IOWA STATE UNIVERSITY
Digital Repository

Retrospective Theses and Dissertations

Iowa State University Capstones, Theses and Dissertations

1938

Organometallic compounds of group VIII elements

Myrl Lichtenwalter
Iowa State College

Follow this and additional works at: https://lib.dr.iastate.edu/rtd

Part of the Organic Chemistry Commons

Recommended Citation

Lichtenwalter, Myrl, "Organometallic compounds of group VIII elements " (1938). *Retrospective Theses and Dissertations.* 13630.
https://lib.dr.iastate.edu/rtd/13630

www.manaraa.com

NOTE TO USERS

ORGANOMETALLIC COMPOUNDS

OF GROUP VIII ELEMENTS

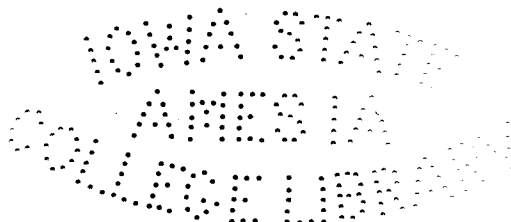by

Myrl Lichtenwalter

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject - Organic Chemistry

Approved:

In charge of Major work

Head of Major Department

Dean of Graduate College

Iowa State College

1938

UMI Number: DP12819

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Henry Gilman for the generous advice and encouragement given during the course of this investigation.

TABLE OF CONTENTS

INTRODUCTION

The paucity of information in regard to the organo-metallic compounds of the group VIII elements makes a study of these compounds highly desirable. The ready availability of iron, cobalt, nickel, and their inorganic compounds, makes the preparation of their organometallic derivatives of particular interest. This thesis was undertaken in an effort to prepare some typical organometallic derivatives of the group VIII elements and to determine some of their properties. Greatest attention was centered on attempts to prepare organoiron compounds, as iron is the cheapest of all the metals.

HISTORICAL

The first organometallic compound of the group VIII elements to be prepared was trimethylplatinum iodide. This compound was prepared by Pope and Peachy (1) through the action of an ether solution of anhydrous platinic chloride on a cold ether-benzene solution of methylmagnesium iodide. A considerable excess of methylmagnesium iodide was required, about twice as much as is indicated by the following equation:

$$PtCl_4 + 3\ CH_3MgI \longrightarrow (CH_3)_3PtI + 2\ MgCl_2 + 2\ MgI_2$$
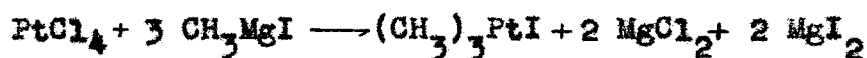
Trimethylplatinum iodide is a bright yellow crystalline powder, freely soluble in hot benzene or chloroform. It is readily soluble in cold ethyl bromide or methyl iodide. It is insoluble in water and very sparingly soluble in ether, alcohol, acetone, or light petroleum ether. It crystallizes in hexagonal plates which apparently belong to the cubic system. The substance is not attacked in the cold by iodine or bromine, nor by concentrated acids or alkalis. Concentrated nitric acid dissolves it slowly on heating and on evaporating the solution a white residue which explodes on further heating is obtained. Trimethylplatinum iodide decomposes gradually on heating in a melting point tube and decomposition

(1) (a) Pope and Peachy, J. Chem. Soc., 95, 571(1909);
(b) Proc. Chem. Soc., 23, 86(1907).

appears to be complete at 250°C. On heating in an open flame
the compound burns with a smoky, lurid flame, leaving a resi-
due of metallic platinum.

With trimethylplatinum iodide for a starting material,
Pope and Peachy (1a) prepared a series of trimethylplatinum
compounds. Diamminotrimethylplatinum iodide was prepared by
heating trimethylplatinum iodide with a mixture of benzene,
alcohol, and concentrated ammonium hydroxide. This compound
is a white, crystalline material, slightly soluble in water,
moderately soluble in benzene or ether, and dissolves very
readily in alcohol, ethyl acetate, or acetone; it is practi-
cally insoluble in chloroform or light petroleum ether. It
yields free ammonia on heating with potassium hydroxide.

Trimethylplatinum hydroxide was prepared by boiling a
solution of trimethylplatinum iodide in moist acetone with
silver hydroxide. This compound forms colorless transparent
plates which are fairly soluble in ether, alcohol, acetone,
ethyl acetate, chloroform, or benzene. It is insoluble in
water, alkalis, or light petroleum ether. It is not attacked
in the cold by mineral acids.

Trimethylplatinum sulphate, $[(CH_3)_3Pt]_2SO_4 \cdot 2H_2O$, was
prepared by boiling equivalent quantities of trimethylplatinum
iodide and silver sulphate in moist acetone-benzene solution.
This compound forms small, colorless, rectangular plates. It
is readily soluble in water, alcohol, or acetone, but practi-
cally insoluble in benzene, light petroleum ether, ether, or

chloroform. The substance contains two molecules of water of crystallization which it retains on heating to $100^\circ C$.

Trimethylplatinum nitrate was prepared by the action of hot concentrated nitric acid on trimethylplatinum hydroxide, and also by the action of barium nitrate on an aqueous solution of trimethylplatinum sulphate. This compound forms colorless, crystalline plates which are readily soluble in water. The compound was found to be so highly deliquescent that no analysis was attempted.

Trimethylplatinum chloride was prepared by precipitating an aqueous solution of the nitrate or sulphate with potassium chloride or by dissolving the hydroxide in alcohol and evaporating to dryness after addition of hydrochloric acid. The chloride is practically insoluble in water, dissolves very sparingly in acetone, alcohol, or ethyl acetate, and is moderately soluble in benzene or chloroform. The substance crystallizes from chloroform in colorless, rhombic dodecahedra, which belong to the cubic system. Powder photographs of trimethylplatinum chloride indicate a body centered cubic lattice (2).

Potassium trimethylplatinic platinocyanide was obtained in an impure form by adding potassium platinocyanide to an aqueous solution of trimethylplatinum nitrate. This substance was found to be insoluble in water and the usual organic sol-

(2) Cox and Webster, Z. Krist., 90, 561(1935)/C. A. 29, 7732(1935)/.

vents with the exception of acetone and alcohol, in which it dissolved freely; but on evaporation of its solutions it remained as an amorphous, resinous film of a greenish-yellow color.

None of the compounds of trimethylplatinum prepared by Pope and Peachey (1a) were characterized by melting points. They underwent decomposition on heating without melting. Pope and Peachey (1a) gave no yields of products in the various transformations described by them.

Menzies (3) obtained seven and one-half grams of trimethylaplatinum iodide from twenty grams of chloroplatinic acid by a modification of the method of Pope and Peachey (1a). As he was unable to dissolve anhydrous platinic chloride in dry ether, he dissolved the salt in the minimum quantity of absolute alcohol and added this solution to a large excess of methylmagnesium iodide.

Starting with trimethylplatinum iodide, Menzies (3), and Menzies and Wiltshire (4) prepared a series of chelate derivatives of trimethylplatinum with β-diketones and β-ketonic esters. The chelate derivatives of trimethylplatinum with acetylacetone, dipropionylmethane, and ethyl acetoacetate are white crystalline substances soluble in organic solvents. Trimethylplatinum benzoylacetone was prepared only in an impure form. These compounds were prepared by the reaction of tri-

(3) Menzies, J. Chem. Soc., 565(1928).
(4) Menzies and Wiltshire, ibid., 21(1933).

methylplatinum iodide with the corresponding chelate deriva-
tive of thallium. The compounds do not have definite melting
points but do have rather definite decomposition points.

Phenylplatinum bromide results by the action of phenyl-
magnesium bromide on an ether solution of dehydrated bromo-
platinic acid (5).

No organoplatinum compound is formed by the action of
the nascent ethyl radical, produced by electrolysis of the
$C_2H_5Na/Zn(C_2H_5)_2$-system, on a platinum anode (6). Oil drops
are formed at the anode, but these are probably due to poly-
merization of the ethyl radical through intermediate adsorption
on the platinum anode, as the anode is completely unaffected.

In an earlier attempt to prepare an organoplatinum
compound, Buckton (7) observed that diethylzinc reacted vigor-
ously with platinic chloride with deposition of platinum black
and with evolution of a gas. Frankland (8) found that the
halide compounds of platinum reacted violently with diethyl-
zinc but the organic group did not unite with the platinum.
However, when he heated platinous chloride in contact with the
chloride of cacodyl, two equivalents of hydrogen in the cacodyl
were replaced by a biatonic molecule of platinum, producing a
chloride of cacoplatyl.

(5) Krause and v. Grosse, "Die Chemie der Metall-organischen
     Verbindungen", Gebruder Borntraeger, Berlin, p. 788(1937).
(6) Hein and Segitz, Z. anorg. allgem. Chem., 158, 153(1926).
(7) Buckton, Ann., 109, 225(1859).
(8) Frankland, J. Chem. Soc., 13, 188(1860).

$$(C_2H_5)_2AsCl + PtCl_2 \rightleftharpoons (C_2H_5)AsCl(C_2H_3Pt^{"}) + 2HCl$$
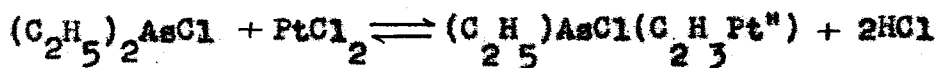
Cacoplatyl forms a series of compounds analogous to those of cacodyl.

The formation of double salts from organoarsenic compounds and platinous or platinic chloride is a general reaction (9), the organoarsenic compounds being too unreactive to cleave the platinum to chlorine bond and thus form an organoplatinum compound. The composition of the double salt may be varied according to the ratio of reactants and the general experimental procedure.

Organoantimony compounds also react with platinic or platinous chloride with the formation of double salts (10) (9a)(9b). The reaction in the case of platinic chloride differs in some cases, however, from the reaction of platinic chloride with organoarsenic compounds. The first phase of the

(9) (a) Hofmann, Ann., 103, 357(1857); (b) Cahours and Gal, Compt. rend., 71, 208(1870); (c) Michaelis, Ann., 321, 141 (1902); (d) Cahours, Ann., 122, 210(1862); (e) LaCoste and Michaelis, Ann., 201, 184(1880); (f) Michaelis and Link, Ann., 207, 193(1881); (g) Michaelis, Ann., 320, 271(1902); (h) Mannheim, Ann., 341, 182(1905); (i) Morgan and Micklethwait, J. Chem. Soc., 95, 1473(1909); (j) Phillips, Ber., 19, 1031(1886); (k) Dehn, Am. Chem. J., 40, 114(1909); (l) Dehn and Wilcox, ibid., 35, 31(1906).
(10) (a) Landolt, Ann., 84, 44(1852); (b) Michaelis and Reese, Ann., 233, 39(1886); (c) Partheil and Mannheim, Arch. Pharm., 238, 166(1900); (d) Morgan and Yarsley, J. Chem. Soc., 127, 184(1925); (e) Buckton, ibid., 13, 119(1860); (f) Löwig, J. prakt. Chem., 64, 415(1854); J. Chem. Soc., 8, 262(1855).

reaction between platinic chloride and the relatively more reactive organoantimony compounds may consist of a reduction of the platinic chloride to platinous chloride. The platinous chloride then forms a double salt with any excess organoantimony compound. As is the case with organoarsenic compounds, the composition of the double salt may be varied according to the procedure used in the preparation. Morgan and Yarsley (10d) made a thorough study of the reaction of trimethylantimony with platinic chloride. They found the first step of the reaction to be a reduction of the platinic chloride to platinous chloride, which then reacts with excess trimethylantimony giving rise to one or two additive compounds according as to whether the reaction is carried out in water or in alcohol. In water the compound formed is an orange colored insoluble solid of the composition $[Pt,4(CH_3)_3Sb]PtCl_4$. This compound is formed in alcohol along with a soluble yellow crystalline compound of the composition $[2(CH_3)_3Sb,PtCl_2]$. Either of these products on treatment with excess trimethylantimony yield the same compound having the composition $[Pt,4(CH_3)_3Sb]Cl_2$. The reactions take place in the following manner:

$$H_2PtCl_6 + (CH_3)_3Sb \longrightarrow H_2PtCl_4 + (CH_3)_3SbCl_2$$

$$\underbrace{H_2PtCl_4 + (CH_3)_3Sb}$$

$[Pt,4(CH_3)_3Sb]PtCl_4$ $[2(CH_3)_3Sb,PtCl_2]$

Orange insoluble   yellow soluble

excess (CH_3)_3Sb   excess (CH_3)_3Sb

$[Pt,4(CH_3)_3Sb]Cl_2$
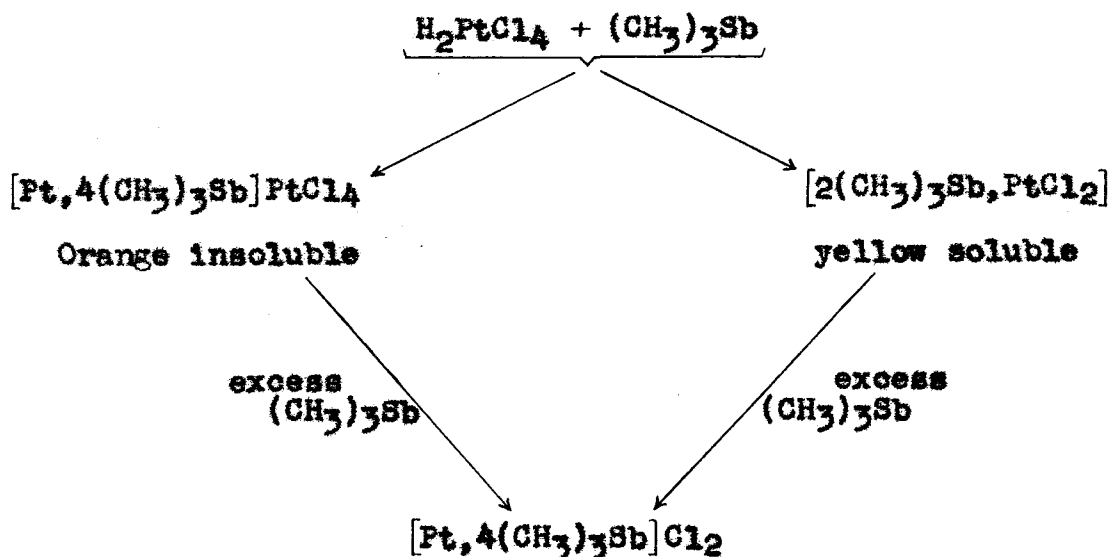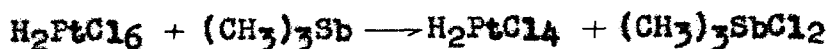
The orange colored insoluble compound reacts with palladous chloride to replace part of the platinum with palladium (10d).

$$[Pt,4(CH_3)_3Sb]PtCl_4 + PdCl_2 \longrightarrow [Pt,4(CH_3)_3Sb]PdCl_4 + PtCl_2$$
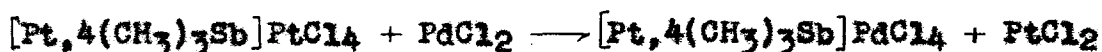
Trimethylantimony reacts with palladous chloride in the same manner as with platinous chloride.

$$(CH_3)_3Sb + PdCl_2 \longrightarrow [2(CH_3)_3Sb,PdCl_2]\xrightarrow[\;(CH_3)_3Sb\;]{excess}[Pd,4(CH_3)_3Sb]Cl_2$$

Triethylarsenic reacts in the same manner with palladous chloride to form the double salt $(C_2H_5)_3As.PdCl.$ (9b) (91).

No organoplatinum or organopalladium compounds are formed in any of the reactions of organoarsenic or organo-antimony compounds with platinum or palladium chlorides.

Platinic halides form complex coordination compounds with unsaturated compounds of the types $K(Un.PtX_3)$, and

$(Un.PtCl_2)_2$, in which Un is an unsaturated molecule containing an ethylene bond. The first compound of the type $K(Un.PtX_3)$ was obtained by Zeise (11), who isolated a compound with the empirical formula $K(C_2H_4.PtCl_3).H_2O$, from the reaction of chloroplatinic acid and alcohol. Birnbaum (12) prepared similar compounds with propylene and amylene, and Chojnack (13) obtained $K(C_2H_4.PtBr_3)$, with platinic bromide.

Biilmann and co-workers have(14) extended the work to unsaturated alcohols, acids, and aldehydes. Pfeiffer and Hoyer (15) have prepared similar compounds from allyl alcohol, allyl acetate, crotyl alcohol, and crotyl aldehyde.

Anderson (16) obtained $(C_2H_4.PtCl_2)_2$ by refluxing ethyl alcohol with sodium chloroplatinate.

A general method for the preparation of complexes of the types $(Un.PtCl_2)_2$ or $(Un.PtBr_2)_2$ has recently been developed by Karasch and Ashford (17). It differs radically from the method of Anderson (16) in that anhydrous platinic chloride or bromide in an anhydrous solvent is used instead of the metallic haloplatinates. It differs further in that the

(11) Zeise, Pogg. Ann., 21, 497(1831).
(12) Birnbaum, Ann., 145, 67(1869).
(13) Chojnacki, Jahresber., 510(1870).
(14) Biilmann, Ber., 33, 2196(1900); Biilmann and Anderson, Ber., 36, 1565(1903); Biilmann and Hoff, Rec. trav. chim. 36, 306(1916).
(15) Pfeiffer and Hoyer, Z. anorg. allgem. Chem., 211, 241(1933).
(16) Anderson, J. Chem. Soc., 971(1934).
(17) Kharasch and Ashford, J. Am. Chem. Soc., 58, 1733(1936).

unsaturated compounds are used instead of the alcohols. Coördination compounds were prepared by this procedure from cyclohexene, dipentene, pinene, ethylene, isobutylene, styrene, stilbene, and trans-dichloroethylene. This method has not been found applicable to unsaturated acids and their esters.

The general electronic structure proposed by Kharasch and Ashford (17) for all compounds of the type $(Un.PtCl_2)_2$
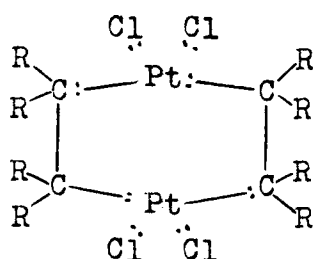
was specifically exemplified by the following formula for cyclohexene platinous chloride.
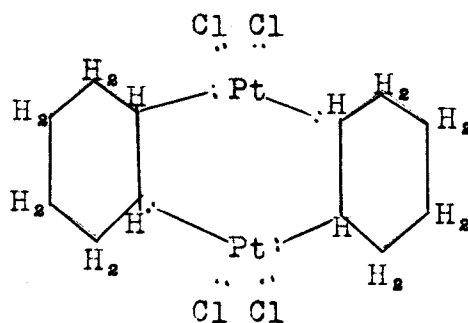
The compounds of the type $K(Un.PtX_3)$ are obviously derivatives of the type $(Un.PtX_2)_2$.

The coördination compounds of platinum with unsaturated compounds are well-defined crystalline substances. They do not have definite melting points and vary widely in stability. When treated with pyridine the substances decompose, liberating the olefin and forming the pyridine platinous chloride. They are decomposed by concentrated hydrochloric acid with liberation of the olefin and by bromine to form the bromine addition product of the unsaturated compound.

These compounds may exist in two or more stereoisomeric forms depending on the olefin from which they are derived.

A number of mixed carbonyl compounds of platinum are known (18). Schützenberger (19) in 1868 passed chlorine and carbon monoxide over platinum sponge at 250°C. and obtained a yellow sublimate from which three distinct compounds were isolated: $PtCl_2.CO$, $PtCl_2.2CO$, and $PtCl_2.3CO$. These compounds dissolve unchanged in carbon tetrachloride but are decomposed by water.

$$PtCl_2.CO + H_2O \longrightarrow Pt + 2HCl + CO_2$$
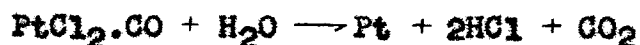
Pullinger (20) prepared platinum carbonyl dibromide, $PtBr_2CO$, by passing dry carbon monoxide over platinous bromide

(18) See, Blanchard, Chem. Rev. 21, 3-38(1937) for a more detailed discussion of carbonyl compounds of the group VIII elements.
(19) Schützenberger, Ann. chim. phys., [4] 15, 100(1868); 21, 35, 350(1870; Bull. soc. chim., [2] 14, 97(1870).
(20) Pullinger, Trans. Chem. Soc., 59, 598(1891).

at 180°C. Platinum carbonyl di-iodide was obtained by Mylius
and Foerster (21) by adding dilute hydriodic acid to a solu-
tion of platinum carbonyl dichloride in hydrochloric acid.
Platinum carbonyl monosulphide, PtS.CO, is thrown down as a
brown precipitate when hydrogen sulphide is passed into a so-
lution of platinum carbonyl dichloride (20). A double salt
of platinum carbonyl thiocyanate, $Pt(CNS)_2.CO$, with potassium
thiocyanate is obtained by adding a solution of potassium thio-
cyanate to one of platinum carbonyl dichloride.

The carbonyl compounds of platinum are crystalline
solids. They decompose on heating to give metallic platinum.
Manchot (22) made use of the platinum chloride carbonyls in
the separation of platinum from palladium.

Pd   Organopalladium compounds have been postulated as
intermediates in the catalytic hydrogenation of aryl halides
(23). This assumption is based on the varying yields of
biphenyl obtained in the catalytic hydrogenation of bromoben-
zene under varying conditions. When bromobenzene is heated
to boiling in methyl alcoholic potassium hydroxide in the
presence of palladiumated calcium carbonate, without introduc-
tion of hydrogen, biphenyl results in fifteen to twenty percent
yields. If high pressures of hydrogen are used, in an auto-
clave, benzene is formed. At lower pressures of hydrogen,

(21) Mylius and Foerster, Ber., 24, 2424(1891).
(22) Manchot, Ber., 58, 2518(1925).
(23) Busch and Weber, J. prakt. Chem., 146, 1-55(1936).

biphenyl is formed. The reaction is postulated to proceed in the following manner:

$$PdH_2 + BrC_6H_5 \longrightarrow HBr + C_6H_5PdH$$

If the phenylpalladium hydride so formed contacts hydrogen, benzene results.

$$C_6H_5PdH + H_2 \longrightarrow PdH_2 + C_6H_6$$
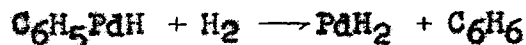
In low concentrations of hydrogen the following reaction may take place:

$$C_6H_5PdH + BrC_6H_5 \longrightarrow (C_6H_5)_2Pd + HBr$$

The labile diphenylpalladium then may react with hydrogen to form biphenyl and palladium hydride.

$$(C_6H_5)_2Pd + H_2 \longrightarrow C_6H_5-C_6H_5 + PdH_2$$
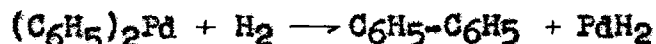
In alcohol, where bromobenzene is soluble, biphenyl is formed as would be expected according to the above equations. In water, where bromobenzene is insoluble, benzene results.

Further coupling is produced to some extent and this is postulated to occur in the following manner:

$$C_6H_5PdH + H-C_6H_4Br \longrightarrow PdH_2 + C_6H_5-C_6H_4Br$$

$$C_6H_5PdH + Br-C_6H_4-C_6H_5 \longrightarrow HBr + C_6H_5-Pd-C_6H_4-C_6H_5$$

$$C_6H_5-Pd-C_6H_4-C_6H_5 + H_2 \longrightarrow PdH_2 + C_6H_5-C_6H_4-C_6H_5$$
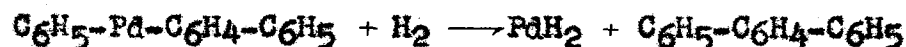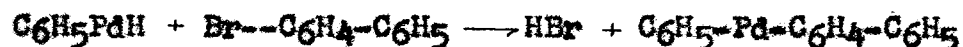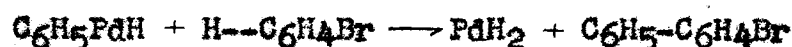
etc., this series of reactions leading to the formation of coupling products up to sedeciphenyl, $C_{96}H_{66}$, all of which were isolated.

Palladium chloride, $PdCl_2$, forms a complex with tri-methylethylene (24). This complex forms stable orange crys-

(24) Kondakov, Balas, and Vit, Chem. Listy., 23, 579-87(1929); 24, 1-8, 26-31(1930) [C. A., 24, 3455(1930)].

tals, decomposing at $85^{\circ}-90^{\circ}$, which correspond to the formula $PdCl_2 \cdot C_5H_{10}$.

Palladium forms a halogen carbonyl complex of the composition $PdCl_2 \cdot CO$, which is the least stable of all such complexes formed by the platinum metals. This compound was obtained by the action of carbon monoxide, saturated with the vapor of methyl alcohol, on palladium chloride at $0^{\circ}C$. (25). This complex is decomposed by water.

$$PdCl_2 \cdot CO + H_2O \longrightarrow Pd + CO_2 + 2HCl.$$
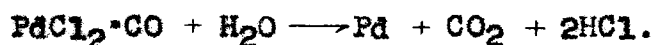
No organometallic compounds of osmium, iridium, rhodium, or ruthenium are recorded in the literature. Pope and Peachey (1b) reported that the chlorides, or in some cases the oxides, of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum, reacted vigorously with methylmagnesium iodide, but they reported no products from any of these reactions other than the formation of trimethylplatinum iodide from platinic chloride.

Manchot and Gall (26) prepared a sublimable carbonyl chloride of iridium. Dry iridium trichloride in a current of completely dry carbon monoxide at $150^{\circ}C$. gave a white, sublimable, crystalline substance of the composition $Ir(CO)_2Cl_2$. This compound decomposes in water with evolution of carbon monoxide.

(25) Manchot and König, Ber., 59, 883(1926).
(26) Manchot and Gall, Ber., 58, 232(1925).

Manchot and König (27) heated osmium trichloride in a current of carbon monoxide at 270°C. and obtained a white sublimate whose composition approximated the formula $OsCl_2 \cdot 3CO$. This compound is unaffected by water and acids. It is soluble in sodium hydroxide solution, and after neutralization of such a solution with nitric acid all of the chlorine is precipitated by silver nitrate, leaving the osmium and carbon monoxide in solution as an apparently stable complex.

No simple carbonyl halide of rhodium has been prepared, but the compound, $RhCl_2 \cdot RhO \cdot 3CO$, was prepared by Manchot and König (28) through the action of carbon monoxide on moist rhodium trichloride. This substance is decomposed slowly by water or by heating to 300°C.

Ruthenium trihalides react with carbon monoxide according to the equation (29):

$$RuX_3 + 2CO \longrightarrow Ru(CO)_2X_2 + 1/2X_2.$$

Ruthenium triiodide reacts rapidly and completely with carbon monoxide at 250°C. and one atmosphere, yielding an ochre-colored residue of the composition $Ru(CO)_2I_2$, which is insoluble in water or organic solvents. It is very resistant to the action of concentrated hydrochloric and sulphuric acids. Ruthenium tribromide reacts much more slowly under the same conditions to give a sublimable product of the composition

(27) Manchot and König, Ber., 58, 229(1925).
(28) Manchot and König, Ber., 58, 2173(1925).
(29) Manchot and König, Ber., 57, 2130(1924).

$Ru(CO)_2Br_2$. At high pressures of carbon monoxide there is a further reduction of the bromide to $Ru(CO)Br$, a colorless crystalline substance (30). Ruthenium trichloride reacts still more slowly than the bromide, yielding $Ru(CO)_2Cl_2$. High pressures of carbon monoxide give a halogen-free, non-volatile carbonyl. Mond (31) prepared the same halogen free carbonyl by the action of carbon monoxide on ruthenium sponge. Its composition approximated the formula $Ru(CO)_2$.

Manchot and Manchot (32) prepared a series of ruthenium carbonyls. The pentacarbonyl was first prepared from ruthenium sponge and carbon monoxide at 700 atmospheres and $400^\circ C$. A more effective method of preparation, however, was found to be the action of carbon monoxide, under 455 atmospheres pressure at $175^\circ C$., on ruthenium iodide in the presence of finely divided silver. Ruthenium pentacarbonyl condenses to colorless crystals which melt at $-22^\circ C$. It decomposes slowly above its melting point into the enneacarbonyl, $Ru_2(CO)_9$. The pentacarbonyl is very sensitive to light while the enneacarbonyl is stable. The pentacarbonyl decomposes to ruthenium and carbon monoxide on heating.

$$Ru(CO)_5 \longrightarrow Ru + 5CO$$
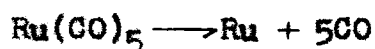
An amorphous green carbonyl of the composition $[Ru(CO)_4]_x$ was also obtained.

(30) Manchot and Enk, Ber., 63, 1635(1930).
(31) Mond, Hirtz and Cowap, Z. anorg. allgem. Chem., 68, 207 (1910); Mond and Wallis, J. Chem. Soc., 121, 32(1922).
(32) Manchot and Manchot, Z. anorg. allgem. Chem., 226, 385 (1936).

In an attempt to obtain the free ethyl radical, Frankland (33) found that heating of ethyl iodide with iron at 150°C. to 200°C. for twelve hours scarcely effected the decomposition of a trace of ethyl iodide. Later, Frankland (34) reported that iron was capable, under the influence of light, of combining readily with the organic groups, methyl, ethyl, and amyl. He gave no further details.

Ullmann (35) found that finely divided iron reacted with p-iodotoluene when heated to 250°C. and gave low yields of bi-p-tolyl. Zeltner (36) was of the opinion that an organoiron compound was formed as an intermediate in this coupling reaction.

Spencer and Harrison, (37), in an attempt to ascertain whether metals of the sixth, seventh, and eighth groups of the periodic system could be caused to react with alkyl halides in the manner of the metals of the first and second groups, found that iron and nickel reacted with alkyl halides, but only when heated in a sealed tube for several hours, while cobalt would not react even under these conditions. The reaction between the metals iron and nickel with iodobenzene took place very completely with the formation of biphenyl in extremely large yields. Freshly reduced nickel heated in a

(33) Frankland, J. Chem. Soc., 2, 295(1848-1849).
(34) Frankland, ibid., 6, 66(1853).
(35) Ullmann, Ann., 332, 38(1904).
(36) Zeltner, J. prakt. Chem., 77, 397(1907).
(37) Spencer and Harrison, Proc. Chem. Soc., 26, 118(1910).

sealed tube with iodobenzene at 280°C. for several hours gave
an eighty-five percent yield of biphenyl. In the case of iron
a similar reaction took place at 180°C. This reaction could
not be brought about with any other halogen compounds with
the exception of p-iodotoluene. It was the opinion of these
investigators that iron, cobalt, and nickel had no tendency
to form organometallic compounds. Patten (38) found ethyl
chloride to have no action on iron, nickel, platinum, palla-
dium, or cobalt at 0°C.

Thomas, Bowden, and Jones (39) studied the action of
iron, cobalt, and nickel on triphenylmethyl halides. Iron was
found to react readily with triphenylmethyl chloride or bromide
in benzene, toluene, or ether solution. No free triphenyl-
methyl was formed and the evidence seemed to indicate the ex-
istence in solution of a stable triphenylmethylferrous chloride
complex. Triphenylmethyl chloride in benzene, toluene, bromo-
benzene, hexane, or ether was found to be unattacked by cobalt
or nickel. Rapid and complete reduction of triphenylmethyl
chloride to triphenylmethyl was produced by cobalt in acetone
solution. No evidence of any triphenylmethyl iron or tri-
phenylmethyl cobalt was reported. Pyrophoric iron reduces tri-
phenylmethyl chloride to triphenylmethyl (40).

(38) Patten, J. Phys. Chem., 7, 153(1903).
(39) Thomas, Bowden, and Jones, J. Chem. Soc., 473(1930).
(40) Schmidlin, "Das Triphenylmethyl", Ferdinand Enke, Stutt-
     gart(1914), p. 31.

Iron, like platinum, is unaffected by the nascent

ethyl radical produced by electrolysis of the $NaC_2H_5/Zn(C_2H_5)_2$-

system (6). A strong evolution of gas was noted at the anode.

Frankland and Duppa (41) in an attempt to prepare an

organoiron compound by the action of iron on diethylmercury

at 150^oC. obtained large quantities of inflammable gases but

no ethyliron compound. They considered the gases to be due to

the thermal decomposition of diethylmercury entirely independent

of any action by the iron. Diphenylmercury on distillation

from powdered iron gives biphenyl (42). Powdered iron reacts

with dimethylantimony bromide to remove the bromine without

forming an organoiron compound (43).

$$(CH_3)_2SbBr + Fe \longrightarrow FeBr_2 + (CH_3)_2Sb_2 + (CH_3)_3Sb$$
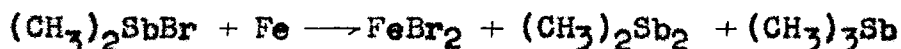
Triphenylantimony, in alcohol or ether solution, re-

duces ferric chloride slowly to ferrous chloride (44). Di-

methylarsenic hydride reduces ferric chloride promptly to

ferrous chloride (45). No organoiron compound is formed.

$$(CH_3)_2AsH + 2FeCl_3 \longrightarrow (CH_3)_2AsCl + 2FeCl_2 + HCl$$
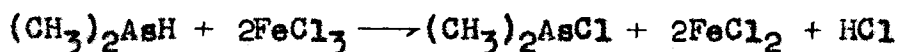
Bennett and Turner (46) have reported the formation

of an organoiron compound from the reaction of phenylmagnesium

(41) Frankland and Duppa, J. Chem. Soc., 17, 35(1864).
(42) Dreher and Otto, Ann., 154, 129(1870).
(43) Morgan and Davies, Proc. Roy. Soc.(London), [A], 110, 526(1926).
(44) Michaelis and Reese, Ann. 233, 49(1886).
(45) Dehn and Wilcox, Am. Chem. J., 35, 30(1906).
(46) Bennett and Turner, J. Proc. Roy. Soc. N. S. Wales, 53, 100(1919) [C. A., 14, 414(1920)].

bromide with ferric chloride in ether solution. Hydrolysis of
the reaction mixture with water and sulphuric acid gave a dark-
colored solid residue which was freed of biphenyl by extrac-
tion with petroleum ether. The ochre-colored residue was dis-
solved in benzene and precipitated by petroleum ether. A
greenish solid resulted, which contained iron, was soluble in
benzene, and depressed the melting point of biphenyl when mixed
with that substance. No melting point or analysis was given
for the substance. In a previous report (47) these workers
reacted three equivalents of phenylmagnesium bromide with one
of ferric chloride. They obtained only a small amount of bi-
phenyl and no organoiron compound. The ferric chloride was
not reduced to ferrous chloride.

According to other investigators (48), the reaction of
phenylmagnesium bromide with ferric chloride proceeds exclu-
sively to the formation of biphenyl and metallic iron. Benzyl-
magnesium bromide reacts with ferric chloride or ferric bromide
to give quantitative yields of bibenzyl (48a) (49). p-Tolyl-
magnesium bromide and phenylmagnesium bromide react with ferric
chloride, ferrous chloride, and ferric thiocyanate to give ex-

(47) Bennett and Turner, J. Chem. Soc., 105, 1062(1914).
(48) Oddo, Gazz. chim. ital., 44, II 268(1914); (b) Job and
     Champatier, Compt. rend., 89, 1089(1929); (c) Michailenko
     and Sassypinka, J. Russ. Phys.-Chem. Soc., 53, 343(1921)
     [Chem. Zentr., 94, III 1014(1923)]; (d) Kondyrew and Fomin,
     ibid., 47, 190(1915) [Chem. Zentr., 87, I 832(1916)]; (e)
     Champetier, Bull. soc. chim., [4] 47, 113(1930).
(49) Michailenko and Protassowa, J. Russ. Phys.-Chem. Soc., 53,
     347(1921) [Chem. Zentr., 94, III 1014(1923)].

cellent yields of bi-p-tolyl and biphenyl, respectively (48d).
With ethylmagnesium bromide these iron salts react to give
ethane and ethylene, and with propylmagnesium bromide to give
propane (48d). n-Butylethynylmagnesium bromide reacts with
ferric chloride to give di-n-butyldiacetylene (50). Organo-
iron compounds may be formed as intermediates in these re-
actions (48a)(48e)(50).

The reaction of one mole of phenylmagnesium bromide
with one mole of ferric chloride gives a quantitative yield of
ferrous chloride (48e).

$$2C_6H_5MgBr + 2FeCl_3 \longrightarrow C_6H_5-C_6H_5 + 2FeCl_2 + MgBr_2 + MgCl_2$$
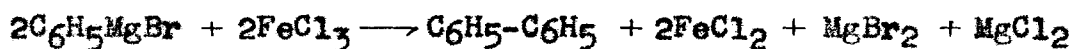
If two more moles of phenylmagnesium bromide are added the iron
is reduced to the metal (48e).

$$2C_6H_5MgBr + FeCl_2 \longrightarrow C_6H_5-C_6H_5 + Fe + MgBr_2 + MgCl_2$$
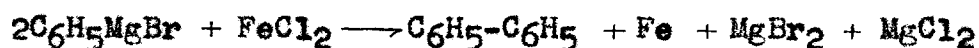
Weichfelder and Thiede (51) found the reaction of
phenylmagnesium bromide with ferric chloride, in an atmosphere
of nitrogen, to give a bright reddish-brown deposit which soon
became black. The deposit was found to consist of colorless
prismatic crystals and a black powder. This solid substance
glowed on exposure to air giving off a smoke which smelled of
biphenyl. No phenyliron compound could be isolated although
some organic substance apparently bound to iron was present in
the solid deposit. When the reaction of phenylmagnesium bro-
mide with ferric chloride was carried out in an atmosphere of

(50) Danehy and Nieuwland, J. Am. Chem. Soc., 58, 1609(1936).
(51) Weichselfelder and Thiede, Ann., 447, 64(1926).

hydrogen, the products were one molecule of benzene, one molecule of biphenyl, and a hydride of iron, FeH_6. Phenylmagnesium bromide and ferrous chloride reacted in an atmosphere of hydrogen giving only benzene and another hydride of iron, FeH_2.

Sims and Mardles (52) carried out some anti-knock studies on solutions prepared from the action of a phenylmagnesium halide on an iron halide in benzene. They assumed a phenyliron compound to be present. The solution was without effect as an anti-knock agent. They described the phenyliron compound as being very unstable.

According to unpublished work by Krause and Wendt (53), when the reaction between phenylmagnesium bromide and ferric chloride was carried out under nitrogen, a greenish-yellow, ether insoluble reaction product was obtained. This product dissolved in alcohol with an intense green color, which in the air gave a red color. With water, the green solution gave ferrous hydroxide and the red solution gave ferric hydroxide. Under ether, the green insoluble substance went in air to a red, ether-soluble substance. The red solution so obtained was decolorized by addition of triethylalumimum etherate.

(52) Sims and Mardles, Trans. Faraday Soc., 22, 368(1926).
(53) Krause and v. Grosse, "Die Chemie der Metall-organischen Verbindungen", Gebruder Borntraeger, Berlin(1937), p. 784.

Job and Champetier (54) reacted phenylmagnesium bromide with ferric chloride in the presence of acetylene. They obtained a brown powder, very unstable in the air, which contained all of the iron initially used in the form of an organometallic. On hydrolysis of the brown powder the iron was eliminated and a black powder remained which weighed the same as the total of acetylene employed plus the weight of the phenyl groups employed. This black powder was found to consist of a mixture of unsaturated hydrocarbons of high molecular weight which oxidized in the air to give mainly benzoic acid. Three molecules of phenylmagnesium bromide were consumed for one molecule of ferric chloride when the ferric chloride was introduced into the Grignard reagent. This reaction was represented as follows:

$$2(6C_6H_5MgBr + FeCl_3 + nC_2H_2) \longrightarrow 2(C_6H_5C \equiv C)_3Fe + 3MgBr_2 + 3MgCl_2.$$
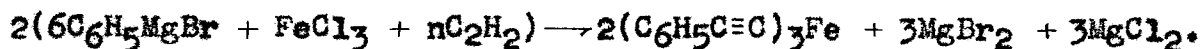
Six molecules of phenylmagnesium bromide were consumed when the Grignard reagent was introduced into a ferric chloride solution.

$$2(6C_6H_5MgBr + FeCl_3 + nC_2H_2) \longrightarrow 2(C_6H_5C \equiv C)_6Fe + 3BrMg-C \equiv C-MgBr + 3MgBr_2 + 3MgCl_2.$$
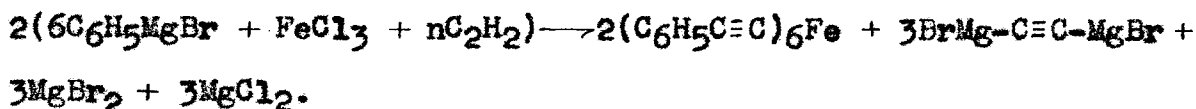
Active iron, produced by the action of phenylmagnesium bromide on ferric chloride, reacted in the presence of phenylmagnesium bromide and acetylene to give an organoiron compound.

$$2(3C_6H_5MgBr + Fe + mC_2H_2) \longrightarrow 2(C_6H_5C \equiv C)_3Fe + 3BrMg-C \equiv C-MgBr.$$
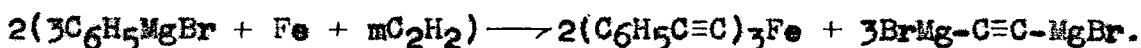
(54) Job and Champetier, Compt. rend., 89, 1089(1929); Bull. soc. chim., [4] 47, 279(1930).

The products of hydrolysis were the same as previously mention-
ed for the other reactions.

Wanklyn and Carius (55) observed that diethylzinc re-
acted vigorously with ferrous iodide in ether solution to give
a mixture of ethane, ethylene, and hydrogen, while the iron was
reduced to a mixture of iron and a hydride of iron, FeH_2. No
ethyliron compound was isolated. Job and Reich (56) reported
ethane, ethylene, and iron from the action of diethylzinc on
ferrous iodide. They state that diethyliron is probably formed,
but that it is too unstable to exist and breaks down.

Job and Reich (57) have reported the preparation of
ethyliron iodide from ethylzinc iodide and ferrous iodide in
ether solution.

$$C_2H_5ZnI + FeI_2 \longrightarrow C_2H_5FeI + ZnI_2$$
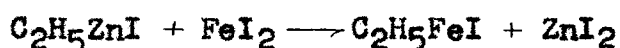
They observed the action of organozinc chlorides on a large
number of anhydrous metallic chlorides and became convinced
that the organometallics exist in all the series and probably
without exception. Their attempts were carried out on the
chlorides of iron, nickel, cobalt, chromium, molybdenum, tung-
sten, uranium, vanadium, thorium, the chlorides of the rare
earths, and copper.

(55) Wanklyn and Carius, Ann., 120, 70(1861).
(56) Job and Reich, Compt. rend., 177, 1439(1923).
(57) Job and Reich, ibid., 174, 1358(1922); Bull. soc. chim.,
       32, 1390(1922).

They explain the formation of ethyliron iodide from
ethylzinc iodide and ferrous iodide or chloride as being due
to a much milder reaction than that of the Grignard reagent
with iron halides.

Equal molecular quantities of ethylzinc iodide and
ferrous iodide were refluxed together in ether solution for
six hours. No gas was evolved during the reaction. The so-
lution so obtained gave on hydrolysis a green precipitate of
ferrous hydroxide and ethane. These products were explained
according to the following equation:

$$C_2H_5FeI + H_2O \longrightarrow C_2H_6 + Fe(I)OH$$
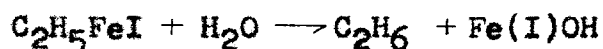
The solution reacted with absolute alcohol to form iron ethyl-
ate. No organoiron compound was isolated from the reaction
and no further evidence for the existence of an organoiron
compound was offered.

The reaction of ethylzinc iodide with ferric chloride
was found to consist of a reduction of the ferric chloride
to ferrous chloride.

$$2FeCl_3 + C_2H_5ZnI \longrightarrow 2FeCl_2 + C_2H_5I + ZnCl_2$$
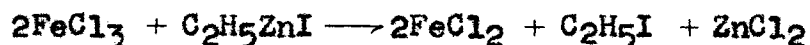
If an excess of ethylzinc iodide was present the reaction con-
tinued to form ethyliron chloride. The ethyliron chloride
was not isolated.

Champetier (48e) compared the action of organomagnesium
and organozinc compounds on halogen salts of iron. He found
one mole of ferric chloride to react with three moles of phenyl-
magnesium bromide. The ether solution so obtained contained

biphenyl and magnesium salts. A black deposit was formed which consisted of active iron which decomposed cold water giving off hydrogen, oxidized spontaneously in the air with incandescence, and rapidly reduced ferric chloride to ferrous chloride. From the reaction of ferrous iodide on phenylzinc chloride, he reports the formation of phenyliron iodide.

$$2C_6H_5ZnCl + FeI_2 \longrightarrow 2C_6H_5FeI + ZnCl_2 + ZnI_2$$

Hydrolysis of the reaction mixture gave ferrous hydroxide and benzene with no biphenyl.

$$2C_6H_5FeI + 2H_2O \longrightarrow 2C_6H_6 + Fe(OH)_2 + FeI_2$$

The ferrous hydroxide obtained contained only an inappreciable amount of zinc hydroxide. No organoiron compound was isolated from the reaction.

The solution of ethyliron iodide, obtained by the action of ethylzinc chloride on ferrous iodide, on standing deposits a metallic mirror with evolution of gas (58). The gas given off consists of a mixture of ethylene and ethane.

Calcium carbide acts on water solutions of ferrous chloride giving a precipitate containing ferrous acetylide which is stable at ordinary temperatures in the presence of air or water (59). On treatment with hydrochloric acid acetylene is evolved. This compound was not isolated.

(58) Job and Reich, Compt. rend., 177, 1439(1923).
(59) Durand, ibid., 177, 693(1923).

Iron forms three different well-defined carbonyls, a pentacarbonyl, $Fe(CO)_5$, a tetracarbonyl, $Fe(CO)_4$ 3, and an enneacarbonyl, $Fe_2(CO)_9$ (18)(60).

Iron pentacarbonyl is prepared by the action of carbon monoxide on finely divided iron at temperatures ranging from $170^\circ C$. to $400^\circ C$. and at pressures of from 20 to 200 atmospheres (60)(61). It is a clear colorless liquid which boils at $103^\circ C$. and solidifies at $-21^\circ C$. It is easily soluble in most organic solvents. In contact with air iron pentacarbonyl is oxidized, ferric oxide is deposited, and carbon monoxide is liberated. Halogens liberate carbon monoxide from the pentacarbonyl and form iron halides with the iron. At low temperatures the addition compounds, $Fe(CO)_5X_2$ (X = halogen), can be isolated as intermediates. These intermediates lose carbon monoxide at room temperature to leave $Fe(CO)_4X_2$, which with water lose all of their carbon monoxide and leave FeX_2 (62). Iron pentacarbonyl may be decomposed by heat into carbon monoxide and iron. Iron prepared in this manner is of especially high purity and as such has use in catalytic processes.

(60) See, Schmidt, "Organometallverbindungen", Wissenschaftliche Verlagsgesellschaft, m. b. h., (1934) Tiel II, on carbonyl compounds of iron and nickel.
(61) (a) Mond and Quincke, Chem. News, 63, 301(1891); 64, 20 (1891); (b) Mond and Langer, J. Chem. Soc., 59, 1090(1890); (c) Berthelot, Compt. rend., 112, 1343(1891); (d) Mittasch, Angew. Chem., 41, 827(1928).
(62) Hieber and Bader, Ber., 61, 1717(1928); Z. anorg. allgem. Chem., 190, 193(1930).

Iron pentacarbonyl decomposes in sunlight to iron enneacarbonyl. Carbon monoxide is liberated.

$$2\ Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO$$
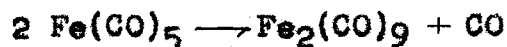
The enneacarbonyl forms orange crystals which are very stable in air (63). This compound is insoluble in ether, petroleum ether, and benzene, somewhat soluble in alcohol, and more soluble in pyridine.

Iron tetracarbonyl may be prepared by well regulated thermal decomposition of iron enneacarbonyl (64). It may also be prepared directly from the pentacarbonyl (65). The pentacarbonyl is shaken with alkali, and a suspension of manganese dioxide is added. The pentacarbonyl disproportionates with the formation of a hydride.

$$Fe(CO)_5 + CH_3ONa + H_2O \longrightarrow Fe(CO)_4H_2 + CH_3O \cdot CO \cdot ONa$$
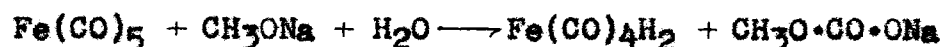
The hydride is then oxidized.

$$Fe(CO)_4H_2 + MnO_2 \longrightarrow 1/3\left[Fe(CO)_4\right]_3 + H_2O + MnO$$
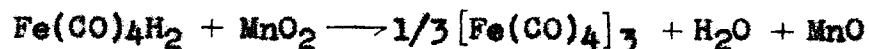
Iron tetracarbonyl forms green crystals which are soluble in benzene, ether, or acetone.

Iron carbonyl hydride has been isolated as a very volatile liquid when prepared in an oxygen free atmosphere (66).

(63) Speyer and Wolf, Ber., 60, 1424(1927).
(64) (a) Freundlich and Cuy, Ber., 56, 2264(1923); (b) Freundlich and Malchow, Z. anorg. allgem. Chem., 141, 317(1924); (c) Dewar and Jones, Proc. Roy. Soc. (London) [A] 76, 558 (1905); [A] 79, 66(1907).
(65) Hieber and Leutert, Z. anorg. allgem. Chem., 204, 165(1932).
(66) Hieber and Leutert, Ber., 64, 2832(1931).

It is extremely unstable. The acidity of this hydride is of about the same order of magnitude as that of carbonic acid (18).

A large number of mixed carbonyl compounds of iron are known. These include amine carbonyl complexes, halogen carbonyl complexes, and nitrosyl carbonyl complexes (18)(60).

Nickelous chloride apparently reacts with diethylzinc in the same manner as ferrous iodide (55).

Nickelous chloride reacts with ethylmagnesium bromide to give ethane and ethylene, with propylmagnesium bromide to give propane, with phenylmagnesium bromide to give biphenyl, and with p-tolylmagnesium bromide to give bi-p-tolyl, all in excellent yields (48d). In an atmosphere of hydrogen, nickelous chloride reacts with phenylmagnesium bromide to give benzene and a hydride of nickel, NiH_2 (51)(67). The action of phenylmagnesium bromide on nickelous chloride has been used as a means of preparing a highly reactive form of colloidal nickel (58)(67). Colloidal nickel prepared in this manner rapidly absorbs hydrogen, carbon monoxide, ethylene, acetylene, or nitric oxide. Job and Reich (58)(68) assumed an organonickel compound to be formed as an intermediate in the reaction of phenylmagnesium bromide with nickelous chloride. Weichselfelder and Thiede (51) attempted the preparation of diphenylnickel from the action of phenylmagnesium bromide, in ether solution, on anhydrous nickelous chloride. They varied the amounts and con-

(67) Schlenk and Weichselfelder, Ber., 56, 2230(1923).
(68) Job and Reich, Compt. rend., 179, 330(1924).

centration of Grignard reagent used manifoldly, but were unable to prepare any diphenylnickel in a pure form. In the reactions the ether solutions were colored brownish-black, and a black powder of pyrophoric nature separated out. This powder burned in the air with an odor resembling biphenyl. In ether suspension it rapidly absorbed oxygen. If it was allowed in a dry condition to react slowly with air, a sublimate melting about $60^{\circ}C$. was obtained. In an atmosphere of hydrogen a hydride of nickel, NiH_2, was obtained. The reaction of n-amylmagnesium chloride/with nickelous chloride was found to proceed in the same manner only more slowly. Gilman and Kirby (69) found nickelous cyanide, $Ni(CN)_2$, to react with phenylmagnesium bromide in ether with sufficient vigor to cause refluxing of the ether. A brownish reaction mixture was obtained which gave only a trace of biphenyl on hydrolysis. Jones (70) reacted phenylmagnesium bromide with nickel tetracarbonyl and obtained biphenyl and benzoin. Gilliland and Blanchard (71) obtained triphenylmethane, triphenylvinyl alcohol, pentaphenylethane, and tetraphenylethylene from the same reaction. No mention of organonickel compounds being formed was made.

Calcium carbide acts on a water solution of nickelous chloride to give a precipitate containing nickelous acetylide, C_2Ni (59). This compound was not isolated. It liberated acetylene on treatment with hydrochloric acid.

(69) Gilman and Kirby, Rec. trav. chim., 48, 157(1929).
(70) Jones, Chem. News, 90, 144(1904).
(71) Gilliland and Blanchard, J. Am. Chem. Soc., 48, 410(1926).

Nickel tetracarbonyl was the first metal carbonyl compound to be prepared (72). It is prepared through the action of carbon monoxide on finely divided nickel at a temperature of 30°-100^oC. Nickel tetracarbonyl is a colorless liquid which boils at 43^oC. and solidifies at -25^oC. It is soluble in most organic solvents. It decomposes on heating to 180°-200^oC. into nickel and carbon monoxide. Nickel tetracarbonyl is very sensitive to oxygen, exploding when heated to 60^oC. in air. Chlorine, bromine, iodine, and cyanogen react with nickel tetracarbonyl forming the corresponding nickel salts and liberating carbon monoxide (73). Nickel tetracarbonyl reacts with pyridine and ammino-compounds to form complexes (18)(60).

Cobaltous chloride reacts with Grignard reagents in the same manner as has already been described for nickelous chloride (48d)(51). If pyridine is used as the solvent, rather than ether, the reaction proceeds a great deal more slowly.

Sims and Mardles (52), tested an assumed solution of naphthylcobalt for anti-knock properties and found it to be without effect. The supposed naphthylcobalt was prepared from a naphthylmagnesium halide acting on an anhydrous halide of cobalt. Naphthylcobalt was described by them as being very unstable.

Cobaltous acetylide, CoC_2, was prepared by the action of calcium carbide on a water solution of cobaltous chloride

(72) Mond, Langer, and Quincke, J. Chem. Soc., 57, 749(1890).
(73) Dewar and Jones, Proc. Chem. Soc., 19, 5(1904).

(59). This compound reacted with hydrochloric acid to liberate acetylene. The compound was not isolated.

Cobalt forms two carbonyl compounds, cobalt tetracarbonyl, $Co_2(CO)_8$, and cobalt tricarbonyl, $Co_4(CO)_{12}$ (74). The tricarbonyl is prepared by careful heating of the tetracarbonyl. Cobalt tetracarbonyl is a yellow, crystalline substance. It melts at 51ºC. It is soluble in most organic solvents.

Cobalt tricarbonyl forms black-glistening crystals which are sparingly soluble in benzene and pentane and insoluble in most other ordinary solvents. The cobalt carbonyls form complex compounds with amines.

Cobalt carbonyl hydride, $H_2Co(CO)_4$, may be prepared by the action of barium hydroxide on cobalt tetracarbonyl (75). This substance is a clear, yellow liquid which solidifies at -33ºC. The acid strength of this hydride has been found to be between that of formic acid and of acetic acid (18). Cobalt carbonyl nitrosyl, $Co(CO)_3NO$, is formed by the action of a mixture of carbon monoxide and nitric oxide on cobalt (76).

The assumption may be drawn that the catalytic action of metals on the decomposition of diphenylmercury and dibenzylmercury, forming biphenyl and bibenzyl respectively, may be due

(74) Hieber, Muhlbauer, and Ehmann, Ber., 65, 1090(1932); Mond, Hirtz and Cowap, J. Chem. Soc., 97, 798(1910).
(75) Hieber, Angew. Chem., 49, 463(1936); Hieber and Schulten, Z. anorg. allgem. Chem., 232, 29(1937).
(76) Blanchard, Rafter, and Adams, J. Am. Chem. Soc., 56, 16 (1934).

to the migration of phenyl or benzyl radical from mercury to the metal employed as a catalyst, with the subsequent decomposition of the new organometallic into the coupling product and metal (77). This conclusion is substantiated, in part, by the fact that those metals, with the exception of platinum, effective in this reaction are those of which no organometallic compound has been prepared or of which the organometallic compounds decompose readily. Rasuwajew and Koton (77) studied the catalytic action of finely divided metals on diphenylmercury and dibenzylmercury by heating without solvent, as well as in the presence of hydrogen under pressure. Iron, cobalt, nickel, copper, silver, gold, palladium, and platinum were used. The decreasing order of effectiveness in the absence of hydrogen to produce coupling products was found to be for diphenylmercury: $Pd > Pt > Ag > Au > Co > Cu > Fe > Ni$; and for dibenzylmercury: $Pd > Pt > Ag > Au > Cu > Ni > Fe > Co$. The decreasing order of effectiveness, in the presence of hydrogen, for the decomposition of diphenylmercury was found to be: $Pd > Pt > Ni > Ag > Au > Co > Cu > Fe$; and for dibenzylmercury: $Pd > Pt > Ni > Au > Ag > Fe > Co > Cu$. Dibenzylmercury on hydrogenation without a catalyst forms benzene and no diphenyl. In the presence of a catalyst both benzene and biphenyl are formed. The interpretation of experimental results on the basis of intermediate organometallic compounds is in accord with the interpretation given by Busch and Weber (23) on the hydrogenation of bromobenzene.

(77) Rasuwajew and Koton, Ber., 66, 854(1933).

EXPERIMENTAL

The Reaction of Iron, Cobalt, and Nickel with some Organic Halides.

To several tubes containing n-butyl bromide were added powdered iron, nickel, and cobalt, respectively. The tubes were sealed and heated to 180°. The tubes containing iron exploded. No reaction occurred on sixteen hours heating in the tubes containing cobalt and nickel. Bromobenzene and powdered iron gave no reaction on heating in a sealed tube for eight hours at 210°.

Iron amalgam was added to ethyl iodide in a tube. The tube was sealed and allowed to stand in sunlight for six months. No reaction occurred. The ethyl iodide was recovered unchanged.

To a solution of 0.1 mole of n-butylmagnesium bromide in ether was added 0.05 mole of anhydrous ferrous chloride. The reaction was refluxed for six hours. The evolution of gas was complete at this time. Ten grams (0.05 mole) of iodobenzene in 25 ml. of ether were then added dropwise. Vigorous refluxing occurred. When the reaction ceased to reflux of its own accord, heat was applied and the reaction mixture was refluxed overnight. Hydrolysis was then effected by addition of an iced solution of ammonium chloride. The ether layer was separated, dried over sodium sulphate, and carefully fractionated. The

fraction boiling at 78° weighed 2.47 grams. This was identified as benzene by means of nitration to m-dinitrobenzene, m. p. 89°. Six grams of iodobenzene were recovered.

The experiment was repeated using bromobenzene in place of iodobenzene. This reaction was not as vigorous as with iodobenzene. The yield of benzene was 1.55 grams from 7.8 grams of bromobenzene. The benzene was identified by nitration to m-dinitrobenzene.

These reactions were checked several times with the same results. Attempts to determine the presence of a phenyl-iron compound in the reaction mixture by means of reactions with functional groups gave negative results. Benzaldehyde, oxygen, and allyl bromide gave no reaction when added to the mixture, while benzoyl bromide gave a 32% yield of ethyl benzoate, but no benzophenone.

To a solution of 0.1 mole of phenylmagnesium bromide in ether was added 0.05 mole of anhydrous ferrous chloride. The reaction was refluxed for four hours. The color test for organometallics was negative. Ten grams (0.05 mole) of iodobenzene in 25 ml. of ether were then added dropwise. No reaction occurred. Heat was applied and the reaction was refluxed for two hours. Hydrolysis was then effected by addition of water. A vigorous reaction occurred with the evolution of large quantities of gas and the formation of ferrous hydroxide. The ether layer was separated, dried, and fractionated. No benzene could be detected. Nine and eight-tenths grams of iodobenzene

were recovered. This reaction was repeated with the same results.

The Reaction of Iron Halides with Phenylmagnesium Halides and Phenyllithium.

Many attempts were made to prepare phenyliron compounds through the action of phenylmagnesium iodide, phenylmagnesium bromide, or phenyllithium on ferric chloride, ferrous chloride, ferric bromide, or ferrous iodide. These reactions were carried out at varying concentrations and at temperatures ranging from -55°C. to 35°C. The solvent employed was varied from 100% ether to a solution containing five parts of benzene to one part of ether. In some cases the organometallic solution was added to the iron halide and in some cases the iron halide was added to the organometallic solution. In none of these reactions could any evidence be found for the formation of an organoiron compound. In most cases the reactions were vigorous and biphenyl was formed in quantitative yield. The reaction mixtures turned black, depositing an iron mirror on the walls of the flask. Ferrous chloride failed to react with the Grignard reagents or with phenyllithium at -55°C. in two hours of stirring. The color test remained positive and unchanged ferrous chloride remained in the flask. On warming to -20°C., a vigorous reaction would set in and biphenyl was formed in quantitative yields. The reaction of ferrous iodide with phenyllithium and with the

Grignard reagents gave a mixture consisting of two layers. Hydrolysis of an aliquot from the larger, upper layer gave the same amount of biphenyl as was obtained on hydrolysis of an aliquot from the smaller, lower layer. Both aliquots indicated a quantitative yield of biphenyl. However, the amount of ferrous hydroxide obtained from the lower layer was many times that obtained from the upper layer. This proved that the biphenyl was not formed from hydrolysis of a phenyliron compound. Numerous attempts to determine the presence in solution of an organoiron compound, by reacting the solutions with functional groups, gave no evidence of the existence of an organoiron compound even at -55°C. Benzoyl halides yielded ethyl benzoate in 80 to 90% yields, phenyl isocyanate gave a quantitative yield of its trimer, and benzaldehyde gave no reaction.

In an attempt to stabilize the primary valence of iron, by filling the secondary valence, ferrous chloride tetrapyridine was prepared (78) and reacted with an ether solution of phenylmagnesium bromide. The only effect of the pyridine was to decrease the rate of reaction. Five days stirring were required to obtain a negative color test. Hydrolysis at this point gave a quantitative yield of biphenyl.

The chlorides and bromides of nickel and cobalt were found to react in the same manner as the chlorides and bromides

(78) This compound was prepared according to the directions of
Weinland, Effinger and Beck, Arch. Pharm., 265, 374(1927)
[C. A., 21, 2231(1927)].

of iron. They reacted with phenylmagnesium halides to produce biphenyl in quantitative yields. No evidence of organocobalt or organonickel compounds was obtained.

The Reaction of α-Naphthylmagnesium Bromide with Ferrous Chloride.

An ether-benzene solution containing 0.1 mole of α-naphthylmagnesium bromide was cooled to -10° in an ice-salt bath. To this solution was added 12.8 grams (0.1 mole) of anhydrous ferrous chloride. No apparent reaction occurred. After stirring for twenty-four hours in an ice-salt bath, the color test was still strongly positive and large amounts of ferrous chloride, which was free of organic matter, were still present in the flask. The reaction was then allowed to come to room temperature. The color test was negative after four hours, the solution was black, and a metallic mirror covered the inside of the flask. The reaction was then hydrolysed by addition of iced-water. A large amount of ferrous hydroxide formed. The benzene layer was separated, dried over sodium sulphate, filtered, and distilled. Ten grams of naphthalene (78%) and 2 grams (16%) of bi-α-naphthyl were obtained. No iron was present in the benzene layer.

This reaction was repeated and 0.05 mole of benzoyl bromide was added as soon as a negative color test was obtained. The reaction mixture was stirred for two hours and then hydrolysed. No α-benzoylnaphthalene was obtained.

The Reaction of α-Naphthyllithium with Ferrous Iodide.

To a solution of 0.05 mole of α-naphthyllithium in ether, cooled to -55° in a dry-ice acetone bath, was added 0.05 mole of ferrous iodide in ether solution. Two layers formed in the reaction mixture. The larger, upper layer was almost colorless. The lower layer was black and viscous. No solid was formed. The color test was soon negative. To this mixture was added 0.05 mole of benzoyl bromide. The reaction was stirred at -55° for one-half hour and then allowed to warm to room temperature. The reaction was then hydrolyzed with distilled water. A large amount of ferrous hydroxide was formed. The benzoyl bromide was recovered as benzoic acid. Three and nine-tenths grams (60%) of naphthalene was obtained. One and three-tenths grams (20%) of the bi-α-naphthyl were obtained. No α-benzoylnaphthalene was obtained.

The Reaction of Ferric Fluoride with Grignard Reagents.

To a solution of 0.1 mole of phenylmagnesium bromide in ether was added 5.65 grams (0.05 mole) of anhydrous ferric fluoride. Five days stirring of the reaction mixture were required to obtain a negative color test. No trace of metallic iron was present in the reaction flask. A reddish-brown precipitate mixed with white crystals was present in the solid phase. The ether layer was light-red in color. The ether layer was filtered through sintered glass and hydrolyzed. A

very slight amount of ferric hydroxide was formed on hydrolysis
of the ether layer. Careful fractionation of the ether layer
gave six grams (77%) of liquid boiling at 78°. This was identi-
fied as benzene by nitration to m-dinitrobenzene. A solid
residue remained in the flask after removal of the benzene
fraction. This was distilled in steam. The solid collected in
the distillate weighed 1.2 grams (15.5% yield) and melted at
69°. It gave no depression in melting point with known bi-
phenyl. The benzene and biphenyl obtained accounted for 92.5%
of the phenylmagnesium bromide employed in the reaction.

The red solid present in the original reaction flask
was soluble in benzene. Removal of the benzene from the solu-
tion gave a red, hygroscopic solid which contained no organic
matter. This red solid was not identified.

Repeated experiments using varying amounts of ferric
fluoride and phenylmagnesium bromide showed that three equi-
valents of Grignard reagents to one of ferric fluoride were
consumed in the reaction. The addition of more than three
equivalents of Grignard reagent gave a reaction mixture which
continued to give a positive color test after standing a year.

To a solution of 0.2 mole of methylmagnesium bromide
in ether was added 11 grams (0.1 mole) of ferric fluoride.
The mixture was stirred for two weeks with no apparent reaction.
The contents of the reaction flask were then transferred to a
Schlenk tube and sealed. The tube was opened after standing
for five months. Only a very slight pressure was present in

the tube. There was no evidence of any reaction having occurred as the solution gave a very strong color test and the ferric fluoride was unchanged in the tube.

The Reaction of Phenylzinc Chloride with Ferrous Iodide.

This reaction was carried out according to the directions of Champetier (48e) for the preparation of phenyliron iodide. To a solution of 0.05 mole of phenylmagnesium bromide in ether was added 0.05 mole of anhydrous zinc chloride in ether. To the phenylzinc chloride, so obtained, was added 0.05 mole of ferrous iodide in 50 ml. of ether. No warming occurred. This mixture was then refluxed for two hours. Seven grams (0.05 mole) of benzoyl chloride were added to the reaction mixture. A slight warming occurred. This reaction was stirred for one hour and then allowed to stand overnight. The products isolated on hydrolysis were, 3 grams of ethyl benzoate, 0.22 gram of benzoic acid, 1.4 grams of benzophenone (19% yield), 0.35 gram of biphenyl, and 1.45 grams of benzene. Some tar was also obtained. The hydroxides formed on hydrolysis were filtered off and washed free of chlorides. Analysis of the hydroxides for iron and zinc showed them to consist of 3 atoms of iron to 2 atoms of zinc.

An ether solution containing 0.5 mole of phenylmagnesium bromide was filtered into a one liter flask under nitrogen. To this Grignard solution was added a solution of 0.5 mole of

zinc chloride in ether. The solid phenylzinc chloride formed
was washed with ether and then covered with 500 ml. of an ether
solution containing 0.5 mole of ferrous iodide. This mixture
was stirred and refluxed for two hours. A 10 ml. portion of
the reaction mixture was then hydrolysed with distilled water.
The hydroxides formed were filtered off and washed free of
halides. The hydroxides so obtained gave a voluminous precipi-
tate of zinc sulphide when a qualitative test was made for zinc.
After seven hours more of refluxing, another sample of the re-
action mixture was removed. The hydroxides obtained at this
point were found to consist of approximately 50% ferrous hy-
droxide and 50% zinc hydroxide. Analysis was made by igniting
the mixed hydroxides to the oxides and extracting the soluble
zinc oxide with dilute acetic acid. The zinc was reprecipi-
tated by addition of sodium hydroxide to the neutral point of
methyl orange, filtered, washed, and weighed. The iron oxide
was washed, ignited, and weighed. The yield of biphenyl as
isolated by ether extraction of the hydrolysis products was 47%
at this point. After another five hours refluxing another
sample was hydrolysed. The yield of biphenyl was 63% and the
hydroxides consisted of 67% iron hydroxide and 33% zinc hy-
droxide. After twelve hours more of refluxing, the yield of
biphenyl was 88% and the hydroxides obtained were 90% ferrous
hydroxide. The reaction was refluxed another twenty-four hours.
Hydrolysis of a portion of the reaction mixture gave a 96% yield
of biphenyl and the hydroxides obtained gave only a slight test

for zinc. One-half of the remainder of the reaction mixture was then treated with benzoyl bromide. No benzophenone was isolated on hydrolysis. Ethyl benzoate and biphenyl were the only products isolated. The bottom of the initial reaction flask was covered with a black solid which reacted vigorously with water to form large quantities of inflammable gas and ferrous hydroxide. No difference could be found in the chemical reactivity of phenylzinc chloride and the mixture obtained by adding ferrous iodide to phenylzinc chloride and refluxing for two hours according to the direction of Champetier (48e) for the preparation of phenyliron iodide. Addition of acid halides produced ketones in both cases, while neither would react with allyl bromide on standing sixteen hours.

The Reaction of Ethylzinc Iodide with Ferrous Iodide.

To a solution of 0.1 mole of ethylzinc iodide in ether, prepared according to the directions of Job and Reich (79), was added 0.1 mole of ferrous iodide in ether according to the directions of Job and Reich (57) for the preparation of ethyliron iodide. The outlet of the condenser was connected to a gas collecting flask, with a calcium chloride tube connected intermediately. The reaction was then refluxed for six hours. The evolution of gas from the reaction was slow but continuous. The gas collected was passed through a cooling coil at $-10^{\circ}C$. to remove any ether which might be present. A total volume of

(79) Job and Reich, Bull. soc. chim. [4] 33, 1414(1923).

575 ml. of gas was collected. This was analysed with a modified William's gas analyser.

<u>Anal.</u>   Total unsaturated gases, 39%.

Saturated gases, 58%.

Selective oxidation over copper oxide showed no hydrogen to be present. Combustion data gave a value of 3.18 for the average number of carbon atoms in the saturated gases. This indicated a probable mixture of ethane and butane.

The reaction mixture was hydrolysed with distilled water. The hydroxides formed consisted of 39.4% ferrous hydroxide and 60.6% zinc hydroxide. No organic material other than a small amount of ethyl iodide was isolated from the products of hydrolysis.

This experiment was repeated using twice as large a run. The gas evolved measured 1320 ml. Analysis of the gas gave 37% unsaturated gases and 63% saturated gases. The hydroxides obtained on hydrolysis contained 44.8% zinc hydroxide and 55.2% ferrous hydroxide.

The Reaction of Ferric Chloride with Tetraethyllead.

To a solution containing 11.5 grams of anhydrous ferric chloride in 200 ml. of dry ether was added 20.6 grams of freshly distilled tetraethyllead. A slight warming occurred with the formation of a voluminous precipitate. This precipitate was extracted with boiling ether until free of lead. The residue consisted of 9 grams of anhydrous ferrous chloride which

was identified by analysis.

Anal. Calcd. for $FeCl_2$: Fe, 44.1; Cl, 55.9.

Found: Fe, 44.02; Cl, 56.00.

The ether extracts consisted of organic lead compounds containing chlorine. From their decomposition points they were probably a mixture of triethyllead chloride and diethyllead dichloride. No organoiron compound was formed.

Tetraethyllead was found to be without action on ferrous iodide, ferrous chloride, cobaltous bromide, and nickelous bromide. Chloroplatinic acid was reduced immediately by tetraethyllead to deposit metallic platinum.

The Reaction of Ferrous Iodide with Tri-p-anisyllead.

This reaction was run using ferrous iodide alone with tri-p-anisyllead and using ferrous iodide in the presence of iron powder. The results were the same in both cases.

Ten grams of tri-p-anisyllead were added to a solution of 0.019 mole of ferrous iodide in 20 ml. of ether and 150 ml. of dry benzene. A yellow precipitate of lead iodide formed immediately. The black color of ferrous iodide disappeared leaving a yellow solution which would blacken immediately on exposure to air. The solution gave no color test with Michler's ketone. This solution was filtered under nitrogen from the solid precipitate. The solution after filtration was divided

into two equal parts. One part was treated with 1.85 grams of benzoyl bromide. This was refluxed for two hours and hydrolysed. The benzoyl bromide was recovered as benzoic acid. No ketone was formed.

The residue in the initial reaction flask was extracted with benzene. This gave 4 grams of tetra-p-anisyllead, m. p. 143°. A mixed melting point with tetra-p-anisyllead gave no depression. There remained 1.58 grams of lead iodide which was identified by dissolving in ammonium acetate and precipitating as lead chromate.

The half of the filtered solution which was not treated with benzoyl bromide was hydrolysed. The hydrolysis products were extracted with ether, the ether extracts dried and distilled. No anisole was obtained. A mixture of organolead compounds consisting chiefly of a yellow compound melting at 122°, was obtained. This yellow solid was identified as di-p-anisyllead diiodide by means of a mixed melting point with a sample of di-p-anisyllead diiodide later prepared by Mr. J. C. Baillie (80). The yield of pure product was 0.9 gram.

The iron from the ferrous iodide remained in solution until hydrolysis was effected. It then precipitated as ferric hydroxide. This reaction is analagous to the reaction obtained by Mr. J. C. Baillie from triaryllead compounds with magnesium iodide in which he obtained no Grignard reagent.

(80) Unpublished work in this laboratory.

This reaction was repeated with the same results. The reaction was also run using powdered iron along with ferrous iodide and tri-p-anisyllead. The results were also the same in this case.

The Reaction of Cobalt Bromide with 2,4,6-trimethylphenyl-magnesium Bromide.

To a solution of 0.05 mole of 2,4,6-trimethylphenyl-magnesium bromide in an ether-benzene solution (2 parts of ether to 1 part benzene) was added slowly 0.05 mole of anhydrous cobaltous bromide, $CoBr_2$. The reaction mixture was cooled in an acetone-dry ice bath. No reaction was apparent at this low temperature. The color test for organometallics remained as strong after three hours stirring as at the start. The reaction was then allowed to warm up to -20° in an ice-salt bath. An immediate reaction set in, the solution became black, and the color test soon became negative. Hydrolysis of this solution gave a 20% yield of bimesityl. No organic material containing cobalt could be isolated.

The Reaction of Phenylmagnesium Bromide with Nickel Cyanide.

Anhydrous nickel cyanide, $Ni(CN)_2$, was prepared by dehydration of the hydrated salt. This was accomplished by heating to 230° under nitrogen until no more water was evolved.

This solution was then filtered through a sintered glass plate and standardized by acid titration. All work was carried out in an atmosphere of nitrogen.

A slight excess of phenylmagnesium iodide solution, prepared in the above manner, was placed in a clean, dry, three-neck flask under nitrogen. The solution was then cooled by means of an ice-salt bath until a small amount of benzene had frozen around the edge of the flask. To this well-stirred mixture was slowly added the anhydrous metal halide by flushing from a dropping funnel with an ether-benzene solution. All halides were added as solids in this manner.

The Reaction with Ferrous Chloride.

To a solution of 0.03 mole of phenylmagnesium iodide was added 1.27 grams (0.01 mole) of anhydrous ferrous chloride, $FeCl_2$. The solution turned black and deposited a black solid. The color test for organometallics was positive after one hour of stirring in ice bath. The solution was then hydrolysed by filtration through a sintered glass plate into an iced solution of ammonium chloride. The hydrolysis products were extracted with ether. The ether extracts were dried over anhydrous sodium sulphate, filtered, and the ether and benzene were removed under reduced pressure. Steam distillation of the solid residue gave 1.51 grams of biphenyl melting at 68°-9°. A mixed melting point with a known sample of biphenyl gave no depression.

The yield of biphenyl was 98% of the theoretical based on the amount of ferrous chloride employed in the reaction. No other organic material could be isolated from the reaction. The solid residue remaining in the reaction flask reacted vigorously with water giving ferrous hydroxide and a gas, but no organic material. This reaction was repeated with the same results.

The Reaction with Cobalt Bromide.

To a solution of 0.03 mole of phenylmagnesium iodide was added 2.19 grams (0.01 mole) of anhydrous cobaltous bromide, $CoBr_2$. A black solution resulted with a black deposit in the flask. The color test for organometallics remained positive. The reaction was worked up in the same manner as described for ferrous chloride. This gave 1.52 grams of biphenyl melting at $68^{o}-9^{o}$. A mixed melting point with known biphenyl gave no depression. The yield of biphenyl was 98% of the theoretical based on the amount of cobalt bromide employed in the reaction. The solid residue remaining in the flask contained no organic material, and no organic material other than biphenyl was isolated from the reaction. This reaction was repeated with the same results.

The Reaction with Nickel Bromide.

To a solution of 0.095 mole of phenylmagnesium iodide was added 6.54 grams (0.03 mole) of anhydrous nickelous bromide, $NiBr_2$. The solution became black and a black deposit was obtained. The color test for organometallics remained positive. The reaction mixture was worked up in the manner described for ferrous chloride. This gave 4.6 grams of biphenyl melting at 67°-9°. The melting point was not depressed by known biphenyl. The yield of biphenyl was quantitative based on the amount of nickel bromide employed in the reaction. No other organic material was isolated. The residual solid in the reaction flask contained no organic matter. This reaction was repeated with the same results.

The Reaction with Ruthenium Chloride.

One gram of commercial ruthenium chloride was dehydrated in an electric furnace at 380^oC. in an atmosphere of chlorine. This gave 0.75 grams of anhydrous ruthenium trichloride, $RuCl_3$. This halide was added to a slight excess of phenylmagnesium iodide. A prompt reaction occurred. The color test for organometallics remained positive. This reaction was worked up in the manner described for ferrous chloride giving 0.82 gram of biphenyl melting at 68°-9°. A mixed melting point with known biphenyl gave no depression. The yield of biphenyl was 99% of the theoretical based on the amount of ruthenium trichloride em-

ployed. No other organic material was isolated from the re-
action. The ruthenium was reduced to ruthenium metal which
was deposited on the bottom of the reaction flask. This metal-
lic deposit did not react with water. It gave a metallic
streak when rubbed on a porous plate. When viewed under a
microscope, it appeared as a gray metal without crystalline
form which had the appearance of having been fused. Pits and
extrusions were visible on the surface. This reaction was not
repeated.

The Reaction with Rhodium Chloride.

One gram of commercial rhodium trichloride, $RhCl_3$, was
dehydrated by heating to $440^\circ C$. in an atmosphere of chlorine.
This gave 0.75 gram (0.0036 mole) of anhydrous rhodium tri-
chloride, $RhCl_3$, which was added to 0.013 mole of phenylmagnes-
ium iodide. A slow reaction set in and the solution gradually
became black with deposition of a black solid. The reaction
mixture was allowed to stand overnight after having been stirred
for six hours in an ice-salt bath. The color test for organo-
metallics was positive. The reaction was worked up in the
same manner as described for ferrous chloride. This gave 0.81
gram (97.5%) of biphenyl melting at $68^\circ-9^\circ$. A mixed melting
point with known biphenyl gave no depression. Metallic rhodium
remained in the reaction flask. This gave a metallic streak
when rubbed on a porous plate. When viewed under a microscope,

this solid showed a metallic luster. It consisted of amorphous lumps, with many pits and extrusions, having cracks visible across the surface. No organic material other than biphenyl was obtained. This reaction was not repeated.

The Reaction with Palladium Chloride.

One gram of anhydrous palladium chloride, $PdCl_2$, (0.00566 mole) was reacted with 0.0163 mole of phenylmagnesium iodide. This gave a vigorous reaction and a black deposit of metallic palladium appeared immediately. The reaction was stirred for three hours in an ice-salt bath and then allowed to stand overnight. The color test for organometallic compounds remained positive. The reaction was then worked up in the manner previously described for ferrous chloride. This gave 0.85 gram of biphenyl melting at 68°-9°. A mixed melting point with known biphenyl gave no depression. This was a 98% yield of biphenyl based on the palladium chloride employed in the reaction. The black deposit of metallic palladium was amorphous but gave a metallic luster. No organic material other than biphenyl was isolated from the reaction. This reaction was not repeated.

The Reaction with Osmium Chloride.

Osmium trichloride was prepared by heating ammonium chlorosmate to 350^oC. in a current of chlorine. The 0.82 gram

of sublimed salt was added to a slight excess of phenylmagnesium
iodide. A prompt reaction took place and the solution became
dark. Hydrolysis gave 0.34 gram (53%) of biphenyl melting at
$68°-9°$. A mixed melting point with known biphenyl gave no de-
pression. A small amount of black, tarry, organic material con-
taining osmium remained after removal of the biphenyl. This
material could not be induced to crystallize. The larger part
of the osmium was precipitated as metallic osmium black during
the reaction. This reaction was not repeated.

The Reaction with Iridium Chloride.

One gram of commercial iridium trichloride was de-
hydrated in a current of chlorine at $320°C$. This gave 0.9 gram
of anhydrous iridium trichloride, $IrCl_3$. This was added to a
slight excess of phenylmagnesium iodide. No apparent reaction
took place. After two hours stirring in an ice-salt bath the
reaction was allowed to come to room temperature. After three
weeks stirring, a negative color test was obtained. The re-
action was hydrolysed with iced ammonium chloride solution,
the benzene layer was separated and dried, and the benzene was
removed under reduced pressure. Steam distillation of the
residue gave 0.2 gram of biphenyl melting at $69°$. A mixed
melting point with known biphenyl gave no depression. The yield
of biphenyl was only 28% of the theoretical based on the iridium
chloride. A small amount of a brown amorphous solid, resem-

bling that obtained from the reaction of platinic chloride
with phenylmagnesium iodide, was obtained. This solid burned,
on heating in a flame, leaving a residue of metallic iridium.
This material was difficultly soluble in benzene, alcohol,
acetone, and ether. It was readily soluble in dioxane. It
appeared to be a mixture as it was only partially soluble in
some solvents. This reaction was not repeated.

The Reaction with Platinic Chloride.

Two and one-tenth grams of anhydrous platinic chloride,
$PtCl_4$, prepared according to the method of Kharasch and Ash-
ford (17), were added to six equivalents of phenylmagnesium
iodide. A reaction set in at once with the appearance of
beautiful golden crystals in the reaction mixture. The re-
action was stirred for thirty minutes at room temperature after
the addition of platinic chloride was completed. The color
test for organometallics was negative at this point. The con-
tents of the flask were then poured into ice water and ex-
tracted repeatedly with benzene. The benzene extracts were
dried over sodium sulphate, filtered, and concentrated under
reduced pressure. A heavy, reddish-brown powder separated
from the benzene. This solid was only slightly soluble in
benzene, alcohol, or chloroform. It was readily soluble in
dioxane and insoluble in water. The temperature of the solvent

had no apparent effect on the solubility of this material. On heating in an open flame, the substance burned with a smoky flame leaving a residue of metallic platinum. It gave an excellent qualitative test for iodine. Chlorine tests were negative. This material was analysed for platinum by burning and weighing the platinum residue.

Anal. Found: Pt, 37.9, 37.7.

This analysis does not correspond to the calculated value for any expected compound and solubility tests indicated that the material was a mixture of various compounds. No crystalline material could be isolated.

A portion of this solid was dissolved in hot concentrated nitric acid. The solution deposited, on cooling, white needles, which after crystallization from alcohol melted at 229° and gave no depression in melting point when mixed with a known sample of 4,4'-dinitrobiphenyl. Biphenyl was found to nitrate to 4,4'-dinitrobiphenyl under the same conditions. However, the platinum-containing solid had been washed several times with benzene, in which biphenyl is very soluble, so it appears unlikely that the 4,4'-dinitrobiphenyl was derived directly from biphenyl contained in this material.

In a second run, four equivalents of phenylmagnesium iodide were reacted with 1.1 grams of platinic chloride. The color test for organometallics was negative after one hour. Another four equivalents of phenylmagnesium iodide were then added to the reaction mixture. The color test again became

negative after one hour. The addition of two more equivalents of phenylmagnesium iodide left a solution which gave a positive color test after stirring overnight. The golden precipitate which appeared at the start of the reaction was gone and a heavy white precipitate was present in the reaction flask. No metallic platinum was visible. The white precipitate was extracted repeatedly with ether to remove unreacted Grignard reagent and magnesium salts. The ether extracts contained some platinum. This precipitate darkened on exposure to air. It gave a qualitative test for magnesium and iodine, which could not be removed by repeated extraction with ether. Qualitative tests for chlorine were negative. This white precipitate gave no color test. It reacted vigorously with water to give a brown, platinum-containing substance which from platinum analysis was the same as that previously described. This white precipitate was analysed for platinum and magnesium. Samples were procured by adding dry ether to the reaction flask; stirring then produced a suspension, which was forced out into a sintered glass filter plate, sealed in a tube. The sample was dried in a stream of nitrogen and weighed in a bulb. The sample was decomposed by dilute sulphuric acid, which dissolved the magnesium but not the platinum. The insoluble platinum containing portion was washed free of magnesium, burned, and the residual platinum was weighed. The magnesium was precipitated as magnesium ammonium phosphate, ignited and weighed as the pyrophosphate.

Anal.   Found: Pt, 18.66, 18.52;   Mg, 5.78, 5.72.
This analysis shows a ratio of 2.5 atoms of magnesium to 1 of platinum. Hydrolysis of the white precipitate remaining in the reaction flask gave 0.5 gram of the brown, platinum-containing powder. No biphenyl was formed during this hydrolysis. This material had no melting point. On heating in a melting point tube, it decomposed at around 185°-200°. The material consisted of a mixture of compounds as it varied slightly in solubility and the percentage of platinum varied from 30.3% to 47.8% on various fractions of this material.

A check on the amount of phenylmagnesium iodide required to give an excess of Grignard reagent in the reaction with platinic chloride gave the same results, ten equivalents of Grignard reagent being added before a permanent color test could be obtained.

Due to the amorphous nature of the material, and the lack of melting point, no individual compounds could be isolated.

The Reaction of Methylmagnesium Iodide with Platinous Chloride.

One and eight-tenths grams of platinous chloride, $PtCl_2$, prepared according to the directions of Kharasch and Ashford (17), were added slowly to a solution of six equivalents of methylmagnesium iodide in an ether-benzene solution. The reaction mixture was cooled in an ice-salt bath and was stirred at this temperature for two hours. The reaction was then al-

lowed to stand overnight. This gave a dark-brown solution with
a small amount of solid in the bottom of the reaction flask.
Hydrolysis was effected by addition of water while the reaction
was cooled in an ice-bath. Ammonium chloride was then added to
dissolve the magnesium hydroxide. The benzene layer was sepa-
rated, dried over sodium sulphate, filtered, and evaporated to
dryness. A very slight amount of unidentified solid remained.
The main product of the reaction consisted of a very difficultly
soluble, amorphous, dark-brown powder. This powder was slightly
soluble in acetone or alcohol, and was insoluble in water,
petroleum ether (b.p., 60-8°), chloroform, or benzene. Analysis
of the substance indicated it to be dimethylplatinum diiodide.

<div align="center">

Anal. Calcd. for $C_2H_6PtI_2$: Pt, 40.75; I, 52.99;

C, 5.01; H, 1.25.

Found: Pt, 40.59; I, 53.5; C, 5.00; H, 1.87.

</div>

Di-α-Naphthylplatinum.

To a solution of 0.02 mole of α-naphthylmagnesium bro-
mide in ether-benzene solution, cooled in an ice-salt bath,
was added slowly 0.5 gram of platinous chloride, $PtCl_2$. The
reaction was stirred for six hours. A brown solution resulted.
This solution was poured onto cracked ice and extracted with
benzene. The benzene solution was dried, filtered, and concen-
trated to a small volume under reduced pressure. Addition of
alcohol precipitated a brown powder, which was washed several

times with hot alcohol and ether to remove any naphthalene or
bi-α-naphthyl. The weight of product was 0.55 gram (61%)
based on the platinous chloride used in the reaction. This
product was very soluble in benzene and chloroform. It was
very slightly soluble in alcohol, ether, or petroleum ether.
The temperature of the solvent had no effect on the solubility
of this material. It could not be induced to crystallize from
any of these solvents. On heating, this product decomposed with-
out melting. Decomposition produced a strong odor of naphtha-
lene. Sodium fusion gave no test for halogen. Analysis of the
product indicated an impure form of di-α-naphthylplatinum.

<u>Anal</u>. Calcd. for $C_{20}H_{14}Pt$: Pt, 43.43; C, 53.45;

H, 3.12.

Found: Pt, 45.11; C, 51.95; H, 3.35.

To a solution of 0.45 gram of di-α-naphthylplatinum in
50 ml. of dry m-xylene was added 5 grams of benzoyl bromide.
This solution was refluxed for five hours. Evolution of large
amounts of hydrogen bromide was noted. The solution was cooled,
filtered, and distilled. Five grams of an oil boiling at 187°-
189° at 17 mm. were obtained. This product was identified as
2,4-dimethylbenzophenone by preparation of its oxime, m. p. 126°.
A mixed melting point with a known sample of the oxime of 2,4-
dimethylbenzophenone gave no depression.

Refluxing of benzoyl bromide in xylene without platinum
being present gave no reaction.

Platinic chloride was also found to act as a condensing
agent for the preparation of 2,4-dimethylbenzophenone from ben-
zoyl bromide and meta-xylene. Seven and five-tenths grams of
benzoyl bromide, 30 ml. of meta-xylene, and 1 gram of anhydrous
platinic chloride were heated to refluxing of the xylene for
eight hours. The evolution of hydrogen bromide was vigorous.
Six grams (71%) of 2,4-dimethylbenzophenone were obtained on
working up the reaction. The ketone was identified by prepar-
ation of its oxime, m. p. 126°. A mixed melting point with a
known sample of the oxime gave no depression.

The Reaction of Methylmagnesium Iodide with Platinic Chloride.

This reaction was carried out by Pope and Peachey (1)
for the preparation of trimethylplatinum iodide. However, the
reaction is much more complicated than would be indicated by
their report. Compounds other than trimethylplatinum iodide
are obtained. As trimethylplatinum iodide was the compound de-
sired in this study, attempts were made to discover the condi-
tions necessary to obtain optimum yields of this compound. The
conditions described below were found to be the most satisfac-
tory.

Anhydrous platinic chloride was prepared according to
the directions of Kharasch and Ashford (17).

A solution of methylmagnesium iodide was prepared from
15 grams (0.105 mole) of methyl iodide, 40 ml. of anhydrous

ether, and 2.5 grams (0.105 atom) of magnesium. The resulting Grignard solution was diluted with 160 ml. of dry benzene. This solution was filtered through glass wool into a clean, dry flask. The Grignard solution was then cooled to -10° and 8.5 grams (0.025 mole) of anhydrous platinic chloride were added in small portions to the well-stirred reaction. Stirring was continued for four hours after the addition of platinic chloride was complete. Hydrolysis was then effected by the addition of water while the reaction was cooled in an ice bath. The reaction products were extracted repeatedly with benzene, the benzene extracts were dried over sodium sulphate, filtered, and concentrated to a small volume under reduced pressure. A heavy reddish-brown powder separated from the concentrates. Sufficient benzene was added to increase the volume to 50 ml. The benzene was heated to boiling and filtered from the residue. The residue was extracted with another 50 ml. portion of boiling benzene. The benzene extracts were combined and concentrated to 10 ml. followed by cooling in an ice-bath. Three and seven-tenths grams (40%) of trimethylplatinum iodide were obtained by filtration from the benzene. This product was recrystallized from a mixture of chloroform and alcohol and identified by analysis in a pearl tube for platinum and iodine.

<u>Anal</u>. Calcd. for C_3H_9PtI: Pt, 53.14; I, 34.60.

Found: Pt, 53.20; I, 34.48.

A slight residue remained from the original benzene extracts after the two extractions with 50 ml. portions of boiling

benzene. This residue was washed with hot acetone. A brick-red powder weighing 24 mg. remained. On examination under a microscope, this substance was found to consist of long slender needles. This compound was analysed for platinum and iodine.

Anal. Found: Pt, 43.30; I, 47.93.

This analysis does not correspond to any simple compound. The compound has not been identified. It is practically insoluble in chloroform, acetone, water, ether, and ethyl acetate. It is very slightly soluble in hot benzene, xylene, and toluene.

The benzene from which the trimethylplatinum iodide was crystallized was removed by a current of dry air. A slight residue remained. This was covered with 5 ml. of petroleum ether (b.p., 60°-8°) and allowed to stand for thirty minutes. The petroleum ether was filtered off and concentrated to a very small volume. Eighteen mg. of a crystalline material containing no halogen was obtained. This was identified as tetramethylplatinum by analysis. The analysis was slightly low.

Anal. Calcd. for $C_4H_{12}Pt$: Pt, 76.48.

Found: Pt, 75.46.

The residual hydrolysis products, which were not extracted by benzene, were filtered. The solid which remained on the filter was washed with alcohol, then with acetone, and finally with ether until the washings were colorless. Concentration of these washings gave a large quantity of a red hygroscopic platinum containing complex which was readily soluble in ether, alcohol, acetone, or water. This complex was not identified.

The residue on the filter was then treated with 10% hydrochloric acid with which it reacted to give a black, water solution. The water soluble material was extracted repeatedly with small portions of ethyl acetate which removed the color from the water layer. The ethyl acetate extracts were dried over sodium sulphate and filtered. The ethyl acetate was removed in a vacuum dessicator and the residue was then washed with acetone until the acetone washings were colorless. There remained 0.1 gram of black crystals which were no longer easily soluble in ethyl acetate or water. Analysis of these crystals indicated a probability of their being methylplatinum pentaiodide.

Anal. Calcd. for CH_3PtI_5: Pt, 23.10; I, 75.10.

Found: Pt, 23.32; I, 75.16.

These crystals on dissolving in water or alcohol and heating the solution on a steam bath for a short time deposited a black, amorphous powder which analysis indicated was methylplatinum triiodide.

Anal. Calcd. for CH_3PtI_3; Pt, 33.05; I, 64.41.

Found: Pt, 33.20; I, 63.05.

This material burned with a luminous flame in an atmosphere of oxygen. This substance is insoluble in all ordinary solvents excepting alcohol in which it is very slightly soluble. Attempts to obtain this substance in a crystalline condition were unsuccessful.

The acetone-soluble portion of the ethyl acetate extracts was evaporated to dryness. The residue was dissolved in ether which was allowed to evaporate slowly in an effort to crystallize the material. This left, on standing, 2.15 grams of a black material which was no longer soluble in ether, ethyl acetate, water or acetone. This material was analysed for platinum and iodine. The analysis approximated the composition for dimethylplatinum diiodide.

Anal. Calcd. for $C_2H_6PtI_2$: Pt, 40.75; I, 52.99.

Found: Pt, 40.20; I, 51.42.

This material burned with a luminous flame in an atmosphere of oxygen.

Four grams of difficultly soluble, black material remained on the filter after the original extraction with ethyl acetate. This material was placed in a Sohxlet cup and extracted with alcohol in which it all dissolved on long extraction. This material was analysed for platinum and iodine. The analysis indicated a possibility of the material being methylplatinum triiodide.

Anal. Calcd. for CH_3PtI_3: Pt, 33.05; I, 64.41.

Found: Pt, 31.95; I, 62.95.

This material could not be obtained in a crystalline form. It burned with a luminous flame in an atmosphere of oxygen.

All of the products of the reaction, which contained halogen and platinum, contained iodine. No product containing platinum contained chlorine with the possible exception of the hygroscopic complex which was not analysed.

It is necessary that the greatest attention be paid
to details if a satisfactory yield of trimethylplatinum iodide
is to be obtained from the reaction of methylmagnesium iodide
with platinic chloride. The Grignard solution must be diluted
with at least four parts of benzene, the reaction mixture must
be cooled until the benzene starts to freeze around the edge
of the flask, and the platinic chloride must be added slowly
in small portions to the reaction. If these conditions were
not strictly followed, the yield of trimethylplatinum iodide
dropped to zero in some cases. In case no trimethylplatinum
iodide was obtained, the reaction products consisted entirely
of the black, highly iodinated platinum compounds described
above.

Hexamethyldiplatinum.

Attempts to prepare this compound by the action of
sodium on trimethylplatinum iodide in liquid ammonia were un-
successful. Trimethylplatinum iodide was found to be insoluble
in liquid ammonia. Addition of sodium caused the trimethyl-
platinum iodide to dissolve in the liquid ammonia, giving a
water soluble complex which regenerated trimethylplatinum iodide
on addition of hydrochloric acid.

Six-tenths gram of trimethylplatinum iodide was dis-
solved in 20 ml. of dry benzene and refluxed with two equi-
valents of powdered potassium for ten hours. The reaction mix-

ture was then allowed to stand for two days. The potassium
was almost completely reacted. Traces of metallic platinum
had precipitated. A few drops of n-amyl alcohol were added to
destroy any remaining potassium. The solution was filtered
and the solvent removed. The residue was washed with water
to remove inorganic salts. The residue was extracted with
ether. Removal of the ether left pale-yellow crystals which
were recrystallized from a benzene-petroleum ether solution by
slow concentration of the solvent. Colorless crystals of
hexamethyldiplatinum were obtained. The yield of hexamethyl-
diplatinum was 0.24 gram (60%). These crystals were very sol-
uble in ether, acetone, or benzene. They were insoluble in
water, and only slightly soluble in cold petroleum ether (b.p.,
60-8°). Considerable difficulty was experienced in the analysis
of this compound due to its explosive nature. It explodes
sharply, on heating, with a brilliant shower of sparks. Anal-
ysis for platinum was finally obtained by exploding the com-
pound in a bulb with capillary openings. The capillaries were
plugged with about one inch of glass wool to prevent escape of
platinum. After the compound was exploded, a slow current of
air was passed through the bulb and it was burned to constant
weight. Analysis for carbon and hydrogen was obtained by
scattering a weighed sample of the material over a length of
about four inches in the combustion tube and igniting a few
particles at a time. A constant series of small explosions ac-
companied the combustion.

<u>Anal.</u>   Calcd. for $C_6H_{18}Pt_2$:   Pt, 81.25; C, 14.95;

H, 3.76.

Found: Pt, 81.13; C, 14.55; H, 3.92.

Molecular weight determinations, by lowering of the freezing point of benzene, indicated the compound to be undissociated.

<u>Mol. Wt. Determination.</u>

	Gms. substance	Gms. benzene	ΔT_f
1.	0.1000	17	0.06
2.	0.1440	17	0.09

Mol. Wt. found: 502, 482.

Calcd. for $C_6H_{18}Pt_2$: 480.4.

Twenty mg. of hexamethyldiplatinum were dissolved in 10 ml. of ether. To this solution was added 12.7 mg. of iodine. The resulting solution was refluxed for several hours until the color of iodine was gone. A precipitate had formed in the flask. This precipitate was crystallized from benzene and identified as trimethylplatinum iodide by analysis for platinum and iodine.

<u>Anal.</u>   Calcd. for C_3H_9PtI: Pt, 53.14; I, 34.60.

Found: Pt, 53.07; I, 34.46.

The yield of trimethylplatinum iodide was 12 mg. (45%).

<u>Tetramethylplatinum.</u>

To a solution containing four grams of dimethylmercury in 60 ml. of benzene-free hexanes was added 1.5 grams of sodium.

This mixture was stirred for two days. The methylsodium formed was forced, by means of nitrogen pressure, through a small tube into a dry flask. Dry mercury was added to remove any particles of metallic sodium which might be present. The suspension of methylsodium was then forced over into another flask.

To this suspension of methylsodium was added 1 gram of trimethylplatinum iodide. The reaction was stirred for twenty-four hours and then hydrolysed by the addition of 2 ml. of n-amyl alcohol followed by ethyl alcohol and finally water was added. The hexane layer was separated, dried over sodium sulphate, filtered, and evaporated to dryness. The residue was covered with 20 ml. of petroleum ether (b.p., 60-80). After standing for thirty minutes, the petroleum ether was filtered off and concentrated slowly. Large hexagonal crystals of tetramethylplatinum were deposited. The yield of tetramethylplatinum was 0.32 gram or 46%. Tetramethylplatinum is a colorless solid, readily soluble in the cold in benzene, acetone, ether, and petroleum ether (b.p., 60°-68°). It is much less soluble in cold alcohol or chloroform. It is insoluble in water and only slightly soluble in acetic acid. It is the most soluble of the organoplatinum compounds so far prepared. Its chief distinction in regard to solubility is its ready solubility in cold petroleum ether (b.p., 60-8°). This compound has no melting point. It decomposes with a slight explosion on heating in an open flame, but does not explode with anything near the violence of hexamethyldiplatinum. Tetramethylplatinum was identified by analysis.

Anal. Calcd. for $C_4H_{12}Pt$: Pt, 76.48; C, 18.80;

H, 4.72.

Found: Pt, 76.84; C, 18.32; H, 4.31.

Methyllithium was found to be ineffective for the transformation of trimethylplatinum iodide to tetramethylplatinum. On adding trimethylplatinum iodide to an ether solution of methyllithium, a white precipitate formed. The reaction mixture was refluxed for ten hours. Hydrolysis by means of dilute hydrochloric acid regenerated trimethylplatinum iodide.

To a solution of 0.2 gram of tetramethylplatinum in 10 ml. of benzene was added 1 ml. of benzoyl chloride. This solution was refluxed for one-hundred hours. No reaction occurred. The tetramethylplatinum was recovered unchanged.

To a solution of 0.1 gram (.0004 mole) of tetramethylplatinum in 10 ml. of chloroform was added 0.1 gram (.0008 atom) of iodine. This solution was refluxed for twenty-four hours with no reaction. The tetramethylplatinum was recovered unchanged.

A solution containing 0.1 gram of tetramethylplatinum in 10 ml. of petroleum ether (b.p., 60-8°) was heated to boiling. Dry hydrogen chloride was passed into the solution. White crystals of trimethylplatinum chloride soon began to deposit from the solution. After about fifteen minutes the precipitation was complete. The crystals were removed and analysed for platinum and chlorine.

Anal. Calcd. for C$_3$H$_9$PtCl: Pt, 70.75; Cl, 12.90.

Found: Pt, 70.20; Cl, 13.10.

Cleavage Reactions of Tetramethyltin.

In order to compare the chemical reactivity of tetra-
methylplatinum with that of tetramethyltin, some cleavage re-
actions of tetramethyltin were run under the same conditions as
were employed in cleavage reactions with tetramethylplatinum.

To a solution of 0.72 grams (0.004 mole) of tetramethyl-
tin in 100 ml. of chloroform was added 1 gram (0.008 atom) of
iodine. This solution was refluxed. The iodine coloration was
gone at the end of four hours. The solution was then saturated
with ammonia gas which precipitated 1.2 grams (100%) of the am-
monia addition compound of trimethyltin iodide. This substance
was identified by analysis for iodine.

Anal. Calcd. for C$_3$H$_9$SnI·NH$_3$: I, 41.24.

Found: I, 41.21.

This experiment was repeated with the same results with the ex-
ception that a faint iodine coloration persisted after four
hours refluxing.

A solution containing 0.72 grams (0.004 mole) of tetra-
methyltin in 100 ml. of petroleum ether (b.p., 60-8°) was heated
to boiling under reflux. Dry hydrogen chloride was passed into
the solution for five minutes. The solution was then cooled and
the excess hydrogen chloride was removed by reduced pressure.

The solution was then saturated with ammonia gas and the petroleum ether was removed in the cold under reduced pressure. No evidence of cleavage of the tetramethyltin was obtained. This experiment was repeated with the exception that hydrogen chloride was passed into the boiling solution for fifteen minutes. Sixty mg. of the ammonia addition compound of trimethyltin chloride were obtained.

The Attempted Preparation of a Methyliridium Compound.

To a solution containing 0.05 mole of methyllithium in equal parts of ether and benzene was added 4 grams (0.0133 mole) of anhydrous iridium trichloride. This mixture was stirred for five days at room temperature. The ether-benzene solution was filtered from the solid in the flask and hydrolysed. Three and six-tenths grams of iridium trichloride remained unreacted in the flask. This material was identified by analysis for iridium.

Anal. Calcd. for $IrCl_3$: Ir, 64.45.

Found: Ir, 64.42.

No methyliridium compound was isolated from the reaction.

The Reaction of Methylmagnesium Iodide with Osmium Chloride.

One gram of osmium was placed in a boat in a quartz tube and heated to 1000° in a current of chlorine for four hours. The chlorine was dried by passage through three feet of anhydrous calcium chloride followed by passage through sulphuric

-79-

acid. The exit end of the quartz tube was connected to a calcium chloride tube to exclude moisture. The osmium chlorides formed were deposited in the cool portion of the tube from which they were extracted with anhydrous ether. The solution of osmium chlorides was added slowly to an ether-benzene solution of methylmagnesium iodide which was cooled in an ice-salt bath. The reaction was stirred for four hours. A brown solution resulted with a black deposit in the flask. Hydrolysis was effected by pouring the reaction mixture onto an iced ammonium chloride solution. Besides osmium black, only a very small amount of tarry material could be isolated from the reaction. This material could not be induced to crystallize.

Miscellaneous Attempts to Prepare Group VIII Organometallics.

Di-p-tolylmercury was refluxed for six hours in xylene with powdered iron. No reaction occurred.

Powdered iron was heated with tetraphenyllead for eight hours at 150°. No reaction occurred.

A benzene solution containing 0.05 mole of di-p-tolylmercury was refluxed with 0.05 mole of anhydrous nickelous bromide for six hours. No reaction occurred. The benzene was replaced by quinoline to increase the solubility of the nickelous bromide. This mixture was refluxed for eighteen hours with no reaction.

Three and one-half grams of diphenylmercury was dissolved in ether and refluxed for eight days with 0.01 mole of anhydrous cobaltous bromide. No reaction occurred.

Attempts were made to prepare the methyl derivatives of iron, cobalt, nickel, and platinum according to the procedure of Hilpert and Ditmar (81) for the preparation of dimethylmercury. Twenty grams of ferrous chloride were dissolved in 130 grams of ten percent hydrochloric acid. This solution was heated to 90° in a water bath and 15 grams of aluminum carbide were slowly added with shaking. The ferrous chloride was unchanged. Similar experiments were carried out using ferric chloride, cobaltous bromide, nickelous chloride, and platinic chloride. Ferric chloride was reduced to ferrous chloride and the platinic chloride was reduced to platinum. No reaction occurred with cobaltous bromide and nickelous chloride.

Ethynylsodium was prepared by the action of acetylene on 2 grams of sodium in liquid ammonia. To this solution was added 0.1 mole of ferrous iodide in 100 ml. of ether. The ferrous iodide formed an insoluble complex with the ammonia before actually hitting the liquid. The mixture was stirred for twelve hours in liquid ammonia with no reaction. The liquid ammonia was then replaced with ether. This was allowed to stand for three weeks prior to hydrolysis. No apparent reaction occurred and no organoiron compound was obtained on hydrolysis.

(81) Hilpert and Ditmar, Ber., 46, 3738(1913).

DISCUSSION

The metals of group VIII show no tendency for direct union with organic halides to form organometallic compounds (37)(p. 40). It is possible that organometallic compounds are formed as intermediates in the reaction of iron with organic halides to form coupling products (36), but that the conditions necessary to bring about this reaction are too strenuous to permit the existence of organoiron compounds for a measurable period of time. In an effort to bring about a reaction of iron with an organi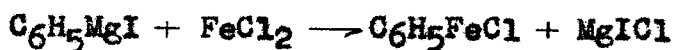c halide under milder conditions, in which an organoiron compound might be stable, a mercury-iron amalgam was prepared and added to ethyl iodide. This method proved ineffective as no reaction occurred. As the finely divided, pyrophoric iron, produced by the action of Grignard reagents on iron halides, shows a high degree of reactivity toward oxygen, with which it reacts to burn spontaneously, and toward water, with which it reacts rapidly to displace hydrogen and form ferrous hydroxide (48e)(54), it was hoped that this active form of iron might react with organic halides in the same manner as magnesium and thus produce organoiron compounds. This active form of iron was produced by the action of n-butylmagnesium bromide on ferrous chloride. To the ether suspensions of finely divided iron, prepared in this manner, was added iodobenzene and bromobenzene, respectively. Vigorous reactions occurred and benzene was ob-

tained on hydrolysis in every case. However, no evidence of an
organoiron compound was obtained and as active iron produced
from the action of phenylmagnesium bromide on ferrous chloride
gave no reaction with iodobenzene, it is probable that a hydride
of iron was formed, in the reaction of n-butylmagnesium bromide
with ferrous chloride, which reduced the iodobenzene and bromo-
benzene to benzene. A hydride of iron has been shown to be
formed in the reaction of diethylzinc with ferrous iodide (55).
The possibility that the reduction might be due to hydrogen,
formed from the action of iron on water during hydrolysis, is
ruled out as no reduction to benzene occurred when pyrophoric
iron, produced by the action of phenylmagnesium bromide on fer-
rous chloride, was hydrolysed in the presence of iodobenzene.
The reduction of iodobenzene to benzene probably takes place
according to the equation:

$$2 \; C_6H_5I + FeH_2 \longrightarrow 2 \; C_6H_6 + FeI_2.$$
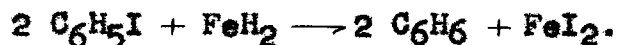
There is no definite evidence that organometallic com-
pounds are formed, even as intermediates, in the reaction of
Grignard reagents or organolithium compounds with the halides
of iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium,
or iridium. In the reaction of phenylmagnesium iodide with fer-
rous chloride, for example, the products of the reaction are bi-
phenyl and iron. These products may be due to the intermediate
formation of an organoiron compound (48a)(48e)(50).

$$C_6H_5MgI + FeCl_2 \longrightarrow C_6H_5FeCl + MgICl$$
$$2 \; C_6H_5FeCl \longrightarrow C_6H_5-C_6H_5 + Fe + FeCl_2$$

-83-

While there is no direct evidence that organoiron compounds are formed as intermediates in the reaction of Grignard reagents with iron halides, there is indirect evidence, by analogy with other coupling reactions, that the reaction occurs in this manner. Undoubtedly, organocopper and organosilver compounds are formed as intermediates in the reaction of Grignard reagents with copper and silver halides, respectively, as is indicated by experiments purposefully carried out to establish this point (82). Under ordinary conditions copper and silver halides are excellent coupling reagents for the production of R-R compounds from RMgX compounds (48c)(48d)(83)(84). However, some organosilver and organocopper compounds have been prepared from the action of Grignard reagents on silver and copper halides, respectively (84). Organogold compounds have also been prepared from the Grignard reagent and gold chloride (85). The most characteristic reaction of the copper, silver, and gold compounds is their prompt and complete decomposition to R-R compound and metal.

$$2\ C_6H_5M \longrightarrow C_6H_5\text{-}C_6H_5 + 2\ M$$

(82) (a) Gilman and Kirby, Rec. trav. chim., 48, 155(1929);
     (b) Danehy and Nieuwland, J. Am. Chem. Soc., 58, 1609(1936).
(83) (a) Krizewsky and Turner, J. Chem. Soc., 115, 559(1919);
     (b) Turner, J. Proc. Roy. Soc. N. S. Wales, 54, 37(1920)
     [C. A., 15, 669(1921)]; (c) Sakellarios and Kyrimis, Ber.,
     57, 322(1924).
(84) (a) Reich, Compt. rend., 177, 322(1922); (b) Krause and
     Wendt, Ber., 56, 2064(1923); (c) Gilman and Straley, Rec.
     trav. chim., 55, 821(1936).
(85) Kharasch and Isbell, J. Am. Chem. Soc., 52, 2919(1930).

The first instance of that particular type of reaction between
a Grignard reagent and a metal salt which involves the reduction
of the salt and the coupling of the organic radicals was ob-
served by Bennett and Turner (86) who treated phenylmagnesium
bromide with chromic chloride in an attempt to prepare organo-
chromium compounds. They obtained biphenyl and chromous chlo-
ride in almost theoretical yields.

$$2\ CrCl_3 + 2\ C_6H_5MgBr \longrightarrow C_6H_5-C_6H_5 + 2\ CrCl_2 + 2\ MgBrCl$$

Later, Hein and co-workers (87) succeeded in preparing a series
of organochromium compounds, including the phenyl compounds,
from Grignard reagents and chromic chloride. Strong cooling of
the reactions was necessary in order to avoid coupling products.
These compounds were unstable and decomposed spontaneously with
the formation of coupling products. Thus it has been shown in
several cases that the reaction of Grignard reagents with some
metal salts which ordinarily give coupling products may be em-
ployed in the preparation of the organic derivatives of these
metals and that the organic derivatives, so formed, decompose
readily with the formation of coupling products. This makes
the possible formation of organoiron compounds, as intermediates
in the reaction of Grignard reagents with iron salts, seem
reasonable. This same reasoning may be applied to the reaction
of Grignard reagents with the halides of all of the group VIII
metals which have definitely shown strong coupling tendencies.
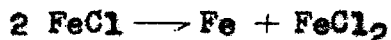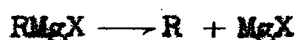
(86) Bennett and Turner, J. Chem. Soc., 105, 1057(1914).
(87) Hein and co-workers, Ber., 54, 1916, 1936, 2710, 2727(1921);
     Ber., 57, 8, 899(1924); Ber., 59, 362, 751(1926); Ber., 61,
     2255(1928); Ber., 62, 1151(1929).

A possible mechanism for the reaction of iron halides, etc., with Grignard reagents, which does not involve the assumption of organometallics as intermediates, is that a stepwise reduction of the halide occurs due to disproportionation of RMgX into R and MgX. The MgX, which is an excellent reducing agent (88), might then reduce ferric chloride, for example, to ferrous chloride. Two R groups might then unite to R-R. The first step of the reaction would be represented as follows:

$$RMgX \longrightarrow R + MgX$$

$$2 R \longrightarrow R-R$$

$$FeCl_3 + MgX \longrightarrow FeCl_2 + MgXCl$$
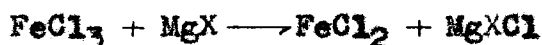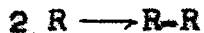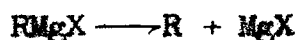
The first step of the reaction of ferric chloride with Grignard reagents has been shown to be a reduction to ferrous chloride with formation of R-R compound (48e). The second step of the reaction, according to the above theory, would consist of a reduction of ferrous chloride to a mono-chloride of iron, FeCl, which might then disproportionate to ferrous chloride and iron.

$$RMgX \longrightarrow R + MgX$$

$$2 R \longrightarrow R-R$$

$$FeCl_2 + MgX \longrightarrow FeCl + MgXCl$$

$$2 FeCl \longrightarrow Fe + FeCl_2$$

The ferrous chloride formed by disproportionation could then react in the same manner thus producing a chain of reactions

(88) Gomberg and co-workers, J. Am. Chem. Soc., 49, 236(1927); ibid., 52, 2455, 4967(1930); ibid., 51, 2229(1929); Rec. trav. chim., 48, 847(1929).

which would yield the same final products as obtained by a possible decomposition of an intermediate organoiron compound. The results reported by Weichfelder and Thiede (51), who obtained only benzene and a hydride of iron, FeH_2, from the reaction of phenylmagnesium bromide and ferrous chloride in an atmosphere of hydrogen, might be considered as evidence for this mechanism. The phenyl radical, which would be formed if this mechanism is correct, might be readily reduced by hydrogen to form benzene rather than coupling to biphenyl which was obtained in an atmosphere of nitrogen. While the possibility exists that an intermediate phenyliron compound might be cleaved by hydrogen to form benzene, this possibility is remote as no organometallic compound, with the possible exception of the highly reactive organoalkali compounds, has been found which cleaves with such extreme ease in an atmosphere of hydrogen. On the other hand, benzene might be formed readily during the disproportionation of an intermediate phenyliron compound if this substance disproportionated to give phenyl radicals as intermediates in the formation of biphenyl. The results obtained by these authors in the reaction of ferric chloride with phenylmagnesium bromide in an atmosphere of hydrogen indicate that the mechanism of the reduction of ferric chloride to ferrous chloride may differ from the mechanism of reduction of ferrous chloride to metallic iron as they obtained both biphenyl and benzene in this reaction.

In the reaction of α-naphthylmagnesium bromide and α-naphthyllithium with ferrous chloride and ferrous iodide, the yields of coupling products are low (89). This suggests the possibility of the existence in solution of a stable organoiron compound. However, naphthalene is obtained on addition of water while benzoyl bromide, which reacts with such unreactive organometallic compounds as di-p-tolylmercury (90) (which is unaffected by water under the same conditions) to give ketones, gave no ketone when added to the reaction mixtures obtained from α-naphthylmagnesium bromide or α-naphthyllithium with ferrous halides. Also, Mr. J. C. Baillie obtained only a trace of α-naphthyllead compound on reaction of α-naphthylmagnesium bromide with lead chloride although a negative color test was obtained promptly in the reaction. Therefore, it is probable that the low yields of coupling product are not due to an organoiron compound, which is stable in solution, but to some intermediate complex between the Grignard reagent and the iron halide. However, it is known that the stability of such relatively unstable organometallic compounds as those of copper, silver, and gold (91) increases

(89) These results have been verified in unpublished work by Mr. F. J. Prochaska in this laboratory.
(90) Gilman, "Organic Chemistry", John Wiley and Sons, New York (1938), Vol. I, p. 418.
(91) See Kharasch and Isbell, J. Am. Chem. Soc., 52, 2919(1930) and Gilman and Straley, Rec. trav. chim., 55, 821(1936). See also, Krause and v. Grosse, "Die Chemie der Metallorganischen Verbindungen", Gebruder Borntraeger, Berlin (1937), p. 745 for a discussion on the relation between the nature of the radical and the ability to form stable organometallic compounds.

greatly as the electronegativity of the radical attached to the metal is increased, and as a low yield of coupling product was also obtained in the reaction of 2,4,6-trimethylphenylmagnesium bromide with cobaltous bromide, the highly electronegative radicals seem to offer the best promise for the preparation of organometallic derivatives of iron, cobalt, nickel, ruthenium, rhodium, and palladium. With the other three members of the group VIII elements, osmium, iridium, and platinum, the tendency to produce coupling products, in the reaction of their halides with phenylmagnesium iodide, is much less with the tendency to produce coupling decreasing in the order: osmium, iridium, platinum. If this tendency to produce coupling may be used as a criterion for the ability to form organometallic derivatives, then organoosmium compounds will be prepared with most difficulty, organoiridium compounds will be prepared more readily, while organoplatinum compounds may be readily prepared if proper precautions are observed. On the basis that the ability to form organometallic derivatives increases as one goes from left to right in the triads of the group VIII elements, organometallic compounds of nickel should be prepared more readily than organorhodium or organoruthenium compounds.

In the reaction of ferric fluoride with phenylmagnesium bromide, benzene was produced on hydrolysis. No evidence of an intermediate organoiron compound was obtained. The formation of benzene might be attributed to the possibility that the ferric fluoride was not anhydrous. If this were the case, then

methylmagnesium bromide which showed no reaction with ferric
fluoride in six months should have reacted with ferric fluoride.
The reaction is not understood by the author at present.

The reactions of phenylzinc chloride and ethylzinc
iodide with ferrous iodide have been reported to produce phenyl-
iron iodide and ethyliron iodide, respectively (48e)(57). The
evidence offered for the existence of a phenyliron compound was
the formation, on hydrolysis, of benzene and ferrous hydroxide,
which according to the author contained only a negligible amount
of zinc hydroxide. The evidence offered for the existence of
the ethyliron compound was the formation of ferrous hydroxide
on hydrolysis accompanied by evolution of ethane. It was also
stated that no gas was evolved during the reaction of ethylzinc
iodide with ferrous iodide. The solution of ethyliron iodide
deposited iron on standing and evolved gases which consisted
of a mixture of ethane and ethylene (58). The reactions of
phenylzinc chloride and ethylzinc iodide with ferrous iodide
were investigated in this thesis work. The evidence obtained
indicated that the reaction of phenylzinc chloride with ferrous
iodide proceeded to the formation of biphenyl and metallic iron.
The hydroxides obtained on hydrolysis at the end of the reaction
period given by Champetier (48e), for the completion of reaction
between phenylzinc chloride and ferrous iodide, were found to
contain large amounts of zinc hydroxide rather than the inappre-
ciable quantities indicated by Champetier (48e). Checks of the
ratio of zinc hydroxide to ferrous hydroxide and of benzene to

biphenyl, obtained on hydrolysis of aliquots at various inter-
vals, showed that the amount of biphenyl increased regularly as
the amount of ferrous hydroxide increased. Furthermore no dif-
ference in reactivity was found between phenylzinc chloride and
the supposed phenyliron iodide. Both solutions reacted with
benzoyl chloride to give benzophenone, and neither gave a re-
action with allyl bromide. The reaction of ethylzinc iodide
with ferrous iodide was found to proceed in a similar manner.
The evolution of gas during the reaction was slow, but contin-
uous. Measurements of the volume of gas collected from the
reaction together with the ratio of zinc hydroxide to ferrous
hydroxide, obtained on hydrolysis, indicated the reaction to be
proceeding slowly, but without the formation of an organoiron
compound. The results obtained in this study have convinced the
author that no organoiron compound is obtained in either reaction,
but that the reactions proceed in the same manner as do the re-
actions of the corresponding Grignard reagents with ferrous
iodide, with the exception that the reactions are much slower.

Gilman and Kirby (69) have reported the reaction of
nickelous cyanide, $Ni(CN)_2$, with phenylmagnesium bromide to pro-
ceed with sufficient heat of reaction to maintain a gentle re-
fluxing of the ether used as a solvent. They obtained only a
trace of biphenyl on hydrolysis. This result gave promise of
the reaction as a satisfactory method for the preparation of a
phenylnickel compound. No mention was made in their report as
to whether the nickelous cyanide employed by them was anhydrous.

In this thesis work, anhydrous nickelous cyanide was prepared by dehydration of the hydrated salt. Addition of this anhydrous salt to phenylmagnesium bromide gave no reaction of sufficient vigor to cause any warming of the ether. The color test remained positive after three weeks stirring and hydrolysis at this point gave a twenty-seven percent yield of biphenyl. It is probable that the commercial nickelous cyanide employed by Gilman and Kirby (69) was not anhydrous and that the reaction of anhydrous nickelous cyanide with phenylmagnesium bromide is unusually slow, but proceeds ultimately to biphenyl and metallic nickel.

As the reaction of the Grignard reagent and organolithium compounds on iron, cobalt, or nickel halides gave little promise of yielding organometallic compounds, other methods were investigated in attempts to prepare these substances.

Organoaluminum compounds have been prepared by cleavage of organolead compounds with anhydrous aluminum chloride (92). This reaction suggested the possibility that organoiron compounds might be prepared in the same manner, that is, by cleavage of organolead compounds with iron halides. The addition of anhydrous ferric chloride to tetraethyllead effected a prompt and complete reduction of the ferric chloride to ferrous chloride. This reaction furnishes a convenient method for the preparation of pure anhydrous ferrous chloride. Tetraethyllead was found to

(92) Unpublished studies in this laboratory by Mr. L. D. Apperson.

be without action on ferrous iodide, ferrous chloride, cobaltous bromide, and nickelous bromide. Chloroplatinic acid was reduced immediately by tetraethyllead to deposit metallic platinum.

Grignard reagents may be obtained by the action of the binary system, $MgX_2 + Mg$, on some trivalent organolead compounds (93). This suggested the possibility that organoiron compounds might be formed in a similar manner from trivalent organolead compounds and a mixture of iron and ferrous iodide in ether. The reaction was attempted and an immediate reaction occurred which was quite complex. Although the color of ferrous iodide disappeared and lead chloride and tetra-p-anisyllead were precipitated, the iron, in some unknown form, remained in ether solution. No evidence as to the nature of the iron compound was obtained. Addition of benzoyl bromide to the solution gave no ketone, while addition of water precipitated ferric hydroxide. Di-p-anisyllead diiodide was obtained from the hydrolysis products along with a mixture of other unidentified organolead compounds. A search was made for anisole, which should have been formed on hydrolysis if a p-anisyliron compound was hydrolysed, in the hydrolysis products, but none was found. The same results were obtained when tri-p-anisyllead and ferrous iodide were brought together in ether solution without metallic iron being present. The reaction was not due, therefore, to a binary system of $Fe + FeI_2$. The reaction is analogous to the reaction

(93) Unpublished studies in this laboratory by Mr. J. C. Baillie.

obtained by Mr. J. C. Baillie (93), who obtained similar results
from the reaction of trivalent organolead compounds with mag-
nesium iodide in the absence of metallic magnesium. He obtained
no Grignard reagent from this reaction, therefore it is probable
that no organoiron compound was formed in the reaction of fer-
rous iodide with tri-p-anisyllead. The mechanism of the reaction
is not understood.

Di-p-tolylmercury could not be induced to react with
anhydrous nickelous bromide by refluxing the two together for
six hours in benzene, followed by eighteen hours refluxing in
quinoline. The quinoline was used in an effort to increase the
solubility of the nickelous bromide. Diphenylmercury gave no
reaction with anhydrous cobaltous bromide on refluxing the ether,
used as a solvent, for eight days. The organomercury compounds
are evidently of too low an order of reactivity to react with
these halides.

Attempts to prepare methyl derivatives of iron, cobalt,
nickel, and platinum through the action of aluminum carbide and
hydrochloric acid on the halides of these metals were unsuccessful.
No reaction was obtained excepting in the cases of ferric chlo-
ride and platinic chloride. The ferric chloride was reduced to
ferrous chloride and the platinic chloride was reduced to metal-
lic platinum. This reaction had been employed by Hilpert and
Ditmar (81) for the preparation of methylmercury, methylbismuth,
and methyltin compounds.

Organometallic compounds in which the carbon attached to metal is connected by a triple bond to the adjacent carbon have been shown in some cases to be the most stable class of organometallic derivatives (50)(87). n-Butylethynylmagnesium bromide gives no organometallic derivative of iron when reacted with ferric chloride (50). In the hope that an ethynyliron compound might be more stable than an n-butylethynyliron compound, the reaction of ethynylsodium with ferrous iodide was attempted in liquid ammonia. Liquid ammonia was used as a solvent media as it is an excellent solvent for ethynylsodium, which is insoluble in ether, and has the additional advantage of maintaining a low temperature. However, when the reaction was attempted, the ferrous iodide formed a complex with ammonia which was so insoluble that no reaction took place.

Organoplatinum compounds are readily prepared by the action of Grignard reagents on anhydrous platinum halides. Certain of the methylplatinum compounds are crystalline and may be readily purified and identified. Aside from those methylplatinum compounds which are crystalline there is no crystalline organoplatinum compound described in the literature and none, other than methyl derivatives, was isolated in this thesis work. None of the organoplatinum compounds so far isolated have melting points.

Anhydrous platinic chloride reacted readily with phenylmagnesium iodide with the formation of a complex compound. The first precipitate to appear in the reaction mixture had a golden

color. On addition of sufficient Grignard reagent to give an excess (ten equivalents of phenylmagnesium iodide were added in the reaction before a solution was obtained which persisted in giving a color test), the golden precipitate was no longer in evidence and a heavy white precipitate was present in the reaction flask. This precipitate contained magnesium in the ratio of two and five-tenths atoms to one of platinum. This amount of magnesium fails to account for the Grignard reagent introduced into the reaction. However, the ether layer contained platinum in some soluble compound which may have had a larger proportion of magnesium. The magnesium in the insoluble precipitate could not be removed by repeated extraction with ether. This precipitate evidently contained Grignard reagent in the form of a complex with the platinic chloride, or a reaction product of the platinic chloride with the Grignard reagent, as it was sensitive to air and moisture. The Grignard reagent was not present in a normal reactive condition as this precipitate did not give a color test. Hydrolysis of the complex produced magnesium-free organic material containing platinum. This material was amorphous and evidently consisted of a mixture of compounds as some solvents would only partially dissolve the material and analyses for platinum varied with differing fractions of the material. This material contained iodine and was undoubtedly a mixture of phenylplatinum compounds as treatment of the material with boiling nitric acid gave 4,4'-dinitrobiphenyl thus proving the presence of phenyl groups in the material. The possibility

exists that some biphenyl was present in the material and was nitrated to form 4,4'-dinitrobiphenyl. This possibility is remote as the material had been extracted several times with benzene in which biphenyl is very soluble. The 4,4'-dinitrobiphenyl may have been formed by cleavage of the phenylplatinum bond with the formation of biphenyl which was subsequently nitrated, or the phenyl groups may have been nitrated prior to cleavage.

It is not surprising that a mixture of compounds would result from the action of phenylmagnesium iodide on platinic chloride as the action of methylmagnesium iodide on platinic chloride produces a mixture of compounds. The amorphous nature of the phenylplatinum compounds together with their lack of melting points made it impossible to separate the components of the mixture into definite individual compounds.

The reaction of methylmagnesium iodide with platinic chloride is very complex and has not been worked out in a satisfactory manner. Pope and Peachey (1) reported trimethylplatinum iodide from the reaction, but they gave no yields of this product and reported no other products. In this thesis work, an attempt was made to isolate all of the products of the reaction. As trimethylplatinum iodide was the product desired in this work as a starting material for the preparation of other compounds, the optimum conditions for the preparation of this compound were also studied. Under the best conditions found the yield of trimethylplatinum iodide was forty percent. A very small amount of tetra-

methylplatinum was also isolated from the reaction. This compound was identified by crystal form, solubility, and analysis for platinum. A small amount of a black, crystalline solid which was apparently a pure compound was isolated. Analyses of this compound indicated the compound as being methylplatinum pentaiodide. The presence of a methyl group was not proved, but a methyl group would exactly account for the portion of the compound which was not platinum and iodine. Furthermore, the ratio of iodine to platinum in the compound was five atoms to one. No inorganic platinum iodide has such a composition. Also on warming a solution of the methylplatinum pentaiodide on a steam plate, a black, amorphous, insoluble material was precipitated which contained one less mole of iodine. Analyses of this material for platinum and iodine corresponded to the calculated values for methylplatinum triiodide. Various fractions of difficultly soluble platinum-containing materials were isolated from the reaction. Analyses of these fractions for platinum and iodine corresponded to the calculated values for methylplatinum triiodide and dimethylplatinum diiodide, respectively. However, as these materials were not crystalline and had no melting points, it was impossible to identify them as definite chemical compounds. Much of the material isolated from this reaction underwent changes in solubility during the isolation process. The mechanism of these solubility changes remains undetermined, but may be due to breaking down of a double compound. The only absolute evidence obtained as to the nature of the difficultly

soluble materials was that they contained platinum and iodine and would burn in a current of oxygen. No chlorine was found in any of the platinum-containing products of the reaction with the possible exception of an easily soluble complex which contained large amounts of magnesium. This material was not analysed.

Methylmagnesium iodide reacted with platinous chloride with the formation, on hydrolysis, of an amorphous, difficultly soluble material which analysis indicated as being dimethylplatinum diiodide. This material was the same in appearance and solubility as the material obtained from the reaction of methylmagnesium iodide with platinic chloride which analysed for dimethylplatinum diiodide. It is surprising to obtain what is apparently a tetravalent platinum compound by the action of a Grignard reagent, which is normally a strong reducing agent, on a divalent platinum halide without disproportionation and deposition of metal. The reaction may not have been due to an oxidation of the platinous chloride by the Grignard reagent but may have been due to preliminary formation of methylplatinum iodide, followed by addition of methyl iodide which was present in the solution.

The reaction of α-naphthylmagnesium bromide with platinous chloride proceeded to the formation of di-α-naphthylplatinum. The formation of a divalent platinum compound in this case, instead of a tetravalent compound as was formed from methylmagnesium iodide, may probably be attributed to the steric

hindrance of the much larger α-naphthyl groups. Di-α-naphthyl-platinum was not obtained in a pure condition due to its lack of crystalline structure. This compound decomposed on heating with a very distinct odor of naphthalene. An attempt to prepare α-benzoylnaphthalene by refluxing a m-xylene solution of di-α-naphthylplatinum with benzoyl bromide gave a very unexpected result. The platinum compound acted as a condensing agent with the formation of 2,4-dimethylbenzophenone in a good yield. This reaction was repeated with anhydrous platinic chloride, rather than di-α-naphthylplatinum, as the condensing agent. An equally good yield of 2,4-dimethylbenzophenone was obtained. Thus it is apparent that some platinum compounds may be employed as catalysts for the preparation of 2,4-dimethyl-benzophenone from benzoyl bromide and m-xylene. Platinum compounds may be found to be effective condensing agents for the preparation of other ketones.

In a preliminary attempt to prepare hexamethyldiplati-num, trimethylplatinum iodide was added to liquid ammonia. Liquid ammonia failed to dissolve this compound. Addition of sodium to the liquid ammonia caused the trimethylplatinum iodide to dissolve and removed the color of sodium from the liquid ammonia. Evaporation of the liquid ammonia left a water soluble compound which regenerated trimethylplatinum iodide on addition of hydrochloric acid. The nature of the water soluble compound was not investigated. Hexamethyldiplatinum was prepared by boiling a benzene solution of trimethylplatinum iodide with potassium.

$$2 \ (CH_3)_3PtI \ + 2 \ K \longrightarrow (CH_3)_3Pt\text{-}Pt(CH_3)_3 \ + 2 \ KI$$
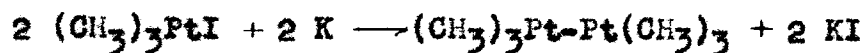
This compound is apparently completely undissociated at the freezing point of benzene as molecular weight determinations gave values slightly higher than the calculated value for hexamethyldiplatinum. The compound is of a somewhat unsaturated nature, however, as it absorbed iodine readily with the formation of trimethylplatinum iodide.

$$(CH_3)_3Pt\text{-}Pt(CH_3)_3 \ + \ I_2 \longrightarrow 2 \ (CH_3)_3PtI$$
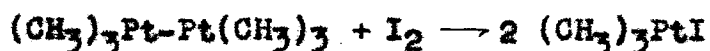
The iodine in trimethylplatinum iodide may be replaced by a methyl group, forming tetramethylplatinum, through the action of methylsodium.

$$(CH_3)_3PtI \ + \ CH_3Na \longrightarrow (CH_3)_4Pt \ + \ NaI$$
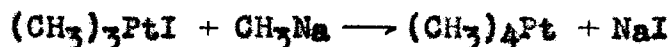
Methyllithium was found to be ineffective for this transformation. This may be due to the unusually strong platinum to iodine bond in trimethylplatinum iodide or it may be due to the formation of an insoluble complex between trimethylplatinum iodide and methyllithium. A white precipitate was formed immediately on adding trimethylplatinum iodide to a solution of methyllithium. The insolubility of the complex together with the added steric hindrance effects may account for the difficulty of replacement of the iodine by a methyl group in the reaction of trimethylplatinum iodide with methyllithium. Some tetramethylplatinum was probably formed in this reaction as a very small amount was isolated from the reaction of methylmagnesium iodide with platinic chloride, but the properties of tetramethylplatinum were unknown at the time the reaction was

carried out and no tetramethylplatinum was isolated.

The organoplatinum compounds are apparently the least reactive of all known organometallic compounds with the possible exception of the organotin compounds. Tetramethylplatinum was found to be unaffected by iodine in boiling chloroform in a period of twenty-four hours, while tetramethyltin was cleaved to trimethyltin iodide by iodine under the same conditions in four hours. Thus tetramethylplatinum is less reactive toward iodine than is tetramethyltin. However, tetramethylplatinum was quantitatively cleaved by hydrogen chloride in boiling petroleum ether (b.p., 60-8°) to trimethylplatinum chloride in fifteen to twenty minutes. Tetramethyltin under the same conditions showed but a trace of cleavage to trimethyltin chloride. Due to the extreme difficulty of recovering a small amount of unchanged tetramethyltin from a large amount of petroleum ether (b.p., 60-8°), unchanged tetramethyltin was not recovered and the possibility exists that the highly volatile tetramethyltin may have been lost during the attempted reaction. Further work is being carried out on this reaction. On the basis of present evidence, it may be concluded that tetramethylplatinum is more reactive toward hydrogen chloride than is tetramethyltin. Neither tetramethyltin nor tetramethylplatinum have been found to react with acid chlorides to form ketones. Thus the relative reactivities of tetramethyltin and tetramethylplatinum are as yet only partially determined.

As the methyl compounds of platinum are the only crys-

talline organoplatinum compounds so far reported, and as the reaction of phenylmagnesium iodide with osmium trichloride and iridium trichloride, respectively, gave promise that organometallic derivatives of these metals might be prepared, attempts were made to prepare the methyl derivatives of these metals in the hope of obtaining crystalline compounds. The reaction of methylmagnesium iodide with osmium chloride gave no crystalline product. A slight amount of black, tarry, osmium-containing material was obtained. The prediction appears to be warranted, however, that organoosmium compounds will be prepared and identified when larger amounts of osmium are available. A slight change in technique in carrying out the reaction of Grignard reagents with osmium halides may be necessary. The reaction of phenylmagnesium iodide with iridium trichloride proceeded so slowly, probably due to the extreme insolubility of iridium trichloride, that the more highly reactive methyllithium was used in an attempt to prepare a methyliridium compound from iridium trichloride. The reaction was stirred for five days prior to hydrolysis. The larger portion of the iridium trichloride was recovered unchanged. No methyliridium compound was found in the reaction products. It is the opinion of the author that if a more soluble anhydrous iridium halide could be prepared and reacted with methylmagnesium iodide under the same conditions employed in preparing trimethylplatinum iodide, that a satisfactory yield of a methyliridium compound would result.

SUMMARY

The literature has been surveyed in regard to organo-
metallic compounds of the group VIII elements.

The preparation of organometallic derivatives of iron,
cobalt, and nickel was attempted by several methods. No evi-
dence for the formation of these compounds was obtained.

The reaction of phenylmagnesium iodide with ferrous
chloride, cobaltous bromide, nickelous bromide, ruthenium tri-
chloride, and palladium chloride proceeds to the formation of
the corresponding metal and biphenyl in quantitative yields.
The yields of biphenyl in the reaction of phenylmagnesium
iodide with osmium trichloride, iridium trichloride, and pla-
tinic chloride are less than quantitative with the yields de-
creasing in the order: $Os > Ir > Pt$. Platinic chloride reacts
with phenylmagnesium iodide with the formation of a mixture of
amorphous phenylplatinum compounds.

Dimethylplatinum diiodide is obtained from the reaction
of methylmagnesium iodide and platinous chloride. Di-α-naph-
thylplatinum is obtained from the reaction of α-naphthylmagnesium
bromide and platinous chloride.

The reaction of methylmagnesium iodide with platinic
chloride is complex. Trimethylplatinum iodide may be obtained
from this reaction in forty percent yields, along with a slight

amount of tetramethylplatinum, methylplatinum pentaiodide, and some amorphous platinum compounds whose analyses correspond to the calculated values for methylplatinum triiodide and dimethylplatinum diiodide, respectively.

Hexamethyldiplatinum is obtained by the action of metallic potassium on trimethylplatinum iodide. Tetramethylplatinum is obtained by the action of methylsodium on trimethylplatinum iodide.

No crystalline product was obtained from the action of methylmagnesium iodide on osmium chloride.

Iridium trichloride gave no reaction in five days with methyllithium. The lack of reaction was probably due to the extreme insolubility of iridium trichloride.

The prediction is made that organometallic compounds of osmium and iridium will be prepared.