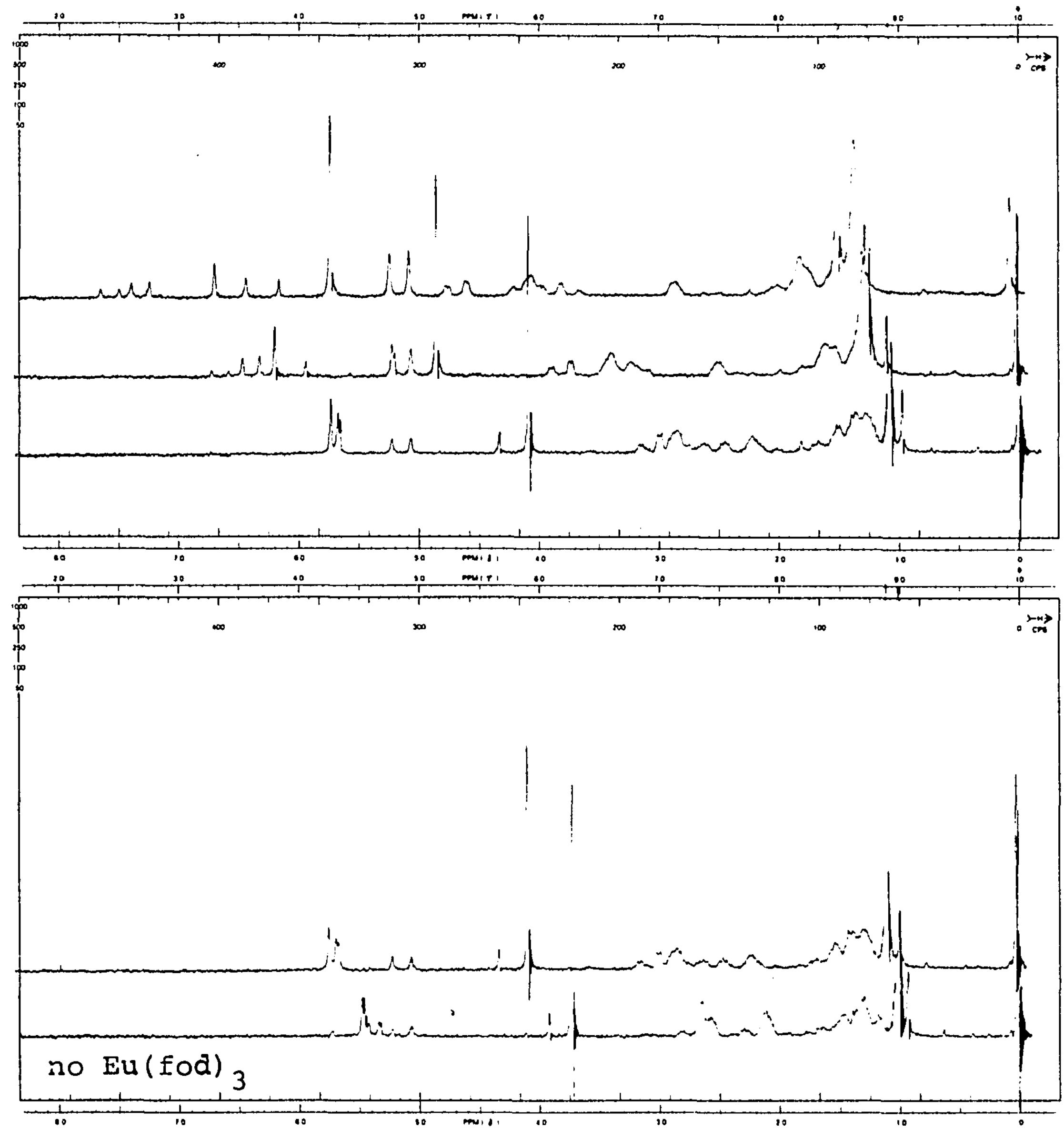
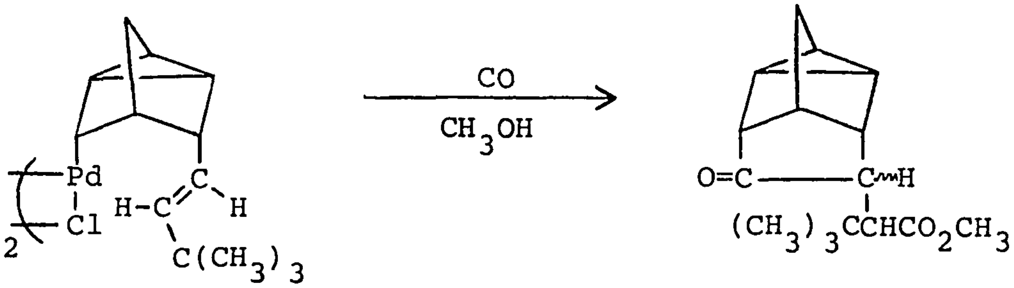


Figure 3. ^{1}H nmr spectrum of compound 12 with successive additions of Eu(fod)$_3$

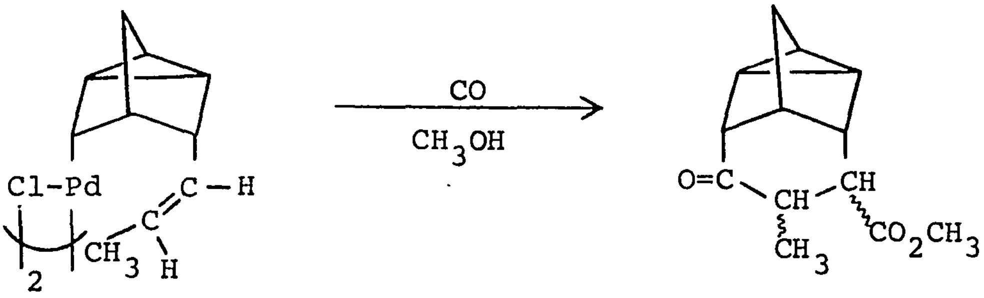
dimethyl-1-butenylmercuric chloride with carbon monoxide in methanol at room temperature forms as the major product a cyclic ketone 13 (Eq. 42). The vinyl nortricyclylpalladium



11 13

(42)

derivative of di(cis-propenyl)mercury was also carbonylated in methanol,[372] however it is reported to form a different cyclic ketone 14 (Eq. 43). Although the observed effect of

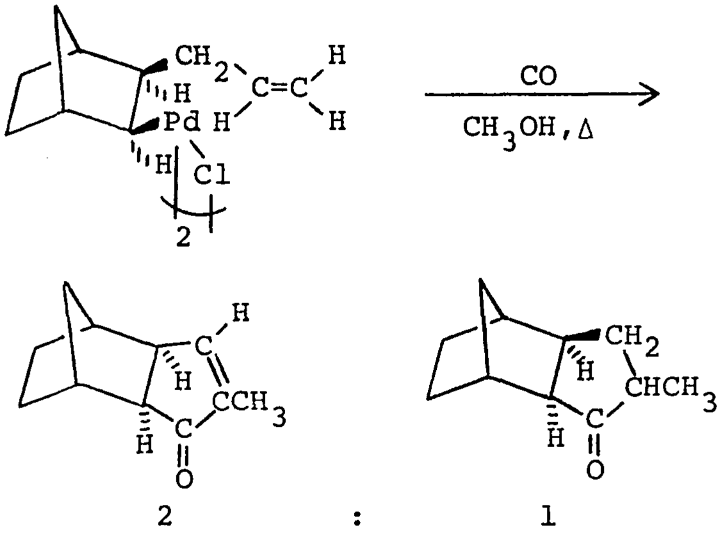


14

(43)

the tert-butyl group upon ring closure is dramatic and perhaps unpredictable, consideration and comparison of the spectral data, especially the IR spectrum argues for the cyclopentanone derivative and against the cyclohexanone derivative. Although the ^{1}H nmr and mass spectrum may not be predictably different, the carbonyl absorption of cyclic ketones is sensitive to ring strain. The carbonyl absorptions of cyclobutanone, cyclopentanone and cyclohexanone occur at 1780, 1745 and 1715 cm^{-1} respectively. The ketone absorption in the cyclohexanone derivative **14** reported by Vedejs occurs at 1727 cm^{-1} whereas the ketone absorption occurs at 1780 cm^{-1} in the carbonylated derivative of trans-3,3-dimethyl-1-butenylmercuric chloride, **13**. Regardless of the reason for the observed direction of ring closure, the original structural formula of the palladium species as a nortricyclylpalladium compound is further established by the carbonylation product.

The observed formation of the methyl ester and the cyclic ketone in these two different palladium derivatives derived from trans-3,3-dimethyl-1-butenylmercuric chloride is especially interesting when the carbonylation of similar allyl norbornylpalladium compounds is considered. J. P. Burkhart and R. C. Larock investigated the carbonylation of allyl norbornylpalladium species under different conditions.[382] Carbonylation of the allyl norbornylpalladium chloride in refluxing methanol produces two cyclic ketones in a 2:1 ratio (Eq. 44). Carbonylation of the allyl norbornylpalladium hexafluoroacetylacetonate in refluxing methanol forms a 1:1 ratio of the allyl norbornyl methyl ester and the saturated cyclic ketone (Eq. 45). Carbonylation of either the allyl norbornylpalladium chloride or allyl norbornylpalladium hexafluoroacetylacetonate forms exclusively the allyl norbornyl methyl ester when triethylamine is added and the carbonylation begun at -78°C and allowed to warm to room temperature (Eqs. 46 and 47). Because the effect of the tert-butyl group upon forma-



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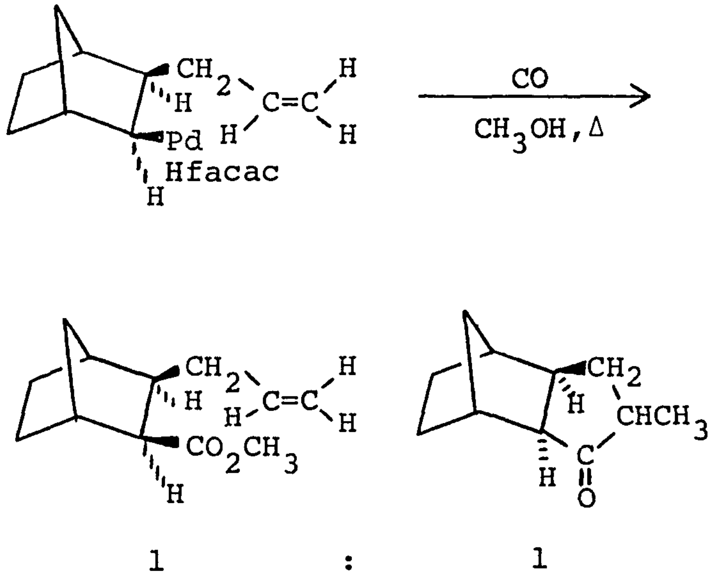

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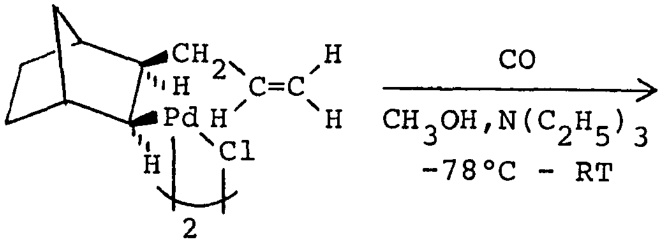

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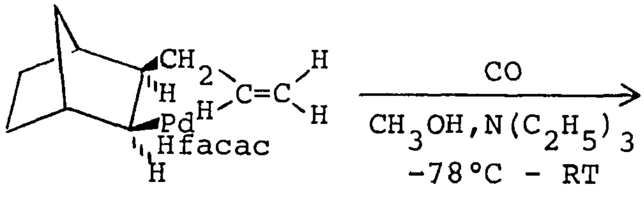
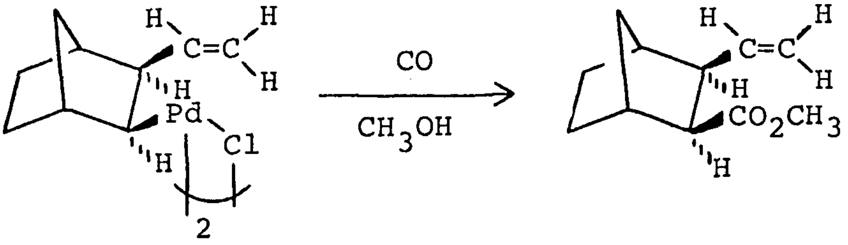


(47)

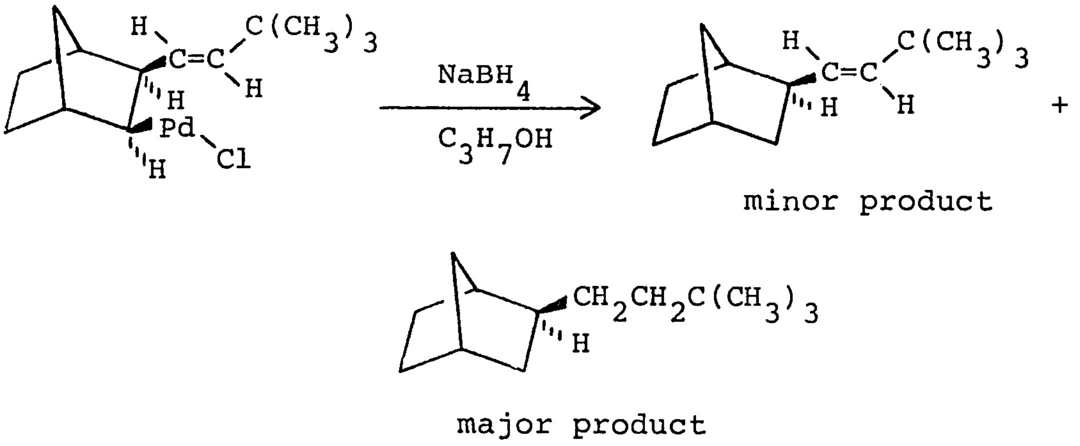
tion of the vinyl norbornyl methyl ester was not known, the vinyl norbornyl palladium compound derived from vinylmercuric chloride was carbonylated in refluxing methanol. The major product (greater than 80%) obtained is the vinyl norbornyl methyl ester (Eq. 48). Traces of other compounds were



(48)

also noticed in the Gas chromatographic analysis. While the carbonylation of these two vinyl norbornylpalladium compounds clearly illustrate the propensity toward ring closure does not depend upon the terminal alkyl substituents of the olefin, the factors which promote ring closure have not been elucidated. With respect to the carbonylation of vinyl norbornyl palladium compounds, the alkyl substitution of the terminal carbon of the olefin is unimportant as a possible factor influencing either ester formation or ring closure. The effect of alkyl substitution on the internal olefinic carbon has not been examined. Therefore, carbonylation of the vinyl norbornylpalladium compound derived from E-4,4-dimethyl-2-pentenylmercuric chloride might be interesting. Although time did not permit, carbonylation of the vinyl nortricyclylpalladium compound derived from norbornadiene palladium dichloride and vinylmercuric chloride might also be interesting in light of the two different directions of ring closure reported so far. Finally, the carbonylation of the trans-β-chlorovinylmercuric chloride derivative may also be useful in elucidating the structure of the original palladium compound.

b. Reduction Initially it was also expected that the structure of the vinyl norbornylpalladium compounds might also be verified by characterization of reduction products. A brief investigation of the reaction of the vinyl norbornylpalladium compound derived from trans-3,3-dimethyl-1-butenylmercuric chloride with sodium borohydride in isopropanol (Eq. 49) or THF (Eq. 50) indicates that predominantly two



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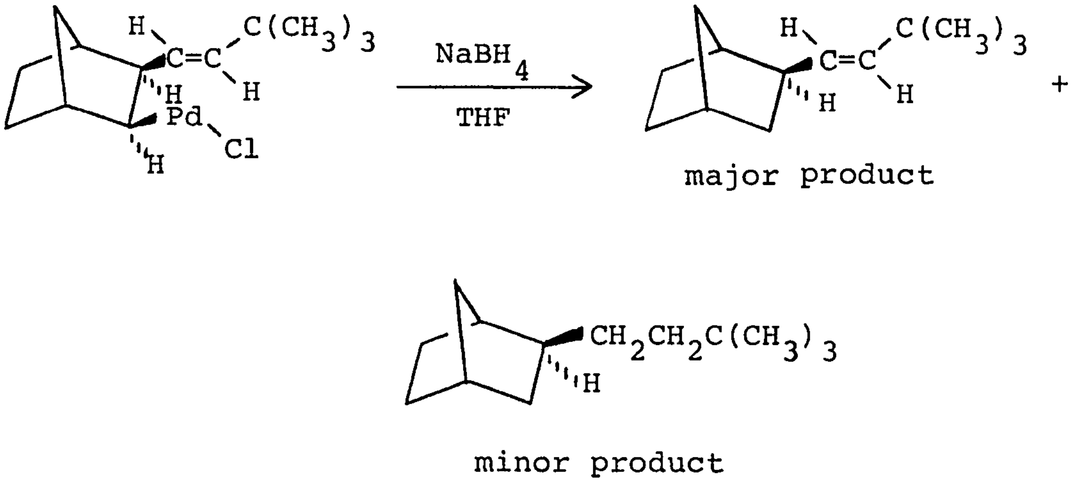
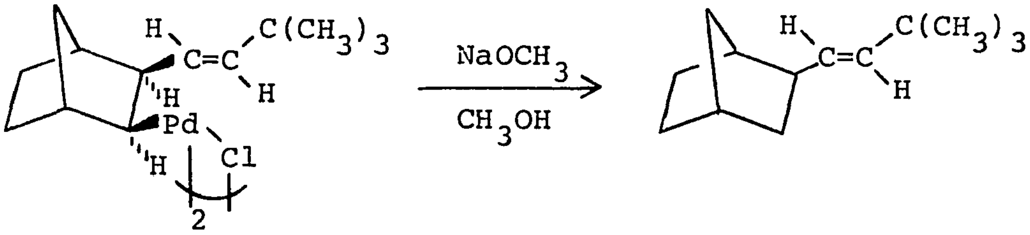


(50)

hydrocarbons are formed. The major and minor products in isopropanol are reversed in THF. It has been proposed that the formation of borane in the reduction of the palladium moiety may be responsible for partial reduction of the olefins.[269]

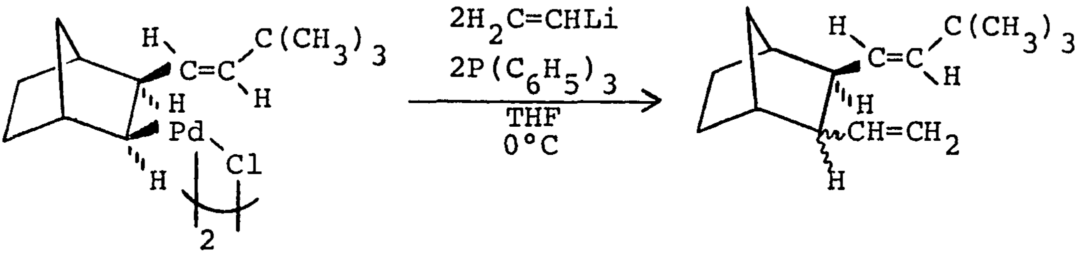
c. Anionic displacements The reaction of several anionic species with these sigma palladium compounds was also considered. The vinyl norbornylpalladium compound derived from trans-3,3-dimethyl-1-butenylmercuric chloride was employed as the model system for these studies due to its availability and the simplicity of its ^1H nmr spectrum. The reaction of compound 4 with sodium methoxide in methanol does not form the methyl ether, but forms instead the hydrocarbon (Eq. 51). While this investigation was in progress, the catalytic reduction of arylpalladium species with sodium methoxide was reported (Eq. 52).[402] A palladium hydride is proposed to be involved.[403]



(51)

$$C_6H_5Br + NaOCH_3 + 0.05\ Pd[P(C_6H_5)_3]_4 \xrightarrow[DMF]{100°C} C_6H_6 \qquad (52)$$

The replacement of the palladium moiety with carbanion species, such as organolithium compounds was also briefly investigated. GLPC analysis indicated that the reaction of compound 4 with an equivalent of either methyl lithium, vinyl lithium or *n*-butyl lithium in HMPA also forms the reduced hydrocarbon and none of the expected alkylated products. Following a report by Murahashi and coworkers that the addition of triphenylphosphine improves the coupling of vinyl lithium and arylpalladium compounds,[404] GLPC-mass spectroscopy indicated that employing two equivalents of both vinyl lithium and triphenylphosphine produces a vinylated derivative (Eq. 53).



(53)

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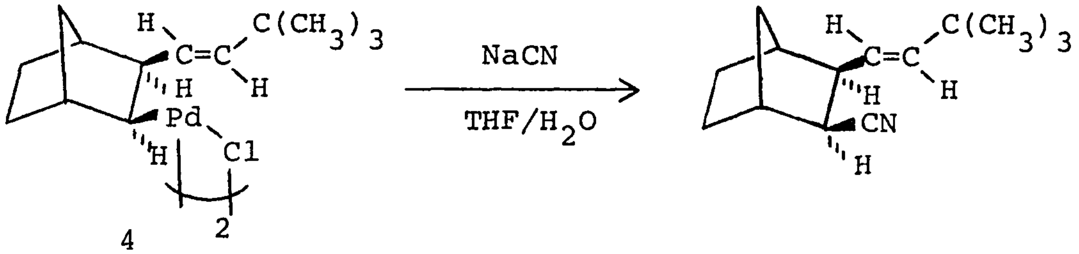
Although the reactions of compound 4 with sodium cyanide in 50:50 THF:water with or without triphenylphosphine remain colorless and do not turn black, a new GLPC peak is observed which is possibly the nitrile (Eq. 54). Since the nitrile



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(54)

might also be reduced to the aldehyde and from it the allylic prostaglandin side chain elaborated, the formation of the nitrile may be synthetically useful.

d. Insertion of olefinic species The functionalization of organopalladium compounds by olefins initially investigated by Heck might also be synthetically useful in developing the allylic side chain of prostaglandin analogs. The reactions of compound **4** with isobutyl vinyl ether and methyl acrylate with or without three equivalents of triethylamine require heating before the reaction mixture turns black. Although a black semi-solid was obtained from the reactions with isobutyl vinyl ether, GLPC analysis also indicated a peak of longer retention time than the reduction product, but it was not characterized. A longer retention time peak was also observed in the reaction of compound **4** and vinyl acetate which turned black at room temperature. Unfortunately, it also was not characterized completely. Allyl chloride and compound **4** were allowed to react at room temperature for several days. Although no color changes occurred to indicate a possible reaction, a new, but very small GLPC peak was observed. No further characterization was attempted.

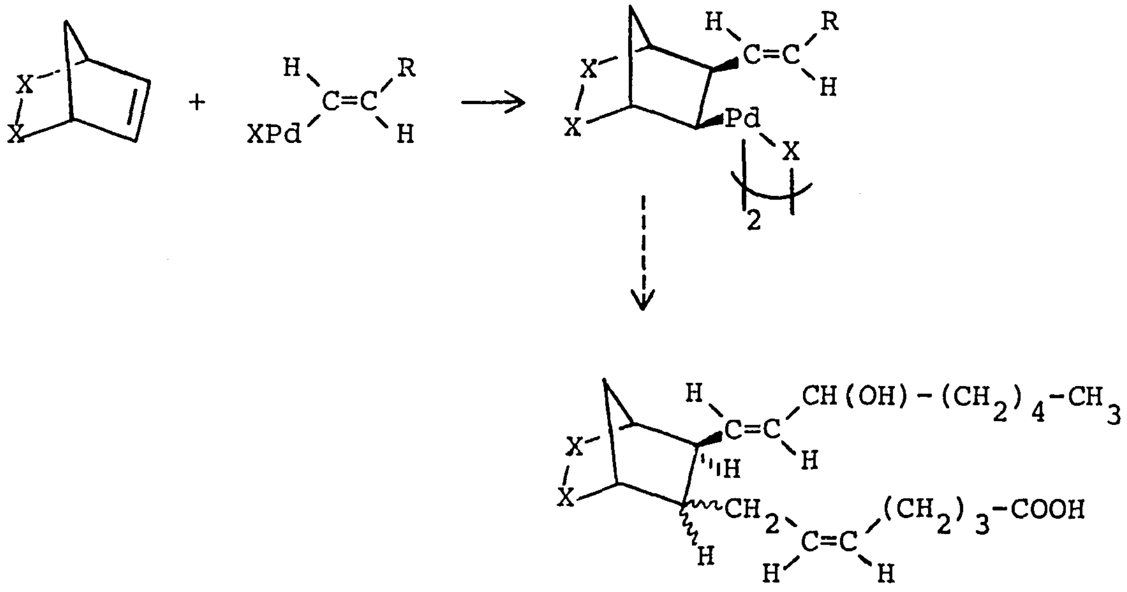
C. Conclusion

Further investigation into the reaction of a vinylmercurial, dilithium tetrachloropalladate and norbornene demonstrates that in addition to the various vinylmercurials employed, different bicyclic olefins such as bicyclo[2.2.2]-oct-2-ene, N,N-bis-carboethoxy-5,6-diazabicyclo[2.2.1]hept-2-ene and bicyclo[3.2.1]oct-6-en-3-one may also be utilized. However, substituting norbornadiene for norbornene under the usual conditions results in the formation of a vinyl nortricyclylpalladium compound.

In the analogous addition of π-allylpalladium compounds to norbornene,[375-381] x-ray diffraction was first utilized to establish the stereochemistry of addition. Later ^1H nmr was also used to support the observed cis,exo addition of both the allyl and palladium moieties.[381] Consequently, ^1H nmr spectroscopy was the predominant tool used in this thesis to verify that the addition of the intermediate vinylpalladium species to norbornene and other bicyclic olefins is also cis and exo. The further functionalization of the palladium moiety, especially the characterization of the carbonylated product, also supports the cis-exo addition of the vinylpalladium species to norbornene.

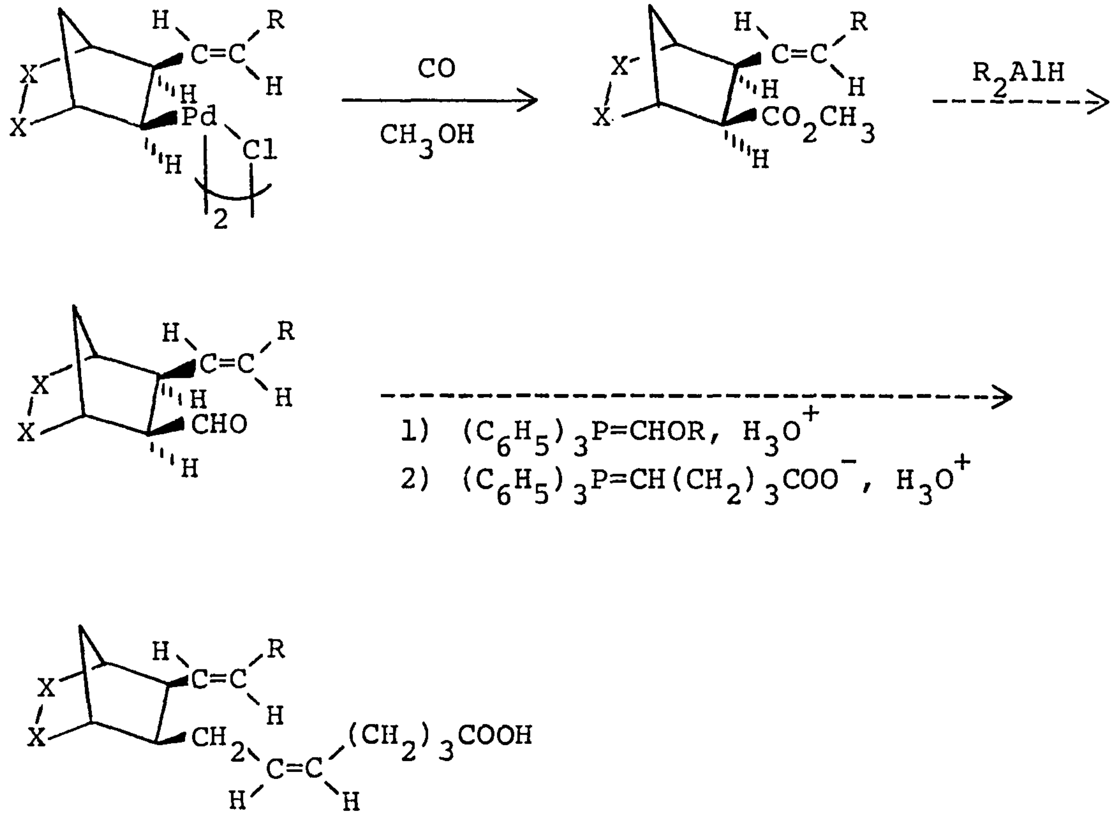
The ease and stereospecificity of the addition of a vinylpalladium species to norbornene, as well as the crude resemblance of an appropriately substituted norbornene skeleton to prostaglandin endoperoxides suggested the possibility of using this addition reaction as a synthetic entry into cis prostaglandin endoperoxide analogs. The modification of existing reactions or the development of new palladium mediated carbon-carbon bond formations and functionalizations for the addition of the allylic side chain is the most obvious area for further investigation (Scheme 13). Although the

Scheme 13



allylic prostaglandin side chain may be constructed in several steps from the ester (or acid) via reduction to the aldehyde Scheme 14, a carbon-carbon bond forming reaction between the

Scheme 14



palladium moiety and a derivative of the entire allylic side chain or a two carbon fragment with subsequent addition of the remaining five carbon fragment would be more efficient and desirable. Since the actual vinyl side chain in naturally occurring prostaglandins also contains an allylic alcohol, the formation of a vinylmercurial containing the protected allylic alcohol is also necessary. Alternatively, further investigation of the formation of these vinyl alkylpalladium compounds from a borane, a protected form of 1-octyn-3-ol, palladium acetate and the bicyclic olefin might resolve the same problem more directly. Although the actual number of palladium mediated carbon-carbon bond formations investigated in this thesis are very few, the initial results are promising, suggesting a more intensive study of these and other synthetic reactions.

D. Experimental Section

1. General

The description of the instruments used as well as routine reagents and solvent purifcation have been described previously. Norbornene, norbornadiene and bicyclo[2.2.2]oct-2-ene were utilized as obtained from Aldrich. N,N-bis-carboethoxy-5,6-diazabicyclo[2.2.1]hept-2-ene[405] and bicyclo-[3.2.1]oct-6-en-3-one[406] were prepared according to literature procedures. Unusual difficulty was experienced with reproducing the bicyclo[3.2.1]oct-6-en-3-one literature synthesis. By rigorously degassing all materials and performing the reaction under argon, a reduced yield of bicyclo[3.2.1]oct-6-en-3-one was isolated. Trimethylamine oxide was dried as suggested by Hickinbottom prior to use.[407] Vinylmercuric chloride was obtained from Orgmet. The other vinylmercurials were prepared according to literature procedures.[254,255] Palladium chloride was generously loaned by Engelhard and Matthey Bishop. Norbornadiene palladium dichloride was also prepared according to a literature procedure.[408] Eu(fod)$_3$ was obtained from Norell.

2. Synthesis of vinyl alkylpalladium compounds

The following synthesis of the (*trans*-1-octenyl)norbornylpalladium compound (Table I, Entry 4) is representative. The procedure is identical to that developed by M. A. Mitchell earlier. 0.85 Grams (20 mmoles) lithium chloride, 1.77 grams (10 mmoles) palladium chloride and 9.49 grams (100 mmoles) norbornene were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 100 ml THF was added by syringe. After cooling to 0°C, 3.39 grams (10 mmoles) *trans*-1-octenylmercuric chloride was added all at once while backflushing with nitrogen. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight, approximately 16 hours. Ether and charcoal were then added to the reaction mixture which was filtered and washed twice with saturated ammonium chloride. The combined washings were re-extracted with ether and the combined ether extractions dried (anhydrous Na_2SO_4). Removal of the solvent affords 2.94 grams (85%) of pale yellow solid which was recrystallized from dichloromethane giving 1.56

grams (46% recrystallized yield). In some cases, washing the chloroform or dichloromethane solution with saturated ammonium chloride solution prior to concentrating and cooling the solution provides slightly higher recrystallized yields and reduces some decomposition which is evidenced by the formation of palladium(0) which is black. Although extensive decomposition occurs upon melting, the observed melting points are different enough to be characteristic: mp 112-115°C. The other characterization includes: ^{1}H nmr ($CDCl_3$) δ0.9-1.7 (17H, m, aliphatic), 2.28 (2H, m, allylic), 2.65 (2H, m, bridgehead), 2.80 (2H, m, endo norbornyl), 3.97 (1H, dd, J = 14 Hz, J = 3 Hz, internal vinyl), 5.60 (1H, m, external vinyl); IR (KBr) 3040 vw, 2960 s, 2930 s, 2880 s, 2860 s, 1540 w, 1470 ms, 1380 mw, 1340 w, 1310 mw, 1295 mw, 1260 mw, 1215 w, 1200 w, 1190 mw, 1160 w, 1130 mw, 1110 m, 1080 ms, 1030 mw, 1010 mw, 980 w, 950 w, 935 mw, 920 w, 880 w, 860 w, 845 w, 800 ms, and 770 mw cm^{-1}. Anal. Calcd for $C_{15}H_{22}ClPd$: C, 51.88; H, 7.26. Found: C, 51.99; H, 7.09.

The vinylnorbornylpalladium compound (Table I, Entry 3) was prepared similarily: recrystallized from dichloromethane, mp 194-195°C; ^{1}H nmr ($CDCl_3$) δ0.9-1.7 (6H, m, norbornyl), 2.34 (1H, m, bridgehead nearest vinyl group), 2.55 (1H, m, bridgehead near palladium), 2.65 (1H, d, J = 9 Hz, endo norbornyl nearest vinyl group), 2.82 (1H, dd, J = 9 Hz, J = 3 Hz, endo norbornyl near palladium), 4.0-4.5 (2H, m, internal vinyl and external cis vinyl), 4.82 (1H, dd,

$\underline{J}$ = 14 Hz, $\underline{J}$ = 2 Hz, external trans vinyl); IR (KBr) 3040 w, 2995 ms, 2950 s, 2910 s, 2875 s, 1530 mw, 1465 w, 1455 ms, 1400 mw, 1315 ms, 1305 ms, 1290 w, 1265 mw, 1220 w, 1200 w, 1190 mw, 1165 w, 1140 ms, 1100 ms, 1040 ms, 1020 mw, 985 s, 975 s, 960 s, 940 ms, 900 mw, 850 mw, 800 w and 770 ms cm^{-1}. Anal. Calcd for $C_9H_{13}ClPd$: C, 41.09; H, 4.98. Found: C, 41.02; H, 5.08.

The [trans(3,3-dimethyl-1-butenyl)]bicyclo[2.2.2]octylpalladium compound (Table I, Entry 6) was prepared similarly by substituting bicyclo[2.2.2]oct-2-ene for norbornene: recrystallized from dichloromethane, mp 159-162°C; ^1H nmr ($CDCl_3$) δ0.9-1.7 (8H, m, bicyclooctyl), 1.2 (9H, s, $-C(CH_3)_3$), 2.0 (2H, m, bridgehead), 2.95 (2H, m, "endo" bicyclooctyl near palladium and the vinyl moiety), 4.23 (1H, dd, $\underline{J}$ = 14 Hz, $\underline{J}$ = 3 Hz, internal vinyl), 6.03 (1H, d, $\underline{J}$ = 14 Hz, external vinyl); IR (KBr) 3010 w, 2970 s, 2940 s, 2910 s, 2870 s, 1540 w, 1480 m, 1460 m, 1395 m, 1370 m, 1265 s, 1235 w, 1200 w, 1100 s, 1025 s, 910 w, 850 m, 800 s cm^{-1}. Anal. Calcd for $C_{14}H_{23}ClPd$: C, 50.47; H, 6.96. Found: C, 50.26; H, 7.23

Employing only 1.1 equivalent of the bicyclic olefin under otherwise identical reaction conditions, the (trans-3,3-dimethyl-1-butenyl) diazabicyclo[2.2.1]heptyl- (Table I, Entry 7) and bicyclo[3.2.1]octylpalladium compounds (Table I, Entry 8) were prepared. (trans-3,3-Dimethyl-1-butenyl)diazabicyclo[2.2.1]heptylpalladium compound: recrystallized from dichloromethane, mp 132-135°C; ^{1}H nmr (CDCl$_3$) δ1.10-1.20 (2H, m, bridge), 1.20 (9H, s, C(CH$_3$)$_3$), 1.28 (6H, t, *J* = 7 Hz, -CH$_3$) 2.94 (2H, m, bridgehead), 3.38 (1H, m, endo norbornyl type nearest the vinyl group), 3.5 (1H, d, *J* = 12 Hz, endo norbornyl type near palladium), 4.2 (4H, overlapping q, *J* = 7 Hz, -O-CH$_2$-), 4.77 (1H, m, internal vinyl) 5.88 (1H, d, *J* = 14 Hz, external vinyl); IR (KBr) 3020 w, 2995 s, 2985 s, 2950 s, 2920 ms, 2880 ms, 1755-1715 s, 1540 w, 1485 ms, 1475 ms, 1450 ms, 1405 s, 1380 s, 1320-1295 s, 1255 s, 1175 s, 1130 s, 1110 s, 1055 ms, 1030 ms, 910 w, 875 mw, 860 mw, 770 s cm^{-1}. Anal. Calcd for $C_{15}H_{27}ClN_2O_4Pd$: C, 43.89; H, 5.85. Found: C, 44.15; H, 5.98.

(trans-3,3-Dimethyl-1-butenyl)bicyclo[3.2.1]octylpalladium compound: recrystallized from dichloromethane, mp 199-200°C; ^{1}H nmr (CDCl$_3$) δ0.9-2.0 (2H, m, bridge methylene), 1.18 (9H, s, -C(CH$_3$)$_3$), 2.20 (1H, d, *J* = 4 Hz, a methylene adjacent to carbonyl), 2.30 (2H, m, methylene adjacent to carbonyl), 2.38 (1H, d, *J* = 4 Hz, a methylene adjacent to carbonyl), 2.56 (1H, m, bridgehead nearest vinyl moiety), 2.88 (1H, m, bridgehead near palladium), 3.10 (1H, m, endo norbornyl type nearest the vinyl group), 3.20 (1H, m, endo norbornyl type near palladium), 3.97 (1H, dd, *J* = 14 Hz, *J* = 3 Hz, internal vinyl), 4.78 (1H, dd, *J* = 14 Hz, *J* = 1 Hz, external vinyl); IR (KBr) 3005 w, 2960 s, 2940 s, 2910 m, 2870 ms, 1720 vs, 1540 w, 1480 mw, 1460 mw, 1410 mw, 1395 mw, 1370 mw, 1355 mw, 1340 w, 1310 w, 1260 w, 1240 w, 1220 mw, 1190 w, 1175 w, 1150 w, 1080 ms, 1030 mw, 1000 w, 940 mw, 905 ms, 870 mw and 800 w cm^{-1}. Anal. Calcd for $C_{14}H_{21}ClOPd$: C, 48.44; H, 6.10. Found: C, 48.70; H, 6.39.

Compounds prepared previously by M. A. Mitchell but incompletely characterized include the following. (trans-3,3-Dimethyl-1-butenyl)norbornyl palladium compound (Table I, Entry 5): recrystallized from chloroform, mp 165-166°C; ^1H nmr ($CDCl_3$) δ0.9-1.6 (6H, m, norbornyl), 1.12 (9H, s, $-C(CH_3)_3$), 2.30 (1H, m, bridgehead nearest vinyl group), 2.68 (1H, m, bridgehead near palladium), 2.78 (1H, d, J = 11 Hz, endo norbornyl nearest vinyl group), 2.98 (1H, d, J = 11 Hz, endo norbornyl near palladium), 3.98 (1H, dd, J = 14 Hz, J = 3 Hz, internal vinyl), 5.80 (1H, d, J = 14 Hz, external vinyl); IR (KBr) 3030 w, 2940 s, 2900 s, 2860 s, 1535 mw, 1470 ms, 1450 ms, 1390 mw, 1365 ms, 1325 mw, 1305 mw, 1295 mw, 1240 ms, 1210 w, 1200 mw, 1180 ms, 1125 ms, 1110 ms, 1075 s, 1035 ms, 1020 ms, 1000 ms, 980 ms, 930 ms, 900 ms, 850 ms, 800 ms, and 750 mw cm^{-1}. Anal. Calcd for $C_{13}H_{21}ClPd$: C, 48.92; H, 6.63. Found: sample 1, C, 46.72; H, 6.52; sample 2, C, 50.88; H, 6.78.

E-4,4-Dimethyl-2-pentenyl)norbornyl palladium compound (Table I, Entry 2): recrystallized from chloroform, mp 210-213°C; ^1H nmr ($CDCl_3$) δ0.9-1.6 (H, m, norbornyl), 1.25

(9H, s, -C$(CH_3)_3$), 1.84 (3H, s, -CH_3), 2.38 (1H, m, bridgehead nearest vinyl group), 2.64 (1H, m, bridgehead near palladium), 2.80 (1H, d, _J_ = 10 Hz, endo norbornyl nearest vinyl group), 2.88 (1H, d, _J_ = 10 Hz, endo norbornyl near palladium), 5.18 (1H, s, external vinyl); IR (KBr) 3050 w, 2995 ms, 2960 s, 2870 s, 1520 w, 1480 mw, 1450 ms, 1395 w, 1380 w, 1365 ms, 1320 mw, 1310 w, 1295 w, 1280 w, 1265 s, 1215 mw, 1200 ms, 1185 mw, 1160 w, 1125 s, 1100 ms, 1060 ms, 1020 ms, 980 ms, 975 mw, 950 w, 940 mw, 920 w, 895 mw, 870 w, 860 w, 800 s, and 750 mw cm^{-1}. Anal. Calcd for $C_{14}H_{23}ClPd$: C, 50.47; H, 6.96. Found: C, 49.84; H, 7.02.

(_trans_-Styryl)norbornylpalladium compound: (Table I, Entry 1) recrystallized from dichloromethane, mp 230-232°C; ^1H nmr (d_6-DMSO; insoluble in $CDCl_3$) δ0.85-1.4 (6H, m, norbornyl), 2.26 (1H, m, bridgehead nearest vinyl group), 2.50 (partially obscured by solvent impurity) (1H, m, bridgehead near palladium), 2.80 (1H, m, endo norbornyl nearest vinyl group), 3.35 (partially obscured by solvent impurity) (1H, m, endo norbornyl near palladium), 5.24 (1H, dd, _J_ = 14 Hz, _J_ = 3 Hz, internal vinyl), 6.97 (1H, d, _J_ = 14 Hz, external vinyl), 7.55-7.95 (5H, m, -C_6H_5); IR (KBr) 3030 w, 3015 w, 3005 w, 2980 s, 2960 s, 2930 s, 2880 s, 2870 s, 1540 w, 1490 w, 1470 w, 1450 ms, 1305 mw, 1250 w, 1210 mw, 1190 w, 1150 w, 1125 mw, 1075 mw, 1030 w, 1105 mw, 975 mw, 935 w, 875 w, 865 w, 750 s and 690 s cm^{-1}. Anal. Calcd for $C_{15}H_{17}ClPd$: C, 53.12; H, 5.05. Found: C, 53.34; H, 5.16.

The adduct formed from *trans*-β-chlorovinylmercuric chloride, dilithium tetrachloropalladate and norbornene is discussed later.

3. *Attempted formation of the (trans-3,3-dimethyl-1-butenyl)-norbornylpalladium chloride compound from a vinylborane, palladium acetate and norbornene*

A 250 ml round bottom flask equipped with a septum inlet, a gas inlet tube and a magnetic stirring bar was thoroughly dried and flushed with nitrogen. 25 Ml THF was added by syringe and the flask immersed in an ice bath. 1.83 Ml (2.74 M BH_3/THF) (5 mmoles) BH_3/THF was added by syringe followed by 0.82 grams (10 mmoles) cyclohexene which was also added by syringe. After 3 hours, during which time the reaction warmed to room temperature, the flask was recooled in an ice bath and 0.41 grams (5 mmoles) 3,3-dimethyl-1-butyne was added by syringe. After an additional 3 hour reaction time, the flask was recooled again and another 25 ml THF was added by syringe. 4.71 Grams (50 mmoles) norbornene and 1.12 grams (5 mmoles) palladium acetate were added all at once while back-flushing with nitrogen. The mixture was then allowed to slowly warm to room temperature and stirred overnight. 2.12 Grams (50 mmoles) lithium chloride, charcoal and ether were then added to the reaction mixture which was carefully filtered into a separatory funnel. The organic layer was then washed three times with saturated ammonium chloride solution, dried (anhydrous Na_2SO_4) and carefully concentrated. $CDCl_3$ was added and a ^1H nmr spectrum of the crude mixture contained a tert-butyl singlet and vinyl hydrogens identical to those observed in the organopalladium compound derived from trans-3,3-dimethyl-1-butenylmercuric chloride, dilithium tetrachloropalladate and norbornene. Subjecting this crude brown semi-solid several times to column chromatography on basic alumina and eluting with dichloromethane gradually separates the palladium compound from the organoboron residue, but suffers from being a tedious purification procedure.

The reaction was also repeated several times with the addition of 2 equivalents anhydrous trimethylamine oxide to the reaction mixture after the addition of 3,3-dimethyl-1-butyne and before the addition of palladium acetate and norbornene. In one run, the mixture was heated at 65°C for 2 hours after the addition of trimethylamine oxide. A small amount of a brown semi-solid was also obtained from these reactions. The ^1H nmr spectrum of the obtained solids in each case contained both a broad peak assigned to the cyclohexyl hydrogens observed in the reactions without trimethylamine oxide as well as a tert-butyl singlet identical to that observed in the previous reactions.

4. Formation of the organopalladium compound from trans-β-chlorovinylmercuric chloride, dilithium tetrachloropalladate and norbornene

Several preparations of trans-β-chlorovinylmercuric chloride were attempted[277] by passing acetylene into a cold solution of 36 grams mercuric chloride dissolved in 37.5 ml half concentrated hydrochloric acid. In each trial less than 10% of the desired precipitate was obtained. After filtering, washing with water, drying, and extracting with and recrystallizing from chloroform, a crystalline material of mp 116-118°C was obtained (lit.[277] mp 123-124°C). An ^{1}H nmr spectrum indicated the presence of trans vinyl hydrogens.

Since the purity of the starting mercurial, especially with respect to the relative amounts of trans-β-chlorovinylmercuric chloride and bis(trans-β-chlorovinyl)mercury was unknown, the following reaction was performed as indicated. 0.35 Grams (8 mmoles) lithium chloride, 0.71 grams (4 mmoles) palladium chloride and 3.76 grams (40 mmoles) norbornene were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After sweeping the system with nitrogen, 40 ml THF was added by syringe, and the reaction vessel placed in an ice bath. 0.65 Grams of mercurial [2 mmoles $(ClHC{=}CH)_2Hg$ or 2.2 mmoles $ClHC{=}CHHgCl$] were added all at once while backflushing with nitrogen and the reaction mixture stirred and allowed to warm to room temperature. After reaching room temperature, the red color characteristic of palladium chloride remained, so an additional 0.65 grams of the vinylmercurial was added. The reaction mixture subsequently turned black. Ether and charcoal were added and the reaction mixture filtered into a separatory funnel. The organic layer was washed 3 times with saturated ammonium chloride solution, dried (anhydrous Na_2SO_4) and concentrated to yield 0.70 grams (59% crude yield) of a yellow solid. The solid was recrystallized from dichloromethane yielding 0.40 grams (38%), mp 173-176°C. The A-60 ^1H nmr spectrum was nearly identical to that of M. A. Mitchell's A-60 ^1H nmr spectrum. Other data includes HA-100 ^1H nmr ($CDCl_3$) δ1.1-1.7 (6H, m, norbornyl), 2.46 (1H, m, bridgehead near the vinyl moiety), 2.73 (1H, m, bridgehead near the palladium), 3.26 (1H, m, possibly an endo norbornyl), 4.27 (1H, m (possibly a t) with $\underline{J} \cong 5$ Hz, a vinyl type hydrogen), 5.77 (1H, dd, $\underline{J} = 5$ Hz, $\underline{J} = 1$ Hz, a vinyl type); IR (KBr) 3035 w, 3000 ms, 2950 s, 2930 s, 2900 s, 2860 s, 1470-1460 s, 1450 ms, 1440 ms, 1400 w, 1320 ms, 1305 mw, 1290 ms, 1260 mw, 1240 w, 1210 w, 1190 mw, 1185 ms, 1170 w, 1145 w, 1120 mw, 1115 ms, 1065 s, 1025 w, 1000 mw, 970 w, 960 w, 945 mw, 935 w, 920 ms, 875 w, 855 mw, 810 w, 790 mw, 775 ms, 730 w and 710 s cm^{-1}. Anal. Calcd for $C_9H_{12}Cl_2Pd$: C, 36.34; H, 4.07. Calcd for $C_9H_{11}ClPd$: C, 41.41, H, 4.25. Calcd for $C_9H_{11}Cl_2Pd$: C, 36.46; H, 3.74. Found: C, 41.95; H, 4.99.

5. Formation of the vinyl nortricyclylpalladium compound (compound 11) via trans-3,3,dimethyl-1-butenylmercuric chloride, dilithium tetrachloropalladate and norbornadiene

1.77 Grams (10 mmoles) palladium chloride and 0.85 grams (20 mmoles) lithium chloride were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 100 ml THF was added by syringe. The flask was cooled in an ice bath and 9.21 grams (100 mmoles) norbornadiene was added by syringe. Lastly, 3.19 grams (10 mmoles) trans-3,3-dimethyl-1-butenylmercuric chloride was added all at once while back-flushing with nitrogen. After slowly warming to room temperature, the reaction was stirred an additional 16 hours at room temperature before ether and charcoal were added. The mixture was then filtered into a separatory funnel. The ether extracts were washed with saturated ammonium chloride solution and dried (anhydrous Na_2SO_4). After solvent removal, 2.85 grams (90%) of a yellow-green solid were obtained. Recrystallization from methylene chloride (not all the crude material dissolves) produced 0.82 grams (26%) recrystallized yield, mp 187-189°C. Acetonitrile appears to be better at dissolving the compound, but the crystals obtained after the addition of ether and hexane to decrease the solubility are noticeably darker. Spectral data includes: ^1H nmr ($CDCl_3$) δ1.24 (9H, s, $-C(CH_3)_3$), 1.46-2.80 (8H, m, nortricyclyl), 5.25 (1H, d, *J* = 14 Hz, vinyl), 5.35 (1H, d, *J* = 14 Hz, vinyl). After the addition of triphenylphosphine, the ^{1}H nmr spectrum changes to δ0.7-2.25 (8H, m, nortricyclyl), 1.30 (9H, s, $C(CH_3)_3$), 6.05 (1H, d, *J* = 14 Hz, vinyl), 6.35 (1H, d, *J* = 14 Hz, vinyl), 7.2-7.8 (15H, m, $P(C_6H_5)_3$); IR(KBr) 3045 ms, 3035 ms, 3020 w, 3005 s, 2980 s, 2950 s, 2920 s, 2880 s, 1530 w, 1585 s, 1560 mw, 1500 ms, 1475 ms, 1465 w, 1450 ms, 1410 mw, 1395 m, 1380 ms, 1370 ms, 1330 ms, 1195 mw, 1175 w, 1130 w, 1100 w, 1065 s, 1050 s, 1040 ms, 1030 ms, 1000 ms, 970 ms, 965 ms, 940 ms, 900 s, 890 ms, 860 s, 820 ms, 810 s, 795 s, 760 s, 705 w, and 660 ms cm^{-1}. Anal. Calcd for $C_{13}H_{19}ClPd$: C, 49.23; H, 6.04. Found: C, 49.23; H, 6.04.

6. <u>Formation of the vinyl nortricycylpalladium compound via trans-3,3-dimethyl-1-butenylmercuric chloride and norbornadiene palladium dichloride</u>

2.70 Grams (10 mmoles) norbornadiene palladium dichloride was weighed into a 250 ml round bottom flask equipped with a septum inlet, a gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 100 ml THF was added by syringe. Since the norbornadiene palladium dichloride did not dissolve completely, it was not cooled, but 3.19 grams (10 mmoles) *trans*-3,3-dimethyl-1-butenylmercuric chloride was added all at once while backflushing with nitrogen. The mixture was allowed to stir 18 hours at room temperature after which time the slurry was light green. Ether only partially dissolved the slurry so eventually dichloromethane and acetonitrile were added. The solution was then filtered. Almost no palladium(0) was evident. The organic solution was washed several times with saturated ammonium chloride solution and dried (anhydrous Na_2SO_4). Upon removal of the solvent, 3.0 grams (95%) of a light green yellow solid was obtained. The melting point, solubility and spectral characteristics were identical to the vinyl nortricyclylpalladium compound obtained from trans-3,3-dimethyl-1-butenylmercuric chloride, dilithium tetrachloropalladate and norbornadiene.

7. Attempted formation of the vinyl norbornenyltriphenylphosphinepalladium compound

0.85 Grams (20 mmoles) lithium chloride, 1.77 grams (10 mmoles) palladium chloride and 5.25 grams (20 mmoles) triphenylphosphine were weighed into a 250 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. After flushing with nitrogen and cooling the flask in an ice bath, 100 ml THF was added by syringe. After the solids dissolved, 3.19 grams (10 mmoles) trans-3,3-dimethyl-1-butenylmercuric chloride was added all at once while backflushing with nitrogen. After 1.5 hours, during which time the mixture slowly warmed to room temperature, the reaction was recooled to 0°C and 0.92 grams (10 mmoles) norbornadiene was added by syringe. The reaction was slowly warmed to room temperature and stirred at room temperature an additional 12 hours. Following the addition of ether and charcoal the mixture was filtered into a separatory funnel, and the organic layer washed with a saturated ammonium chloride solution, dried (anhydrous Na_2SO_4) and the solvents removed. The vinyl region of the ^1H nmr spectrum indicated more signals than present in the spectrum of the vinylmercurial itself. The additional peaks occurred at δ5.25(d, J = 15 Hz), δ5.45(m) and δ5.83(d, J = 15 Hz). The integration, however, suggested an unusually large amount of triphenylphosphine was present, further suggesting that the product was probably not a pure compound. Attempts to remove some of the triphenylphosphine by adding pentane to a dichloromethane solution of the compound and filtering removed successive amounts of triphenylphosphine, but caused further decomposition.

8. Attempted formation of the vinyl norbornenyltriphenylphosphine palladium compound immediately followed by carbonylation

0.21 Grams (5.0 mmoles) lithium chloride, 0.44 grams (2.5 mmoles) palladium chloride, 1.31 grams (5.0 mmoles) triphenylphosphine and 0.80 grams (2.5 mmoles) trans-3,3-dimethyl-1-butenylmercuric chloride were weighed into a 50 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing the system with nitrogen and cooling the flask in an ice bath, 25 ml THF was added by syringe. After 1.5 hours, during which time the mixture slowly warmed to room temperature, the reaction was recooled to 0°C and 4.60 grams (50 mmoles) norbornadiene added by syringe. The reaction was slowly warmed to room temperature and stirred at room temperature an additional 12 hours. The solvent and excess norbornadiene were then removed on the rotary evaporator leaving a light green solid. A condenser was added and the gas inlet tube replaced. The flask was cooled to -78°C, 25 ml methanol added by syringe, flushed with carbon monoxide and placed under a carbon monoxide atmosphere. After slowly warming to room temperature and stirring an additional 8 hours at room temperature, the reaction mixture had not yet turned black so the temperature was increased to reflux. After four days reflux, the palladium(0) coagulated together leaving a nearly colorless solution. Following filtration, some methanol was removed by distillation, and pentane and water added to try to remove the organic product from the excess triphenylphosphine. This procedure was not as ideal as imagined and some product was lost. The pentane solution was further purified by preparative gas chromatography. Although the spectral evidence here is incomplete it is presented. The GLPC purified material was too dilute; however, the crude ^1H nmr spectrum indicated peaks at δ0.9-1.2 (m + s), 2.0 (m), 2.50 (m), 3.55 (m), 3.70 (s), 5.40 (m), 5.75 (d, $\underline{J}$ = 15.5 Hz), 6.95 (d,

$\underline{J}$ = 15.5 Hz), 7.50 (m); IR (CCl_4) 3080 w, 3020 w, 2010 w, 2980 s, 2950 m, 2920 m, 2880 m, 1485 mw, 1470 m, 1370 ms, 1350 w, 1315 mw, 1305 mw, 1290 mw, 1270 w, 1260 w, 1240 mw, 1040 w, 980 s, 950 w, 940 mw, 910 w, and 880 ms cm^{-1}; m/e 210.11834 (calculated for $C_{13}H_{19}Cl$: 210.11753). In addition, GC-MS of the crude mixture showed a peak of M = 234, possibly $C_{15}H_{22}O_2$ corresponding to the vinyl norbornenyl ester.

9. Carbonylation of compound 4 (Table I, Entry 5)

0.3192 Grams (1 mmole) compound 4 was weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen and cooling to -78°C, 10 ml methanol was added by syringe. After flushing with carbon monoxide, a balloon containing carbon monoxide was attached to the gas inlet tube and the reaction warmed to room temperature slowly. After 24 hours at room temperature, GLPC analysis indicated no product was formed. Upon refluxing, GLPC analysis indicated one product was formed which continuously increased in size for approximately 48 hours. After this time the palladium coagulated as a small black clump in a nearly colorless solution. Previously it had been an opaque black solution. The reaction was filtered to remove the palladium. The methanol was removed by distillation and the oil remaining purified by preparative gas chromatography (1/4" x 10' 10% DC-550 at 225°C). Since the initial oil still contained methanol and material was lost during preparative GLPC, the yield was not obtained. The spectral data includes: ^1H nmr ($CDCl_3$) $\delta 0.95$ (9H, s, $-C(CH_3)_3$), 1.0-1.75 (6H, m, norbornyl), 1.85-2.10 (2H, m, bridgehead), 2.5 (2H, m, endo norbornyl near the vinyl and ester moieties), 3.55 (3H, s, $-OCH_3$), 5.05 (1H, ddd, $\underline{J}$ = 15 Hz, $\underline{J}$ = 7 Hz, $\underline{J}$ = 1 Hz, internal vinyl), 5.45 (1H, d, $\underline{J}$ = 15 Hz, external vinyl). The gradual addition of $Eu(fod)_3$ enabled observation of the coupling constant of the endo cis hydrogens, $\underline{J}$ = 10 Hz, and clarified the appearance of the trans vinyl hydrogens (Figure 3); IR (CCl_4) 3030 w, 2980 vs, 2950 ms, 2910 m, 2890 s, 1740 vs, 1480 m, 1465 m, 1440 s, 1400 w, 1375 s, 1355 w, 1310 m, 1290 m, 1250 mw, 1220 mw, 1220 s, 1185 m, 1175 s, 1155 s, 1125 ms, 1045 m, 975 m, 945 w, 915 vw, and 810 w cm^{-1}; m/e 236.17967 (calculated for $C_{15}H_{24}O_2$: 236.17764). (Table I, Entry 3) was carbonylated and purified in a similar manner: ^1H nmr spectrum not obtained, solution too dilute; IR (CCl_4) 3040 w, 2980 ms, 2970 ms, 2960 ms, 2880 mw, 1740 vs, 1640 w, 1510 w, 1470 w, 1435 mw, 1420 w, 1360 mw, 1300 w, 1280 w, 1240 w, 1220 mw, 1190 ms, 1170 ms, 1150 s, 1115 mw, 1040-1030 mw, 1000 mw, 950 ms, and 870 w cm^{-1}; m/e 180.11526 (calculated for $C_{11}H_{16}O_2$: 180.11503).

10. Carbonylation of compound **11**

0.3171 Grams (1 mmole) compound **11** was weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and a magnetic stirring bar. After flushing with nitrogen and cooling to -78°C, 10 ml methanol was added by syringe. After flushing with carbon monoxide, a balloon containing carbon monoxide was attached to the gas inlet tube and the reaction warmed to room temperature slowly. After 24 hours at room temperature, GLPC analysis indicated product formation had occurred. It was also observed that the previously opaque black solution was now colorless with the palladium coagulated in a small black clump. The reaction was filtered to remove the palladium, the methanol removed by distillation, and the remaining oil purified by preparative gas chromatography. Since the initial oil still contained methanol and material was lost during preparative GLPC, the yield was not determined. The spectral data includes: ^{1}H nmr ($CDCl_3$) δ0.9-1.25 (3H, m, nortricyclyl), 1.0 (9H, s, $-C(CH_3)_3$), 1.55 (2H, m, nortricyclyl), 2.00 (2H, m, nortricyclyl), 2.25 (2H, m, hydrogen adjacent to ketone and ester), 2.50 (1H, m, hydrogen on carbon adjacent to ketone and cyclopropane), 3.33 (3H, s, $COOCH_3$); IR (CCl_4) 3070 w, 2995 m, 2970 s, 2950 s, 2920 w, 2880 s, 2845 mw, 1780 vs, 1740 ms, 1480 ms, 1470 ms, 1405 mw, 1375 ms, 1350 ms, 1330 mw, 1320 mw, 1310 mw, 1285 mw, 1275 mw, 1270 mw, 1255 mw, 1240 mw, 1230 mw, 1210 mw, 1200 mw, 1185 ms, 1180 ms, 1160 ms, 1130 mw, 1120 ms, 1080 w, 1070 m, 1060 ms, 1040 ms, 1010 m, 980 mw, 957 mw, 960 ms, 950 w, 940 w, 935 m, 910 w, 890 w and 860 w cm^{-1}; m/e 262.15909 (calculated for $C_{16}H_{23}O_3$: 262.15689).

11. Reduction of compound 4 with sodium borohydride

0.3192 Grams (1.0 mmole) compound 4 was weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 10 ml 2-propanol was added by syringe and the flask subsequently cooled in an ice bath. While backflushing with nitrogen, 0.0370 grams (1.0 mmole) $NaBH_4$ was added all at once and the reaction mixture immediately turned black. It was slowly warmed to room temperature and stirred overnight. GLPC analysis indicated two large peaks with the first peak smaller than (approximately one-fourth the size of) the second peak. On a 1/4" x 10' 10% DC-550 column at 140°C, both peaks have shorter retention times than *n*-tridecane. Alternatively, a 1/4" x 10' 10% SE-30 column at 140°C may also be employed with *n*-tridecane as an internal standard.

The same reaction with THF as the solvent in place of 2-propanol turned black a little slower (within 15 minutes), in place of the instantaneous color change previously observed. GLPC analysis indicated the same 2 large peaks, but the first peak was now larger than (approximately twice the size of) the second. The superimposability of the first peak with that observed in the reactions of sodium methoxide in methanol and methyl-, vinyl- or n-butyl lithium in HMPA suggests the first peak is 2-[trans-3,3-dimethyl-1-butenyl]norbornane.

12. Attempted alkylations of compound 4 with organolithium reagents

The alkylation procedure with vinyl lithium described below is representative of the reaction with methyl lithium or n-butyl lithium also in HMPA. 0.3192 Grams (1.0 mmole) compound 4 was weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet tube and magnetic stirring bar. After flushing with nitrogen, 10 ml HMPA was added by syringe and the flask cooled in an ice bath. 0.84 Ml (1.0 mmole) 1.2 M vinyl lithium was also added by syringe, at which time the reaction mixture immediately turned black. After slowly warming to room temperature, the reaction was stirred an additional 16 hours at room temperature. GLPC analysis of the crude mixture showed one major peak with a retention time identical to the first peak of the previously described sodium borohydride reactions. Upon extraction of the reaction mixture with pentane, washing the pentane extracts with saturated ammonium chloride solution, drying (anhydrous Na_2SO_4) and evaporation of the solvent, an oil was produced which was purified by preparative GLPC. The GC-MS analysis of this compound (M^+= 178) indicated it was the reduced species, 2-[trans-3,3-dimethyl-1-butenyl]norbornane. The same product [observed m/e = 178.16924, calculated for $C_{13}H_{22}$= 178.17216] was observed in the reaction of compound 4 and methyl lithium under similar reaction conditions. (That experiment was performed by M. A. Mitchell). The product peak in the GLPC analysis of a similar reaction between compound 4 and n-butyl lithium also possessed the same retention time as the reduced product.

13. The successful vinylation of compound 4 with 2 equivalents vinyl lithium and 2 equivalents triphenylphosphine

0.1596 Grams (0.5 mmoles) compound 4 and 0.2623 grams (1.0 mmoles) triphenylphosphine were weighed into a 25 ml round bottom flask equipped with a septum inlet, gas inlet and magnetic stirring bar. After flushing with nitrogen, 5 ml THF was added and the reaction mixture stirred at room temperature one hour. After cooling the flask in an ice bath, 0.84 ml (1.0 mmole) vinyl lithium was added by syringe. Immediately, the reaction mixture turned from yellow to dark orange. After slowly warming to room temperature, the reaction was stirred an additional 16 hours at room temperature. Following filtration to remove the palladium(0), water and pentane were added to the reaction mixture, the layers separated and the pentane extracts washed with saturated sodium chloride solution, dried (anhydrous Na_2SO_4) and concentrated leaving an oily residue. GLPC analysis of the pentane solution indicated the major peak possessed a longer retention time than the previously observed reduced product, 2-[3,3-dimethyl-1-butenyl]norbornane. GC-MS analysis was consistent with the formation of the vinyl-substituted product, $M^+ = 204$, and a smaller amount of the reduced product, $M^+ = 178$.

14. Displacement of the palladium moiety in compound 4 with cyanide

0.2450 Grams (5 mmoles) sodium cyanide was weighed into a 25 ml round bottom flask equipped with a septum inlet, condenser with a gas inlet tube and a magnetic stirring bar. In one experiment, 0.2623 grams (1.0 mmole) triphenylphosphine was also weighed in at the beginning. After flushing with nitrogen, 2.5 ml THF and 2.5 ml water were added by syringe and the mixture stirred until the sodium cyanide dissolved and subsequently cooled in an ice bath. While backflushing with nitrogen, 0.1596 grams (0.5 mmoles) compound 4 was added all at once. The reaction mixture was allowed to warm to room temperature slowly and was then stirred overnight at room temperature. Both reactions were still slightly cloudy but nearly colorless solutions, so the reactions were heated at reflux for 2 days. Despite the lack of a visible change in appearance, the reactions were extracted with pentane, the pentane extracts washed with saturated ammonium chloride solution, dried (anhydrous Na_2SO_4)

and concentrated. GLPC analysis indicated the presence of a new peak. A crude mass spectrum of this peak yielded an odd numbered mass which is consistent with the presence of nitrogen and might possibly suggest that the nitrile was formed. However, this result requires further verification.

15. Attempted "Heck" type insertion of olefins into compound 4

The procedure used with vinyl acetate is representative. 0.1596 Grams compound 4 was weighed into a 25 ml round bottom flask equipped with a septum inlet, a gas inlet tube and a magnetic stirring bar. After flushing with nitrogen, 5 ml vinyl acetate was added by syringe and the reaction allowed to stir at room temperature. After 24 hours, the crude solution was GLPC analyzed directly. A peak with a retention time longer than the reduction product was observed, but not further characterized.

III. CONCLUSION

In Part I of this thesis the transmetalation of an organomercury compound with various rhodium(III) species formed diorganorhodium(III) species which reductively eliminate forming new carbon-carbon bonds. In addition to the already known rhodium catalyzed diene and biaryl formations and diaryl ketone formation, a facile rhodium catalyzed divinyl ketone synthesis from vinylmercurials has been presented. While the vinyl-aryl coupling of vinyl bromide and arylmercurials is successful with catalytic amounts of Wilkinson's catalyst, the investigated methyl-vinyl and methyl-aryl couplings were stoichiometrically successful, but catalytically unsuccessful.

The transmetalation of an organomercurial with another transition metal salt was also important in Part II of this thesis. Transmetalation of a vinylmercurial with dilithium tetrachloropalladate forms an organopalladium species which adds to norbornene and other bicyclic olefins forming stable vinyl alkylpalladium compounds similar to the previously reported addition of π-allyl- or phenylpalladium species. Since the addition is demonstrated to be highly stereospecific, with both the vinyl and palladium moieties being cis and exo, the vinyl alkylpalladium compounds which are formed are potentially attractive synthetic intermediates. The similarity of an appropriately substituted norbornane skeleton to prostaglandin endoperoxides suggests the synthesis of various prostaglandin endoperoxide analogs via known or proposed carbon-carbon bond formation and functionalizations involving the palladium moiety. Currently the many facets of this study are being pursued by Larock and other members of his research group. The development of new general methods of olefin, arene and ketone formation and the specific syntheses of a class of compounds potentially valuable as intermediates in the synthesis of prostaglandin endoperoxide analogs illustrate the versatility of organomercury, -rhodium and -palladium reagents in organic synthesis.

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