1994

Synthesis, reactions, and rearrangement of X(PEt3)2Pt[C(=PR)X] (X = Cl, Br; R = 2,4,6-tri-tert-butylphenyl), a synthetic precursor for bridged cyaphide, semi-bridged isocyaphide metal complexes

Hyoung Jun
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Jun, Hyoung, Ph.D.

Iowa State University, 1994

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by

Hyoung Jun

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For the Major Department

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For the Graduate College

Iowa State University
Ames, Iowa

1994

DEDICATION

To my wife

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GENERAL INTRODUCTION

Dissertation Organization

This dissertation contains two papers describing the research I performed at Iowa State University. Preceding these papers is a general introduction, which is a literature review of phosphaalkenes ($RP{=}CR_2$) and phophaalkynes ($R\text{-}C{\equiv}P$). This introduction mainly covers the syntheses, properties, and reaction chemistry of these compounds and their various coordination modes in transition metal complexes. In the introduction as well as in the papers, the literature citations, tables, figures, and schemes pertain only to the papers in which they appear. Following the final section is a general summary. References cited in the General Introduction are listed following the general Summary.

Introduction

The investigation of unstable and metastable compounds has played a key role in the development of many intriguing areas of modern chemistry. The recent emergence of the chemistry of doubly and triply bonded trivalent phosphorus is an illustrative example of this.[1] Over a comparatively short period, this field has developed from theoretical consideration of hypothetical structures and experimental studies of ephemeral or illusive molecules, to the synthesis of stable compounds containing phosphorus $p\pi$ multiple bonds.

In the early sixties, heavy nonmetallic elements such as phosphorus, silicon, and arsenic were found to violate the so-called double bond rule by forming compounds containing real $p\pi$ multiple bonds.[2] The first example of a compound exhibiting PC multiple bonds

was phosphaacetylene (H-C≡P),[3] which was prepared by Gier by passing PH_3 through an electric arc between graphite electrodes and is stable only below -120 °C. In the mid-seventies, Nixon et al. succeeded in obtaining a series of short-lived phosphaalkenes by eliminating hydrogen halides from alkyl halophosphines or (haloalkyl)phosphines.[4] At the same time, Becker reported the synthesis of the first stable acyclic compound containing a localized PC-double bond. This was accomplished by a silatropic movement from the phosphorus to the oxygen.[5] The first examples of stable phosphaalkynes were obtained five years later by Becker et al. also via the sodium hydroxide catalyzed β elimination of hexamethyldisiloxane from $(Me_3SiO)(t\text{-}Bu)C{=}P(SiMe_3)$.[6]

The above results appeared to be a substantiation of novel theoretical concepts developed in the mid-sixties and seventies. They were also further reflected in the three approaches used for the stabilization of the pπ-hybridized phosphorus state. Chronologically, the first approach is of thermodynamic origin and consists of stabilizing the $(p\text{-}p)_\pi$–bond by including it in a conjugated system. Stabilization of this type is observed in phosphamethine cyanine cations and phospha-benzenes.[7] The second approach aims at increasing overlap between the 3p-orbital of phosphorus and 2p-orbital of the other element at the expense of generating a positive charge on the phosphorus atom.[8] The third and most rewarding approach is the kinetic stabilization of the pπ-bond based on spatial screening effects imposed by the introduction of bulky substituents.[9]

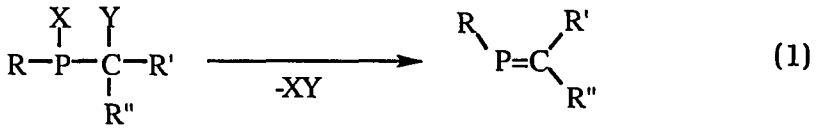
After the first review article of CP multiple bond compounds by Appel,[10] many other reviewers have added up-dated summaries of the progress in this area.[11] This review will focus mainly on the synthesis and reactions of phosphaalkenes and phosphaalkynes and their coordination modes in organometallic complexes.

Phosphaalkenes

Formation of PC double bond

The main routes to phosphaalkene formation will be categorized in three types of reactions, 1,2-elimination, condensation, and 1,3-trimethylsilyl migration.

1,2-Elimination Analogous to the chemistry of olefins, 1,2-elimination with suitable organyl phosphanes has proven useful. Molecules with substituents having inverse polarities give thermodynamically favored leaving molecules XY (eq 1). The formation of XY is

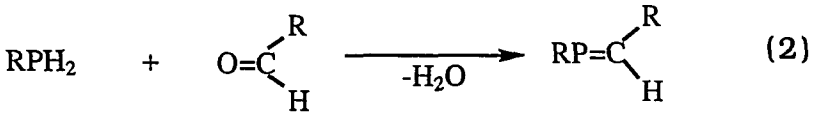


(1)

initiated thermally by bases or metals. Dehydrohalogenation from alkyhalophosphines (X = Cl, Y = H) is one of the most popular ways to generate PC double bonds by 1,2-elimination.[12] Alkyl halophosphines used in dehydrohalogenation should contain a sufficiently acidic α-proton and have substituents which provide kinetic or thermodynamic stabilization of the forming PC double bond. Thermally induced elimination of $SiMe_3X$ (X = Cl, $OSiMe_3$) from vicinal chloro- (or Me_3SiO-)

and trimethylsilyl-substituted phosphines also leads to phosphaalkenes in almost quantitative yield.[13]

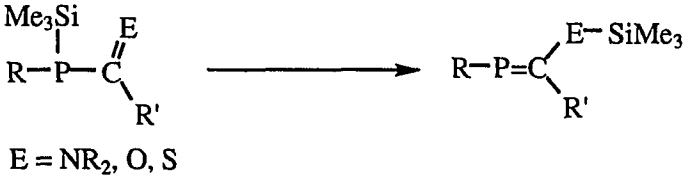
Condensation It is possible in many cases to create PC double bonds via condensations which result in the elimination of halosilane, siloxane,[14] or even water.[15] For example, formaldehyde or benzaldehyde reacts with 2,4,6-tri-*tert*-butylphenylphosphane, forming the phosphaalkene, when performed in the presence of dehydrating agents (P_4O_{10} or $CaO/CaCl_2$) (eq 2). This method is exceptionally favorable for



(2)

the synthesis of compounds that stabilize the PC double bond with ring formation as in 1,3-benzazaphospholes, 1,3-benzoxaphospholes, and 1,3-benzthiaphospholes.[16]

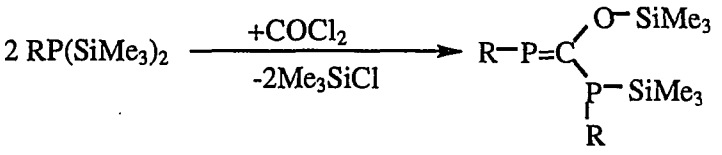
1,3-Trimethylsilyl Migration Another well-established process that is available for the preparation of PC double bonds is the migration of phosphorus-bonded silyl groups to an α-positioned, doubly-bonded element such as N, O, or S (eq 3). By this intra-molecular silatropic movement, which is energetically favored, the double bond is shifted to the phosphorus atom along with the formation of a stable bond



(3)

between silicon and the other element (N, O, or S).

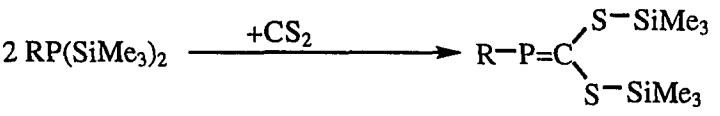
This method of synthesis can also be used in combination with the preceding condensation or addition reactions. Condensations followed by silyl migrations are achieved easily with carbon acid chlorides [RC(=O)Cl],[5] imid chlorides [RC(=NR')Cl],[17] and suitable derivatives of carbonic acid ($COCl_2$ or Cl_2C=NR).[18]



(4)

After the primary condensation to the corresponding silylacylphosphane, a fast, irreversible migration of the silyl group usually takes place, forming the phosphaalkene compound (eq 4).

The silatropic migration process can also be combined with an addition reaction of certain compounds to $RP(SiMe_3)_2$, including RN=C=NR,[19] CS_2,[20] and CO_2.[21] In this process, the first step, insertion into the P-Si bond, is followed by a silyl migration (eq 5).



(5)

Structure and proof of genuine pπ bonds

X-ray analysis of more than 50 different phosphaalkenes shows PC bond lengths ranging between 1.61 Å and 1.71 Å. The average value is 1.67 Å, in contrast to the single bond length of 1.85 Å. Moreover, two isomers (E and Z) have been observed by ^{31}P NMR and were identified by X-ray structure. The more stable E isomer of R-P=C(H)Ph (R = 2,4,6-tri-

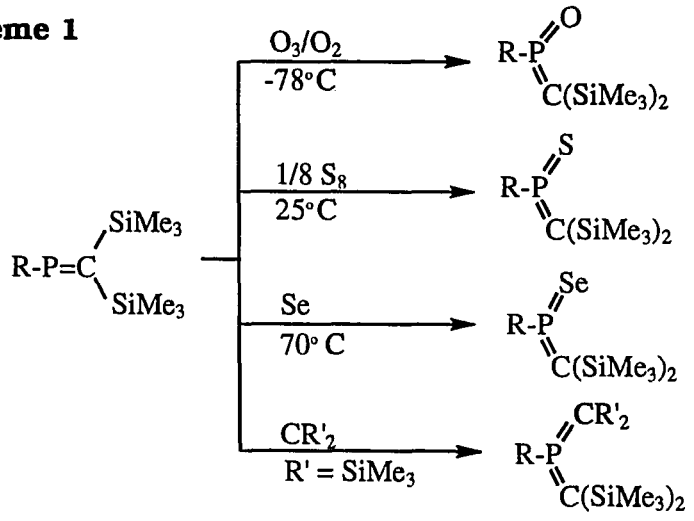
tert-butylphenyl)[22] melts at 148 °C, and the Z isomer melts at 84 °C. Also, in the ^{13}C NMR data, the sp^2-hybridized carbon produces characteristic shift values between 170 ppm and 210 ppm relative to TMS. In addition, the ^{31}P NMR signal of the sp^2-hybridized two coordinated P atom is typically shifted toward lower field (300 ppm - 200 ppm). A compilation of the ^{31}P NMR data is given in Ref.[23]

Reactivity

Phosphaalkenes have three different reactive centers, the (λ^3, σ^2) P atom, the π-bond, and the sp^2 carbon.

(λ^3, σ^2) P atom A reaction at the P atom can be realized with special phosphaalkenes using ozone, sulfur, selenium, or some carbenes (Scheme 1).[24] These reactions preserve the double bond and culminate

Scheme 1

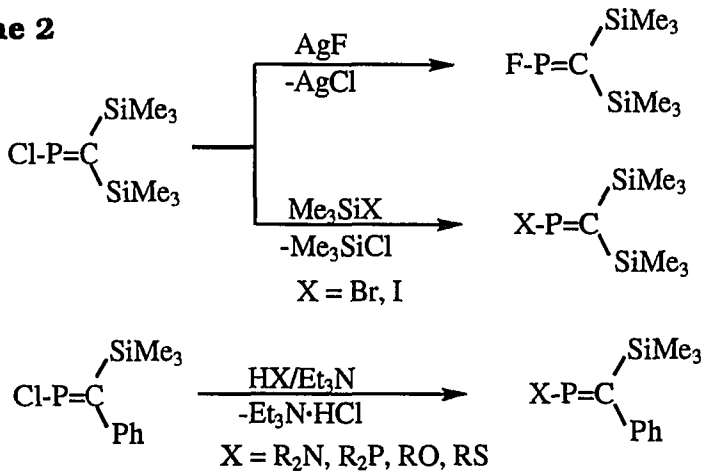


in an oxidative increase in the coordination of phosphorus.

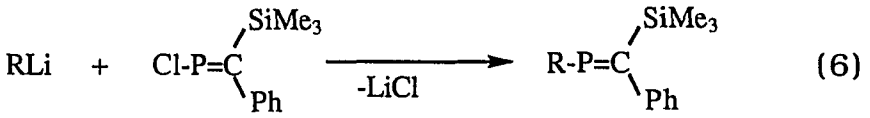
P-(halo)phosphaalkenes allow derivatization of the two coordinate phosphorus. For instance, with AgF[25a] or $AgBF_4$[25b], P-fluoromethylene-phosphines are obtained (Scheme 2). Substitution of the chlorine at the

two coordinate phosphorus atom in (Cl)P=C(SiMe$_3$)$_2$ by bromine and iodine is accomplished by using Me$_3$SiBr and Me$_3$SiI. These reactions proceed as readily as with chlorophosphines.[25a] The reactions of (Cl)P=C(SiMe$_3$)(Ph) with proton donor nucleophilic reagents illustrates the use of nucleophilic substitution for obtaining novel phosphaalkenes, such as the alkoxy-, alkylthio-, and phosphino-substituted compounds (Scheme 2).[25c]

Scheme 2



Despite the fact that organolithium and organomagnesium compounds show high nucleophilicity and add to the PC double bond, in some cases it is possible to realize the selective substitution of chlorine in P-chlorophosphaalkenes by alkyl and aryl groups (eq 6).[26]

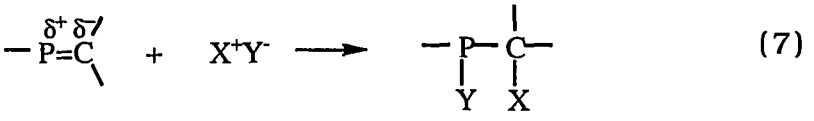


(6)

R = t-Bu, Ph, 4-tert-butylphenyl

π-Bond The second characteristic center of reactivity within phosphaalkenes is the (2p-3p)-π bond. The reactivity is more similar to

the C=C than to the corresponding C=N or P=N double bond. This is in accordance with the tendency of phosphaalkenes to have π-orbitals as their highest occupied molecular orbital energy levels as in olefins. The olefinic character is also demonstrated by the lower polarity of the P-C bond in comparison with the C-N or P-N bond. In these compounds the carbon atom is mostly negative and the phosphorus is mostly positive. Therefore, the direction of addition of highly polar reagents (hydrogen halides, alcohols, or amines) towards P=C versus N=C bonds is generally opposite (eq 7).



(7)

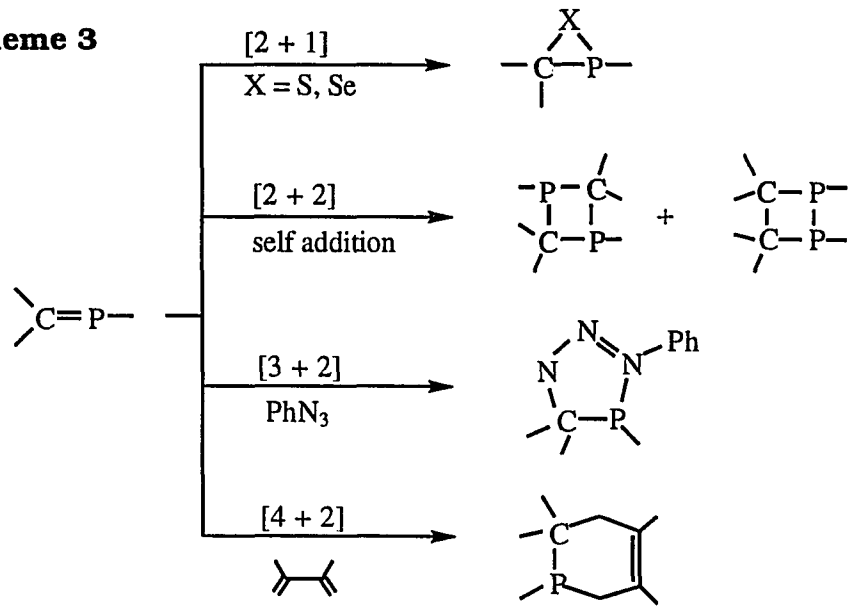
The similarity between olefins and phosphaalkenes can also be demonstrated by quite a number of [2 + n] cycloadditions (Scheme 3). However, under certain conditions, the simple phosphaalkenes containing poorly stabilized P=C double bonds are oligomerized by [2+2] cycloaddition, whereas simple olefins do not cyclodimerize. The reason for the abnormal behaviour of phosphaalkenes lies in the stepwise character of their cyclodimerization reactions which presumably involve ionic or biradical intermediates.

Reactions of phosphaalkenes with sulfur or selenium proceed predominantly via oxidation of the phosphorus atom to the corresponding methylenethio- or methyleneselenooxophosphoranes, which to some extent can be transferred to the λ^5-thiaphosphiranes with sulfur.[24c] On the contrary, phosphaalkenes containing π-donor substituents react with

sulfur or selenium, forming 1,2-λ^3-thiaphosphirane or 1,2-λ^3-selenium phosphirane, respectively, via a [2+1] cycloaddition.[27]

[2+2]-Cycloaddition of phosphaalkenes results in the formation of 1,3-diphosphetanes (head-to-tail dimerization) or 1,2-diphosphetanes (head-to-head dimerization). In most cases, phosphaalkenes undergo head-to-tail cyclodimerization. However, phosphaalkenes containing bulky substituents at the phosphorus and small substituents at the carbon atom will usually lead to head-to-head dimerization.[28]

Scheme 3



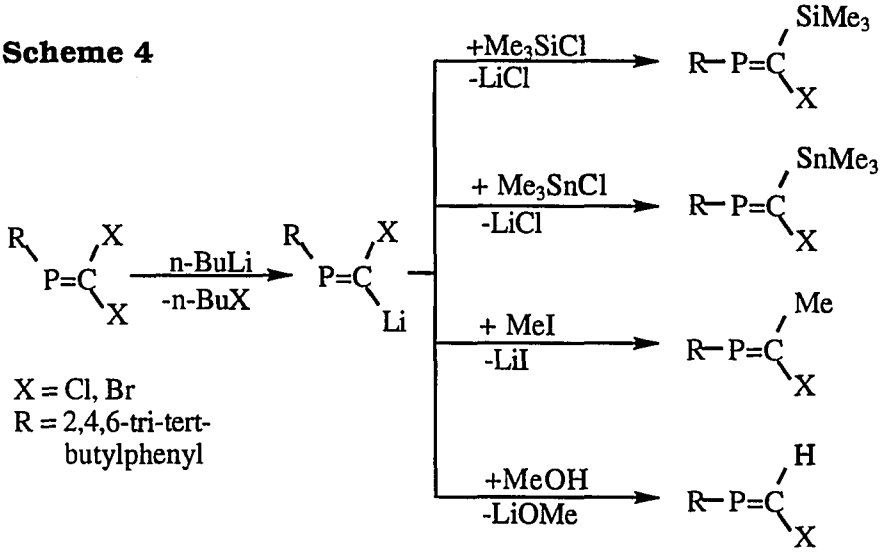
The formation of five-membered rings via addition to an open-chained phosphaalkene takes place with a number of 1,3-dipolar reagents (PhN_3, Ph_2CN_2, and Mes-C=N-O).[29]

Significant attention was paid to the study of [4+2] cycloaddition (Diels-Alder) reactions with the participation of PC double bonds. The P=C bond reacts mainly as the dienophile.[30] 2,3-Dimethylbutadiene,

cyclopentadiene, and orthoquinones are used as diene components. These [4+2] cycloadditions generally proceed at much lower temperatures than analogous C=C systems, indicating a drastic reduction of the energy of activation, which has been observed and calculated for other electrocyclic reactions of the PC double bond.

***sp*^{2} carbon** Inspite of the impressive developments in phophaalkene chemistry, there are certain aspects which have so far received less attention. Very few reactions have been done with the relatively electron rich sp^2 carbon atom. One route that has received some attention is the reaction of phosphaalkenes which are halogenated at the carbon atom. Substitution of the halogens by other groups has produced new functionalized phosphaalkenes (Scheme 4).

Scheme 4



Appel et al.[31] have described this halogen-metal exchange and the subsequent derivatization of X_2C=P-R (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl). In this study, they also observed an interesting conversion

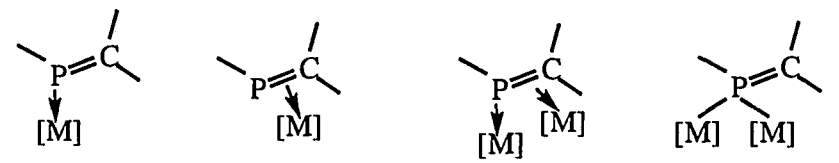
of the lithiated phosphaalkene [(Li)(Cl)C=P-R)] to the phosphaalkyne (R-C≡P) by warming the lithiated phosphaalkene by itself (eq 8). Although

(8)

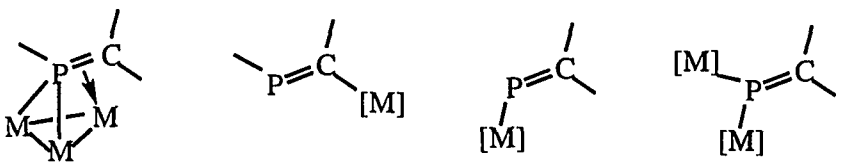
they did not observe any intermediates during this conversion, they proposed C≡P-R, a phosphorus analog of C≡N-R, as a transient intermediate.

Phosphaalkene transition metal complexes

Compounds with PC-double bonds can react with transition metal derivatives to form various complexes.[32] The most significant ones are represented by structures **A-H** . Both ab initio STO/3G calculations[33] and photoelectron spectroscopic results on phosphaalkenes indicate that the σ phosphorus lone pair and the π-orbitals are very close in energy.



A **B** **C** **D**

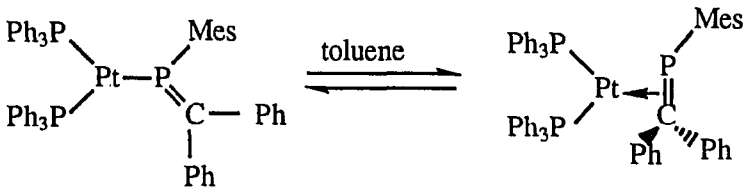


E **F** **G** **H**

It is also agreed that in the parent compound $H_2C{=}PH$, the π-orbital is probably the HOMO, and the π^*-orbital is probably the LUMO. Clearly, the quasi-degeneracy of the σ- and π-type orbitals is likely to be affected in substituted phosphaalkenes. Likewise the energy differences between η^1- and η^2-ligating modes in transition metal phosphaalkene complexes might be expected to be rather small, and in favorable cases $\eta^1 \longleftrightarrow \eta^2$ interconversion is possible.

The η^1-mode of coordination (type **A**) was the first type of coordination of phosphaalkenes. This was reported by Kroto and Nixon[34] and Bickelhaupt et al.[35] utilizing the stable all-alkyl-substituted phosphaalkene $Ph_2C{=}P(Mes)$ (Mes = mesityl). This mode of coordination was established for Cr(0), W(0), Rh(0), Pt(II), Ni(0), and Fe(0). The majority of η^1-phosphaalkene complexes were derived via ligand exchange reactions.

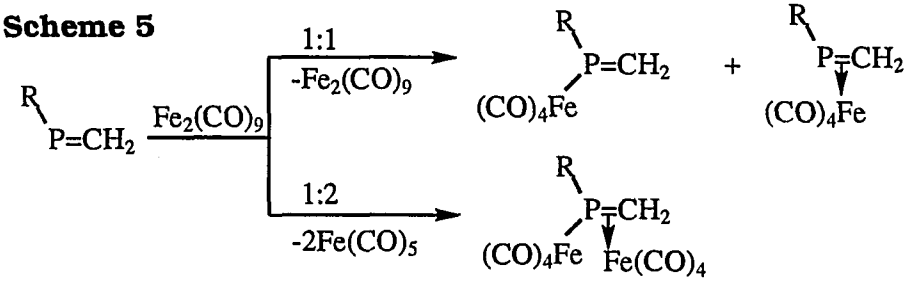
The η^2-mode of coordination (type **B**) is known for several Ni(0), Rh(0), and Pt(0) compounds. Pt(0) complexes of phosphaalkenes can be η^1- or η^2-ligated, depending on the other ligands present. A particularly interesting example is $(PPh_3)_2Pt[P(Mes){=}CPh_2]$, which is η^1 in the solid state as evidenced by a single crystal X-ray structural determination but η^2 in solution, where the characteristically low value of $^1J_{PtP(alkene)}$ (505 Hz) was diagnostic of the side-bonded phosphaalkene.[36]



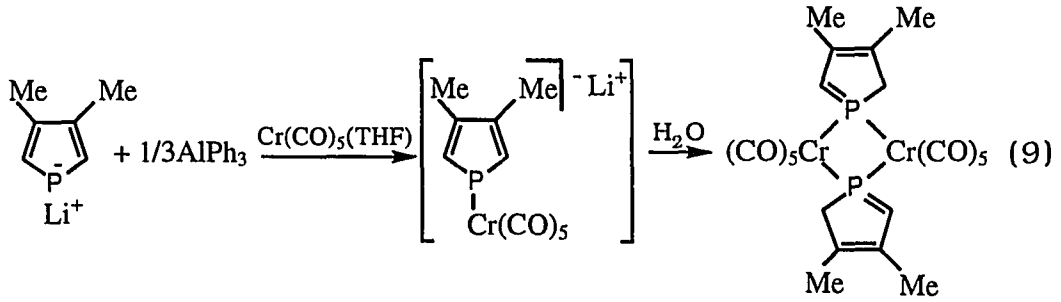
It is interesting to note that the P-C bond is substantially lengthened by the η^2 coordination (from ca. 1.69 to 1.83 Å) whereas in η^1-complexes the P-C bond is comparable (slightly shorter) with that of the free phosphaalkene.

The coordination mode of type **C** has been established by Mathey et al..[37] More recently, Appel and co-workers[38] have obtained the novel η^1,η^2-complex $[[Fe(CO)_4]_2(RP{=}CH_2)]$ (R = 2,4,6-tri-*tert*-butylphenyl) (Scheme 5). Interestingly, treatment of $[Fe_2(CO)_9]$ with 1 equiv of $RP{=}CH_2$ gives a mixture of the η^1 and η^2 $[Fe(CO)_4]$ complexes.

Scheme 5

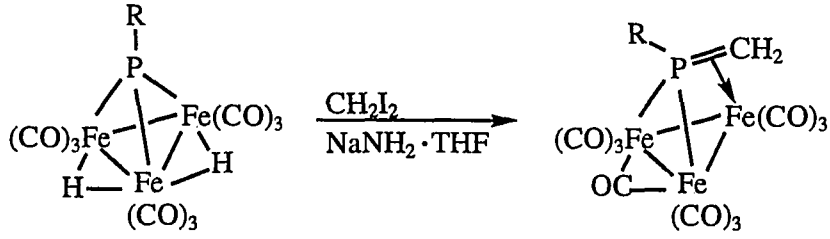


Mathey et al.[37] also described the first and only example of type **D** coordination in a 2*H*-phosphole complex obtained in the reaction sequence shown below (eq 9).



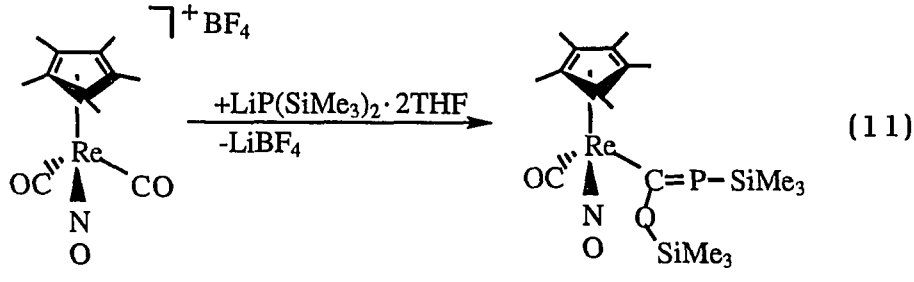
(9)

Huttner et al.[39] have reported the stabilization of the phospha-alkene $RP{=}CH_2$ as an η^2-(μ_3) bridging ligand (type **E**). Thus, twofold deprotonation of the triiron cluster $[Fe_3(CO)_9(\mu_3\text{-}PR)(\mu_2\text{-}H)_2]$ followed by treatment with CH_2I_2 gave the neutral phosphaalkene complex, in which one of the P-Fe bonds is bridged by a CH_2 group (eq 10).



(10)

Alternatively, phosphaalkenes can be substituted by transition metals (type **F**) instead of organic groups. Weber et al.[40] have reported the synthesis of (E)-$(\eta^5\text{-}C_5Me_5)(CO)(NO)Re[C(=PSiMe_3)OSiMe_3]$ by using $[(\eta^5\text{-}C_5Me_5)(CO)_2(NO)Re]BF_4$ and $LiP(SiMe_3)_2{\cdot}2THF$ via 1,3-silatropic



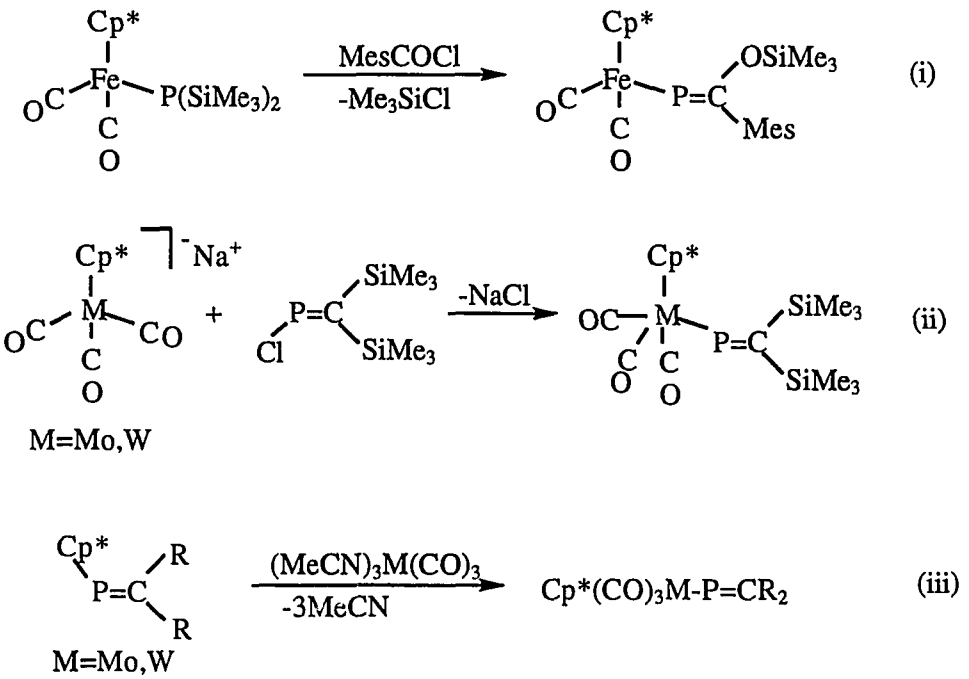
(11)

movement (eq 11). The C=P bond distances in these types of complexes(1.70 Å) are comparable with that of free phosphaalkenes (1.69 Å).

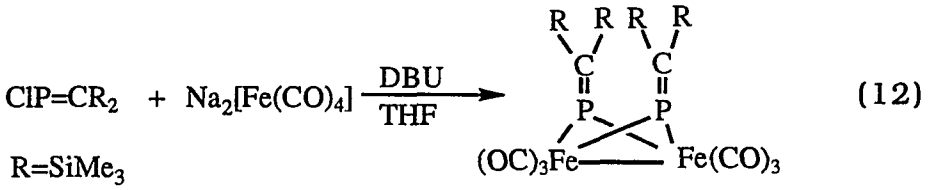
Another interesting coordination mode of phosphaalkenes is type **G**. At present, there are three main synthetic approaches to these

compounds: (i) formation of the PC-double bond in the coordination sphere of a transition metal via trimethylsilyl- or acylphosphido-complexes,[41] (ii) nucleophilic substitution of P-chlorophosphaalkenes with carbonylmetallate anions,[42] and (iii) rearrangement of complexes of Cp*-substituted phosphaalkenes with transfer of the Cp*-ligand from phosphorus to a metal center (Scheme 6).[43]

Scheme 6



Finally, the reaction of a chloro-phosphaalkene with $Na_2[Fe(CO)_4]$ results in formation of the bridging phosphaalkenyl complex (type **H**), the structure of which was established by an X-ray study (eq 12).[44]



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Phosphaalkynes

Formation of PC triple bond.

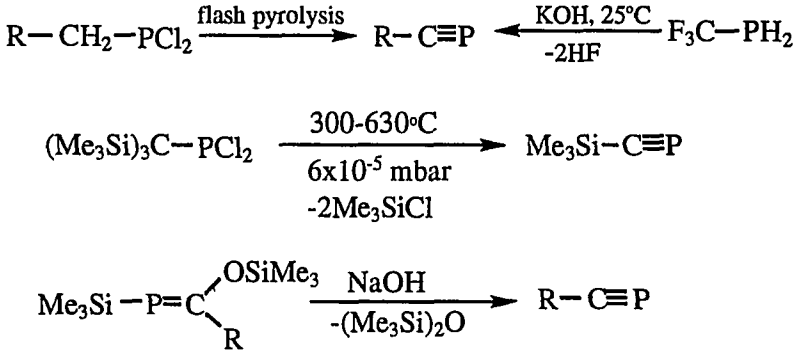
The main routes to phosphaalkyne formation will also be categorized in the two types of reactions, 1,2-elimination and 1,3-tri methylsilyl migration.

Elimination reactions The 1,2-elimination methodology has acquired the most significance for the construction of PC triple bonds. The thermal elimination of HCl plays a dominating role in the generation of the short lived phosphaalkynes whereas NaOH (or KOH) catalyzed elimination of hexamethyldisiloxane is used for the synthesis of the kinetically stabilized phosphaalkynes.

The simplest phosphaalkynes are produced by vapor phase pyrolysis of organohalophosphines[45] or low temperature dehydrohalogenation of haloalkylphosphines on the surface of strong bases such as NaOH (or KOH) (Scheme 7).[46] Owing to a high level of impurities and rather low thermal stability, the products of these reactions are nomally hard to obtain in their pure state. These were characterized by microwave, photoelectron, and NMR spectra. Thus, phosphaalkyne HC≡P obtained from flash vaccum thermolysis of CH_3PCl_2

followed by HCl removal is characterized by a 5 min half-life period at -10°C.[47]

Scheme 7

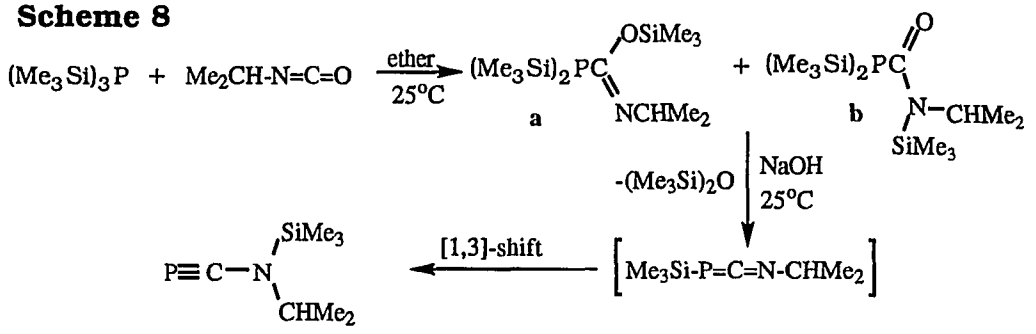


Successes in phosphaalkyne synthesis are associated with the application of elimination reactions involving stable compounds of two coordinate phosphorus. In 1981, Appel et al. established that thermally induced elimination of Me_3SiCl from the vicinal chloro- and trimethylsilyl-substituted phosphaalkenes led to phosphaalkynes in almost quantitative yield.[6]

Becker et al.[48] suggested the most significant route to phosphaalkynes by NaOH-promoted elimination of hexamethyldisiloxane from phosphaalkenes. This approach was applied successfully to the synthesis of a wide variety of stable phosphaalkynes.

Rearrangement reactions Phosphaalkynes can also be prepared by various rearrangement reactions. The decisive step in the preparation of a donor-substituted phosphaalkyne is the [1,3] shift of a trimethylsilyl group.[49] Reactions of this type are well known in carbodiimide

Scheme 8



chemistry. The starting materials are $(Me_3Si)_3P$ and isopropyl isocyanate, which react to form a tautomeric mixture of **a** and **b** (Scheme 8). The latter mixture is then subjected to the NaOH-catalyzed elimination of hexamethyldisiloxane.[50]

Physical properties

The two phosphaalkynes H-C≡P and ^{t}Bu-C≡P have been thoroughly investigated with regard to their general thermal behavior and spectroscopic properties as typical representatives of the short-lived and kinetically stabilized phosphaalkynes.[11]

Phosphaalkyne (HC≡P) is very reactive and pyrophoric; it is best handled in dilute solutions. It can be stored for longer periods of time in toluene solution at -70 °C. On allowing the solution to warm, white phosphorus, among other products, is formed. Under reduced pressure, HC≡P is even capable of existence at room temperature; its occurence in interstellar space has been confirmed.

In contrast, *tert*-butylphosphaacetylene (^{t}Bu-C≡P) is a stable liquid boiling at 61 °C. At temperatures higher than 130 °C, it undergoes slow cyclotetramerization. However, it is able to take part in reactions with

dienophiles at even higher temperatures. In comparison to HC≡P, the sensitivity of ^{t}Bu-C≡P toward oxygen is considerably less.

The ionization potentials of both of these phosphaalkynes are lower than those of the corresponding nitriles. This property is also reflected in the much more diverse ligand behavior of the phosphaalkynes compared with that of their nitrogen analogous. The C≡P stretching frequency of ^{t}Bu-C≡P is 1533 cm^{-1} [51] and that of HC≡P is 1559 cm^{-1}.[52] The C≡P distance in R-C≡P (R = 2,4,6-tri-*tert*-butylphenyl) of 1.516 (13) Å[53] which is determined by X-ray structural study, is comparable to that of ^{t}Bu-C≡P (1.536 (2) Å) and HC≡P (1.5421 (5) Å) which were determined by other methods. The ^{13}C NMR signals of the C≡P carbon are observed in the region 150-200 ppm with a wide range of PC coupling constants ($^{1}J_{PC}$ = 15-55 Hz). The ^{31}P NMR resonances are found in the high field region (-15~-70 ppm). But the presence of silyl and aryl substituents gives rise to paramagnetic shifts in the signals.

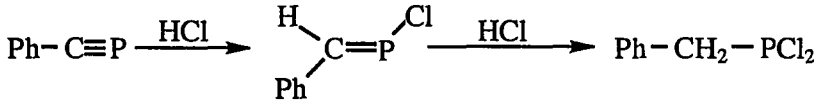
Reactivity

The reactivity of the PC triple bond is molded by its addition behavior. However, for synthetic purposes, the most interesting feature is the clean conversion of a λ^3 σ^1-phosphorus atom into a λ^3 σ^2-phosphorus atom which is achieved in [2+1]-, [2+3]-, and [2+4]-cycloaddition processes.

1,2-Addition reaction The ability of phosphaalkynes to undergo addition to hydrogen chloride accompanied the discovery of the compounds themselves. In the case of Ph-C≡P, an initial cis addition of HCl is assumed to be followed by a further addition of HCl in the same

orientation.[6] This specific orientation is followed without exception and reflects the charge distribution in the phosphaalkynes (eq 13).

The 1,2-addition of MeLi to arylphosphaalkynes also shows this same orientation. The lithiated phosphaalkene is the initial product of the 1:1 reaction with the expected orientation of the reaction partners and it can then be hydrolyzed (eq 14).[54]



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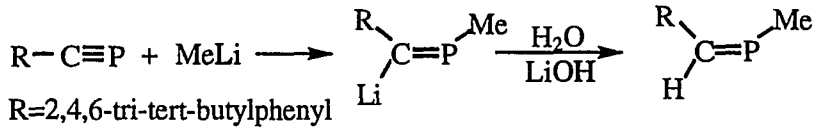

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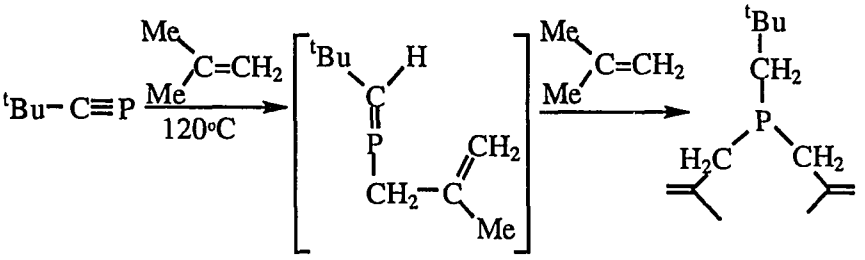


(15)

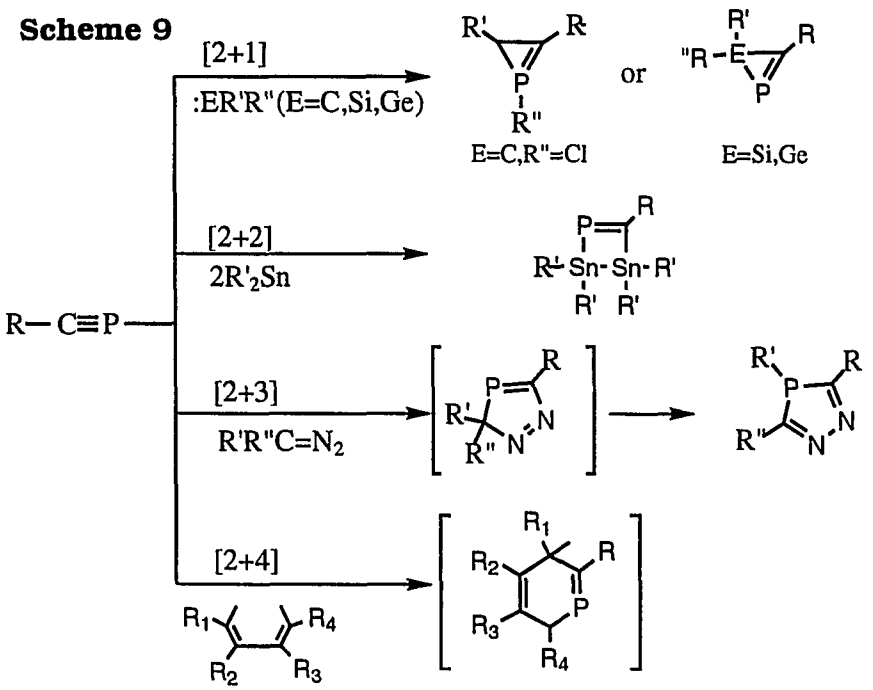
Ene reactions of phosphaalkynes require a remarkable thermal activation. The formation of the final product is most easily explained when it is assumed that the ene reaction of ^{t}Bu-C≡P to give an intermediate is followed by a further ene reaction of the intermediate with another molecule of isobutylene to produce the final product (eq 15).[55]

Cycloaddition reactions Phosphaalkynes show similar reactivity to that of phosphaalkenes in the [2+n] cycloaddition reactions with suitable reagents (Scheme 9).

The [2+1]-cycloaddition reactions between phosphaalkynes and the electron-deficient species carbene,[56] silylene,[57] and germylene,[58] provide a method of obtaining three-membered ring systems containing P=C units. Some of the products thus obtained are also capable of undergoing subsequent rearrangement reactions.

In contrast to the other [2+n] cycloaddition reactions of phosphaalkynes, very little is known about their [2+2] cycloadditions. When a stannylidene is allowed to react with a phosphaalkyne under moderate conditions, the phosphadistanna-cyclobutene is formed.[59]

Scheme 9

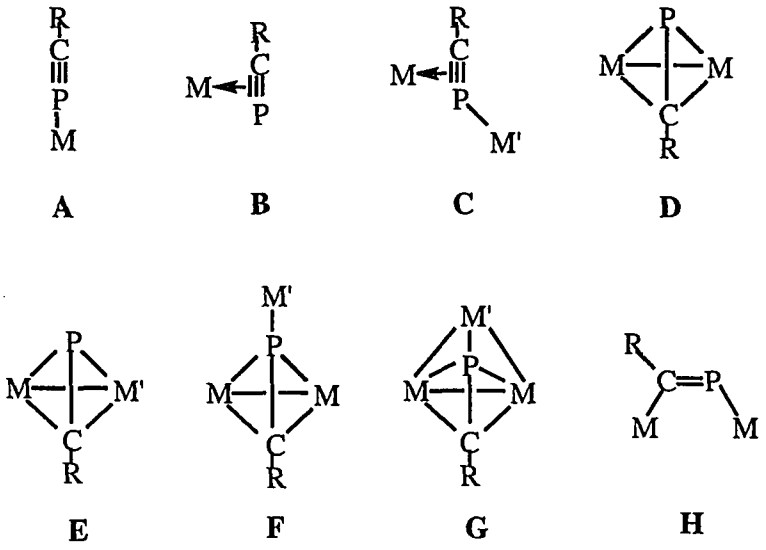


1,3-Dipolar cycloaddition reactions of diazonium (diazo or azide compounds) and nitrilium betaines to phosphaalkynes constitute a major extension of the synthetic methodology for phospholes. Azomethine dipoles also readily undergo addition to the PC triple bond. However, in contrast to the diazonium and nitrilium betaines which add regiospecifically to phosphaalkynes, the formation of regioisomeric heterocyclic products is observed in the reactions with the azomethine dipoles.[60]

The particular fascination with the Diels-Alder reactions of phosphaalkynes is the specific transformation of $\lambda^3\sigma^1$-phosphorus atoms into $\lambda^3\sigma^2$-phosphorus atoms. This provides a method for the construction of 1-phospha-1-cycloalkenes. In general, [4+2]-cycloaddition reactions with 1,3-dienes require an extremely high thermal activation. The reactions with antiaromatic compounds, however, provide the only known exception to this rule.[61]

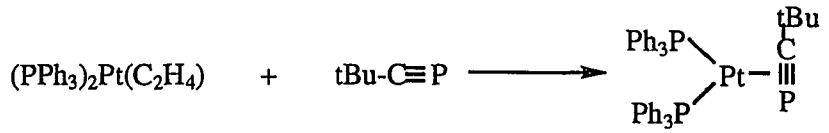
Phosphaalkyne transition metal complexes

Compounds with PC-triple bonds can also form transition metal complexes.[32] Photoelectron spectroscopic studies on a series of phosphaalkynes indicated that the HOMO is of the π-type and the π-n separation is greater than in the corresponding nitrile, indicating that side-on coordination of the R-C≡P ligand should be preferred to P ligation. In mono- and dinuclear metal systems, the following ligation modes are expected, and examples have subsequently been established. Although the alkyne-like behavior of phosphaalkynes dominates their coordination chemistry, the first example of a η^1-bonded phospha-



alkyne metal complex (type **A**) has been reported by Nixon et al.[62] A series of complexes has been obtained by displacement of dinitrogen from *trans*-$M(N_2)_2(R'_2PCH_2CH_2PR'_2)_2$ (M = Mo, W) complexes. In these complexes, only ligands that are long and thin can approach the metal and bind in the axial positions.

η^2-Complexes of type **B** were first reported by Nixon et al.[63] The molecular structure of $(PPh_3)_2Pt(^tBuC{\equiv}P)$, which was determined by an X-ray diffraction study, confirms the η^2-bonding mode and reveals that the P-C bond is considerably lengthened on coordination, consistent with the population of π^* orbitals. This complex is also noteworthy in that the one-bond Pt-P coupling constant ($J_{PtP(in\ CP)}$ = 62 Hz) is the smallest so far recorded, reflecting the low s character of the Pt-P bond (eq 16).



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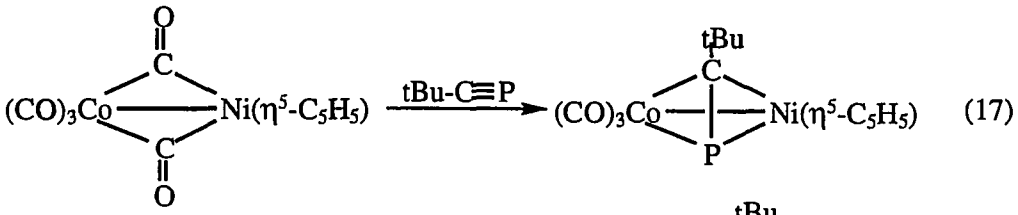

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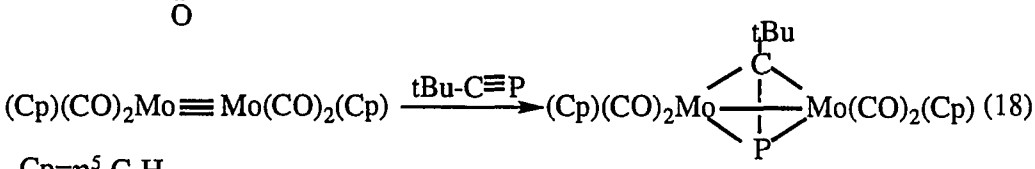
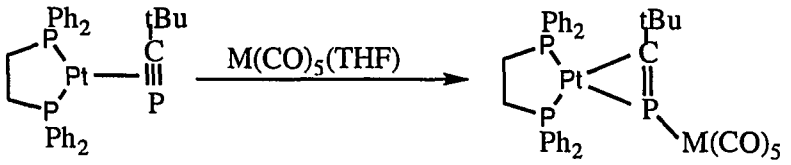


(18)

Cp=η^5-C_5H_5

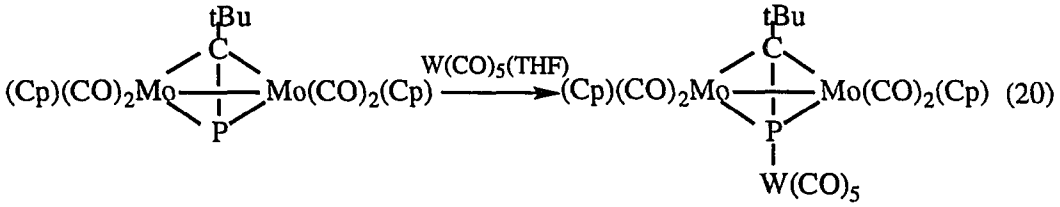
Complexes of types **D** and **E** containing a tetrahedrane structure have been made by analogous reactions to those for alkynes, namely by i) treatment with [$Co_2(CO)_8$] or [$CoNi(CO)_5(\eta^5$-$C_5H_5)$] (eq 17) or ii) via addition across metal-metal multiple bonds (eq 18).[64]

Unlike the analogous alkyne derivatives, complexes of type **B**, **D**, and **E** have further ligating potential by virtue of the availability of the lone pair of electrons at phosphorus.



(19)

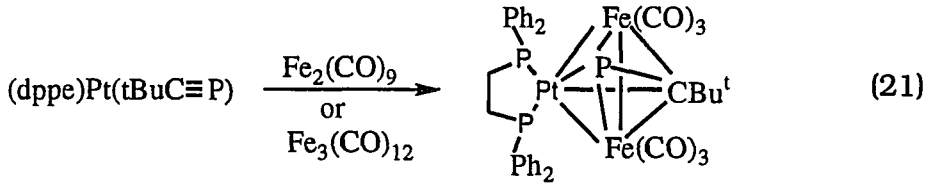
M = Cr, Mo, W



(20)

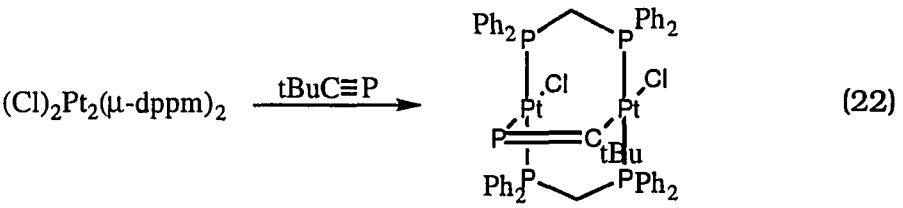
Thus, complexes of type **C** and **F** result from further interaction with other metal centers (eq 19 and 20).[65]

A further type of trimetallic phosphaalkyne complex (type **G**) in which the R-C≡P fragment transversely bridges an M-M bond to afford a μ3-(η2- ⊥) ligating mode has been described.[66] The complex $Fe_2Pt(dppe)(CO)_6(^tBuC{\equiv}P)$ is formed quantitatively from $(dppe)Pt(^tBuC{\equiv}P)$ and either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ (eq 21).



(21)

Recently, Nixon et al.[67] reported an interesting coordination mode of R-C≡P (Type **H**) in the dinuclear metal complex $(Cl)_2Pt(\mu\text{-}dppm)_2(\mu\text{-}tBuC{\equiv}P)$, which shows a μ-parallel bonding instead of μ-perpendicular bonding of phosphaalkyne to the dimetallic center (eq 22).



(22)

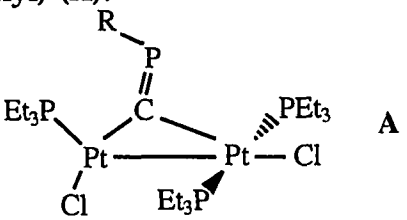
PAPER I. SYNTHESIS, REACTIONS, AND REARRANGEMENT OF $X(PR'_3)_2M[C(=PR)X]$ (M = Pt, Pd; X = Cl, Br; R' = Et, Ph; R =2,4,6-tri-*tert*-butylphenyl): MECHANISM OF THE TRANSITION METAL PROMOTED CONVERSION OF $X_2C=PR$ TO R-C≡P

ABSTRACT

Oxidative addition reactions of $X_2C{=}PR$ (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) with $M(PEt_3)_4$ (M = Pt, Pd) or $(C_2H_4)Pt(PPh_3)_2$ initially yield the *cis* isomer of square planar $(X)(PR'_3)_2M[C(=PR)X]$ (**II**); these complexes (**IIa-IId**), where PR'_3 is PEt_3, rearrange rapidly in the presence of free PEt_3 to give the *trans* isomers (**Ia-Id**). In the contrast, the *cis* isomers (**IIe** and **IIf**), where PR'_3 is PPh_3 and M is Pt, react further to give R-C≡P and *cis*-$X_2Pt(PPh_3)_2$. In polar solvents (CH_2Cl_2 and $CHCl_3$), all the addition products (**I** and **II**) convert to R-C≡P and cis- or trans-$X_2M(PR'_3)_2$ via the surprising phosphabicyclo intermediate $(X)(PR'_3)_2Pt$(X-PBC) (**III** and **IV**); the structure **IIIa** was established crystallographically. In the presence of H_2O, $(X)(PEt_3)_2Pt[C(=PR)X]$ (**Ia** and **Ib** where X = Cl, Br) give the oxy-phosphabicyclo complex $(X)(PEt_3)_2Pt[(H)O{=}PBC]$ (**Va** and **Vb**) which was characterized by X-ray diffraction. A mechanism for the conversion of $(X)(PR'_3)_2M[C(=PR)X]$ to R-C≡P and $X_2M(PR'_3)_2$ is proposed.

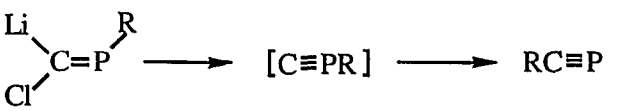
INTRODUCTION

After Gier[1] obtained the first experimental evidence for a compound with a P-C multiple bond in 1961, many stable phosphaalkyne (R-C≡P) and phosphaalkene (R-P=CR_2) compounds have been prepared and studied.[2] Despite the inherent reactivity of P≡C and P=C bonds, such compounds have been stabilized with bulky R-groups. However, there is still no evidence for phosphorus analogs, C≡P-R, of the well known aryl or alkyl isocyanides C≡N-R.[3] In fact, calculations indicate that C≡P-H is 85 kcal/mol less stable than the H-C≡P isomer.[4] Thus, it seems unlikely that free C≡P-R molecules can be prepared. However, we have reported[5] in a preliminary communication that an arylisocyaphide (C≡P-R) can be stabilized as a bridging ligand in (Cl)(PEt_3)Pt(μ-C=P-R)Pt(PEt_3)$_2$(Cl) (R = 2,4,6-tri-*tert*-butyl phenyl) (**A**).



A

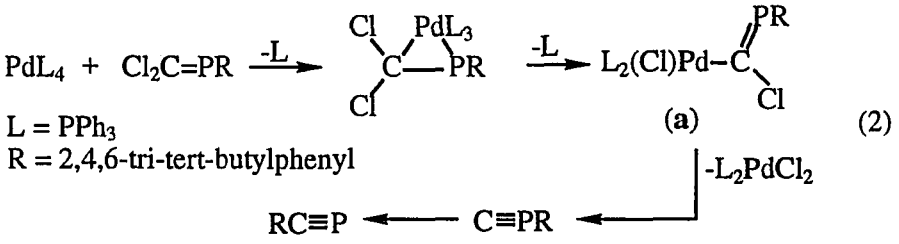
Free aryl isocyaphides (C≡P-R) have been proposed as intermediates in reactions of phosphaalkenes. Appel and co-workers[7] suggested that the formation of R-C≡P from (Li)(Cl)C=P-R proceeds by way of an undetected highly reactive C≡P-R[6] which rapidly rearranges to the R-C≡P product (eq 1). Other research groups[8] have also reported



(1)

in related systems reactions of the type in eq 1. Although no intermediates were observed in these reactions even at the low temperature (-78 °C),[9] C≡P-R was proposed as a transient intermediate.

Recently, Romanenko and co-workers[10] reported the reaction of $Pd(PPh_3)_4$ with $Cl_2C{=}PR$ which gives R-C≡P and $Pd(PPh_3)_2Cl_2$ in greater than 85% yield (eq 2). This reaction involves the overall dechlorination



(2)

of $Cl_2C{=}PR$ and migration of the supermesityl (R) group from the phosphorus to the carbon. While no intermediates were detected, they proposed (eq 2) that the reaction proceeds by way of initial oxidative addition across a C-Cl bond to give an intermediate (**a**) which is analogous to the complex $Cl(PEt_3)_2Pt[C(=PR)Cl]$ that we isolated previously[5] from the reaction of $Pt(PEt_3)_4$ with $Cl_2C{=}PR$. Then, L_2PdCl_2 is eliminated from this intermediate (**a**) to give the free arylisocyaphide C≡PR, which was proposed to rearrange to the R-C≡P product.[2a]

A reaction that is similar to the first steps in eq 2 is the three-fragment oxidative-addition of $Cl_2C{=}N{-}R$ to low valent metal complexes.[11] Such reactions give products with terminal isocyanide ligands, as in eq 3. Recently, we attempted to synthesize the phosphorus analog

$$Pt(PPh_3)_4 \xrightarrow{Cl_2C=NR} Cl_2Pt(PPh_3)(CNR) + Cl_2Pt(PPh_3)_2 \qquad (3)$$

R = 2,4,6-tri-tert-butylphenyl

$Cl_2Pt(PEt_3)(C{\equiv}P\text{-}R)$ of the product in eq 3 by reacting $Cl_2C{=}P\text{-}R$ (R = 2,4,6-tri-*tert*-butylphenyl) with $Pt(PEt_3)_4$.[5] From those trials, only the two-fragment oxidative-addition product $Cl(PEt_3)_2Pt[C(=PR)Cl]$ was obtained. While we were able to convert this to $(Cl)(PEt_3)Pt(\mu\text{-}C{=}P\text{-}R)Pt(PEt_3)_2(Cl)$ (**A**) with a semi-bridging C=PR group, compounds with terminal $C{\equiv}P\text{-}R$ ligands have not yet been prepared.

In this paper, we report an expanded study of the syntheses and reactions of the compounds, $X(PR'_3)_2M[C(=PR)X]$ (M = Pt, Pd; X = Cl, Br; R'= Ph, Et; R = 2,4,6-tri-*tert*-butylphenyl). Also we describe the structure of an unusual intermediate formed in the conversion of $X(PR'_3)_2M[C(=PR)X]$ to $R\text{-}C{\equiv}P$ and $X_2M(PR'_3)_2$. Some of these results were reported in a communication.[12]

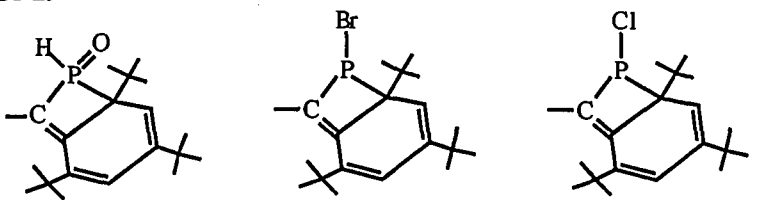
EXPERIMENTAL SECTION

General procedure

All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents under N_2. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while hexanes and dichloromethane (CH_2Cl_2) were distilled from CaH_2. Distilled water was used as solvent or reagent. Chromatography columns (ca. 30 cm in length and 1 cm in diameter) were packed with silica gel (Davisil 62, Davison Chemical).

The ^1H NMR spectra were recorded in C_6D_6 unless otherwise noted using a Nicolet-NT 300 MHz or Varian VXR-300 MHz spectrometer with TMS (δ =0.00 ppm) as the internal standard. The $^{31}P\{^1H\}$ and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer in C_6D_6 using 85% H_3PO_4 (δ=0.00 ppm) as the external standard. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN or Desert Analytics, Tucson, AZ. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. The complexes $(PPh_3)_2Pt(C_2H_4)$,[13] $Pt(PEt_3)_4$,[14] $Pd(PEt_3)_4$[15] and compounds $Cl_2C{=}PR$[16] and $Br_2C{=}PR$[17] were prepared by literature methods. The products, **Ia-Ic**, **IIa**, **IIIa** and **IIIb**, **Va** and **Vb**, and **VIe** are air stable for at least a month. The phosphabicyclo ligand abbreviations, Cl-PBC, Br-PBC, and (H)O=PBC in compounds **IIIa**, **IIIb**, **IVa**, **IVe**, **IVf**, **Va**, **Vb** and **VIe** are shown in Chart I.

Chart I.



(H)O=PBC **Br-PBC** **Cl-PBC**

Preparation of *trans*-(Cl)(PEt$_3$)$_2$Pt[C(=PR)Cl] (R=2,4,6-tri-*tert*-butylphenyl) (Ia).

Method A To a benzene solution (10 mL) of Pt(PEt$_3$)$_4$ (0.67 g, 1.0 mmol) was added a benzene solution (2 mL) of Cl$_2$C=PR (R = 2,4,6-tri-*tert*-butylphenyl) (0.36 g, 1.0 mmol). After the solution was stirred at room temperature for 1 h, the solvent was evaporated under vacuum to yield an oily yellow residue. The residue was extracted with hexanes (50 mL) and filtered by cannula. After reducing the extract to one-fourth of its volume under vacuum, pale yellow crystals of **Ia** were obtained by cooling the solution to -78 °C (0.67 g, 85%).

Method B A cold (-78 °C) THF solution of (Li)(Cl)C=P-R^7 was generated by adding a hexane solution of n-BuLi (0.500 mmol) to a THF solution (5 mL) of Cl$_2$C=P-R (0.180 g, 0.500 mmol) at -78 °C and then stirring the solution for 30 min at the same temperature. This solution was added over a period of 15 min to a cold (-78 °C) THF (5 mL) solution of *trans*-Cl$_2$Pt(PEt$_3$)$_2$ (0.251 g, 0.500 mmol). After 30 min stirring at -78 °C, the reaction mixture was slowly warmed to room temperature over a period of 2 h. In the reaction mixture, both isomers (**Ia** and **IIa**) were observed in the ^{31}P NMR spectrum. This mixture was evaporated to

dryness under vacuum; the residue was extracted into hexanes (30 mL) and the solution was filtered by cannula. This solution was reduced under vacuum to one-half its volume, whereupon **IIa** began to precipitate. Cooling to -30 °C yielded more **IIa**. An additional amount of **IIa** and **Ia** was isolated from the mother liquor by reducing the volume of the solution, cooling to -30 °C several times. The overall yields of **IIa** and **Ia** were 0.205 g (52%) and 0.142 g (36%) respectively. ^{1}H NMR (C_6D_6) δ 7.58 (s, 2H, R), 1.95 (m, 12H, CH_2 of Et),1.71 (s, 18H, CH_3 of R), 1.35 (s, 9H, CH_3 of R), 1.03 (m, 18H, CH_3 of Et). $^{31}P\{^{1}H\}$ NMR (C_6D_6, 85% H_3PO_4 external standard) δ 223.3 (t, $^{3}J_{PP}$ = 25.2 Hz, $^{2}J_{PtP}$ = 657.7 Hz, C=P-R), 15.0 (d, $^{3}J_{PP}$ = 25.2 Hz, $^{1}J_{PtP}$ = 2752.7 Hz, PEt_3). EIMS (70eV) m/e 790 (M^+), 755 (M^+- Cl), 733 (M^+- t-Bu), 698 (M^+- (Cl + t-Bu)). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pt$: C, 47.11; H, 7.46. Found: C, 47.54; H, 7.48.

Preparation of *trans*-(Br)(PEt_3)$_2$Pt[C(=PR)Br] (Ib)

Complex **Ib** was prepared by the same method (**A**) as described above using $Pt(PEt_3)_4$ (0.67 g, 1.0 mmol) and Br_2C=PR (0.45 g, 1.0 mmol). The product **Ib** was obtained as pale yellow crystals (0.49 g, 56%). ^{1}H NMR (C_6D_6) δ 7.50 (s, 2H, R), 2.00 (m, 12H, CH_2 of Et), 1.62 (s, 18H, CH_3 of R), 1.32 (s, 9H, CH_3 of R), 1.00 (m, 18H, CH_3 of Et). $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 234.2 (t, $^{3}J_{PP}$ = 25.2 Hz, $^{2}J_{PtP}$ = 661.2 Hz, C=P-R), 9.5 (d, $^{3}J_{PP}$ = 25.2 Hz, $^{1}J_{PtP}$ = 2712.3 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Br_2P_3Pt$: C, 42.35; H, 6.71. Found: C, 42.17; H, 6.83.

Preparation of *trans*-(Cl)(PEt$_3$)$_2$Pd[C(=PR)Cl] (Ic)

Complex **Ic** was prepared by **method A** used for compound **Ia**; the reactants were Pd(PEt$_3$)$_4$ (0.58 g, 1.0 mmol) and Cl$_2$C=PR (0.36 g, 1.0 mmol). The product **Ic** was obtained as pale yellow crystals (0.55 g, 78%). ^{1}H NMR (C$_6$D$_6$) δ 7.56 (s, 2H, R), 1.86 (m, 12H, CH$_2$ of Et), 1.69 (s, 18H, CH$_3$ of R), 1.34 (s, 9H, CH$_3$ of R), 1.05 (m, 18H, CH$_3$ of Et). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 227.6 (t, $^3J_{PP}$ = 42.7 Hz, C=PR), 16.1 (d, $^3J_{PP}$ = 42.7 Hz, PEt$_3$). Anal. Calcd for C$_{31}$H$_{59}$Cl$_2$P$_3$Pd: C, 53.07; H, 8.41. Found: C, 53.15; H, 8.51.

Conversion of *trans*-(Cl)(PEt$_3$)$_2$Pd[C(=PR)Cl] (Ic) to R-C≡P and *trans*-Cl$_2$Pd(PEt$_3$)$_2$

After complex **Ic** (0.070 g, 0.10 mmol) in 2 mL of dry CH$_2$Cl$_2$ was stirred at room temperature under argon for 24 h, the reaction solution was evaporated to dryness. The residue was extracted with hexanes (10 mL) and filtered through a short column of Celite. The crude products were separated by column chromatography (hexanes, silica) under argon atmosphere to give R-C≡P (0.019 g, 65%) and *trans*-Cl$_2$Pd(PEt$_3$)$_2$ (0.015 g, 36%). A ^{31}P{^{1}H} NMR spectrum of the reaction solution showed that these products were formed in essentially quantitative yield, and no intermediates were observed during the course of the reaction. R-C≡P[10] and *trans*-Cl$_2$Pd(PEt$_3$)$_2$[18b] were characterized by their NMR spectra. ^{1}H NMR (C$_6$D$_6$) for R-C≡P: δ 7.16 (d, $^4J_{PH}$ = 1.2 Hz, 2H, on R), 1.72 (s, 18H, CH$_3$ on R), 1.23 (s, 9H, CH$_3$ on R). ^{31}P{^{1}H} NMR (C$_6$D$_6$) for R-C≡P: δ 33.9 (s). *trans*-Cl$_2$Pd(PEt$_3$)$_2$: δ 17.5 (s).

Conversion of Br_2C=PR to R-C≡P through the intermediate *trans*-$(PEt_3)_2(Br)Pd[C(=PR)Br]$ (Id)

To a CH_2Cl_2 solution (2 mL) of $Pd(PEt_3)_4$ (0.058 g, 0.10 mmol) was added a CH_2Cl_2 solution (1.0 mL) of Br_2C=PR (0.045 g, 0.10 mmol). After the solution was stirred at room temperature for 6 h, the solvent was evaporated under vacuum. The resulting solid was purified by column chromatography (hexanes, silica) under argon atmosphere to give R-C≡P (0.016 g, 50%) and *trans*-$Br_2Pd(PEt_3)_2$ ^{18e} (0.018 g, 36%). As indicated by a $^{31}P\{^1H\}$ NMR spectrum of the reaction solution, these were the only products of the reaction and **Id** was the only intermediate. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) of **Id**: δ 243.0 (t, $^3J_{PP}$ = 41.2 Hz, C=P-R), 12.5 (d, $^3J_{PP}$ = 41.2 Hz, PEt_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) of *trans*-$Br_2Pd(PEt_3)_2$: δ 14.4 (s).

Preparation of *cis*-$(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (IIa)

To a cold (-50 °C) hexanes (10 mL) solution of $Pt(PEt_3)_4$ (0.67 g, 1.0 mmol) was added a hexanes solution (5 mL) of Cl_2C=PR (0.36 g, 1.0 mmol). After being stirred 5 min at the same temperature and then reducing the reaction solution to one-half of its volume under vacuum, white crystals of **IIa** precipitated (0.51 g, 65%). $^{31}P\{^1H\}$ NMR (acetone d_6) δ 224.0 (d,d, $^3J_{PP}$ = 46.3Hz, $^3J_{PP}$ = 12.3Hz, $^2J_{PtP}$ = 365.4 Hz, C=P-R), 6.0 (d,d, $^2J_{PP}$ = 15.1 Hz, $^3J_{PP}$ = 12.3Hz, $^1J_{PtP}$ = 3921.2 Hz, PEt_3), 8.0 (d,d, $^2J_{PP}$ = 15.1 Hz, $^3J_{PP}$ = 46.3 Hz, $^1J_{PtP}$ =2125.4 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pt$: C, 47.12; H, 7.47. Found: C, 47.06; H, 7.56.

Conversion of *cis*-$(PEt_3)_2(Cl)Pt[C(=PR)Cl]$ (IIa) to R-C≡P and *cis*-$(Cl)_2Pt(PEt_3)_2$ through the intermediate *cis*-$(PEt_3)_2(Cl)Pt$(Cl-PBC) (IVa)

After complex **IIa** (0.079 g, 0.10 mmol) in 2 mL of dry CH_2Cl_2 was stirred at room temperature under argon for 24 h, the reaction solution was evaporated to dryness. A $^{31}P\{^1H\}$ NMR spectrum taken during the reaction showed **IVa** as an intermediate. The residue was extracted with hexanes (10 mL) and filtered through a short column of Celite. After reducing the filtrate to one-fourth of its volume under vacuum, white crystals of *cis*-$(Cl)_2Pt(PEt_3)_2$[18a] were obtained upon cooling to -78 °C (0.023 g, 46%). The mother liquor from the crystals was chromatographed (hexanes, silica) under argon atmosphere to give R-C≡P (0.016 g, 55%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) for *cis*-$(Cl)_2Pt(PEt_3)_2$: δ 9.3 ($^1J_{PtP}$ = 3509 Hz). **IVa**: δ 88.2 (d, $^3J_{PP}$ = 18.3 Hz, $^2J_{PtP}$ = 190.7 Hz, P in Cl-PBC), 9.3 (t, $^3J_{PP}$ = 18.3 Hz, $^2J_{PP}$ = 18.3 Hz, $^1J_{PtP}$ = 1793.0 Hz, PEt_3), -0.1 (d, $^3J_{PP}$ = 18.3 Hz, $^1J_{PtP}$=3970.5 Hz , PEt_3).

Conversion of Cl_2C=PR to R-C≡P through intermediates *cis*-$(Cl)(PPh_3)_2Pt[C(=PR)Cl]$ (IIe) and *cis*-$(Cl)(PPh_3)_2Pt$(Cl-PBC) (IVe)

To a CH_2Cl_2 solution (5 mL) of $(PPh_3)_2Pt(C_2H_4)$ (0.075 g, 0.10 mmol) was added a CH_2Cl_2 solution (2 mL) of Cl_2C=PR (0.036 g, 0.10 mmol). After the solution was stirred at room temperature for 12 h, the solvent was evaporated under vacuum to yield an oily yellow residue which was extracted with hexanes. The extracted solution was filtered through a short column of Celite. After reducing the filtrate to one-fourth of its volume under vacuum, white crystals of *cis*-$(Cl)_2Pt(PPh_3)_2$[18d] (0.034 g, 43%) were obtained by cooling to -78 °C. The mother liquor from the

crystals was chromatographed (hexanes, silica) under argon atmosphere to give R-C≡P (0.018 g, 62%). During the 12 h course of the reaction, intermediates **IIe** and **IVe** were identified by the $^{31}P\{^{1}H\}$ NMR spectra as discussed in the Results Section. $^{31}P\{^{1}H\}$ NMR (C_6D_6) data for *cis*-$(Cl)_2Pt(PPh_3)_2$: δ 13.5 (s, $^{1}J_{PtP}$ = 3680 Hz). **IIe**: δ 234.6 (dd, $^{3}J_{PP}$ = 22.5 Hz, $^{3}J_{PP}$ = 45.4 Hz, $^{2}J_{PtP}$ = 354.8 Hz, C=P-R), 17.8 (dd, $^{3}J_{PP}$ = 45.4 Hz, $^{2}J_{PP}$ = 16.4 Hz, $^{1}J_{PtP}$ = 1889.8 Hz, PPh_3), 10.4 (dd, $^{3}J_{PP}$ = 22.5 Hz, $^{2}J_{PP}$ = 16.4 Hz , $^{1}J_{PtP}$ = 4203.2 Hz, PPh_3). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) data for **IVe** : δ 80.0 (dd, $^{3}J_{PP}$ =19.2 Hz, $^{3}J_{PP}$ =5.3 Hz, $^{2}J_{PtP}$ = 142.0 Hz, P in PBC), 16.5 (dd, $^{3}J_{PP}$ = 19.2 Hz, $^{3}J_{PP}$ =18.1 Hz, $^{1}J_{PtP}$ = 1750.0 Hz, PPh_3), 14.2 (dd, $^{3}J_{PP}$ = 18.1 Hz, $^{3}J_{PP}$ = 5.3 Hz, $^{1}J_{PtP}$ = 4150.0 Hz, PPh_3).

Conversion of Br_2C=PR to R-C≡P through the intermediate *cis*-$(Br)(PPh_3)_2Pt$(Br-PBC) (IVf)

In a reaction of Br_2C=PR (0.045 g, 0.10 mmol) and $(PPh_3)_2Pt(C_2H_4)$ (0.075 g, 0.10 mmol) that was carried out as for the reaction directly above, R-C≡P (0.020 g, 69%) was obtained as the final product. The other product *cis*-$Br_2Pt(PPh_3)_2$[18d] was observed by $^{31}P\{^{1}H\}$ NMR spectrometry in the product mixture. Complex **IVf** was identified as an intermediate by its $^{31}P\{^{1}H\}$ NMR spectrum obtained during the course of the reaction. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) data for *cis*-$Br_2Pt(PPh_3)_2$: δ 12.8 (s, $^{1}J_{PtP}$ = 3630 Hz). **IVf**: δ 88.5 (dd, $^{3}J_{PP}$ = 19.2 Hz, $^{3}J_{PP}$ = 6.4 Hz, $^{2}J_{PtP}$ = 144.1 Hz, P in Br-PBC), 13.1 (dd, $^{3}J_{PP}$ = 19.2 Hz, $^{3}J_{PP}$ = 18.1 Hz, $^{1}J_{PtP}$ = 1762.8 Hz, PPh_3), 13.8(dd, $^{3}J_{PP}$ = 18.1 Hz, $^{3}J_{PP}$ = 6.4 Hz, $^{1}J_{PtP}$ = 4204.2 Hz, PPh_3).

Preparation of *trans*-(Cl)$(PEt_3)_2$Pt(Cl-PBC) (IIIa)

After a solution of complex **Ia** (0.40 g, 0.50 mmol) in 10 mL of dry CH_2Cl_2 was stirred at room temperature under argon for 24 h, it was evaporated to dryness. The residue was recrystallized from hexanes at -30 °C to give **IIIa** as colorless crystals (0.36 g, 90%). ^1H NMR (C_6D_6) δ 6.11 (d, $^4J_{HH}$ = 1.46 Hz, 1H, on C6), 6.04 (dd, $^4J_{HH}$ = 1.46 Hz, $^3J_{PH}$ = 18.80 Hz, 1H, on C4), 2.14 (m, 6H, CH_2 of Et), 2.00 (m, 6H, CH_2 of Et), 1.54 (s, 9H, CH_3 of R), 1.10 (s, 9H, CH_3 of R), 1.08 (s, 9H , CH_3 of R), 1.18 (m, 9H, CH_3 of Et), 1.08 (m, 9H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 93.8 (s, $^2J_{PtP}$ = 387.7 Hz, P3), 12.9 (s, $^1J_{PtP}$ = 2737.1 Hz, PEt_3), 11.2 (s, $^1J_{PtP}$ = 2632.5 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Cl_2P_3Pt$: C, 47.11; H, 7.46. Found: C, 47.46; H, 7.61.

Conversion of IIIa to R-C≡P and *trans*-$Cl_2Pt(PEt_3)_2$

A solution of complex **IIIa** (0.016 g, 0.020 mmol) in 0.4 mL of dry C_6H_6 in a NMR tube was monitored by ^{31}P NMR spectroscopy. After 6 h at room temperature, only the two final products R-C≡P[10] and trans-$Cl_2Pt(PEt_3)_2$[18a] were observed. $^{31}P\{1H\}$ NMR (C_6H_6) data for *trans*-$Cl_2Pt(PEt_3)_2$: δ 13.2 (s, $^1J_{PtP}$ = 2405 Hz).

Preparation of *trans*-(Br)$(PEt_3)_2$Pt(Br-PBC) (IIIb)

A solution of complex **Ib** (0.44 g, 0.50 mmol) in 10 mL of dry CH_2Cl_2 was stirred at 0 °C under argon for 8 h; then, it was evaporated to dryness. The residue was recrystallized from hexanes at -78 °C to give **IIIb** as light yellow crystals (0.35 g, 80%). ^1H NMR (C_6D_6) δ 6.18 (d, $^4J_{HH}$ = 1.46 Hz, 1H on C6), 6.07 (dd, $^4J_{HH}$ = 1.46 Hz, $^3J_{PH}$ = 19.04 Hz, 1H on C4), 2.30 (m, 6H, CH_2 of Et), 2.08 (m, 6H, CH_2 of Et), 1.55 (s, 9H,

CH_3 of R), 1.32 (s, 9H, CH_3 of R), 1.04 (s, 9H, CH_3 of R), 1.14 (m, 9H, CH_3 of Et), 1.01 (m, 9H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 92.1 (s, $^2J_{PtP}$ = 393.8 Hz, P3), 7.2 (s, $^1J_{PtP}$ = 2714.6 Hz, PEt_3), 5.3 (s, $^1J_{PtP}$ = 2588.6 Hz, PEt_3). Anal. Calcd for $C_{31}H_{59}Br_2P_3Pt$: C, 42.35; H, 6.71. Found: C, 42.67; H, 6.77.

Conversion of IIIb to R-C≡P and *trans*-$Br_2Pt(PEt_3)_2$

Complex **IIIb** (0.018 g, 0.020 mmol) in C_6H_6 solvent at room temperature in a NMR tube converted to R-C≡P and *trans*-$Br_2Pt(PEt_3)_2$[18c] during a 3 h period. $^{31}P\{^1H\}$ NMR data for *trans*-$Br_2Pt(PEt_3)_2$: δ 6.9 (s, $^1J_{PtP}$ = 2349 Hz).

Preparation of *trans*-(Cl)$(PEt_3)_2$Pt[(H)O=PBC] (Va)

Method A To a solution of complex **Ia** (0.395 g, 0.500 mmol) in 10 mL of dry CH_2Cl_2 was added H_2O (0.009 g, 0.5 mmol). After being stirred at room temperature for 48 h, the solution was evaporated to dryness. The residue was recrystallized from a CH_2Cl_2 /hexanes (4:1) solvent mixture at room temperature by slow evaporation to give **Va** as colorless crystals (0.232 g, 60%).

Method B To a solution of complex **IIIa** (0.040 g, 0.050 mmol) in 2 mL of dry CH_2Cl_2 was added H_20 (0.0009 g, 0.05 mmol). After stirring at room temperature for 24 h, the mixture was evaporated to dryness under vacuum. The residue was recrystallized from the solvent mixture stated above to give **Va** (0.030, 80%). ^1H NMR (C_6D_6) δ 7.3 (d, $^1J_{PH}$ = 435.8 Hz, 1H, on P3), 6.1 (d, $^4J_{HH}$ = 1.7 Hz, 1H, on C5), 5.9 (dd, $^4J_{HH}$ = 1.7 Hz, $^3J_{PH}$ = 17.3 Hz, 1H, on C3), 2.2 (m, CH_2 of Et), 1.8 (m, CH_2 of Et), 1.6 (m, CH_2 of Et), 1.5(s, 9H, t-Bu), 1.3 (s, 9H, t-Bu), 1.0 (s, 9H, t-Bu

), 1.1 (m, 9H, CH_3 of Et), 0.9 (m, 9H, CH_3 of Et). $^{31}P\{^1H\}$ NMR (C_6D_6) δ 25.9 (d, $^3J_{PP}$ = 9.6 Hz, $^2J_{PtP}$ = 147.1 Hz, P in (H)O=PBC), 13.0 (d, $^3J_{PP}$ = 9.6 Hz, $^1J_{PtP}$ = 2680.0 Hz, PEt_3), 11.4 (s, $^1J_{PtP}$ = 2575.0 Hz, PEt_3). Anal. Calcd for $C_{32}H_{62}Cl_3O_1P_3Pt \cdot CH_2Cl_2$: C, 44.86; H, 7.23. Found: C, 45.24; H, 7.56.

Conversion of *trans*-(Br)(PEt$_3$)$_2$Pt[C(=PR)Br] (Ib) to *trans*-(Br)(PEt$_3$)$_2$ Pt[(H)O=PBC] (Vb)

Following **method A** in the above procedure, complex **Ib** (0.088 g, 0.10) was treated with H_2O (0.0018 g, 0.10 mmol) to give complex **Vb** (0.037 g, 45%). Complex **Vb** was identified only by its $^{31}P\{^1H\}$ NMR spectrum. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 25.5 (d, $^3J_{PP}$ =12.4 Hz, $^2J_{PtP}$ = 145.7 Hz, P in (H)O=PBC), 10.1 (d, $^3J_{PP}$ = 12.4 Hz, $^1J_{PtP}$ = 2537.7 Hz, PEt_3), 8.2 (s, $^1J_{PtP}$ = 2583.0 Hz, PEt_3).

Reaction of (PPh$_3$)$_2$Pt(C$_2$H$_4$) with Cl$_2$C=PR and H$_2$O to give *cis*-(Cl)(PPh$_3$)$_2$Pt[(H)O=PBC] (VIe) through intermediates IIe and IVe

To a CH_2Cl_2 solution (5 mL) of $(PPh_3)_2Pt(C_2H_4)$ (0.075 g, 0.10 mmol) and Cl_2C=PR (0.036 g, 0.10 mmol) was added H_2O (0.0018 g, 0.10 mmol). A series of $^{31}P\{^1H\}$ NMR spectra of the solution indicated that **IIe** formed immediately after the addition (within a minute); it then slowly converted to **IVe** and finally to **VIe**. After the solution was stirred at room temperature for 12 h, the solvent was evaporated to dryness. The residue was recrystallized from a CH_2Cl_2 /hexanes (4:1) solvent mixture at room temperature (slow evaporation) to give **VIe** (0.037 g, 35%). Compound **VIe** was characterized only by its ^{31}P NMR spectrum. $^{31}P\{^1H\}$ NMR (C_6D_6) δ 13.0 (d, $^3J_{PP}$ = 3.2 Hz, $^2J_{PtP}$ = 20 Hz, P in (H)O=PBC), 16.4

(dd, $^3J_{PP}$ = 3.2 Hz, $^2J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 1760 Hz, PPh_3), 12.2 (d, $^2J_{PP}$ = 18.1 Hz, $^1J_{PtP}$ = 4150 Hz, PPh_3).

R group rearrangement from Ia to R-C≡P in the presence of $(t\text{-}Bu)_2$ NO.

After adding $(t\text{-}Bu)_2NO$ (1 equiv) to a CH_2Cl_2 solution (2 mL) of **Ia** (0.040 g, 0.050 mmol) at room temperature, the solution was stirred for 24 h. Then, the solvent was evaporated to dryness and the residue was recrystallized from hexanes at -78 °C to give **IIIa** (0.030 g, 75%) as the only product.

Conversion of *trans*-(Cl)$(PEt_3)_2$Pt[C(=PR)Cl] (Ia) to *trans*-(Cl)$(PEt_3)_2$Pt [(H)O=PBC] (Va) with hydrated $AgBF_4$

To a THF solution (2 mL) of **Ia** (0.040 g, 0.050 mmol) was added moist solid $AgBF_4$ (0.0097 g, 0.050 mmol); the mixture was stirred at room temperature for 1 h. A white precipitate formed immediately, and the solution color darkened. After 1 h, the solution was filtered by cannula, and the solvent was removed under vacuum. The residue was recrystallized from hexanes/CH_2Cl_2 (1:1) solvent by slow evaporation at room temperature, giving colorless crystals of **Va** (0.024 g, 60%).

Reactions of *trans*-(Cl)$(PEt_3)_2$Pt[C(=PR)Cl] (Ia) and *trans*-(Cl)$(PEt_3)_2$Pt[Cl-PBC] (IIIa) with dry $AgBF_4$.

To a dry THF solution (2 mL) of **Ia** (0.040 g, 0.050 mmol) was added dry solid $AgBF_4$ (0.0097 g, 0.050 mmol); the solution was stirred at room temperature in a glove box for 1 h. A white precipitate formed immediately. After 1 h, **Ia** was completely converted to a new product, (Cl)$(PEt_3)_2$Pt[BF_4-PBC] (**VII**). Product **VII** slowly decomposed during attempted recrystallizations at -30 °C in THF. The same product **VII** was

also produced quantitatively in the reaction of **IIIa** with dry $AgBF_4$ in dry THF solution. When a drop of H_2O was added to THF solutions of **VII**, **Va** was formed immediately. Due to its instability, **VII** could not be isolated and was only characterized by its ^{31}P NMR spectrum. $^{31}P\{^1H\}$ NMR (THF) of **VII**: δ 139 (dddd, $^3J_{PP}$ = 8.25 Hz, $^3J_{PF}$ = 63.95 Hz, $^1J_{PF}$ = 866.07 Hz, $^1J_{PF}$ = 1055.78 Hz, $^2J_{PtP}$ = 299.68 Hz, P in PBC ligand), 13.3 (d, $^3J_{PP}$ = 8.25 Hz, $^1J_{PtP}$ = 2623 Hz, PEt_3), 10.5 (s, $^1J_{PtP}$ = 2587 Hz, PEt_3).

X-ray crystallographic analyses of $Cl(PEt_3)_2Pt[C(=PR)Cl]$ (Ia) and $Cl(PEt_3)_2Pt[(H)O=PBC]$ (Va)

Diffraction-quality crystals of **Ia** were obtained at -78 °C in hexanes; crystals of **Va** were obtained by slow evaporation of a hexanes/CH_2Cl_2 (1:1) solution of **Va** at room temperature. Data collection and reduction information are given in Table I. Positional parameters and selected bond distances and bond angles are given in Tables II to V. Colorless crystals of **Ia** and **Va** were mounted on glass fibers for data collection at 20 (1) °C (**Ia**) and -50 (1) °C (**Va**) on an Enraf-Nonius CAD4 diffractometer. Cell constants for the data collection were determined from a list of reflections found by an automated search routine. Data collection and reduction information are presented in Table I. Lorentz and polarization corrections were applied. A correction based on nonlinear decay in the standard reflections was applied to the data. An absorption correction based on a series of ψ-scans using the semi-empirical method was applied. The centric space group $P2_1/c$ (**Ia**) and the acentric space group $P2_12_12_1$ (**Va**) were unambiguously determined by systematic absences.

Both structures were solved by direct methods.[19] All non-hydrogen atoms were placed directly from the E-map and refined with anisotropic thermal parameters. Hydrogen atom positions were generated with ideal geometries and refined as riding, isotropic atoms. One exception was the phosphinoxo hydrogen atom (H1) in **Va**, which was located and refined as an isotropic atom. In addition, it was found necessary to refine **Va** as a racemic twin.[19b] The contribution of the minor component was 14.4%.

Table I. Crystal and Data Collection Parameters for $(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (Ia) and $(Cl)(PEt_3)_2Pt[(H)O=PBC]$ (Va)

	Ia	**Va**
Formula	$C_{31}H_{59}Cl_2P_3Pt$	$C_{31}H_{60}ClP_3OPt$
Formula weight	790.72	857.17
Space group	$P2_1/c$	$P2_12_12_1$
a, Å	13.188(1)	9.183(1)
b, Å	12.106(1)	12.265(2)
c, Å	23.990(2)	34.973(8)
β, deg	105.099(2)	
cell vol, Å^3	3697.8(8)	3939(1)
Z	4	4
Dcalcd , g cm^{-3}	1.42	1.445
Crystal size, mm	0.45x0.45x0.40	0.50x0.35x0.35
μ (MoKα), cm^{-1}	41.4	39.10
Data collection instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	MoKα (λ=0.71073 Å)	MoKα (λ=0.71073 Å)
Temperature, °C	20(1)	-50(1)

Table I. continued

Scan method	θ–2θ	θ–2θ
Data col. range, 2θ, deg	4.0-50.0	4.0-50.0
Tot. uniq. reflec.	6850	3910
Uniq. reflec. obs.	4434	3659
No. of para. refined	335	401
Trans. factors, max., min.	0.994, 0.739	0.901, 0.514
Refinement	SHELXTL-PLUS[19a]	SHELXL-93[19b]
R[a]	0.025	0.038
Rw[b] or wR2[c]	0.032 (Rw)	0.101 (wR2)
Quality-of-fit indicator	0.867[d]	1.150[e]
Largest shift/esd, final cycle	0.00	
Largest peak, e/Å^3	0.88	1.031

[a] $R = \Sigma| |Fo|-|Fc| |/\Sigma|Fo|$. [b] $R = \{\Sigma\omega(|Fo|-|Fc|)^2/\Sigma\omega|Fo|^2\}^{1/2}$; $\omega = 1/\sigma^2(|Fo|)$. [c] $wR2 = [\Sigma\{\omega(Fo^2-Fc^2)^2\}/\Sigma\{\omega(Fo^2)^2\}]^{1/2}$; $\omega = q/\{\sigma^2(F_o^2) + (a*p)^2 + (b*p) + d + (e*\sin\theta)\}$, see ref. 19b. [d] Quality-of-fit = $\{\Sigma\omega(|Fo|-|Fc|)^2/(Nobs-Nparameters)\}^{1/2}$. [e] Quality-of-fit = $[\Sigma\{\omega(Fo^2-Fc^2)^2/(n-p)\}]^{1/2}$, see ref. 19b.

Table II. Positional Parameters for Complex (Cl)$(PEt_3)_2$Pt[C(=PR)Cl] (Ia) with Estimated Standard Deviations in Parentheses

	x	y	z	B(Å^2)
Pt	0.58510(1)	0.27816(2)	0.12824(1)	3.496(4)
Cla	0.7142(1)	0.1790(1)	0.24698(5)	4.33(3)
Clb	0.4513(1)	0.2428(2)	0.04228(7)	7.79(4)
P1	0.78281(9)	0.4058(1)	0.21715(5)	3.50(3)
P2	0.4801(1)	0.4106(1)	0.15474(5)	3.83(3)
P3	0.6812(1)	0.1569(1)	0.08771(5)	4.11(3)
C1	0.7012(3)	0.2974(4)	0.2009(2)	3.07(9)
C2	0.8833(3)	0.3729(4)	0.2861(2)	3.14(9)
C3	0.8608(3)	0.3714(4)	0.3429(2)	3.33(9)
C4	0.9271(4)	0.3117(5)	0.3856(2)	4.1(1)
C5	1.0190(4)	0.2620(4)	0.3811(2)	3.8(1)
C6	1.0479(4)	0.2826(4)	0.3303(2)	3.9(1)
C7	0.9861(3)	0.3398(4)	0.2836(2)	3.4(1)
C8	0.7723(4)	0.4362(4)	0.3577(2)	4.3(1)
C9	0.7282(5)	0.5350(5)	0.3178(2)	6.0(1)
C10	0.6833(4)	0.3575(5)	0.3620(2)	5.6(1)
C11	0.8163(5)	0.4901(5)	0.4182(2)	6.3(2)
C12	1.0372(4)	0.3746(4)	0.2348(2)	4.2(1)
C13	1.1559(4)	0.3576(6)	0.2522(3)	6.7(2)
C14	0.9939(4)	0.3148(6)	0.1781(2)	6.2(1)
C15	1.0236(4)	0.5012(5)	0.2256(2)	5.5(1)
C16	1.0878(4)	0.1977(4)	0.4322(2)	4.9(1)
C17	1.1905(6)	0.1569(7)	0.4201(3)	10.0(2)

Table II. continued

C18	1.1182(8)	0.2695(6)	0.4841(3)	12.3(3)
C19	1.0309(6)	0.0958(6)	0.4425(3)	9.7(2)
C20	0.3443(4)	0.4123(5)	0.1104(3)	5.6(1)
C21	0.2739(4)	0.5012(6)	0.1233(3)	6.6(2)
C22	0.4673(4)	0.4009(5)	0.2290(2)	5.1(1)
C23	0.4277(5)	0.2891(6)	0.2422(3)	7.5(2)
C24	0.5274(5)	0.5499(5)	0.1500(3)	5.9(1)
C25	0.5337(6)	0.5814(7)	0.0891(3)	9.4(2)
C26	0.8088(4)	0.1107(4)	0.1311(2)	4.3(1)
C27	0.8848(5)	0.0625(6)	0.0993(3)	7.7(2)
C28	0.7030(5)	0.2203(5)	0.0223(2)	6.3(1)
C29	0.7601(6)	0.3304(7)	0.0332(3)	8.4(2)
C30	0.6156(5)	0.0285(5)	0.0608(3)	6.8(2)
C31	0.5851(5)	-0.0388(7)	0.1062(4)	9.6(2)

Table III. Selected Bond Distances(Å) and Bond Angles(deg) for $(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (Ia)[a]

Distances (Å)			
Pt-Clb	2.377(2)	Pt-P2	2.313(1)
Pt-P3	2.312(1)	Pt-C1	2.013(4)
C1-P1	1.678(5)	C1-Cla	1.790(5)
P1-C2	1.874(5)	P2-C20	1.829(6)
P2-C22	1.836(6)	P2-C24	1.812(7)
P3-C26	1.820(5)	P3-C28	1.835(7)
P3-C30	1.814(7)		
Angles (deg)			
Clb-Pt-P2	90.07(5)	Clb-Pt-P3	83.39(6)
Clb-Pt-C1	176.1(1)	P2-Pt-P3	171.24(5)
P2-Pt-C1	93.2(1)	P3-Pt-C1	93.5(1)
C1-P1-C2	107.6(2)	Pt-C1-Cla	111.8(2)
Pt-C1-P1	126.1(3)	Cla-C1-P1	122.1(3)

[a] Numbers in parentheses are estimated standard deviations.

Table IV. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for $(Cl)(PEt_3)_2Pt[(H)O{=}PBC]$ (Va)

Atom	x	y	z	U(eq)
Pt	0.7316(1)	0.0725(1)	0.8271(1)	0.031(1)
Cl	0.6879(4)	0.1771(3)	0.7707(1)	0.059(1)
P(3)	0.9539(3)	-0.0653(3)	0.8850(1)	0.034(1)
O	1.0509(9)	-0.1386(7)	0.8613(2)	0.053(2)
C(1)	0.7842(12)	-0.0158(8)	0.8734(3)	0.032(2)
C(2)	0.7333(11)	-0.0456(7)	0.9086(2)	0.026(2)
C(3)	0.8591(12)	-0.1065(8)	0.9284(3)	0.033(2)
C(4)	0.9001(11)	-0.0446(9)	0.9638(3)	0.037(3)
C(5)	0.8050(12)	0.0152(9)	0.9827(3)	0.039(3)
C(6)	0.6523(12)	0.0186(9)	0.9696(3)	0.035(2)
C(7)	0.6090(11)	-0.0141(8)	0.9335(3)	0.033(2)
C(8)	0.8471(13)	-0.2328(9)	0.9363(3)	0.040(3)
C(81)	0.7898(11)	-0.2949(8)	0.9012(3)	0.048(3)
C(82)	0.9980(11)	-0.2774(9)	0.9456(3)	0.063(4)
C(83)	0.7405(15)	-0.2542(9)	0.9696(3)	0.049(3)
C(9)	0.8389(13)	0.0726(12)	1.0202(4)	0.054(3)
C(91)	1.0033(17)	0.0778(17)	1.0276(5)	0.099(7)
C(92)	0.7861(31)	0.1874(12)	1.0192(5)	0.129(10)
C(93)	0.7611(28)	0.0135(14)	1.0537(4)	0.107(8)
C(10)	0.4532(13)	-0.0148(9)	0.9204(3)	0.041(3)
C(101)	0.4255(14)	-0.1202(10)	0.8990(4)	0.054(3)
C(102)	0.3484(12)	-0.0078(12)	0.9536(3)	0.052(3)
C(103)	0.4223(12)	0.0820(12)	0.8944(3)	0.055(3)

Table IV. continued

P(1)	0.6976(3)	-0.0760(3)	0.7878(1)	0.041(1)
C(111)	0.5229(14)	-0.729(14)	0.7631(3)	0.054(3)
C(112)	0.3915(15)	-0.0639(16)	0.7873(4)	0.080(5)
C(121)	0.7127(18)	-0.2100(9)	0.8086(3)	0.058(4)
C(122)	0.7062(22)	-0.3077(10)	0.7804(4)	0.078(5)
C(131)	0.8340(12)	-0.0724(13)	0.7497(3)	0.051(3)
C(132)	0.9858(19)	-0.0788(22)	0.7629(5)	0.103(7)
P(2)	0.7903(4)	0.2367(2)	0.8550(1)	0.048(1)
C(211)	0.8059(16)	0.2460(9)	0.9069(3)	0.051(3)
C(212)	0.8640(21)	0.3538(11)	0.9227(4)	0.077(5)
C(221)	0.6626(19)	0.3530(10)	0.8424(4)	0.068(4)
C(222)	0.5069(23)	0.3305(16)	0.8488(6)	0.106(7)
C(231)	0.9592(18)	0.2855(14)	0.8360(5)	0.085(5)
C(232)	1.0851(17)	0.2145(15)	0.8456(6)	0.105(7)
Cl(1')	0.5834(8)	-0.0680(5)	1.1592(2)	0.155(3)
C(1')	0.7118(19)	-0.1643(11)	1.1715(5)	0.081(5)
Cl(2')	0.8864(8)	-0.1247(5)	1.1533(2)	0.126(2)

Table V. Selected Bond Distances (Å) and Angles (deg) for $(Cl)(PEt_3)_2Pt[(H)O{=}PBC]$ (Va)[a]

Distances(Å)			
Pt-C(1)	2.006(10)	Pt-P(2)	2.302(3)
Pt-P(1)	2.304(3)	Pt-Cl	2.388(3)
P(3)-O	1.484(8)	P(3)-C(1)	1.776(3)
P(3)-C(3)	1.844(10)	P(3)-C(2)	2.247(10)
C(1)-C(2)	1.369(13)	C(2)-C(7)	1.485(14)
C(2)-C(3)	1.539(14)	C(3)-C(4)	1.500(14)
C(3)-C(8)	1.58(2)	C(5)-C(6)	1.48(2)
C(5)-C(9)	1.52(2)	C(6)-C(7)	1.38(2)
C(7)-C(10)	1.50(2)		
Angles (deg)			
Cl-Pt-P(1)	84.74(11)	Cl-Pt-P(2)	85.40(11)
P(1)-Pt-P(2)	167.54(11)	C(1)-Pt-P(1)	95.0(3)
C(1)-Pt-P(2)	94.2(3)	O-P(3)-C(1)	126.6(5)
O-P(3)-C(3)	125.1(5)	C(1)-P(3)-C(3)	80.2(5)
C(2)-C(1)-P(3)	90.7(7)	Pt-C(1)-C(2)	142.1(8)
Pt-C(1)-P(3)	126.2(6)	C(1)-C(2)-C(7)	136.0(9)
C(1)-C(2)-C(3)	106.1(8)	C(3)-C(2)-C(7)	116.2(8)
C(2)-C(3)-C(4)	108.2(8)	C(4)-C(3)-C(8)	111.6(8)

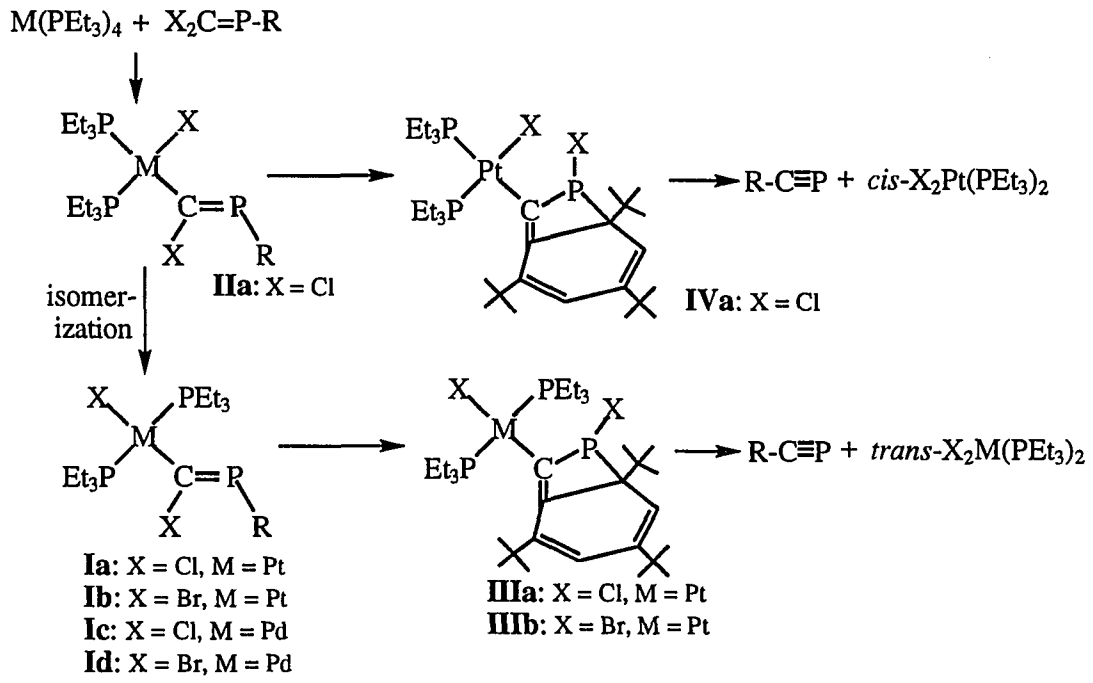
[a] Numbers in parentheses are estimated standard deviations.

RESULTS

Reactions of X_2C=P-R (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) with $M(PEt_3)_4$ (M = Pt, Pd)

The reactions of X_2C=P-R (X = Cl, Br) with $M(PEt_3)_4$ (M = Pt, Pd) in C_6H_6 (or hexanes) solvent at room temperature for 1 h gave only the *trans*-(X)$(PEt_3)_2$M[C(=PR)X] (**Ia**: X = Cl, M = Pt; **Ib**: X = Br, M = Pt; **Ic**: X = Cl, M = Pd) complexes which were isolated in moderate yield (56%-85%). Complex **Id** was unstable in organic solvents (CH_2Cl_2, C_6H_6, and hexanes) and could not be isolated; it reacted further to give the final products R-C≡P and *trans*-$Br_2Pd(PEt_3)_2$. But it was sufficiently stable to be observed by $^{31}P\{^1H\}$ NMR spectroscopy. In the presence of free PEt_3, the first product, *cis*-isomer (**IIa**), slowly isomerized to the *trans*-isomer (**Ia**) even at low temperature (-30 °C).[20] At -50 °C in hexanes, *cis*-(Cl)$(PEt_3)_2$Pt[C(=P-R)X] (**IIa**) separated as white crystals. At this temperature, any *cis*-isomer **IIa** that formed quickly precipitated. When pure isolated **IIa** was allowed to stand in hexanes (or in C_6H_6) in the absence of free PEt_3, no isomerization to **Ia** occurred over a period of 3 days at room temperature. The *cis*-isomer (**IIb**) of **Ib** was also observed but the other *cis*-isomers of **Ic** and **Id** were not observed during the reactions at room temperature. Presumably, the rates of isomerization of the *cis* to the *trans* isomers were so fast that the *cis* isomers were not observed under these reaction conditions. The *trans* **I** products (except **Id**) were very stable in non-polar organic solvents (C_6H_6, hexanes, and CCl_4) and did not undergo further reaction over a period of a week at

Scheme 1



room temperature. But in some polar organic solvents (CH_2Cl_2 , $CHCl_3$, and THF), **Ia, Ib**, and **IIa** were quantitatively converted to **IIIa**, **IIIb**, and **IVa**, respectively, within 24 h at room temperature. At longer times these complexes reacted further to give the final products, R-C≡P and $X_2Pt(PEt_3)_2$ (X = Cl, Br) (Scheme 1). In the conversion of **Ic** and **Id** to the final products, an intermediate of type **III** was not observed. Isolated **IIIa** was stable in polar solvents (at least 24 h in CH_2Cl_2) but slowly converted to the R-C≡P and *trans*-$Cl_2Pt(PEt_3)_2$ final products in hexanes within 6 h. Intermediate **IIIb** was sufficiently stable to be isolated from polar CH_2Cl_2 but readly converted to the final products in hexanes even at -30 °C. Intermediate **IVa** was too unstable to be isolated in all organic

solvents tried (CH_2Cl_2, $CHCl_3$, and THF); it went on to form the final R-C≡P and *cis*-$Cl_2Pt(PEt_3)_2$ products.

The *cis*- and *trans*-(Cl)$(PEt_3)_2$Pt[C(=P-R)Cl] complexes (**Ia** and **IIa**) were also prepared by reaction of *trans*-$Cl_2Pt(PEt_3)_2$ with 1 equivalent of Li(Cl)C=P-R[7] in THF at -78 °C. This reaction may provide

$$\textit{trans}\text{-}Cl_2Pt(PEt_3)_2 + Li(Cl)C{=}PR \longrightarrow \mathbf{Ia} + \mathbf{IIa} \qquad (4)$$

a more general route for the synthesis of complexes containing the [C(=P-R)Cl] ligand from the corresponding chloro-complexes.

Compounds **Ia-Ic**, **IIa**, **IIIa**, and **IIIb** were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectrometry and elemental analysis; structures of **Ia** and **IIIa** were established by X-ray diffraction studies. The very similar $^{31}P\{^1H\}$ NMR chemical shifts and coupling constants for **Ia** and **Ib** indicate that they have the same structures; the J_{PtP} values for the PEt_3 ligands (**Ia**: 2752.7 Hz; **Ib**: 2712.3 Hz) are typical of *trans* complexes as in *trans*-$Pt^{II}(PEt_3)_2(R)(X)$.[21] The ^{195}Pt-P coupling constants (**Ia**: 657.7 Hz; **Ib**: 661.2 Hz) of the phosphorus in the [C(=PR)X] ligands are approximately twice the value of that in the *cis*-isomer (**IIa**: 365.4 Hz) and in $(PPh_3)_2Pt(\eta^2\text{-}RP{=}CPh_2)$ (319 Hz at -50 °C) (where R = 2,6-dimethylphenyl).[22]

The $^{31}P\{^1H\}$ NMR spectrum of the *cis*-isomer (**IIa**) shows the same pattern as that of **IIe** and **IIf**. Of the three signals for **IIa**, the doublet of doublets at 224.0 ppm, assigned to the phosphorus in the phosphaalkene unit Pt[C(=PR)Cl], is slightly upfield from Cl_2C=PR (232.0 ppm). The

^{195}Pt-P coupling constant (365.4 Hz) of this P is similar to that in **IIe** (354.8 Hz) but almost half the value of that (657.7 Hz) in **Ia**. The other two peaks at 6.0 ppm and 8.0 ppm are assigned to the PEt_3 ligands. The one at 6.0 ppm shows a larger ^{195}Pt-P coupling constant (3921.2 Hz) but a smaller P-P coupling constant ($^3J_{PP}$ = 12.3 Hz) than the other at 8.0 ppm ($^1J_{PtP}$ = 2125.4 Hz, $^3J_{PP}$ = 46.3 Hz). On the basis of their P-P coupling constants to the phosphorus in the Pt[C(=PR)Cl] ligand, the peak at 8.0 ppm can be assigned to the PEt_3 ligand which is *trans* to the Pt[C(=PR)Cl] group and the peak at 6.0 ppm can be assigned to the *cis* PEt_3 ligand. The $^{31}P\{^1H\}$ NMR spectra of **Ic** and **Id** exhibit the same pattern as that of **Ia** and **Ib** except there are no ^{195}Pt-satellites. Interestingly, the $^{31}P\{^1H\}$ NMR signals of the phosphorus in the phosphabicyclo ligands of intermediates **IIIa**, **IIIb**, and **IIIc** are not split by coupling to the PEt_3 ligands; in contrast, this coupling is significant (5-20 Hz) in the *cis*-isomers (**IVa**, **IVe** and **IVf**). Also the two PEt_3 ligands in these intermediates (**IIIa**, **IIIb**, and **IIIc**) are not equivalent because they are diastereotopic; but there is no coupling between their phosphorus nuclei.

X-ray crystal structures of Ia and IIIa

Bond distances and angles for **Ia** are presented in Table III. The ORTEP drawing (Fig. 1) of complex **Ia** shows that the platinum atom is in a square planar environment which is defined by the two PEt_3, Cl, and [C(=PR)Cl] ligands. The atoms Pt, P(2), P(3), Clb, and C(1) are all nearly coplanar (within 0.087 (1) Å). The C(1)-P(1) distance (1.678 (5) Å) is very similar to that of a C=P double bond, e.g., as found in $Ph(Me_3Si)C{=}P$-

R (1.676 (6) Å, where R=2,4,6-tri-*tert*-butylphenyl).[23] The C(1)-P(1) distance is also very similar to that (1.679 (4) Å) in the P-bound phosphaalkene in $Cr(CO)_5(\eta^1$-Mes-P=CPh_2),[2d] but it is shorter than that (1.773 (8) Å) of the side-on π bound phosphaalkene in $Ni(PMe_3)_2[\eta^2$-$(Me_3Si)_2CHP=C(SiMe_3)_2]$[24].

The ORTEP drawing of complex **IIIa** (Fig. 2), which was reported briefly in a communication,[12] shows that it contains a remarkable phosphabicyclo ligand. The six-membered ring of this ligand is not aromatic but contains double bonds at C(4)-C(5) (1.348 (7) Å) and C(6)-C(7) (1.339 (8) Å) and single bonds at C(3)-C(4) (1.509 (7) Å), C(2)-C(3) (1.533 (6) Å), and C(2)-C(7) (1.490 (8) Å), while the C(5)-C(6) distance (1.464 (8) Å) is characteristic of the central C-C bond of a diene.[25] In the four-membered ring, C(2)-C(3) (1.533 (6) Å) is a single bond, whereas C(1)-C(2) (1.389 (8) Å) is a somewhat long double bond.[26] The P(3)-C(3) bond (1.911 (6) Å) is also longer than a typical P-C single bond (1.85 Å),[25] but the P(3)-C(1) distance (1.802 (5) Å) is close to that of a single bond.

A comparison of the isomers **Ia** and **IIIa** shows that the geometry around the Pt and the Pt-P and Pt-Cl distances are very similar in both complexes. However, the P-Pt-P angle in **IIIa** (P(1)-Pt-P(2) = 166.9 (1)°) is slightly less linear than that in **Ia** (P(2)-Pt-P(3) = 171.24 (5)°), probably due to the bulkiness of the Cl-PBC ligand.

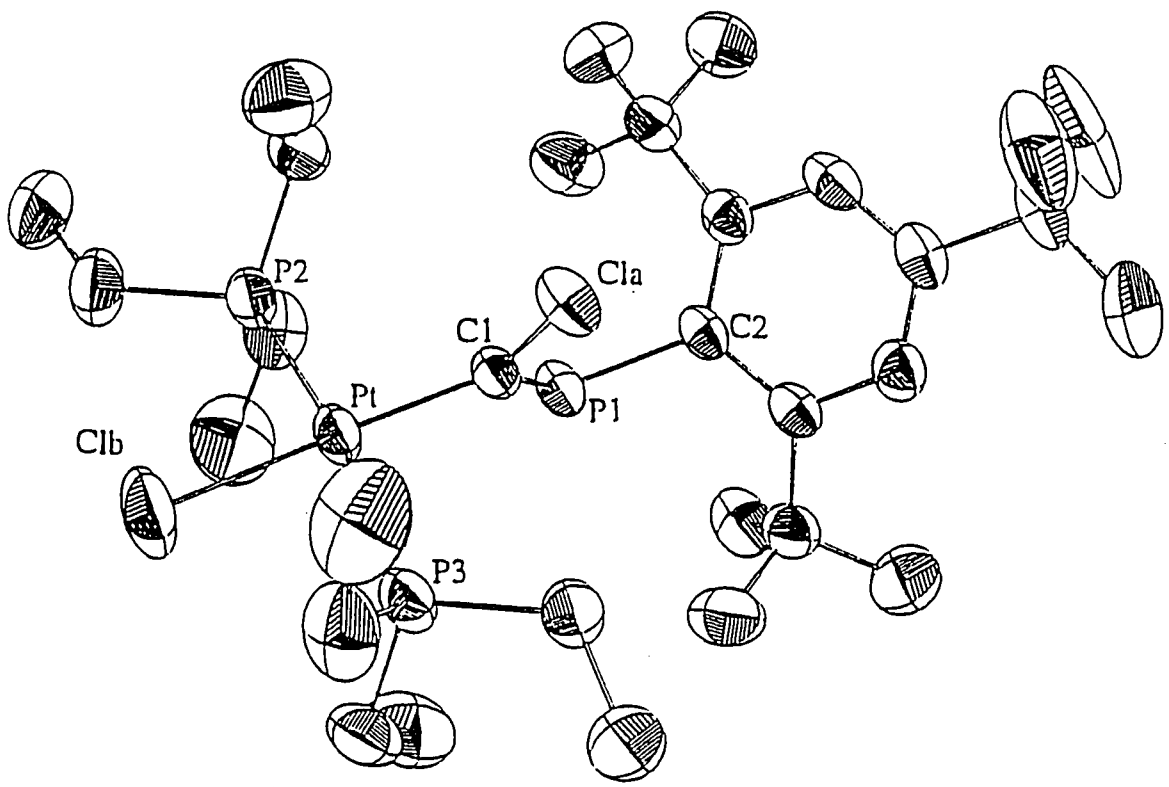


Figure 1. ORTEP drawing of (Cl)(PEt$_3$)$_2$Pt[C(=PR)Cl] (**Ia**).

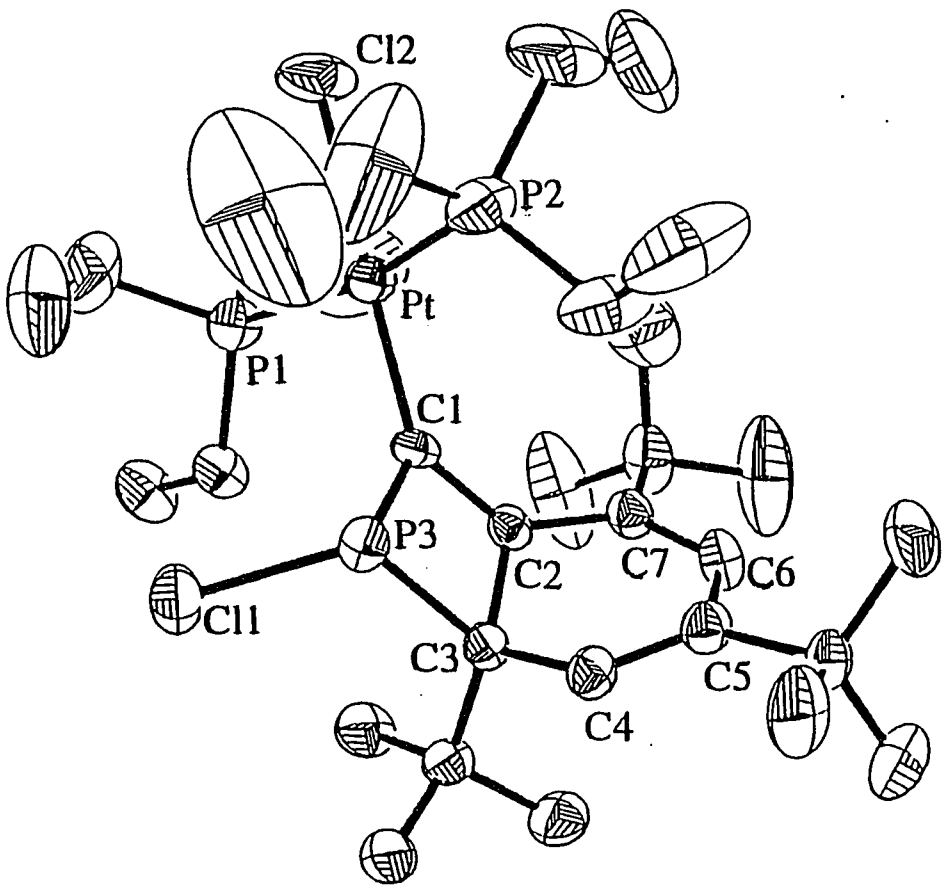
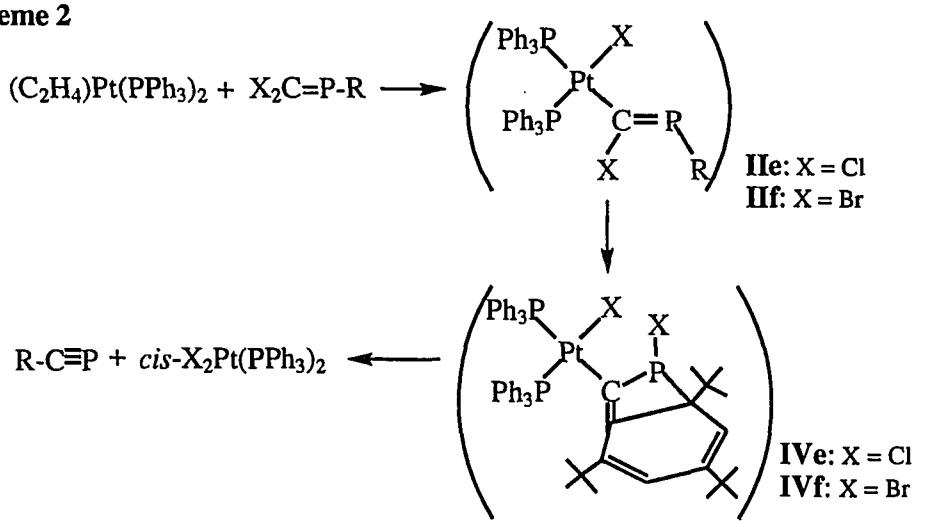


Figure 2. ORTEP drawing of (Cl)$(PEt_3)_2$Pt(Cl-PBC) (**IIIa**).

Reactions of X_2C=P-R (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) with $(PPh_3)_2Pt(C_2H_4)$

The reactions of X_2C=P-R with $(PPh_3)_2Pt(C_2H_4)$ in organic solvents (C_6H_6, CH_2Cl_2, $CHCl_3$, and hexanes for Cl_2C=P-R; C_6H_6 and CH_2Cl_2 for Br_2C=P-R) at room temperature for 12 h gave the final products, R-C≡P (65%-69%) and *cis*-$X_2Pt(PPh_3)_2$, in moderate yield after workup. These products were identified by comparison of their ^1H and $^{31}P\{^1H\}$ NMR spectra with those reported in the literature[10] for these compounds. In non-polar organic solvents (C_6H_6 and hexanes), white crystals of *cis*-$X_2Pt(PPh_3)_2$ precipitated during the reaction. Interestingly, two types of intermediates (**IIe** and **IIf**, **IVe** and **IVf**) were observed during the reaction in polar solvents (CH_2Cl_2) by $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2). They were not separable even at low temperature (-78 °C), but were sufficiently stable to be observed by $^{31}P\{^1H\}$ NMR spectroscopy.

Scheme 2



The $^{31}P\{^{1}H\}$ NMR spectra (described below) of these intermediates show that they all have a *cis* structure; this is evident from the two PPh_3 signals, coupling between the two PPh_3 phosphorus nuclei and the quite different ^{195}Pt-P coupling constants for the PPh_3 ligands, all of which are typical of *cis* square planar $(PR_3)_2Pt^{(II)}(R)(X)$ complexes.[21] Thus, these intermediates, as well as the products *cis*-$X_2Pt(PPh_3)_2$, all have *cis* structures; there was no evidence for *trans* isomers.

The $^{31}P\{^{1}H\}$ NMR spectra of **IIe** and **IIf** show the same pattern as that of **IIa**. Of the three signals for **IIe** (X = Cl), the doublet of doublets at 234.6 ppm, assigned to the phosphorus in the phosphaalkene unit Pt[C(=P-R)Cl], is slightly downfield from Cl_2C=P-R (232.0 ppm). The ^{195}Pt-P coupling constant (354.8 Hz) of this P is similar to that in *cis*-(Cl)$(PEt_3)_2$Pt[C(=P-R)Cl] (**IIa**) (365.4 Hz) but almost the half value of that (657.7 Hz) in *trans*-(Cl)$(PEt_3)_2$Pt[C(=P-R)Cl] (**Ia**). The other two peaks at 17.8 ppm and 10.4 ppm are assigned to the inequivalent PPh_3 ligands. The one at 10.4 ppm which is *trans* to the Cl^- ligand, shows a larger ^{195}Pt-P coupling constant (4203.2 Hz) than the other at 17.8 ppm (1889.8 Hz), which is *trans* to [C(=PR)Cl] ligand. The $^{31}P\{^{1}H\}$ NMR spectra of **IVe** and **IVf** show almost the same pattern. Of the three signals for intermediate **IVe** (X = Cl), the doublet of doublets at 80.0 ppm assigned to the phosphorus in the phosphabicyclo ligand is upfield of that in Cl_2C=PR and also of that in **IIe**. The ^{195}Pt-P coupling constant (142.0 Hz) of the Cl-PBC ligand in **IVe** is significantly smaller than that in **IIe** (354.8 Hz) and that in (Cl)$(PEt_3)_2$Pt(Cl-PBC) (**IIIa**) (387.7 Hz). The other two signals (δ16.5 ppm, $^{1}J_{PtP}$ = 1750.0 Hz; δ14.2 ppm, $^{1}J_{PtP}$ = 4150.0

Hz) assigned to the PPh_3 ligands have chemical shifts and ^{195}Pt-P coupling constants very similar to those in **IIe** (δ17.8 ppm, $^1J_{PtP}$ = 1889.8 Hz; δ10.4 ppm, $^1J_{PtP}$ = 4203.2 Hz). The analogous Br intermediates, **IIf** and **IVf**, show the same $^{31}P\{^1H\}$ patterns and similar chemical shifts as those for **IIe** and **IVe** (see Experimental Section).

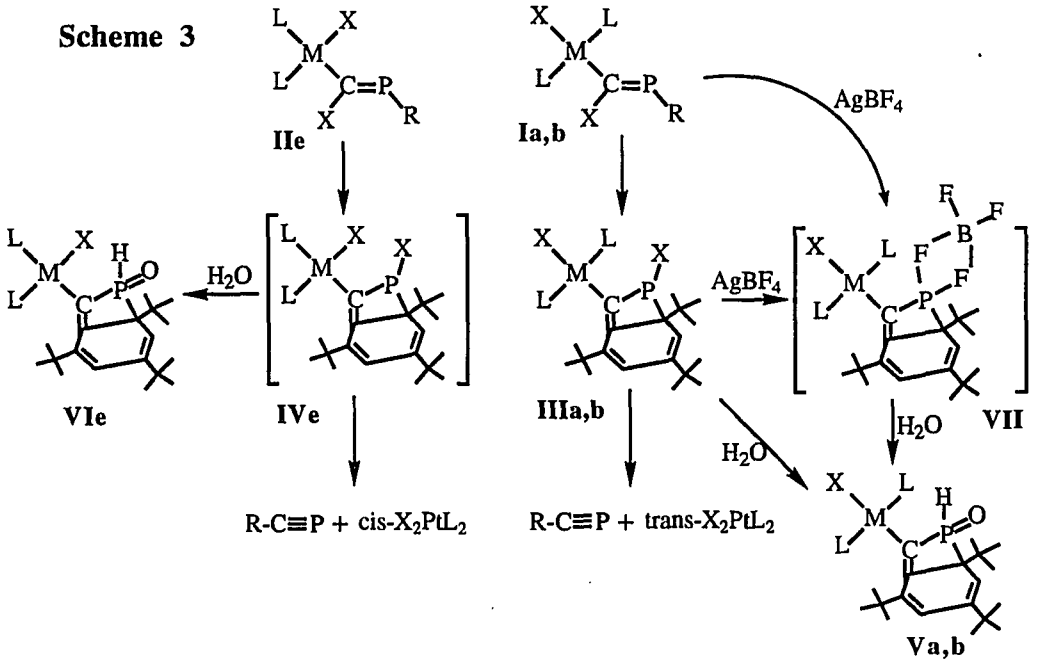
Reactions of Ia and Ib with H_2O and $AgBF_4$, and reactions of $(PPh_3)_2Pt(C_2H_4)$ with Cl_2C=P-R and H_2O

Complexes **Ia** and **Ib** reacted (Scheme 3) with H_2O within 24 h at room temperature under an argon atmosphere in CH_2Cl_2 to give **Va** (X = Cl, L = PEt_3) and **Vb** (X = Br, L = PEt_3) which were isolated as analytically pure compounds and identified by their ^1H and $^{31}P\{^1H\}$ NMR spectra; the structure of **Va** was established by an X-ray diffraction study. A $^{31}P\{^1H\}$ NMR study showed that **Ia** and **Ib** converted to **Va** and **Vb** through intermediates **IIIa** and **IIIb** without forming R-C≡P and $X_2Pt(PEt_3)_2$ (X = Cl, Br). Complex **Va** was also synthesized from the direct reaction of **IIIa** with H_2O in CH_2Cl_2 solvent (80% yield). Of the two $^{31}P\{^1H\}$ NMR signals for the diastereotopic PEt_3 ligands in **Va**, only the doublet at 13.0 ($^1J_{PtP}$ = 2680 Hz) is coupled with the phosphorus in the phosphabicyclo ligand ($^3J_{PP}$ = 9.6 Hz). The ^{195}Pt-P coupling constants of the PEt_3 ligands (2680 Hz, 2575 Hz) in **Va** are typical of *trans*-$Pt^{II}(PEt_3)_2(X)R$ complexes.[21] The ^1H NMR spectrum of **Va** showed three signals in the 7.3-5.9 ppm range. The doublet at 7.3 ppm is assigned to the proton on the phosphorus in phosphabicyclo ligand because of the large one bond coupling to the phosphorus ($^1J_{PH}$ = 435.8 Hz).[27] The other two signals at 6.1 (d, $^4J_{HH}$

=1.7 Hz) and 5.9 (dd, $^4J_{HH}$ =1.7 Hz, $^3J_{PH}$ =17.3 Hz) were assigned to the two protons on the 6-membered ring in the phosphabicyclo ligand.

Reaction of **Ia** with $AgBF_4$ in dry THF solution produced (Scheme 3) an immediate precipitate of AgCl and a new complex **VII** in solution; **VII** was also formed in the reaction of **IIIa** with $AgBF_4$ in dry THF solution. Unfortunately **VII** was not sufficiently stable to be isolated;

Scheme 3



it decomposed to unidentifiable products within 24 h at -30 °C. The reaction of **VII** with H_2O in THF solution immediately gave **Va**, which was identified by its ^{31}P NMR spectrum. The reaction of **Ia** with $AgBF_4$ in the presence of H_2O gave **Va** as the only product. Since **VII** could not be isolated, it was not possible to establish its structure by X-ray diffraction. However, its ^{31}P NMR spectrum suggests the structure shown in Scheme 3. In this spectrum, the splitting of the peak at 139 ppm (d,d,d,d),

assigned to the P in the BF_4-PBC ligand, shows two relatively large coupling constants (1055.78 Hz and 866.07 Hz), which are typical of one-bond ^{31}P-^{19}F coupling; another coupling constant (63.95 Hz) is typical of three-bond ^{31}P-^{19}F coupling constants.[28] The fourth coupling constant (8.25 Hz) is probably due to coupling with a PEt_3 ligand. The ^{195}Pt-P coupling constant (299.68 Hz) of this peak is close to that of **IIIa** (387.7 Hz). These ^{31}P NMR data are consistent with the structure in (Scheme 3) if it is assumed that one of the terminal F atoms does not couple to the phosphorus of the phosphabicyclo ligand. In the absence of further structural characterization, this structural assignment for **VII** must be regarded as tentative.

The reaction of $(PPh_3)_2Pt(C_2H_4)$ and Cl_2C=P-R in the presence of a trace amount of H_2O in CH_2Cl_2 solution proceeded in almost the same manner as that of $(PPh_3)_2Pt(C_2H_4)$ with Cl_2C=P-R in dry CH_2Cl_2 (Scheme 3). In both reactions, monitored by $^{31}P\{^1H\}$ NMR spectrometry, **IIe** formed first and this rearranged to intermediate **IVe**, which converted to the final products, R-C≡P and *cis*-$Cl_2Pt(PPh_3)_2$ (Scheme 2 and 3); however, the reaction with trace H_2O gave a very small amount of a new product (**VIe**). When an amount of H_2O equivalent to Cl_2C=P-R and $(PPh_3)_2Pt(C_2H_4)$ was used, **VIe** was obtained as the major product together with R-C≡P and *cis*-$Cl_2Pt(PPh_3)_2$ as minor products. The $^{31}P\{^1H\}$ NMR spectrum of **VIe** shows a splitting pattern typical of *cis* square planar (X)(R)$Pt^{II}L_2$ (X = halogen; R = alkyl, aryl; L = phosphine) complexes in which the J_{PtP} of the L that is to the halogen

is much larger than that of the L which is *trans* to the R group.[21] Of the three $^{31}P\{^{1}H\}$ NMR signals for **VIe**, that at 16.4 (dd, $^{3}J_{PP}$ = 3.2 Hz, $^{2}J_{PP}$ = 18.1 Hz ,$^{1}J_{PtP}$ = 1760.0 Hz) is assigned to the PPh_3 that is *trans* to the (H)O=PBC ligand while the signal at 12.2 (d, $^{2}J_{PP}$ = 18.1 Hz, $^{1}J_{PtP}$ = 4150.0 Hz) is assigned to the PPh_3 that is *trans* to the Cl ligand. The remaining signal at 13.0 (d, $^{3}J_{PP}$ = 3.2 Hz, $^{2}J_{PtP}$ = 20 Hz) assigned to the phosphorus in the (H)O=PBC ligand was much further up-field than that (80 ppm) in **IVe**. Somewhat unexpected is the observation that the PPh_3 ligand *trans* to the Cl ligand is not split by coupling to the phosphorus in the phosphabicyclo ligand.

In order to explore the possibility that the rearrangement of **Ia** to R-C≡P and *trans*-$Cl_2Pt(PEt_3)_2$ is initiated by radicals, this reaction was performed in the non-polar solvent CCl_4 which is a better Cl radical source than CH_2Cl_2. However, **Ia** did not rearrange or react in CCl_4 for 1 week at room temperature, which suggests that radicals are not involved in this conversion. Also, the rearrangement of **Ia** to **IIIa** in CH_2Cl_2 solvent with added $(t\text{-Bu})_2NO$, which is a good radical scavenger, gave the same product (**IIIa**) quantitatively within 24 h at room temperature; thus, the $(t\text{-Bu})_2NO$ had no effect on the product or rate of the reaction.

X-ray crystal structure of Va

The ORTEP drawing (Fig. 3) of complex **Va** shows that it contains the phosphabicyclo ligand with almost the same structure as in **IIIa** (Fig. 2) except for the oxygen and hydrogen on the phosphorus instead of Cl. The P(3)-O distance (1.473 (7) Å) is slightly shorter than typical P=O double bonds in R_3P=O (1.489 Å).[25] A comparison of the **IIIa** and **Va**

structures shows that geometry around the Pt, the single bonds at C(3)-C(4), C(7)-C(2) and C(5)-C(6) in the six-membered ring, and the single bond at C(2)-C(3) in the four membered ring are very similar in both complexes. On the other hand, the double bond at C(6)-C(7) (1.38 (2) Å) in **Va** appears to be longer than that (1.339 (8) Å) in **IIIa**. In the four membered ring, the C(1)-C(2) bond (1.369 (13) Å) is similar to that (1.389 (8) Å) in **IIIa** . The P(3)-C(3) bond (1.844 (9) Å) is similar to a typical P-C single bond (1.85 Å), whereas the P(3)-C(1) distance (1.766 (11) Å) appears to be shorter than that of a single bond and also shorter than that (1.802 (5) Å) in **IIIa**.

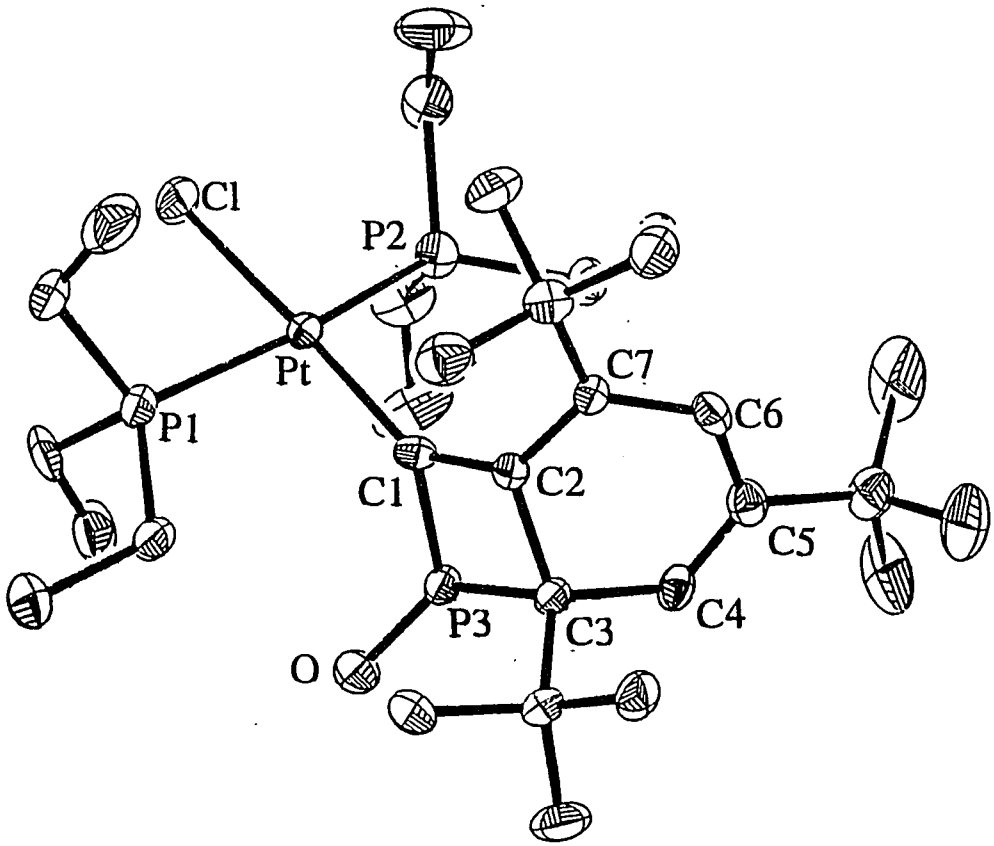


Figure 3. ORTEP drawing of (Cl)$(PEt_3)_2$Pt[(H)O=PBC] (Va).

DISCUSSION

Synthesis and rearrangement of $(X)(PR_3)_2M[C(=PR)X]$ complexes.

Unlikely the reactions of $Pt(PPh_3)_4$ with $Cl_2C=N-R$ (R = C_6H_{11}, C_6H_5, *p*-$C_6H_4NO_2$) which give 3-fragment oxidative addition products (eq 3), the reactions of $M(PEt_3)_4$ (M = Pt, Pd) or $(PPh_3)_2Pt(C_2H_4)$ with $X_2C=P-R$ (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl) give the *cis* products, **II** (Schemes 1 and 2). The *cis* products **IIa-IId** rearrange quickly to the *trans* isomers **Ia-Id** in the presence of free PEt_3, as occurs in other $(PR_3)_2 M^{II}X_2$ (M = Pt, Pd) complexes.[21] The other *cis* products, **IIe** and **IIf**, do not rearrange to the *trans* isomer even in the presence of PPh_3 . Instead they go on to form the products, R-C≡P and *cis*-$X_2Pt(PPh_3)_2$. In non-polar organic solvents (C_6H_6, hexanes, and CCl_4), **Ia-Ic** are stable enough to be isolated. Under the same reaction conditions, **Id** reacts further to give the final products, R-C≡P and *trans*-$Br_2Pd(PEt_3)_2$, without evidence (^{31}P NMR) for intermediates (Scheme 1). But in polar organic solvents (CH_2Cl_2, $CHCl_3$, and THF), all reactions of $M(PEt_3)_4$ (M = Pt, Pd) with $X_2C=P-R$ (X = Cl, Br) give the final products, R-C≡P and *trans*-$X_2M(PEt_3)_2$ (X = Br, Cl, M = Pt, Pd) via intermediates **I** and **III**. Thus, the solvent greatly affects the rate of formation of R-C≡P and *trans*-$X_2M(PEt_3)_2$ from complexes **I**.

In addition, the rate of conversion of the type **I** and **II** complexes to form **III** and **IV** depends on the PR'_3 ligands, the metal, and the halogen of the $X_2C=P-R$ reactant. In non-polar solvents (C_6H_6 and hexanes), the *cis* and *trans* isomers of $Cl(PEt_3)_2Pt[C(=PR)Cl]$ (**Ia** and **IIa**) do not react

further over a period of 72 h, but the *cis*-$(PPh_3)_2Pt[C(=PR)X]$ complexes (**IIe** and **IIf**) easily convert to the final products R-C≡P and *cis*-$X_2Pt(PPh_3)_2$ under the same conditions. On the other hand, in the polar solvent CH_2Cl_2 all of the type **II** complexes are unstable and undergo further reactions. Complex **Ia**, which has a relatively poor leaving group (Cl^-) at the carbon in the phosphaalkene ligand, is more stable than **Ib**, which has a better leaving group (Br^-). In general **Ia, Ib,** and **IIa**, are more stable than the Pd analogs **Ic** and **Id** in polar solvents. The tendency of polar solvents to promote further reactions of **I** and **II** suggests that X^- (X = Cl, Br) dissociation from the [C(=PR)X] ligand is the initial step in these reactions. This is supported by results of the reaction of Ag^+ with **Ia** which gives **VII** within a minute (Scheme 3). However, there is no spectroscopic evidence for terminal isocyaphide complexes $XL_2M(C{\equiv}PR)^+X^-$ expected to result from such a X^- dissociation. Presumably, they are so reactive that they immediately convert to XL_2M[X-PBC]. However, the mass spectrum (EI, at 70 ev) of **Ia** shows a fragment peak at m/e = 755.7 which corresponds to $[M-Cl]^+$. Although the structure of this fragment ion is not known, it could be the terminal isocyaphide complex $[Cl(PEt_3)_2Pt(C{\equiv}P\text{-}R)]^+$.

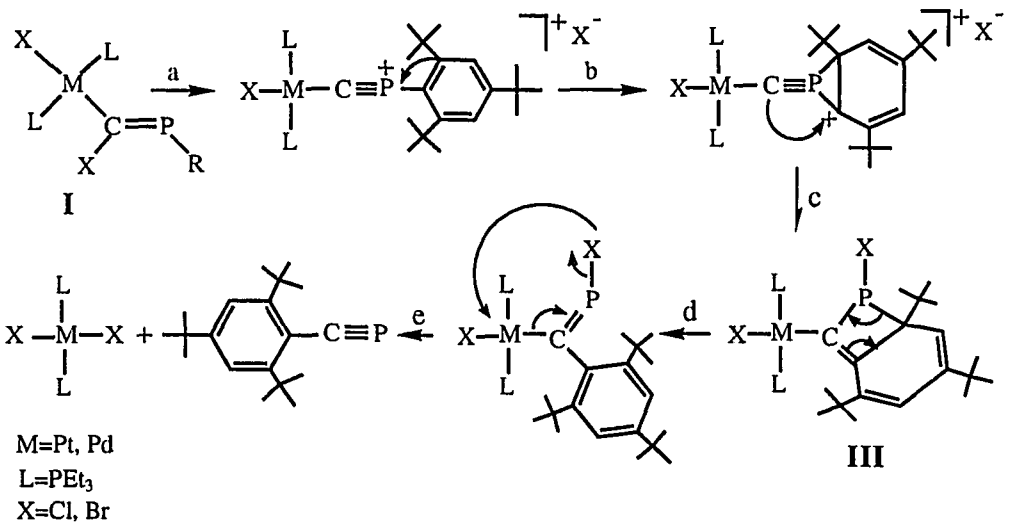
The stabilities of intermediates, **III** and **IV**, also depend on the PR_3 ligands, the halogen on the phosphorus, the structures (*cis* or *trans*) and the solvent. The *cis* type complex **IVa** reacts much more rapidly to give R-C≡P and $Cl_2Pt(PEt_3)_2$ than the *trans* analog **IIIa**. And also **IVa** is more reactive than **IVe.** The trend in increasing reactivity (**IIIa** < **IVe** < **IVa**) follows the trend (Cl < PPh_3 < PEt_3) in *trans* influence[29] of the ligand

trans to the phosphabicyclo ligand. The reactivities of intermediates (**III** and **IV**) also depend on the halogen which is on the phosphorus. The bromo complexes **IIIb** and **IVf** are more reactive than the Cl-analogs, **IIIa** and **IVe**.

A proposed mechanism for the conversion of complexes I to R-C≡P and $X_2M(PEt_3)_2$

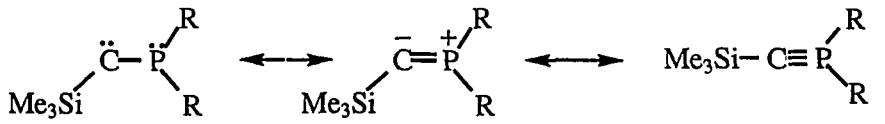
Based on the above reaction studies and the structure of **IIIa**, we propose the mechanism in Scheme 4 for the conversion of **I** to R-C≡P and *trans*-$X_2M(PEt_3)_2$. In step *a*, X^- dissociates to give a highly reactive aryl isocyaphide (C≡P-R) ligand whose positive phosphorus is attacked by an electron rich carbon on the supermesityl to give a λ^5 -phospha-acetylene type transient intermediate (step *b*). Addition of the isocyaphide carbon (step *c*) to the aryl ring carbon gives complex **III**; the structure of **IIIa** was established crystallographically.

Scheme 4



The formation of **III** clearly indicates that it is thermodynamically more stable than its isomer **I**. This is surprising since the supermesityl group loses its aromaticity in this isomerization. The aromaticity is restored in the final steps (*d* and *e*) leading to the final products *trans*-$X_2M(PEt_3)_2$ and R-C≡P.

Support for the proposed λ^5-phosphaacetylene intermediate formed in step *b* may be found in recent studies of Bertrand and co-workers,[30] who reported the synthesis and reactions of the λ^5-phosphaacetylene, Me_3Si-C≡PR_2 (where R = $(i\text{-}Pr)_2N$). Based on NMR



A **B** **C**

studies, they suggested that resonance form **C** best represents the compound.

Effect of H_2O on reactions of I, II, and III

Under conditions where the reactants and solvents are carefully dried, the *cis*- and *trans*-$(X)(PR'_3)_2M[C(=PR)X]$ (**I** and **II**) rearrange (Scheme 1 and 2) to give R-C≡P and $(X)_2M(PR'_3)_2$ through intermediates **III** and **IV**. However, if water is present in the reaction solution (Scheme 3), the major (or sole) products are the $(X)(PR'_3)_2M[(H)O{=}PBC]$ complex (**V** or **VI**); very little if any of the R-C≡P and $(X)_2M(PR'_3)_2$ products are observed. Since water reacts with the halo-phosphabicyclo complex **III** to give **V**, it appears that it is this facile reaction that leads to the

formation of **V**. Thus, small amount of water in this system dramatically change the course of the reaction.

CONCLUSIONS

These studies provide details of the syntheses of the metalla-phosphaalkene complexes $(X)(PR'_3)_2M[C(=PR)X]$ (X = Cl, Br; M = Pt, Pd; R' = Et, Ph; R = 2,4,6-tri-*tert*-butylphenyl) (**I** and **II**) from reactions (Scheme 1 and 2) of $X_2C=P-R$ with $M(PR'_3)_4$ or the reaction of $(Li)(Cl)C=P-R$ with *trans*-$Cl_2Pt(PEt_3)_2$ (eq 4). These complexes spontaneously react (Scheme 3) to give $R-C\equiv P$ and $X_2M(PR'_3)_2$ via phosphabicyclo intermediates **III** and **IV** in which the aromaticity of the 2,4,6-tri-*tert*-butylphenyl group (R) has been disrupted. A mechanism for this conversion has been proposed (Scheme 4). It is likely that the previously reported[10] reaction (eq 2) of $Pd(PPh_3)_4$ with $Cl_2C=P-R$ to give analogous products, $R-C\equiv P$ and $Cl_2Pd(PPh_3)_2$ proceeds by a similar mechanism. One might even speculate that the conversion (eq 1) of $(Li)(Cl)C=P-R$ to $R-C\equiv P$ proceeds by the mechanism in Scheme 4, where lithium plays the role of platinum. In the presence of H_2O, $(X)(PEt_3)_2Pt[C(=PR)X]$ (**Ia** and **Ib**) gives (Scheme 3) the oxy-phosphabicyclo complex $(X)(PEt_3)_2Pt[(H)O=PBC]$ (**Va** and **Vb**) instead of $R-C\equiv P$ and *trans*-$Cl_2Pt(PEt_3)_2$.

Acknowledgment

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PAPER II. BRIDGING CYAPHIDE (C≡P) AND BRIDGING ARYL ISOCYAPHIDE(C=P-R) LIGANDS: SYNTHESIS AND CHARACTERIZATION OF $(X)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$ AND $(X)(PEt_3)Pt(\mu\text{-}C{=}P\text{-}R)Pt(PEt_3)_2(X)$ (X=Cl, Br, R = 2,4,6-tri-*tert*-butylphenyl)

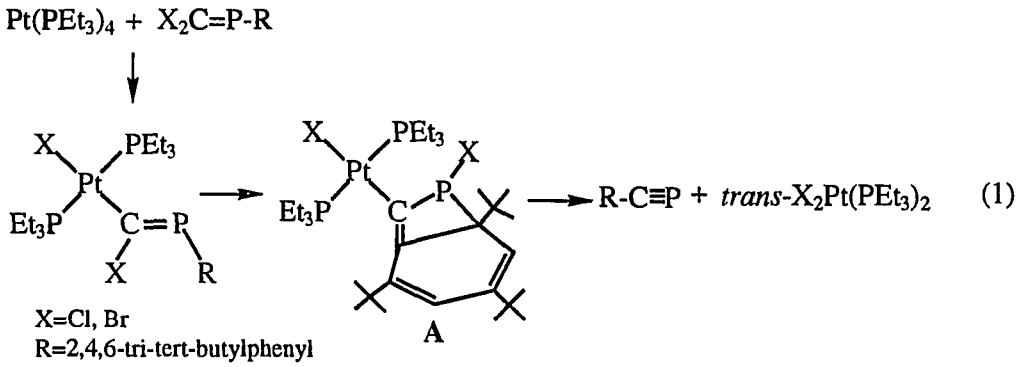
ABSTRACT

The halophosphaalkene platinum complexes, *trans*-$(X)(PEt_3)_2Pt[C(=PR)X]$ (**1a**: X = Cl; **1b**: X = Br; R = 2,4,6-tri-*tert*-butylphenyl) react with $Pt(PEt_3)_4$ to yield $(X)(PEt_3)Pt(\mu$-$C=PR)Pt(PEt_3)_2(X)$ (**3a**: X = Cl; **3b**: X = Br). The molecular structure of **3a** shows that it contains a semi-bridging isocyaphide (C≡P-R) ligand. The platinum complexes *trans*-$(X)(PEt_3)_2Pt[C(=PR)X]$ (**1a**: X = Cl; **1b**: X = Br; R = 2,4,6-tri-*tert*-butylphenyl) react with $Pd(PEt_3)_4$ to give $(X)(PEt_3)_2Pt(C\equiv P)$ (**4**) and $(X)(PEt_3)_2Pd(R)$ (**5**). Complexes **4**, which are tentatively assigned a structure with a terminal cyaphide ($C\equiv P^-$) ligand, react with $Pt(PEt_3)_4$ to give bridging cyaphide di-platinum complexes $(PEt_3)_2Pt(\mu$-$C=P)Pt(PEt_3)_2(X)$ (**6a**: X = Cl; **6b**: X = Br). The molecular structure of **6a** exhibits a bridging $C\equiv P^-$ ligand carbon-bonded to Pt(1) and η^2-bonded to Pt(2). In the structure of **5a**, a methyl group of each of the two o-*tert*-butyl groups of the R ligand sits above (and below) the Pd; however, NMR studies suggest there is little if any agostic interaction.

INTRODUCTION

During the past two decades, bulky alkyl and aryl R groups have been used to stabilize compounds with multiple bonds between carbon and phosphorus. As a result, many phosphaalkynes (RC≡P)[1] have been synthesized and subsequently incorporated as ligands into transition metal complexes.[2] According to photoelectron spectroscopic studies,[3] the HOMO of phosphaalkynes is a π-type orbital and the non-bonding (n) electrons are of lower energy; the π-n separation is greater in phosphaalkynes than in the corresponding nitriles (RC≡N), which generally prefer N-ligation to metals. The relatively high energy of the C≡P π-bond may explain the preference of RC≡P for side-on π-bonding over P-donor coordination in transition metal phosphaalkyne complexes.

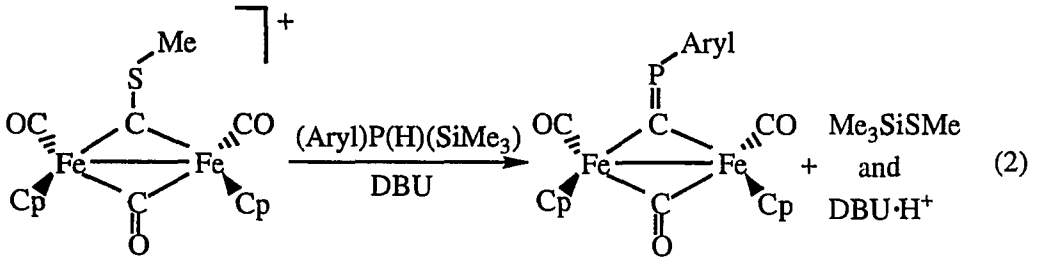
Unlike RC≡P compounds, the isomeric alkyl or aryl isocyaphides (C≡PR)[4] are unknown and are unstable relative to the RC≡P isomer according to ab initio calculations.[5] In fact, these calculations indicate that C≡P-H is 85 kcal/mol less stable than the H-C≡P isomer. Recently, several research groups have proposed free C≡PR



(1)

(where R = 2,4,6-tri-*tert*-butylphenyl) as a transient intermediate in the conversion of Li(Cl)C=PR to LiCl and RC≡P[6a-6d] and in the reaction of $Pd(PPh_3)_4$ with Cl_2C=PR to give $(Cl)_2Pd(PPh_3)_2$ and R-C≡P.[6e] The latter reaction, however, probably does not proceed through free C≡PR; this is suggested by our study[7] of the analogous reaction (eq 1) of $Pt(PEt_3)_4$ with Cl_2C=PR or Br_2C=PR. For this reaction, intermediate **A** has been isolated and characterized by X-ray diffraction studies. Thus, there is no evidence for free C≡PR as a transient intermediate in this reaction.

While there is no experimental evidence for free alkyl or aryl isocyaphides (C≡PR), we communicated[8] previously the synthesis of a di-platinum complex (Cl)(PEt_3)Pt(μ-C=PR)Pt$(PEt_3)_2$ (Cl) (**3a**) with a semi-bridging C≡PR ligand. More recently, Weber and co-workers[9] reported the synthesis (eq 2)



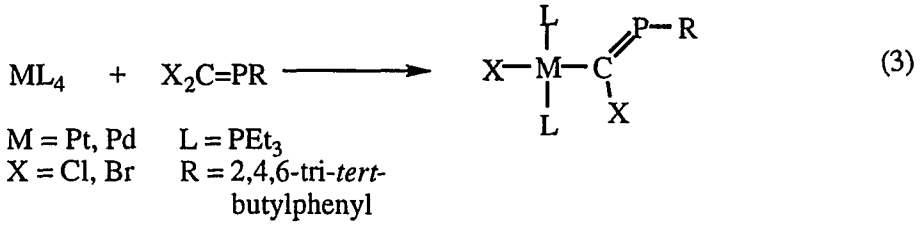
(2)

of a di-iron complex with a bridging C≡PR ligand. In the present paper, we provide details for the synthesis of **3a** and related derivatives.

In addition to our interest in stabilizing C≡PR ligands in transition metal complexes, we have also sought to prepare complexes with the cyaphide[10] ($C\equiv P^-$) ligand, the phosphorus analog of cyanide ($C\equiv N^-$), a well-known ligand in transition metal chemistry.[11] Since $C\equiv P^-$ has not

been detected, little is known about it; however, a MO calculation[12] suggests that its heat of formation is ca. 40 kcal/mol greater than that of $C{\equiv}N^{-\cdot}$ However, as discussed in a communication,[13] we have isolated and characterized crystallographically a di-platinum complex, $(Cl)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$, in which the $C{\equiv}P^-$ is C-bonded to one Pt and π-bonded to the other. Details of the synthesis and characterization of this di-platinum complex are described herein.

The syntheses of both the semi-bridging aryl isocyaphide complex $(Cl)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(Cl)$ (**3a**)[8] and the bridging cyaphide complex $(Cl)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$ (**6a**)[13] begin with the platinum complexes, *trans*-$(X)(PEt_3)_2Pt[C(=PR)X]$ (X = Cl, Br; R = 2,4,6-tri-*tert*-butylphenyl), whose preparations (eq 3) were reported previously.[7,8] In this paper,



(3)

are given details of the syntheses of **3a** and **6a** and related compounds, as well as evidence for the formation of the complexes $(X)(PEt_3)_2Pt(C{\equiv}P)$ (X = Cl, Br) with a terminal cyaphide ($C{\equiv}P$) ligand.

EXPERIMENTAL SECTION

General procedure

All manipulations were carried out under a dry, oxygen-free argon atmosphere, using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while hexanes and dichloromethane (CH_2Cl_2) were distilled from CaH_2.

The ^1H NMR spectra were recorded in C_6D_6 unless otherwise noted using a Nicolet-NT 300 MHz or Varian VXR-300 MHz spectrometer with tetramethylsilane (TMS) (δ = 0.00 ppm) as the internal standard. The $^{31}P\{^1H\}$ and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer in C_6D_6 using 85% H_3PO_4 (δ = 0.00 ppm) as the external standard. Elemental analyses were performed by either Galbraith Laboratories, Inc., Knoxville, TN or Desert Analytics, Tucson, AZ. The complexes $Pt(PEt_3)_4$,[14] $Pd(PEt_3)_4$,[15] *trans*-$(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (**1a**),[7] *trans*-$(Br)(PEt_3)_2Pt[C(=PR)Br]$ (**1b**),[7] and *trans*-$(Cl)(PEt_3)_2Pd[C(=PR)Cl]$ (**1c**),[7] where R = 2,4,6-tri-*tert*-butylphenyl, were prepared by literature methods.

Preparation of $(Cl)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(Cl)$ (3a)

To a benzene solution (5 mL) of *trans*-$(Cl)(PEt_3)_2Pt[C(=PR)Cl]$ (**1a**) (0.395 g, 0.500 mmol) was added a benzene solution (5 mL) of $Pt(PEt_3)_4$ (0.334 g, 0.500 mmol). After the solution was stirred at room temperature under argon for 24 h, the solvent was evaporated to dryness

to yield an oily reddish-yellow residue. The residue was extracted with hexanes (30 mL) and filtered by cannula. After reducing the extract to one-fourth of its volume under vacuum, red crystals of **3a** (0.717 g, 65%) were obtained by cooling (-30 °C) the solution. ^{1}H NMR (C_6D_6) δ 7.46 (s, 2H, R), 2.43 (m, 6H, CH_2), 2.09 (m, 6H, CH_2), 1.49 (m, 6H, CH_2), 1.74 (s, 18H, CH_3 of R), 1.35 (s, 9H, CH_3 of R), 1.26 (m, 18H, CH_3 of Et), 0.82 (m, 9H, CH_3 of Et). ^{31}P NMR (acetone-d_6, 85% H_3PO_4 external standard) (see Figure 1 for atom labels) δ 151.3 (td, $^{3}J_{P1P2}$ = 23 Hz, $^{3}J_{P1P4}$ = 35 Hz, $^{2}J_{Pt1P1}$ = 110 Hz, $^{2}J_{Pt2P1}$ = 321 Hz, P1), 22.8 (d, $^{3}J_{P4P1}$ = 35 Hz, $^{1}J_{Pt2P4}$ = 4814 Hz, $^{2}J_{Pt1P4}$ = 512 Hz, P4 in PEt_3), 19.6 (d, $^{3}J_{P2P1}$ = 23 Hz, $^{1}J_{Pt1P2}$ = 2428 Hz, $^{2}J_{Pt2P2}$ = 67 Hz, P2 and P3 in PEt_3). Anal. calcd for $C_{37}H_{74}Cl_2P_4Pt_2$: C, 40.25; H, 6.78. Found; C, 40.36; H, 6.95.

Preparation of *trans*-(Br)(PEt$_3$)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(Br) (3b)

Complex **3b** was prepared by the same method as described above using *trans*-(Br)$(PEt_3)_2$Pt[C(=PR)Br] (**1b**) (0.088 g, 0.10 mmol) and $Pt(PEt_3)_4$ (0.067 g, 0.10 mmol). The product **3b** was obtained as red crystals (0.072 g, 60%). ^{1}H NMR (C_6D_6) δ 7.47 (s, 2H, R), 2.53 (m, 12H, CH_2 of Et), 2.10 (m, 6H, CH_2 of Et), 1.73 (s, 18H, CH_3 of R), 1.35 (s, 9H, CH_3 of R), 1.25 (m, 18H, CH_3 of Et), 0.82 (m, 9H, CH_3 of Et). ^{31}P NMR (C_6D_6) δ 142.3 (td, $^{3}J_{P1P2}$ = 23 Hz, $^{3}J_{P1P4}$ = 36 Hz, $^{2}J_{Pt1P1}$ = 102 Hz, $^{2}J_{Pt2P1}$ = 352 Hz, P1), 19.9 (d, $^{3}J_{P4P1}$ = 36 Hz, $^{1}J_{Pt2P4}$ = 4754 Hz, $^{2}J_{Pt1P4}$ = 465 Hz, P4 in PEt_3), 14.7 (d, $^{3}J_{P2P1}$ = 23 Hz, $^{1}J_{Pt1P2}$ = 2387 Hz, $^{2}J_{Pt2P2}$ = 53 Hz, P2 and P3 in PEt_3). Anal. calcd for $C_{37}H_{74}Br_2P_4Pt_2$: C, 37.27; H, 6.20. Found: C, 37.49; H, 6.26.

Reaction of *trans*-(Cl)(PEt$_3$)$_2$Pt[C(=PR)Cl] (1a) with Pd(PEt$_3$)$_4$ to give 4a and 5a, then with Pt(PEt$_3$)$_4$ to give (Cl)(PEt$_3$)$_2$Pt(μ-C=P)Pt(PEt$_3$)$_2$ (6a)

To a benzene solution (5 mL) of **1a** (0.395 g, 0.500 mmol) was added a benzene solution (5 mL) of Pd(PEt$_3$)$_4$ (0.289 g, 0.500 mmol). After the solution was stirred at room temperature under argon for 8 h, only two products, **4a** and **5a**, were generated, as established by a $^{31}P\{^1H\}$ NMR spectrum. To this mixture (in situ) was added a benzene solution (5 mL) of equimolar Pt(PEt$_3$)$_4$ (0.334 g, 0.500 mmol). After stirring the reaction solution for 30 min at room temperature, the solvent was evaporated to dryness under vacuum. The residue was extracted with hexanes (30 mL) and filtered by cannula. After reducing the hexanes extract to half of its volume, colorless crystals of **5a** (0.279 g, 90%) were obtained after 2-3 days by cooling to -78 °C. After filtering off **5a** by cannula, the volume of the solution was reduced under vacuum to give pale brown crystals of **6a** (0.376 g, 80%) within ca. 2 weeks upon cooling to -78 °C. Data for **4a**: ^{31}P NMR δ 68.0 (t, $^3J_{PP}$ = 9.2 Hz, $^2J_{PtP}$ = 303 Hz, C≡P), 7.3 (d, $^3J_{PP}$ =9.2 Hz, $^1J_{PtP}$ = 2871 Hz, PEt$_3$). **5a**: ^1H NMR (C_6D_6) δ 7.42 (t, 2H, $^5J_{PH}$ = 0.97 Hz, R), 1.89 (s, 18H, CH$_3$ of R), 1.68 (tq, 12H, $^3J_{PH}$ = 2.69 Hz, $^3J_{HH}$ = 7.08 Hz, CH$_2$ of Et), 1.34 (s, 9H, CH$_3$ of R), 0.88 (m, 18H, $^3J_{HH}$ = 7.08 Hz, CH$_3$ of Et). ^{31}P NMR (C_6D_6) δ -2.75 (s, PEt$_3$). Anal. calcd for $C_{30}H_{59}ClP_2Pd$: C, 57.83; H, 9.73. Found: C, 57.60; H, 9.56. **6a**: ^{31}P NMR (C_6D_6) δ 107.0 (tdd, $^3J_{P1P2}$ = 10.7 Hz, $^2J_{P1P4}$ = 10.7 Hz, $^2J_{P1P5}$ = 13.7 Hz, $^2J_{Pt1P1}$ = 255 Hz, $^1J_{Pt2P1}$ = 58 Hz, C≡P), 18.6 (dd, $^2J_{P1P4}$ = 10.7 Hz, $^2J_{P4P5}$ = 35.1 Hz, $^1J_{Pt2P4}$ = 3619 Hz, $^3J_{Pt1P4}$ = 137 Hz, P4), 15.0 (tdd, $^4J_{P5P2}$ = 4.5 Hz, $^2J_{P5P4}$ = 35.1 Hz, $^2J_{P5P1}$ = 13.7 Hz,

$^{1}J_{Pt2P5}$ = 3155 Hz, P5), 4.9 (dd, $^{3}J_{P2P1}$ = 10.7 Hz, $^{4}J_{P2P5}$ = 4.5 Hz, $^{1}J_{Pt1P2}$ = 2936 Hz, P2 and P3). Anal. calcd for $C_{25}H_{60}ClP_5Pt_2$: C, 31.89; H, 6.38. Found: C, 31.72; H, 6.61.

Reaction of *trans*-(Br)(PEt$_3$)$_2$Pt[C(=PR)Br] (1b) with Pd(PEt$_3$)$_4$ to give 4b and 5b, then with Pt(PEt$_3$)$_4$ to give (Br)(PEt$_3$)$_2$Pt(μ-C=P)Pt(PEt$_3$)$_2$ (6b)

To a benzene solution (1 mL) of **1b** (0.044 g, 0.050 mmol) was added a benzene solution (1 mL) of Pd(PEt$_3$)$_4$ (0.029 g, 0.050 mmol). After the solution was stirred at room temperature under argon for 3 h, only two products **4b** and **5b** were observed in the ^{31}P NMR spectrum. To this reaction mixture (in situ) was added a benzene solution (1 mL) of equimolar Pt(PEt$_3$)$_4$ (0.033 g, 0.050 mmol). After stirring the reaction solution for 30 min at room temperature, only one product **6b** was formed quantitatively; **5b** was also present in the final reaction mixture. ^{31}P NMR (C_6D_6) data for **4b**: δ 68.0 (t, $^{3}J_{PP}$ = 9.6 Hz, $^{2}J_{PtP}$ = 293 Hz, C≡P), 3.8 (d, $^{3}J_{PP}$ = 9.6 Hz, $^{1}J_{PtP}$ = 2877 Hz , PEt$_3$). **5b**: δ -5.4 (s, PEt$_3$). **6b**: δ 107.0 (tdd, $^{3}J_{P1P2}$ = 11.0 Hz, $^{2}J_{P1P4}$ = 9.6 Hz, $^{2}J_{P1P5}$ = 13.7 Hz, $^{2}J_{Pt1P1}$ = 251 Hz, C≡P), 18.4 (dd, $^{2}J_{P1P4}$ = 9.6 Hz, $^{2}J_{P4P5}$ = 37.1 Hz, $^{1}J_{Pt2P4}$ = 3886 Hz, $^{2}J_{Pt2P4}$ = 137 Hz, P4), 14.5 (tdd, $^{4}J_{P5P2}$ = 4.1 Hz, $^{2}J_{P5P4}$ = 37.1 Hz, $^{2}J_{P5P1}$ = 13.7 Hz, $^{1}J_{Pt2P5}$ = 3194 Hz, P5), 1.0 (dd, $^{3}J_{P2P1}$ = 11.0 Hz, $^{4}J_{P2P5}$ = 4.1 Hz, $^{1}J_{Pt1P2}$ = 2950 Hz, P2 and P3).

Reaction of *trans*-(Cl)(PEt$_3$)$_2$Pd[C(=PR)Cl] (1c) with 2 equivalents of Pt(PEt$_3$)$_4$ to give 4a and 5a, then to give 6a as the final product

To a benzene solution (1 mL) of **1c** (0.070 g, 0.10 mmol) was added a benzene solution (1 mL) of Pt(PEt$_3$)$_4$ (0.134 g, 0.200 mmol). After the solution was stirred at room temperature for 12 h, only two products, **5a**

and **6a**, were found in the reaction mixture. These two products were separated by the same recrystallization procedure as that used in the synthesis of **6a** from the reaction of **1a** with $Pd(PEt_3)_4$ followed by $Pt(PEt_3)_4$. Products **5a** (0.045g, 72%) and **6a** (0.061g, 65%) were identified by their ^{31}P NMR spectra.

X-ray crystal structure analyses

Each crystal was attached to the tip of a glass fiber and mounted on the diffractometer for data collection at -50(1) °C. Cell constants were determined from lists of reflections found by an automated search routine. Pertinent data collection and reduction information for **5a** are given in Table I. Lorentz and polarization corrections were applied. A correction for nonlinear decay in the standard reflections was applied to the data for **5a**. Absorption corrections based on a series of azimuthal scans were applied to the data. The centric space group C2/c for **5a** was indicated initially by systematic absences and intensity statistics. The structure was solved by direct methods.[16] All non-hydrogen atoms in **5a** were refined with anisotropic thermal parameters (Table II). All hydrogen atoms in **5a** were refineded as riding atoms with C-H distances equal to 0.96 Å and individual isotropic thermal parameters, except in the case of mehtyl groups which were constrained to group isotropic temperature parameters. The *p-tert*-butyl group was statistically disordered about the crystallographic two-fold rotation axis and these hydrogens were given fixed isotropic temperature factors. All the refinement calculations were performed on a Digital Equipment Micro Vax 3100 computer using the SHELXTL Plus programs[16] for **5a**.

Table I. Crystal and Data Collection Parameters for *trans*-(Cl)(PEt_3)$_2$Pd(R) (5a), R = 2,4,6-tri-*tert*-butylphenyl

Crystal Data	
formula	$C_{30}H_{59}ClP_2Pd$
formula weight	623.6
color and habit	yellow, monoclinic
crystal size, mm	0.55 x 0.40 x 0.37
crystal system	monoclinic
space group	C2/c
a, Å	17.580 (4)
b, Å	12.945 (2)
c, Å	14.877 (3)
β, °	102.99 (2)
V, Å^3	3307.4 (11)
Z	4
D (calcd.)	1.252 g/cm^3
Data Collection and Refinement	
Diffractometer	Siemens P4RA
Radiation	MoKα (K = 0.71073 Å)
monochrometer	highly oriented graphite crystal
scan type	θ–2θ
2θ range, deg	4.0-50.0
no. of data collected	6187
no. of unique data	2907
unique observed data	2690; F > 4.0σ (F)

Table I. continued

no. of parameters refined	186
R^a, $_wR^b$	0.0272 %, 0.0403 %
Goodness-of-fit[c]	1.10

[a] $R = \Sigma| |F_o| - |F_c| | / \Sigma |F_o|$

[b] $_wR = [\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega |F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$

[c] Goodness-of-fit = $[\Sigma\omega(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$

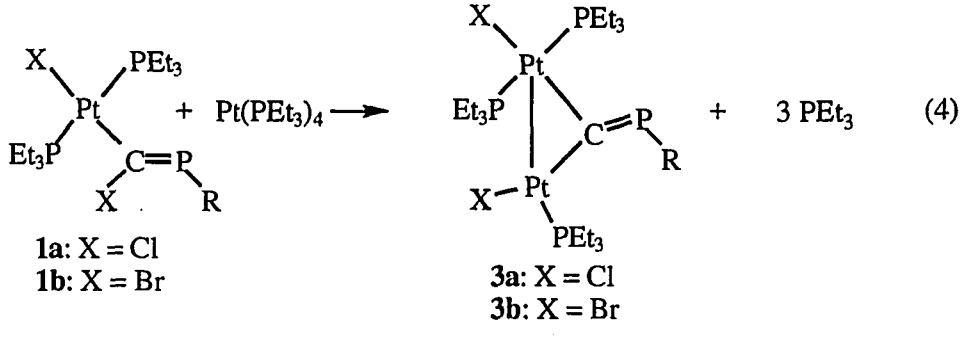
Table II. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Coefficients ($Å^2$ x10^3) for the Compound *trans*-(Cl)$(PEt_3)_2$Pd(R) (5a), R = 2,4,6-tri-*tert*-butylphenyl

atom	x	y	z	U(eq)
Pd	5000	1907(1)	2500	23(1)
Cl	5000	58(1)	2500	49(1)
P	4013(1)	1863(1)	3331(1)	30(1)
C(11)	4302(2)	1010(2)	4338(2)	47(1)
C(12)	3710(2)	596(3)	4824(2)	75(1)
C(13)	3764(2)	3103(2)	3794(2)	45(1)
C(14)	3072(2)	3155(2)	4231(3)	64(1)
C(15)	3047(1)	1401(2)	2716(2)	48(1)
C(16)	3018(2)	375(2)	2224(2)	65(1)
C(1)	5000	3483(2)	2500	23(1)
C(2)	4501(1)	4052(1)	1786(1)	25(1)
C(20)	3890(1)	3640(2)	932(1)	32(1)
C(21)	3078(1)	3945(2)	1035(2)	58(1)
C(22)	4042(2)	4150(2)	43(2)	56(1)
C(23)	3880(1)	2483(2)	743(2)	44(1)
C(3)	4516(1)	5128(1)	1817(1)	30(1)
C(4)	5000	5695(2)	2500	30(1)
C(40)	5000	6883(2)	2500	35(1)
C(41)	5244(4)	7287(4)	1675(4)	59(2)
C(42)	5531(4)	7350(3)	3372(3)	58(2)
C(43)	4154(3)	7258(4)	2479(5)	61(2)

RESULTS AND DISCUSSIONS

Synthesis of semi-bridging isocyaphide platinum complexes, (X)(PEt$_3$)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(X) (3a: X = Cl; 3b: X = Br)

The first examples of stable aryl isocyaphide metal complexes (X)(PEt$_3$)Pt(μ-C=PR)Pt(PEt$_3$)$_2$(X) (**3a**: X = Cl; **3b**: X = Br) were prepared by the reaction of *trans*-(X)(PEt$_3$)$_2$Pt[C(=PR)X] with Pt(PEt$_3$)$_4$ in benzene (or in hexanes) solvent at room temperature (eq 4). This oxidative-addition type reaction was complete within 24 h and afforded **3a** or **3b** as the only product as determined by ^{31}P NMR spectra of the reaction solutions;



1a: X = Cl
1b: X = Br

3a: X = Cl
3b: X = Br

some O=PEt$_3$ impurity was also formed presumably resulting from the reaction of PEt$_3$ with adventitious O$_2$. The reaction leading to the bromo analog **3b** was faster than that to **3a**. But both of these reactions were much slower than those (eq 3) of X$_2$C=PR (X = Cl, Br) with Pt(PEt$_3$)$_4$ which were complete within minutes in the same solvents (C$_6$H$_6$ or hexanes) at room temperature.[7,8] Complexes **3a** and **3b** were isolated in 60-65% yield after recrystallization in hexanes at -78 °C. During recrystallization, red crystals of **3a** or **3b** precipitated after colorless crystals of the O=PEt$_3$ impurity formed. Complexes **3a** and **3b** are stable

in air for at least a month at room temperature and are soluble in organic solvents (C_6H_6, hexanes, acetone, THF, and CH_2Cl_2). Complexes **3a** and **3b** were also prepared by the direct reaction of X_2C=PR (X = Cl, Br) with two equivalents of $Pt(PEt_3)_4$ in benzene (or in hexanes) solvent at room temperature; in this synthesis, both reactions (eq 3 and 4) occur in the same solution. But the yield (<40%) was much lower than that obtained from the reaction of **1a** with $Pt(PEt_3)_4$ (eq 4).

Compounds **3a** and **3b** were characterized by NMR spectroscopy ($^{31}P\{^1H\}$ and ^1H), elemental analysis, and X-ray crystallography (for **3a**). The NMR spectra of both **3a** and **3b** show the same pattern of signals which suggests they have the same structure. And these spectra are consistent with the structure (Figure 1) of **3a** as established crystallographically. The $^{31}P\{^1H\}$ NMR spectrum of **3a** shows three different signals. The peak at 151.3 ppm, assigned to the phosphorus in the C=PR ligand, shows a doublet of triplets with two different Pt satellites, which is consistent with the structure of **3a**; the triplet ($^3J_{PP}$ = 23 Hz) results from coupling of P(1)[17] to the two equivalent PEt_3 ligands on Pt(1) and the doublet ($^3J_{PP}$ = 35 Hz) is caused by coupling to the PEt_3 ligand on Pt(2). Although the two ^{195}Pt-P(1) coupling constants ($^2J_{PtP1}$ = 321 Hz, $^2J_{PtP1}$ = 110 Hz) to the Pt atoms cannot be assigned unambiguously, we can make a best guess based on previous observations[18] that J_{PtP} coupling constants are larger for complexes with lower Pt coordination number. Thus, the large J_{PtP} (321 Hz) may be

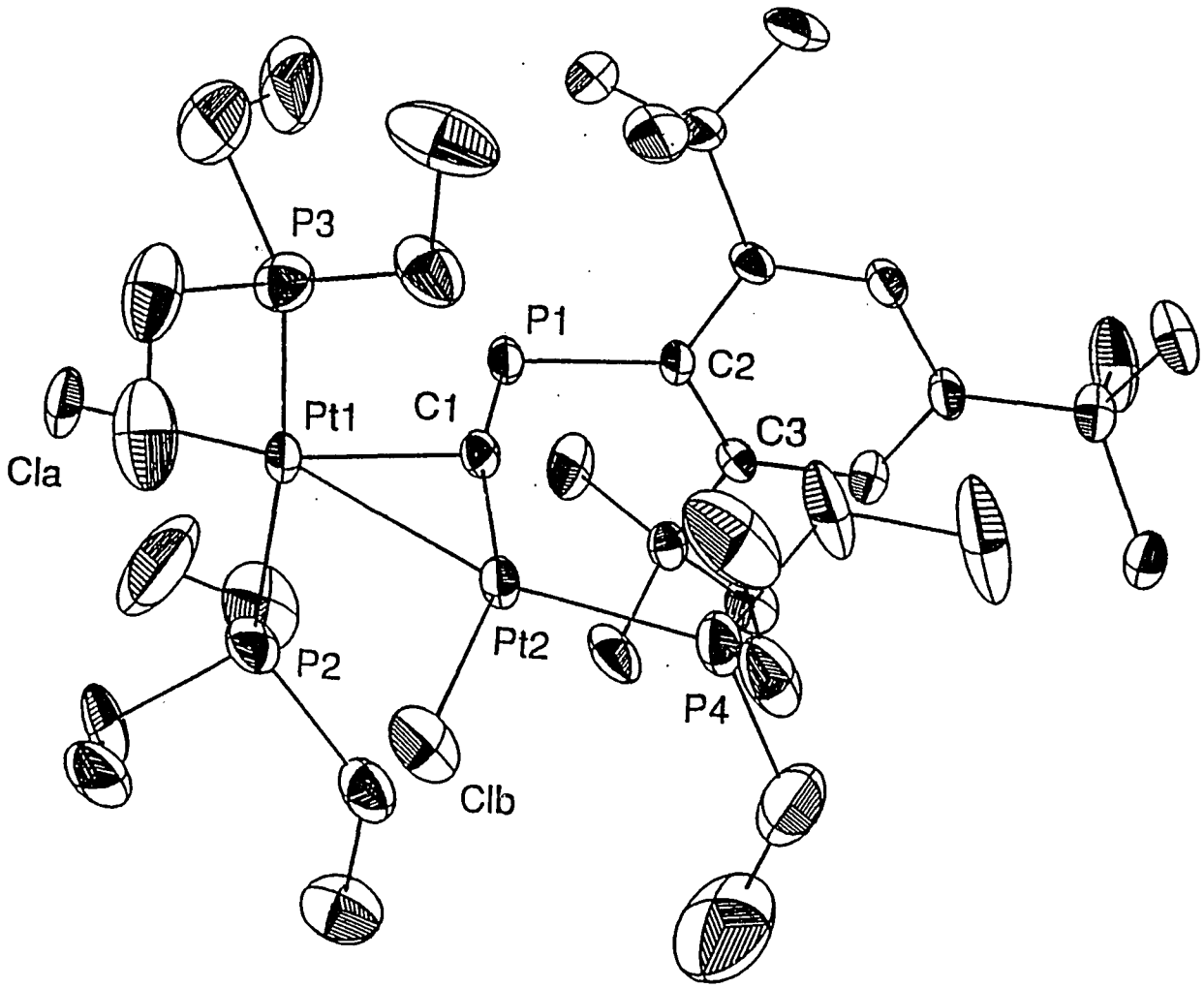


Figure 1. ORTEP drawing of (Cl)(PEt_3)Pt(μ-C=PR)Pt(PEt_3)$_2$(Cl) (**3a**)

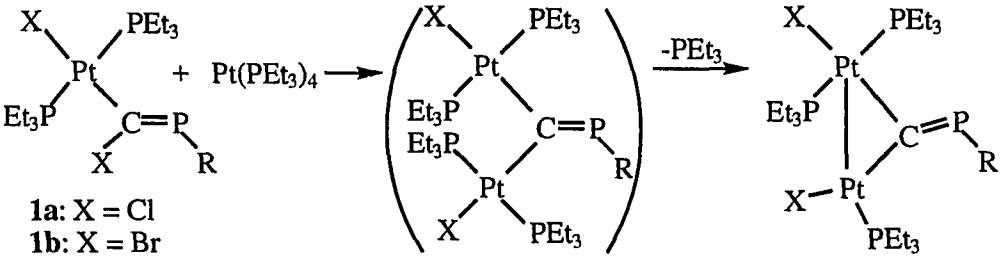
Table III. Selected Bond Distances (Å) and Angles (deg) for the Compound (Cl)(PEt_3)Pt(μ-C=PR)Pt(PEt_3)$_2$ (Cl) (3a), R = 2,4,6-tri-*tert*-butylphenyl

Distances, Å			
Pt(1)-Pt(2)	2.6751(5)	Pt(1)-Cla	2.388(3)
Pt(1)-P(2)	2.338(4)	Pt(2)-Clb	2.398(3)
Pt(1)-C(1)	2.107(9)	Pt(1)-P(3)	2.324(4)
Pt(2)-C(1)	1.89(1)	Pt(2)-P(4)	2.217(3)
P(1)-C(1)	1.67(1)	P(1)-C(2)	1.89(1)
Angles, deg			
Pt(2)-Pt(1)-Cla	155.2(1)	Pt(2)-Pt(1)-P(2)	90.34(9)
Pt(2)-Pt(1)-P(3)	90.4(1)	Pt(2)-Pt(1)-C(1)	44.7(2)
Cla-Pt(1)-P(2)	87.8(2)	Cla-Pt(1)-P(3)	86.4(1)
Cla-Pt(1)-C(1)	159.9(3)	P(2)-Pt(1)-P(3)	167.7(1)
P(2)-Pt(1)-C(1)	96.8(2)	P(3)-Pt(1)-C(1)	92.4(2)
Pt(1)-Pt(2)-Clb	104.76(9)	Pt(1)-Pt(2)-P(4)	163.42(9)
Pt(1)-Pt(2)-C(1)	51.5(3)	Clb-Pt(2)-P(4)	91.5(1)
Clb-Pt(2)-C(1)	156.2(3)	P(4)-Pt(2)-C(1)	112.3(3)
C(1)-P(1)-C(2)	110.7(5)	Pt(1)-C(1)-Pt(2)	83.8(4)
P(1)-C(2)-C(3)	122.1(7)	P(1)-C(2)-C(7)	120.6(7)
Pt(1)-C(1)-P(1)	112.0(5)	Pt(2)-C(1)-P(1)	164.1(6)

assigned to $^{195}Pt(2)$-P(1) and the small value (110 Hz) to $^{195}Pt(1)$-P(1). Similarily, the ^{195}Pt-P coupling constant (2428 Hz) for the two PEt_3 ligands on Pt(1) is smaller than that (4814 Hz) for the PEt_3 ligand on Pt(2). The doublet at 19.6 ppm is assigned to the two equivalent PEt_3 ligands on Pt(1), while the other doublet at 22.8 ppm is assigned to the PEt_3 ligand on Pt(2). The chemical shift of the phosphorus in the semi-bridging isocyaphide ligand (151.3 ppm) is significantly upfield of that for the phosphorus in **1a** (223.3 ppm).

Although no intermediates were observed by ^{31}P NMR spectroscopy during the reaction (eq 4) of **1a** (or **1b**) with $Pt(PEt_3)_4$, a possible mechanism for the formation of **3a** (or **3b**) could involve intermediate **2a** (or **2b**) resulting from oxidative addition of the C-X bond to the $Pt(PEt_3)_4$ (Scheme 1). Loss of PEt_3 from this intermediate followed by Pt-Pt bond formation would give the final product **3a** (or **3b**).

Scheme 1



1a: X = Cl
1b: X = Br

2a: X = Cl
2b: X = Br

3a: X = Cl
3b: X = Br

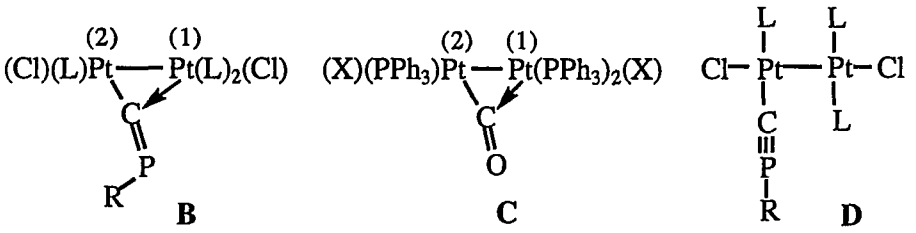
X-ray crystal structure of (Cl)(PEt_3)Pt(μ-C=PR)Pt(PEt_3)$_2$(Cl) (3a)

The ORTEP drawing of complex **3a** (Figure 1), which was reported briefly in a communication,[8] shows a dinuclear complex with a bridging

μ-C=PR ligand. The atoms Cl(a), Pt(1), C(1), P(1), C(2), Pt(2), Cl(b), and P(4) are all coplanar within 0.134 Å; of the coordinated atoms, only P(2) and P(3) are out of this plane, the Pt(1)-P(2) and Pt(1)-P(3) bond vectors being approximately perpendicular to this plane. The C(1)-P(1) distance (1.67 (1) Å) in the μ-C=PR ligand is the same as that (1.678 (5) Å) in the precursor complex (Cl)(PEt_3)$_2$Pt[C(=PR)Cl] (**1a**)[7] and that (1.67 Å) in Ph(H)C=PR, where R = 2,4,6-tri-*tert*-butylphenyl.[19] The Pt-C distances to the bridging C=PR from the inequivalent Pt atoms are significantly different; Pt(1)-C(1) (2.107 (9) Å) is 0.22 Å longer than Pt(2)-C(1) (1.89 (1) Å). Also the Pt-C(1)-P(1) angles are vastly different; the Pt(2)-C(1)-P(1) angle (164.1 (6)°) approaches linearity while Pt(1)-C(1)-P(1) (112.0 (5)°) is sharply bent.

The geometry of the C=P-R ligand in **3a** is not analogous to symmetrically bridging isocyanide ligands as occurs in compounds such as the triangular Pt_3(μ-CNR)$_3$(CNR)$_3$[20] and the dinuclear Cp_2Fe_2(μ-CNR)$_2$(CNR)$_2$,[21] or in the symmetrically bridging isocyaphide ligand in $Cp_2Fe_2(CO)_2$(μ-CO)(μ-C=P-mesityl) (eq 2).[9] The long nonbonding Pt(1)-P(1) distance (3.15 Å) eliminates the possibility that the C=P-R ligand is a four-electron donor with π-donation from the C=P bond to Pt(1). Therefore, the most reasonable description of μ-C=P-R in this complex is that of a semibridging group, which is strongly coordinated to Pt(2) and interacts more weakly with Pt(1) by accepting at C(1) electron donation from the more electron rich Pt(1) (with two PEt_3 donor ligands), as represented in **B** (chart I).

Chart I



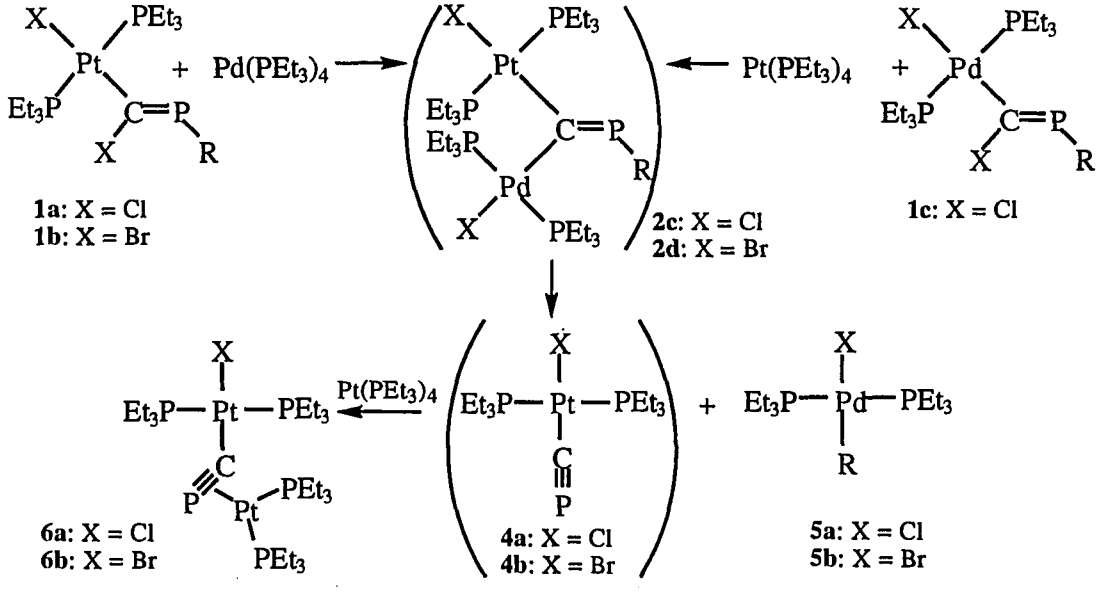
Structure **B** of compound **3a** is very similar to that (**C**) of $(X)(PPh_3)Pt(\mu\text{-}CO)Pt(PPh_3)_2(X)$ (X = Cl[22], Br[23]), both of which have been described as containing a semibridging CO ligand. As in **3a**, the Pt(2)-C-O angle (156 (1)°) is very open and the Pt(2)-C bond distance (1.901 (13) Å) is shorter than that of Pt(1)-C (2.218 (13) Å) in $(Br)(PPh_3)Pt(\mu\text{-}CO)Pt(PPh_3)_2(Br)$.[23] In the absence of a semi-bridging interaction with Pt(1), the C≡PR ligand in **3a** would be terminal and have structure **D**. It is not clear why the C≡PR ligand in **3a** and the CO in **C** prefer the semibridging structure.

Reaction of $(X)(PEt_3)_2Pt[C(=PR)X]$ (1a: X = Cl; 1b: X = Br) with $Pd(PEt_3)_4$ to Give 4 and 5, then with $Pt(PEt_3)_4$ to Give $(X)(PEt_3)Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$ (6a: X = Cl; 6b: X = Br)

When the precursor complexes **1a** and **1b** react with $Pd(PEt_3)_4$ in benzene (or hexanes) solvent at room temperature, the reaction proceeds in a totally different manner (Scheme 2) than that with $Pt(PEt_3)_4$ (eq 4). After stirring the reaction solution of **1a** and $Pd(PEt_3)_4$ for 24 h, the two complexes (**4a** and **5a**) were observed as the only products in the $^{31}P\{^1H\}$ NMR spectrum. These products were quite stable in solution under argon even at room temperature for at least a week. Despite this stability,

all attempts to separate **4a** by fractional crystallization in hexanes solvent at low temperature (-78 °C) were unsuccessful; however, colorless crystals of **5a** (90% yield) readily separated at an early stage of this recrystallization. Complex **5a** was also separated from the mixture by column chromatography (neutral alumina, hexanes).

Scheme 2



Complex **4a** decomposed to unidentifiable products during the chromatography even when performed at low temperature (-30 °C). The spectroscopic characterization of **4a** is described below. The reaction of **1b** with $Pd(PEt_3)_4$ showed exactly the same reaction pattern and gave the analogous products (**4b** and **5b**).

The ^1H and $^{31}P\{^1H\}$ NMR spectra of **5a** in solution are consistent with its structure as determined by X-ray diffraction (Figure 2). The ^1H NMR spectrum of **5a** clearly shows the expected signals, two singlets at δ

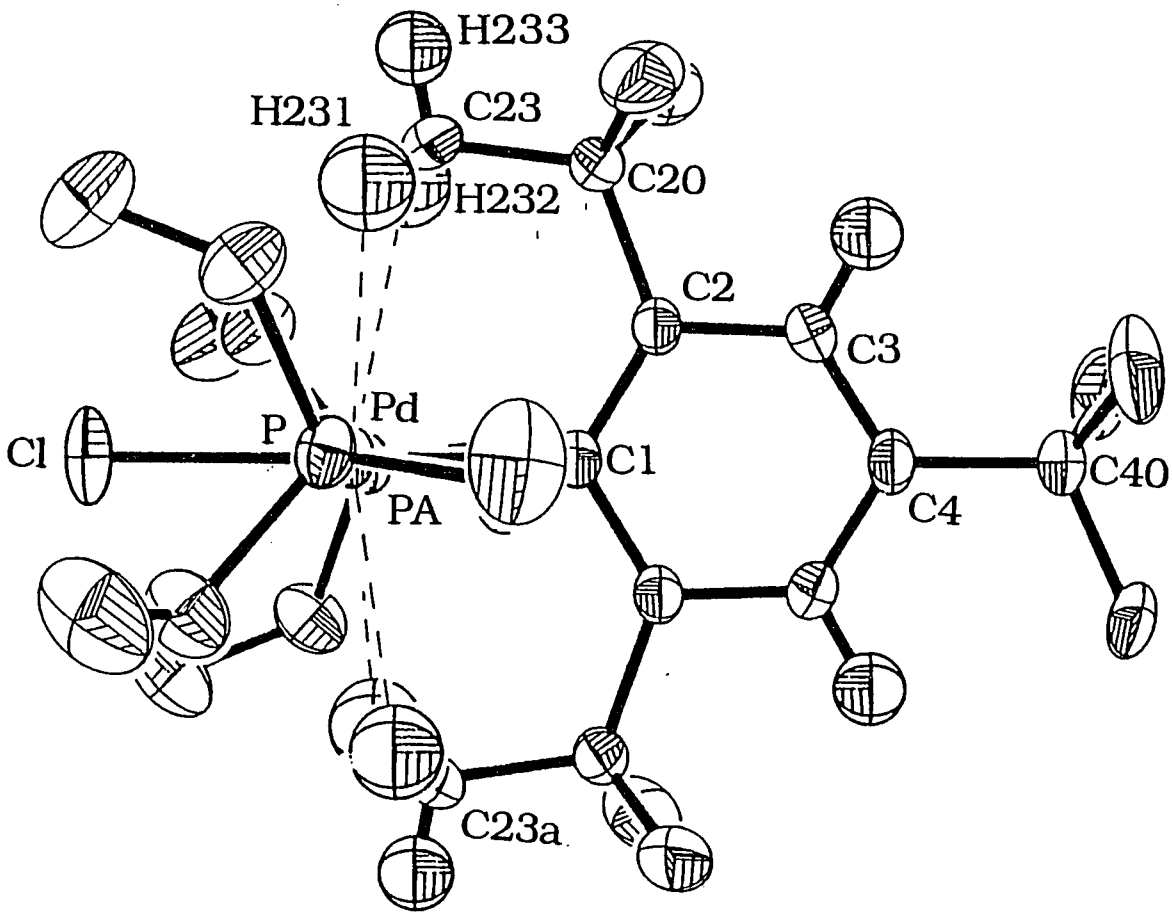


Figure 2. ORTEP drawing of (Cl)(PEt_3)$_2$Pd(2,4,6-tri-*tert*-butylphenyl) (**5a**)

Table IV. Selected Bond Distances (Å) and Angles (deg) for the Complex *trans*-(Cl)$(PEt_3)_2$Pd(R) (5a), R = 2,4,6-tri-*tert*-butylphenyl

Diastances, Å			
Pd-Cl	2.394(1)	Pd-C(1)	2.045(3)
Pd-P	2.348(1)	Pd-PA	2.348(1)
Pd-H(231)	2.495	Pd-H(233)	2.795
Angles, deg			
Cl-Pd-P	88.6(1)	Cl-Pd-C(1)	180.0(1)
P-Pd-C(1)	91.4(1)	Cl-Pd-PA	88.6(1)
P-Pd-PA	177.2(1)	C(1)-Pd-PA	91.4(1)

1.89 ppm (*o-tert*-Bu,18H) and δ 1.34 ppm (*p-tert*-Bu, 9H) and a doublet at δ 7.42 ppm (2H on Ph), for the supermesityl group; it also exhibits two multiplets at δ 1.68 ppm and δ 0.88 ppm, for the CH_2 and CH_3 protons of the PEt_3 ligands. The $^{31}P\{^1H\}$ NMR spectrum of **5a** contains only one singlet at δ -2.75 ppm for the two equivalent PEt_3 ligands.

Although we were unable to isolate and fully characterize **4a**, it may be tentatively assigned to the terminal cyaphide structure in Scheme 2 based on its $^{31}P\{^1H\}$ NMR spectrum in the reaction mixture with **5a**. Of the two signals ascribed to **4a**, the one at δ 7.3 ppm is assigned to the PEt_3 ligands because the chemical shift is characteristic of a PEt_3 bound to Pt(II) and the ^{195}Pt-P coupling constant (2871 Hz) is typical of *trans*-$Pt^{II}(PEt_3)_2X_2$[18] complexes; the small J_{PP} (9.2 Hz) is reasonable for coupling to the more distant phosphorus on the C≡P$^-$ ligand. The signal at δ 68.0 ppm, which we assign to the cyaphide phosphorus, is split (J_{PP}

= 9.2 Hz) into a triplet by the equivalent PEt_3 phosphorus atoms, and the ^{195}Pt satellites show a relatively small J_{PtP} (= 303 Hz) coupling constant.

Although complex **4a** was not isolated, it can be trapped by reaction (Scheme 2) with $Pt(PEt_3)_4$ to give the di-platinum complex **6a**. Complex **6a** formed quickly when $Pt(PEt_3)_4$ was added to a benzene (or hexanes) solution containing the **4a** and **5a** mixture. Complex **6a** was isolated in 80% yield by fractional crystallization over a period of approximately two weeks in hexanes at -78 °C. During this recrystallization, impurity $O{=}PEt_3$ and complex **5a** precipitated first; then **6a** crystallized. Pale brown crystals of **6a** are slightly stable in air at room temperature; they may be handled in air for a maximum of 5 min. The synthesis of the bromo analog **6b** proceeded in the same manner.

Complex **6a** was fully characterized by NMR spectroscopy ($^{31}P\{^1H\}$ and ^1H), elemental analysis, and an X-ray crystal structure determination. The analogous complex **6b** was identified by its $^{31}P\{^1H\}$ NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum of **6a** shows four different signals. The signal at δ 107.0 ppm, assigned to the phosphorus in the bridging C≡P ligand, is a doublet of doublets of triplets with two different ^{195}Pt satellites. The two doublets ($^2J_{P1P4}$ = 10.7 Hz, $^2J_{P1P5}$ = 13.7 Hz) result from coupling to the two PEt_3 ligands on Pt(2) and the triplet is due to splitting by the two equivalent PEt_3 ligands on Pt(1). Of the two ^{195}Pt-P coupling constants obtained from the P(1) signal, the one (255.0 Hz) assigned to $^2J_{Pt1P1}$ is much smaller than that in *trans*-(Cl)$(PEt_3)_2$Pt[C(=PR)Cl] (**1a**) (657.7 Hz)[7] but is quite similar to that (303 Hz) in **4a**. The other coupling constant (58 Hz), assigned to $^1J_{Pt2P1}$, is very similar to that in η^2-(RC≡P)$Pt(PPh_3)_2$

(62 Hz)[24] (where R = t-Bu); such small coupling constants are typical for side-on bound R-C≡P ligands in Pt metal complexes. The two signals at δ 18.6 ppm (dd, $^1J_{Pt2P4}$ = 3619 Hz) and δ 15.0 ppm (ddt, $^1J_{Pt2P5}$ = 3155 Hz) are assigned to the two PEt_3 ligands on Pt(2) based on their splitting patterns and the J_{Pt-P} values which are typical of η^2-(R-C≡P)Pt(L)$_2$ (J_{PtP} = 3200- 3600 Hz).[2] The signal at δ 4.9 ppm (dd, $^1J_{Pt1P2}$ = 2936 Hz) is assigned to the two equivalent PEt_3 ligands on Pt(1); the ^{195}Pt-P coupling constant is similar to that (2871 Hz) in **4a**, which is typical for *trans*-$X_2Pt(PR_3)_2$ complexes.[18]

No intermediates were detected in ^{31}P NMR spectra taken during the reaction (Scheme 2) of **1a** (or **1b**) with $Pd(PEt_3)_4$ to give **4a** (or **4b**) and **5a** (or **5b**). However, we propose that the first step in this reaction is the formation of the mixed Pt-Pd complex **2c** (or **2d**) by oxidative-addition of the C-X bond of **1a** (or **1b**) to the $Pd(PEt_3)_4$. Subsequent transfer of the R group from the P to the Pd would give the products **4a** (or **4b**) and **5a** (or **5b**). To test the proposed intermediacy of **2c**, the Pd complex **1c** was reacted with $Pt(PEt_3)_4$ (Scheme 2). If **2c** is an intermediate in this latter reaction, the same products should be obtained as in the reaction of **1a** with $Pd(PEt_3)_4$. Indeed, **1c** reacts with $Pt(PEt_3)_4$ in C_6H_6 (or hexanes) at room temperature for 24 h to give **4a** and **5a** in quantitative yield as determined by ^{31}P NMR spectra of the product mixture. This experiment not only supports **2c** and **2d** as intermediates in the reaction in Scheme 2, but is also consistent with the suggestion that **2a** and **2b** are intermediates in the reaction in Scheme 1.

X-ray crystal structures of $(Cl)(PEt_3)_2Pd(R)$ (5a) and $(Cl)(PEt_3)_2Pt(\mu$-C=P)$Pt(PEt_3)_2$ (6a)

Data collection information, bond distances, angles, and positional parameters for **5a** and bond distances and angles for **6a** are presented in Tables II to V. The ORTEP drawing of **6a** (Figure 3), which was also reported briefly in a communication,[13] shows that it contains a bridging $C{\equiv}P^-$ ligand carbon-bonded to Pt(1) and η^2-bonded to Pt(2); the Pt atoms are not bonded to each other [Pt(1)-Pt(2) = 3.7868 (3) Å]. The atoms Cl(1), Pt(1), C(1), P(1), Pt(2), P(4), and P(5) are all nearly coplanar (within 0.061 Å), while P(2) and P(3) are 2.292 and 2.279 Å out of this plane. The C(1)-P(1) distance (1.666 (6) Å) is longer than those of triple bonds in phosphaalkynes RC≡P [1.52 (1) Å for R = 2,4,6-tri-*tert*-butylphenyl[25] and 1.536 (2) Å for R = *tert*-butyl][26] but is very similar to that (1.67 (2) Å) in η^2-(RC≡P)$Pt(PPh_3)_2$ (where R = t-Bu).[24] The C(1)-P(1) distance is also very similar to that of a C=P double bond, as found in Ph(H)C =PR (1.67 Å, where R = 2,4,6-tri-*tert*-butylphenyl).[19]

The ORTEP drawing of complex **5a** (Figure 2) shows that it has essentially a square planar geometry with two PEt_3, a Cl, and a C-bonded supermesityl ligand. The atoms Cl, Pd, C(1), C(2), C(3), C(4), and C(40) are all nearly coplanar within 0.009 Å; only P and PA are out of this plane, the Pd-P and Pd-PA bond vectors being approximately perpendicular to this plane. An interesting structural feature of **5a** is the placement of two methyl groups of the two *o-tert*-butyl substituents on the phenyl ring above and below the Pd atom. This geometry suggests that there may be

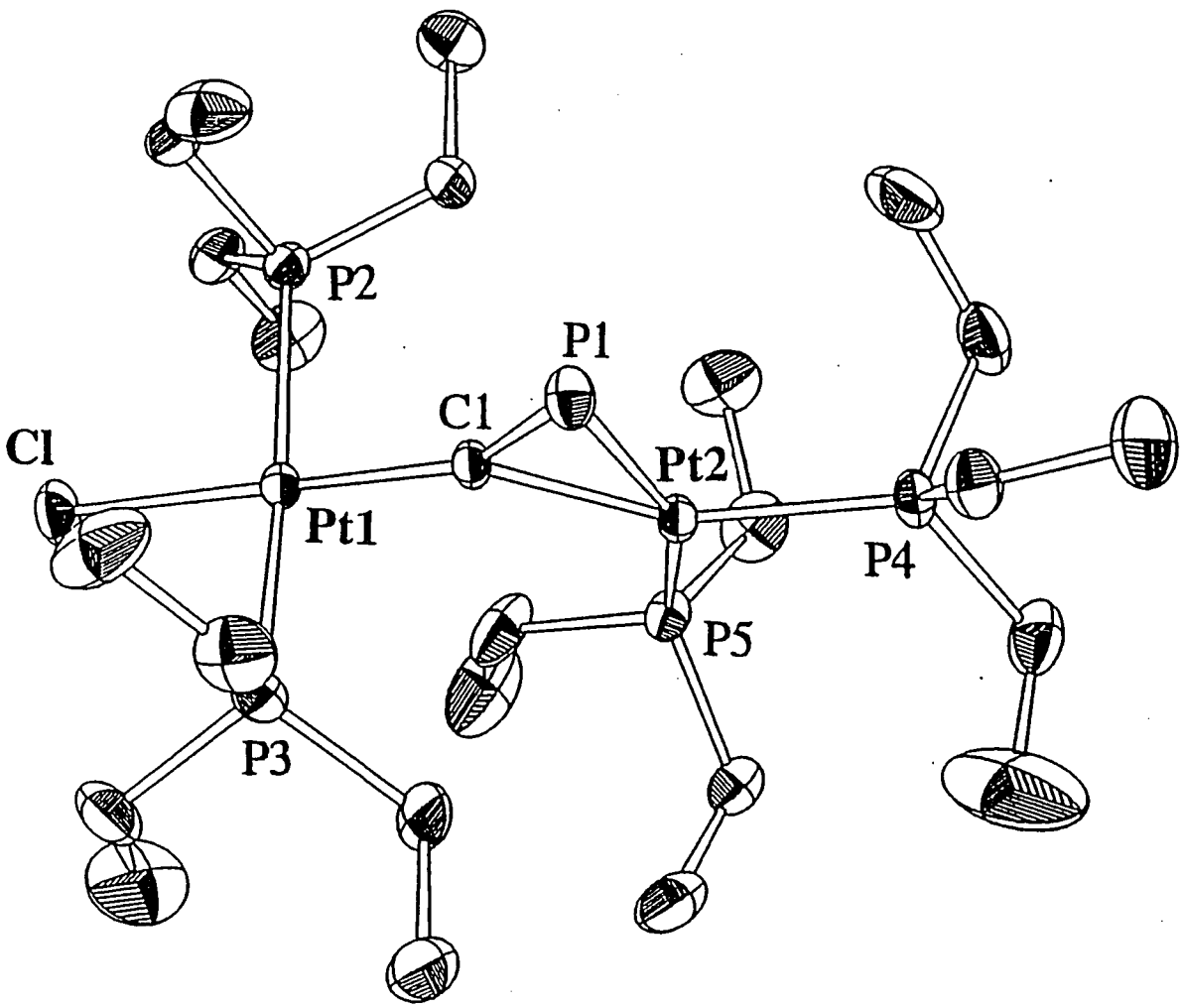


Figure 3. ORTEP drawing of $(Cl)(PEt_3)_2Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2$ **(6a)**

Table V. Selected Bond Distances (Å) and Angles (deg) for the Compound $(Cl)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$ (6a), R = 2,4,6-tri-*tert*-butylphenyl

Distances, Å			
Pt(1)-C(1)	1.950(6)	Pt(1)-Cl	2.412(2)
Pt(1)-P(2)	2.302(2)	Pt(1)-P(3)	2.297(2)
Pt(2)-C(1)	2.083(5)	Pt(2)-P(1)	2.337(2)
Pt(2)-P(4)	2.269(2)	Pt(2)-P(5)	2.277(2)
C(1)-P(1)	1.666(6)		
Angles, deg			
C(1)-Pt(1)-Cl	178.9(2)	C(1)-Pt(1)-P(2)	91.6(2)
C(1)-Pt(1)-P(3)	87.1(2)	Cl-Pt(1)-P(2)	88.05(7)
Cl-Pt(1)-P(3)	93.46(7)	P(2)-Pt(1)-P(3)	168.53(6)
C(1)-Pt(2)-P(1)	43.8(2)	C(1)-Pt(2)-P(4)	146.1(2)
C(1)-Pt(2)-P(5)	109.2(2)	P(1)-Pt(2)-P(4)	102.45(6)
P(1)-Pt(2)-P(5)	152.96(6)	Pt(1)-C(1)-Pt(2)	139.7(3)

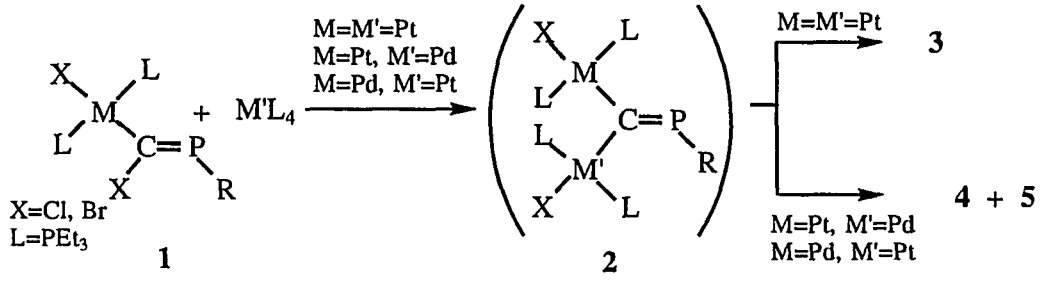
an agostic C-H interaction between the Pd and two H atoms on each CH_3 group. As the distances Pd-C(23) (2.992 Å) and Pd-C(23a) (2.992 Å) are much longer than normal Pd-C bond distance (ca. 2.00 Å), there appears to be no Pd-C bonding. The estimated distances of the Pd·····H(231) (2.495 Å) and Pd·····H(232) (2.795 Å) (assuming 0.96 Å for the methyl C-H distance) are comparable to non-bonding Pd·····H distances to the ortho hydrogens of the phenyl rings in the phosphine

complexes $I_2Pd(PPhMe_2)_2$ (2.84-2.85 Å)[27] and in $Pd(PPh^tBu_2)_2$ (2.6 Å).[28] In $(Br)(PPh_3)_2Pd[C_4(CO_2Me)_4H]$,[29] the agostic Pd·····H (vinyl) distance is only 2.3 Å and agostic vinyl ^1H signal is split into a triplet by coupling to the two PPh_3 ligands on the Pd. Since ^1H and ^{13}C NMR spectra of **5a** in CD_2Cl_2 solvent show no spitting of the CH_3 signal by the PEt_3 ligands and all three methyl carbons and all nine hydrogens of the *o-tert*-butyl groups are equivalent even at low temperature (-75 °C), any agostic interaction between the Pd and the protons in the two *o-t*-butyl groups must be weak or non-existent.

CONCLUSION

The remarkable reactions of $(X)(PEt_3)_2Pt[C(=PR)X]$ (**1a**: X = Cl; **1b**: X = Br) with $Pt(PEt_3)_4$ and $Pd(PEt_3)_4$ have yielded the first examples of complexes containing $C{\equiv}P^-$ and $C{\equiv}PR$ ligands. In these reactions, the first step (Scheme 3) is presumably oxidative-addition of the C-X bond in the [C(=PR)X] ligand to $Pt(PEt_3)_4$ or $Pd(PEt_3)_4$ to give intermediate **2**. If M and M' are both Pt, intermediate **2** is converted to products of type **3**; the bridging arylisocyaphide complexes $(X)(PEt_3)Pt(\mu\text{-}C{=}PR)Pt(PEt_3)_2(X)$ (**3a** and **3b**)

Scheme 3



are prepared in this type of reaction. On the other hand, if M is Pt and M' is Pd, intermediate **2** gives the terminal cyaphide ($C{\equiv}P^-$) complex *trans*-$(X)(PEt_3)_2Pt(C{\equiv}P)$ (**4**) and *trans*-$(X)(PEt_3)_2Pd(R)$ (**5**). Thus, the presence of Pd in intermediate **2** yields products that are dramatically different from those obtained when M and M' in **2** are both Pt. Of additional importance is the reaction of the terminal cyaphide complexes **4** with $Pt(PEt_3)_4$ to give $(X)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$ (**6**), which contains a bridging cyaphide ligand.

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SUMMARY

The synthesis and characterization of *cis*- and *trans*-$(X)(PR'_3)_2M[C(=PR)X]$ and $(X)(PR'_3)_2M[X\text{-}PBC]$ (X = Cl, Br; R' = Et, Ph; M = Pt, Pd; R = 2,4,6-tri-*tert*-butylphenyl) have provided an opportunity to understand the reaction mechanism of the metal promoted R group rearrangement from $X_2C{=}P\text{-}R$ to $R\text{-}C{\equiv}P$ via $(X)(PR'_3)_2M[X\text{-}PBC]$ as an intermediate. In the presence of H_2O, the oxy-phosphabicyclo complex $(X)(PR'_3)_2M[(H)O{=}PBC]$ was formed instead of $R\text{-}C{\equiv}P$ and $X_2M(PR'_3)_2$ via the same intermediate $(X)(PR'_3)_2M[X\text{-}PBC]$.

The halophosphaalkene platinum complex $(X)(PEt_3)_2Pt[C(=PR)X]$ (X = Cl, Br) was used as a precursor for the synthesis of the first examples of bridging cyaphide ($C{\equiv}P^-$) and bridging isocyaphide ($C{\equiv}P\text{-}R$) platinum complexes, $(X)(PEt_3)_2Pt(\mu\text{-}C{=}P)Pt(PEt_3)_2$ and $(X)(PEt_3)_2Pt(\mu\text{-}C{=}PR)Pt(PEt_3)(X)$.

These results suggest that a much broader range of cyaphide ($C{\equiv}P^-$) and isocyaphide ($C{\equiv}P\text{-}R$) complexes are capable of being prepared.

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