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Review

REACTIONS OF COORDINATED PNICTOGEN DONOR LIGANDS

Charles S. Kraihanzel
Department of Chemistry
Lehigh University
Bethlehem, Pennsylvania 18015

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CONTENTS

A. Introduction

Numerous metal complexes of phosphorus, arsenic, antimony and bismuth donor ligands, herein called pnictogen donor ligands, are known. For example, two recent reviews[1,2] of complexes with phosphorus donor ligands summarize the results of investigations reported in over 1900 literature and patent references. Another review[3] of metal complexes with pnictogen donor ligands for the years 1965-1970 contains nearly 500 references. This interest in metal complexes of pnictogen donor ligands, especially of phosphorus donor ligands, remains undiminished. For, in addition to ongoing synthetic, structural and spectral studies (infrared, visible-ultraviolet, ESCA, NMR, mass spectrometry, Mössbauer, etc.), current investigations include the design of multidentate ligands to permit geometric control of complex structures, studies of steric effects of ligands as they affect rates of reactions and stereochemistry of complexes, attempts to develop nitrogen fixation catalysts, catalytic syntheses of organic compounds and structurally specific polymers, and the utilization in organic synthesis of both soluble and insoluble complexes of polymeric ligands whose properties mimic those of simple homogeneous catalysts. In the above-mentioned practical applications of metal complexes with pnictogen donor ligands, it is generally desirable, if not absolutely necessary, that the ligands have good thermal stability and not undergo chemical reactions under the pertinent experimental conditions. Thus, organophosphorus compounds such as triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (Diphos) are found to be among the most widely used as ligands. Yet, even aryl phosphines are chemically reactive and thermally unstable under the right conditions (see e.g. Sec. B.1.h). In contrast, pnictogen donor ligands carrying halogen, alkoxyl, alkylamino or hydrido groups can be expected to be considerably more chemically reactive than alkyl- or arylphosphines by analogy to the differences in the chemical properties of either the uncomplexed phosphorus compounds or their oxide analogs.

This general prediction has been borne out by the results of a number of investigators and the prime purpose of this review is to summarize these observations.

A general metal ligand system M-E(A)(BC)(D···Z) (where M is a metal atom, E is a pnictogen atom and A, BC and D···Z are groups required to complete the covalency of E) is defined for the purposes of illustrating the classes of reactions of coordinated ligands to be considered. These classes are: (1) substitution reactions at phosphorus resulting from cleavage of the E-A bond and subsequent replacement of A; (2) reactions which require cleavage of the metal-ligand bond M-E; (3) reactions involving a bond B-C once removed from the pnictogen site; (4) reactions at a functional site Z which is remote from the pnictogen site and whose reactions are not directly dependent upon the presence of the pnictogen. In addition to summarizing the results of reactions which are clearly reactions of coordinated ligands, a number of reactions have been included which most likely involve a coordinated pnictogen ligand in an intermediate step.

B. REACTIONS OF COORDINATED PNICTOGEN LIGANDS

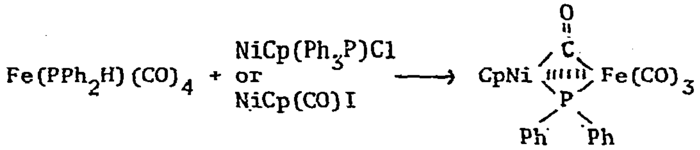
1. Reactions Involving Cleavage of the E-A Bond in an R_2EA Ligand

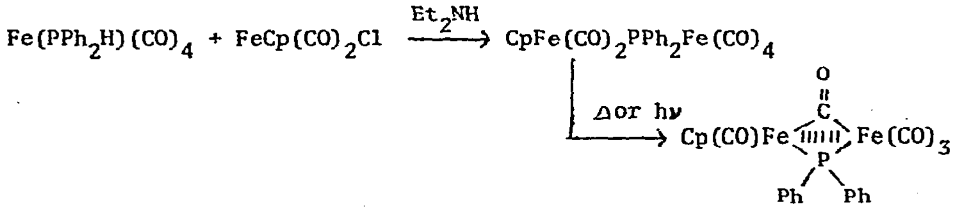
a. General Comment. The reactions of coordinated pnictogen ligands have been categorized in this section according to the A substituent. Most of the substances to be considered are synthesized by a direct reaction between R_2E-A and a precursor metal salt, metal carbonyl or organometallic compound. However, as will become apparent in the ensuing discussion, reactions of some R_2E-A with metal complexes often yield substances in which the E-A bond has been cleaved. Whether the E-A bond is cleaved prior to, coincident with or subsequent to coordination to the metal is not generally known in these cases. For the purpose of this review, the assumption is made that wherever E-A bond cleavage is noted to occur during the interaction between R_2EA and a transition metal compound, the reaction is one which involves a coordinated ligand, unless the nature of the reaction demands otherwise.

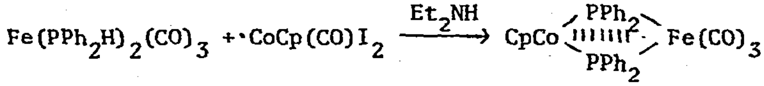
b. The E-Hydrogen Bond. Primary and secondary phosphines, and phosphine itself exhibit Lewis base character and form metal complexes with metal halides, metal carbonyls and other transition metal organometallic derivatives. A most interesting and complicating feature of many of these reactions is the ease which a hydrogen phosphorus bond (P-H) is cleaved to yield a phosphido ligand which may or may not form a bridge in a binuclear complex. The fate of the proton is determined by one or more of the following factors: the metal involved; the other groups attached to phosphorus; the reaction temperatures; the nature of the reagents; solvent.

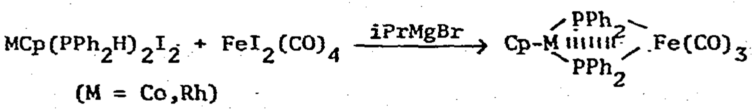
The earliest reports on the complexity of the reactions of secondary phosphines with metal halides were made by Issleib and his coworkers[4,5]. They showed that diphenylphosphine (PPh_2H) did not always yield metal complexes with an intact ligand. For example, the products obtained with anhydrous nickel(II) bromide and palladium(II) chloride were $Ni(Ph_2PH)_2(Ph_2P)_2$ and $[Pd(Ph_2PH)(Ph_2P)Cl]_2$, respectively. Hayter[6] in a more extensive study found that palladium halides and Ph_2PH react to yield a range of products $[PdX(PPh_2)(HPPh_2)]_2$, $PdX_2(HPPh_2)_2$, $[Pd(PPh_2)_2(HPPh_2)_2$ (X=Cl,Br,I) and $[PdBr(HPPh_2)_3]Br$. The elimination of HX from $PdX_2(HPPh_2)_2$ to yield $PdX(PPh_2)(HPPh_2)$ is found to be easiest for X = Cl and hardest for X = I. Hayter[7,8] confirmed an earlier report[4] that unlike Ph_2PH dialkyl- and dicycloalkylphosphines do not readily eliminate HX in reactions with palladium(II) halides. He noted that dimethylphosphine, diethylphosphine and ethylphenylphosphine produced exclusively the simple substitution products cis-$PdX_2(R_2PH)_2$. Elimination of HX from these last-named compounds was shown to require the assistance of weak bases such as p-toluidine and led to bridged complexes. However, $RuCl_2(HPEt_2)_4$ and $RuCl_2(HPPh_2)_4$ could not be made to undergo HCl elimination[8]. Whether or not other complexes such as the cis and trans isomers of $Cl_2(Ph_2PH)_2M$ (M=Ru and Os) will eliminate HX and lead to dimers has not been shown[9]. In the same report[9], Sanders observed the reaction between $Re(O)Cl_3(PPh_3)_2$ and Ph_2PH to yield cis-$ReCl_2(PPh_2)(Ph_2PH)_3$; possibly, the unbridged diphenylphosphido group arose from HCl elimination involving the coordinated PPh_2H.

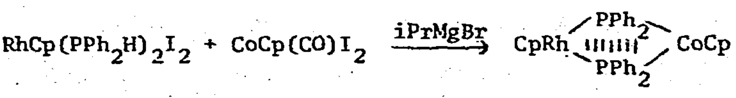
In contrast to the apparent internal HX eliminations cited above, Yasafuku and Yamazaki[10,11,12] have reported a number of examples of reactions of HX elimination between two different organometallic complexes in the presence of diethylamine or the isopropyl Grignard reagent. Their results are summarized in the following reactions:

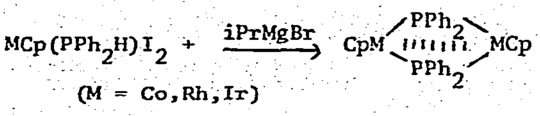








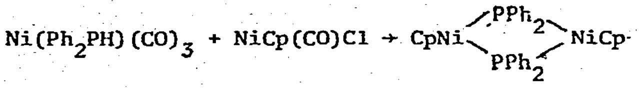




$$MCp(PPh_2H)I_2 + \xrightarrow{iPrMgBr} CpM(PPh_2)_2MCp$$

(M = Co,Rh,Ir)

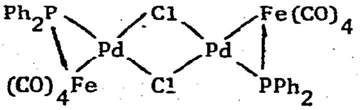
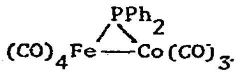
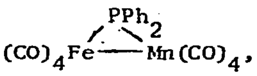
$Ni(Ph_2PH)(CO)_3 + FeCp(CO)_2Cl \rightarrow CpFe(CO)_2PPh_2Ni(CO)_3$



$$Ni(Ph_2PH)(CO)_3 + NiCp(CO)Cl \rightarrow CpNi(PPh_2)_2NiCp$$

The coupling reactions were found to proceed in the presence of diethylamine or isopropyl Grignard as indicated.

Two additional types of elimination reactions involving secondary phosphines have been noted. Benson et al.[13] reacted $Fe(PPh_2H)(CO)_4$ with $[Pd(\pi\text{-allyl})Cl]_2$, $Co(\pi\text{-allyl})(CO)_3$ and $Mn(\pi\text{-allyl})(CO)_4$ and noted elimination of propene and formation of the bridged complexes


,  and ,

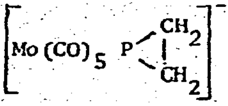
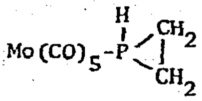
respectively. Some time ago, Hieber and Winter[14] noted that whereas $V(CO)_6$ reacts with either $PPhH_2$ or PPH_2H to generate trans-$V(CO)_4L_2$ complexes without subsequent reaction, PH_3 led to the bridged dimer $(CO)_4V(PH_2)_2V(CO)_4$, presumably by elimination of elemental hydrogen.

A most informative observation by Dobbie, Hopkinson and Whittaker[15] illustrates one of the ways whereby the PH bond of secondary phosphines is cleaved during reactions with metal complexes. These workers noted that the major product found in the reaction between $Fe(CO)_5$ and $P(CF_3)_2H$ between 50° and 100° is $H_2Fe(CO)_6[P(CF_3)_2]_2$ for which both cis and trans isomers were found. They suggested the possibility of the involvement in the reaction mechanism of an oxidative-addition step. The oxidation-addition could occur either in the initial step of the reaction to give a hydrido-phosphido complex $(CO)_4Fe(H)P(CF_3)_2$ or a simple substitution product $(CO)_4FePH(CF_3)_2$ could be formed which subsequently rearranged under the reaction conditions to the hydrido-phosphido complex. In either case, the resulting phosphido complex with the lone pair of electrons on phosphorus can form the isomeric bridged dimers $H(CO)_3Fe(P(CF_3)_2)_2Fe(CO)_3H$. Their observation that $Fe_2(CO)_9$ reacts with $P(CF_3)_2H$ to form $Fe(CO)_4(PH(CF_3)_2)$ which upon heating yields predominantly the bridged dimer supports the second proposed mechanism.

Very recently, Schunn[16] has shown that $[Ir(Ph_2PCH_2CH_2PPh_2)_2]X$, where X is Cl^- or BPh_4^-, adds PH_3 at -78° in dichloromethane. Upon warming to room temperature in a closed system, an oxidative-addition reaction occurs with formation of the hydrido-phosphido complex [<u>cis</u>-$IrH(PH_2)$-$(Ph_2PCH_2CH_2PPh_2)_2]X$. Reductive-elimination of PH_3 from the BPh_4^- salt was found to occur readily at 180° in vacuum or upon heating in refluxing acetonitrile. He also noted that oxidative-addition of PH_3 to $Ir(CO)$-$(Me_2PCH_2CH_2PMe_2)_2$, with elimination of CO, and to $RhCl(PPh_3)_3$, with elimination of PPh_3, occurred readily.

In another study of the reactions of $P(CF_3)_2H$, nickelocene was found to yield two products, $P(CF_3)_2(C_5H_7)$ and $[CpNiP(CF_3)_2]_2$[17]. Formation of the dinickel bridged complex is not unprecedented based upon the previously discussed results. One might expect cyclopentadiene to be obtained by analogy to the elimination to propene observed in the reactions of π-allyl complexes. However, the formation of $P(CF_3)_2(C_5H_7)$ is surprising and could be accounted for by way of a "hydrophosphination" reaction analogous to the well-known metal-catalyzed hydrometallation by the group IV hydrides.

Several investigators have reported the ease with which strong bases remove a proton from a coordinated primary or secondary phosphine ligand as well as from coordinated phosphine. For example, n-BuLi was shown to remove the proton from $M(CO)_5P(C_6F_5)_2H$ (where M = Cr or Mo)[18],

Ph_2^- was found to abstract a hydrogen from $(CO)_5MoPH_3$[19], while both methyllithium and n-butyllithium have been employed with $[FeCp(CO)_2PPhH_2]^+PF_6^-$ [20]. Sodium methoxide in acetone was sufficient to effect removal of the proton from phosphorus in $[FeCp(CO)_2PPh_2H]^+PF_6^-$ [20]. Also, KPH_2 has been used to form  from  [21]. Some reactions of the coordinated phosphido groups which result from proton abstraction will be considered in Section B.1.g.

Finally, Guggenberger, Klabunde and Schunn[22] have reported a most interesting technique which can be employed to effect deuterium-hydrogen exchange for the coordinated PH_3 ligand. These authors prepared $Cr(CO)_5PH_3$, <u>cis</u>-$M(CO)_4(PH_3)_2$ and <u>fac</u>-$M(CO)_3(PH_3)_3$ (where M = Cr, Mo, W) by classical means. The deuterium-hydrogen exchange was carried out by passing benzene solutions of the complexes through an acid-washed aluminum column deactivated with deuterium oxide. The same authors also noted that the PH_3 complexes show line-broadening in their ^{1}H-NMR spectra owing to proton exchange in methanol in the presence of ethylamine. The rate of exchange was said to decrease the more highly substituted the chromium complex. For the <u>cis</u>-$M(CO)_4(PH_3)_2$ complexes the rate of exchange followed the order Cr>Mo>W.

c. The E-halogen Bond

The first well documented reactions of a coordinated pnictogen donor ligand were reported in 1872 by Schutzenberger and Fontaine[23]. They prepared $[PtCl_2(PCl_3)]_2$ and $PtCl_2(PCl_3)_2$ from platinum and phosphorus pentachloride and found these substances to react with water and ethanol to yield complexes containing $P(OH)_3$ and $P(OC_2H_5)_3$ ligands. Somewhat later, Strecker and Schurigin[24] summarized the studies of several previous workers on the syntheses, structures and properties of phosphorus trihalide complexes of the Group VIII metals and presented some of their own results. They did not make any attempts to characterize their products other than to obtain elemental analyses and to note that some of the complexes showed activity toward amines, water and alcohol. In 1936, Davis and Ehrlich[25] prepared $(CuCl)_2 \cdot PCl_3$ and found this to react with aniline, phenol, and aliphatic alcohols although the only complex isolated by them was $CuCl(P(OCH_3)_3)_2$. Inasmuch as the dissociation pressure of PCl_3 above $(CuCl)_2 \cdot PCl_3$ appears to be extensive and inasmuch as PCl_3 is removed from the complex upon washing with benzene or other inert solvents, the question arises as to whether the PCl_3 reacts as a coordinated ligand or if it dissociates from the metal, reacts with the nucleophilic reagent, and then recombines with the metal. Certainly, the possibility exists that this type of reaction occurs in reactions of halophosphine complexes of other metals as well. The extent to which this possible dissociation-recombination occurs has not been determined.

Although the earliest PF_3 complexes to be prepared, $[PtF_2(PF_3)]_2$[26], was reported in 1891, extensive studies of PF_3 as a ligand did not begin until the early 1950's. About that time, Chatt and Williams[27] prepared the analogous $[PtCl_2(PF_3)]_2$ as well as $PtCl_2(PF_3)_2$. In regard to these complexes they stated: "The P-F bond is unfortunately too easily hydrolyzed to allow a thorough study of the properties of the chlorides." This observation contrasts sharply with the comment by Nixon: "A noteworthy feature of all the tetrakisfluorophosphine nickel complexes reported in this paper [NiL_4 where L is PF_3, CF_3PF_2, $(CF_3)_2PF$, CCl_3PF_2, Et_2NPF_2 or $C_5H_{10}NPF_2$] is their enhanced stability towards air and moisture, in sharp contrast to the highly reactive nature of the fluorophosphines."[28]

Several other early observations on the hydrolytic stability of metal complexes of halophosphines were made. Irvine and Wilkinson[29] reported the first preparation of $Ni(PCl_3)_4$ from PCl_3 and $Ni(CO)_4$ and found this thermochroic, nonvolatile solid to be stable toward water over several days, only slowly decomposed in basic solution, and rapidly decomposed in ammonium hydroxide. Edwards and Woodward[30] noted that this compound is soluble in various organic solvents but decomposes slowly to yield green solutions. They obtained some evidence for the formation of hexachloroethane in carbon tetrachloride solutions. Other nickel complexes prepared by Wilkinson[31] were $Ni(PBr_3)_4$, obtained by ligand exchange of PBr_3 with $Ni(PCl_3)$ and $Ni(PF_3)_4$ which was obtained by fluorination of $Ni(PCl_3)_4$ with SbF_3 in fluor lube. The hydrolytic stability of these nickel complexes follows the order $PF_3 > PCl_3 > PBr_3$. Attempts to prepare nickel complexes with AsF_3, $AsCl_3$ and $AsBr_3$ were unsuccessful. The readily hydrolyzed $Ni(CO)_3SbCl_3$ and $Fe(CO)_3(SbCl_3$ were also obtained[32]. Wilkinson[33] also showed that PF_3 can be attached to human hemoglobin in much the same manner as carbon monoxide but is readily hydrolyzed.

An improvement on halogen-exchange reactions of coordinated ligands was reported in 1961 by Seel, Ballreich and Schmutzler[34]. They synthesized $Ni(PF_3)_4$, $Ni(PMeF_2)_4$ and $Ni(PPhF_2)_4$ from KSO_2F and the nickel complexes of the corresponding chlorophosphine ligands. The work has been discussed in a review by Schmutzler[35]. Unpublished results using SbF_3 and KF in tetramethylsulfone as a fluorinating medium have been mentioned.[36]

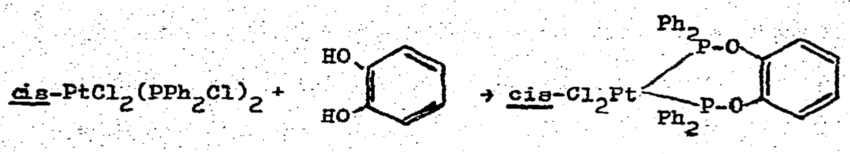
Except for the few examples cited previously, most definitive investigations of the reactions of simple nucleophilic reagents such as water, alcohols, amines, etc., with coordinated pnictogen ligands date from 1966. This is so even though many complexes of halophosphine ligands have been known for a longer period. Austin's thesis[37] contains the results of a substantial study on the reactions of Pt(II) and Pd(II) complexes with PPh_2Cl and $PPhCl_2$ ligands. The two complexes cis-$MCl_2\{PPh_2(OH)\}_2$, where M is Pd or Pt, were obtained by hydrolysis of cis-$MCl_2\{PPh_2Cl\}_2$. The particular thermodynamically unstable tautomeric form of diphenylphosphinous acid found in the complexes is stabilized by complexation. Other investigators have shown that diphenylphosphine oxide, the thermodynamically stable tautomer, reacts with $PdCl_4^{2-}$ [38] and $Mo(CO)_6$[39] to yield metal complexes of the unstable tautomeric form. Other hydrolysis reactions which have led to complexes of diorganophosphinous acids have been reported for cis-$PtX_2(MR_2Cl)(M'R'_3)$ (where: X = Cl, Br or I; M = P or As; R and R' = alkyl or aryl groups)[40] and for $Mo(CO)_5(PMe_2Cl)$[39]. Ligand hydrolysis reactions go faster in the presence of hydroxide or an amine[39]. When a base is employed, a salt of the acid may or may not be obtained depending upon the acid strength of the coordinated phosphinous acid. As an example of how a base affects reaction rates, Kruck and coworkers[41] obtained $Ba[Ni(PF_3)_3(PF_2O)]_2$ and $Ba[Fe(PF_3)_4(PF_2O)]_2$ from $Ba(OH)_2$ and the parent trifluorophosphine complexes under relatively mild conditions, whereas $Ni(PF_3)_4$ may be steam-distilled with minimal decomposition.

In two independent 1972 reports metal carbonyl complexes of diorganochlorophosphines were found to react with water to yield complexes of diphosphoxanes. Vahrenkamp[42] obtained $W(CO)_5PMe_2OPMe_2W(CO)_5$ in the hydrolysis of $W(CO)_5PMe_2Cl$. The arsenic analog was also made. Kraihanzel and Bartish[39] were able to obtain $Mo(CO)_5PMe_2(OH)$ and show that this compound combined with $Mo(CO)_5PR_2Cl$ in the presence of triethylamine to yield $Mo(CO)_5PMe_2OPR_2Mo(CO)_5$. Similar reactions provided $Mo(CO)_5PPh_2OPR_2Mo(CO)_5$, where R = Me or Ph, Several other important reactions of the coordinated phosphinous acid and phosphinate ligands which probably do not involve cleavage of the P-O bond are cited in Section B.3.

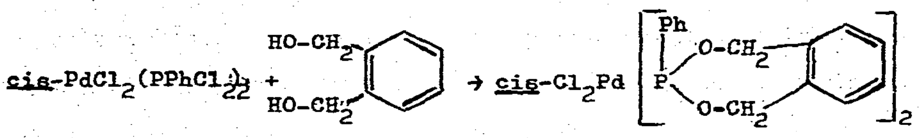
Hydrogen sulfide behaves in the same manner as water in reactions of the P-Cl bond of coordinated ligands. Thus, the salts $[Et_3NH][W(CO)_5(EMe_2S)]$[42], E = P or As, and $[Et_3NH][Mo(CO)_5(PPh_2S)]$[43] have been obtained. The tungsten complexes form $W(CO)_5EMe_2SEMe_2W(CO)_5$ upon continued heating in benzene[42].

Numerous reactions of alcohols with and without added amines, or of alkoxides with coordinated pnictogen donor ligands are known. The following interesting reactions, among others, carried out by Austin[37] may be cited:

cis-$PtCl_2(PPh_2Cl)_2 + HOCH_2CH_2OH \rightarrow$ cis-$PtCl_2(PPh_2OCH_2CH_2OH)_2$

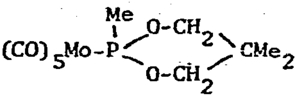


$\underline{cis}$-$PdCl_2(PPhCl_2)_2 + HOCH_2CH_2OH \rightarrow$ $\underline{cis}$-$PdCl_2(PPh(OCH_2CH_2OH)_2)_2$



In another example of a reaction of a coordinated ligand which led to a heterocyclic ligand, the diol $HOCH_2$-CMe_2CH_2OH was reacted with $(CO)_5Mo(PMeCl_2)$

to form



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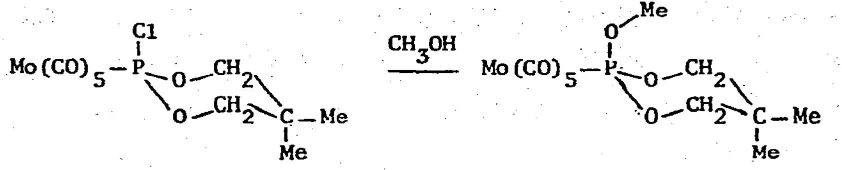
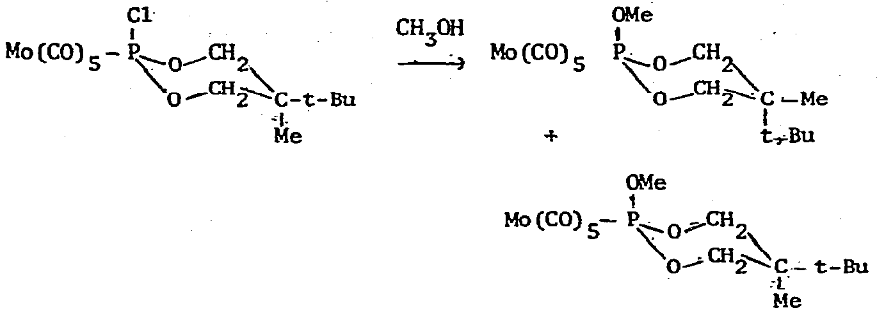
Kruck and coworkers obtained $Ni(P(OMe)_3)_4$ from the reaction of sodium methoxide in methanol with $Ni(PF_3)_4$ [45] and $Ni(PF_2OMe)_4$ from displacement of chloride in $Ni(PF_2Cl)_4$ [46]. The total replacement of chloride in $Ni(PCl_3)_4$ by methoxide was also demonstrated[11]. However, in the absence of methoxide, pure methanol gave a variety of products including methyl chloride, dimethyl phosphinate and solvated nickel(II) ion.[47] In an extraordinary study, Clark and Morgan[48] were able to obtain all of the possible complexes resulting from stepwise replacement of the fluorides by methoxide in $Co(NO)(CO)_x(PF_3)_{3-x}$, where x = 0,1,2. Müller and Fenderl[49] have made one of the few available direct comparisons between the reactivity of arsenic and phosphorus donor ligands. They noted that displacement of one or two of the fluorides from arsenic in $MnCp(CO)_2AsF_3$ by methanol in benzene proceeds readily at 20°. Under identical experimental conditions, the corresponding PF_3 complex is inert.

The methanolyses of two molybdenum complexes of 2-chloro-5,5-disubstituted-1,3,2-dioxaphosphorinanes have been carried out[44] and simple replacement of chloride by the methoxyl group occurred. The second reaction is discussed in greater detail in Section C.



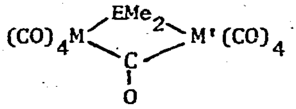


equilibrium concentration (10%)

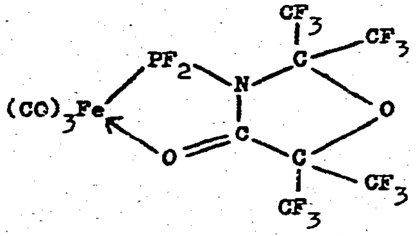
(90%)

Except for the syntheses of Mo(CO)$_5$(PR$_2$SEt), where R = Ph, or Me, from ethanethiol and the corresponding chlorophosphine complexes, no other reactions with thiols have been reported[43].

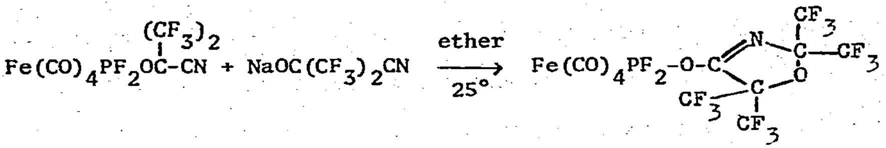
A few reactions of primary and secondary amines and two reactions of ammonia with halophosphine ligands are known. Kruck and coworkers[46] noted that secondary amines react with Ni(PF$_3$)$_4$ to yield a range of complexes Ni(PF$_3$)$_{4-n}$(PF$_2$NR$_2$)$_n$ (n = 4,3.2). Vahrenkamp prepared W(CO)$_5$PMe$_2$NMeH from W(CO)$_5$PMe$_2$Cl and MeNH$_2$ [42]. Subsequent reaction of the aminophosphine complex with **methyllithium** abstracted the amino proton yielding an amido derivative. This in turn was found to displace chloride in W(CO)$_5$PMe$_2$Cl and form W(CO)$_5$PMe$_2$NMePMe$_2$W(CO)$_5$.[42] Kraihanzel and Bartish[43] obtained the expected series of aminophosphine molybdenum complexes Mo(CO)$_5$L (L = PMe$_2$NH$_2$, -NHMe, -NMe$_2$ and PPh$_2$NH$_2$, -NHMe, -NMe$_2$, -NHPh) by reacting ammonia or the appropriate amine with Mo(CO)$_5$PR$_2$Cl. An unusual but related reaction is an apparent ligand substituent exchange noted by Nixon and Sexton[51]. They report that although cis-PtCl$_2$(P(R$_2$N)F$_2$)$_2$ can be prepared by bringing together the free phosphine and platinum(II) chloride, long reaction times lead to loss of phosphorus trifluoride from the reaction mixture and formation of <u>cis</u>-$PtCl_2(P(R_2N)_2F)_2$.[19]

Several reactions have been cited in which transition metal organometallic anions effect halogen displacement from phosphorus. Ehrl and Vahrenkamp[52] showed that $(CO)_5MEMe_2Cl$, where M = Cr, Mo or W and E is P or As, reacted with $NaM'(CO)_5$, where M' is Mn or Re, to yield the binuclear complexes $(CO)_5ME(CH_3)_2M'(CO)_5$. Heating the latter complexes gives rise to $M(CO)_6$ and $[M'(CO)_4EMe_2]_2$ but no  Haines and coworkers[53,54] obtained $Cp(CO)_2Fe(PPh_2)Fe(CO)_4$ in the reaction of $CpFe(CO)_2^-$ with $Fe(CO)_4PPh_2Cl$. Ultraviolet irradiation of the diiron complex effected rearrangement and formation of $CpFe_2PPh_2(CO)_5$ containing both CO and PPH_2 bridges.

Simple inorganic anions and organic anionic species readily displace the bromide from $Fe(CO)_4PF_2Br$ according to Ruff and his coworkers. The simplest displacement reactions of $Fe(CO)_4PF_2Br$ involve such anions as F, SCN^-, N_3^-, etc.,[55] while a more complex reaction is noted with the ambident anion of 2,2,5,5(tetrakistrifluoromethyl)4-oxazolidone[56] for which the followi structure has been proposed.



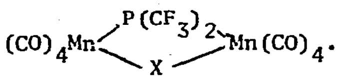
These same workers were able to synthesize a structural isomer of the above mentioned complex according to the following reaction:



Ruff and others[57] have also found $Fe(CO)_4PF_2Br$ to react with a variety of oxygen containing substances (silver permanganate, hexa-n-butyl-distannoxane, silver(I) oxide and copper(I) oxide) to give $(CO)_4FePF_2OPF_2Fe(CO)_4$ in 7 - 40% yield. They mention that mercury and other metals are not effective in trying to make $(CO)_4FePF_2\text{-}PF_2Fe(CO)_4$ by debromination of $Fe(CO)_4PF_2Br$.

Only a few reductions of halophosphine ligands are known. Höfler and Schnitzler[58] used sodium borohydride in tetrahydrofuran for one day at room temperature to convert $MnCp(CO)_2PCl_3$ to $MnCp(CO)_2PH_3$ in 70% yield and $MnCp(CO)_2PPhCl_2$ to $MnCp(CO)_2PPhH_2$ in 64% yield. In contrast, lithium aluminum hydride did not function well as a reducing agent for $Mo(CO)_5PPh_2Cl$ [43].

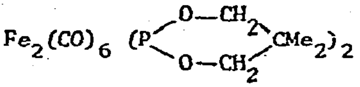
In contrast to the body of information cited above which suggests that complexes of diorganohalophosphines are of good thermodynamic stability, several reactions between halophosphines or haloarsines and metal complexes yield products in which a halogen-pnictogen bond is cleaved. Grobe[59] has shown that reactions between $Mn_2(CO)_{10}$ and $P(CF_3)_2X$, where X is Cl, Br, I, SCF_3 or $SeCF_3$, go beyond the stage of simple substitution and form bridged complexes

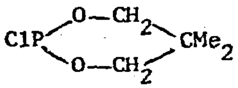
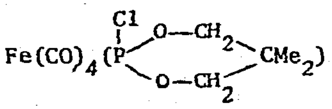


$$(CO)_4Mn\overset{P(CF_3)_2}{\underset{X}{\rightleftarrows}}Mn(CO)_4$$

. On the other hand, $P(CF_3)_2NCO$ and $P(CF_3)_2N(CH_3)_2$ react to form $Mn_2(CO)_8(P(CF_3)_2)_2$. Later, Grobe and Kober[60] showed that the bridge complex $Mn_2(CO)_8AsMe_2X$ was obtained with $AsMe_2X$, where X is I or $P(CF_3)_2$. A similar cleavage reaction occurs with $Me_2PAs(CF_3)_2$, but $AsMe_2Cl$ and $AsMe_2Br$ yielded unidentified polymeric carbonyls while $AsMe_2SCF_3$ reacted only minimally with $Mn_2(CO)_{10}$ at 80°. Iron pentacarbonyl and $E(CF_3)_2I$, where E = P or As, was shown to yield not only the expected

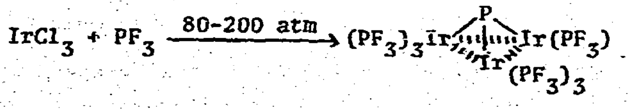
$Fe(CO)_4(E(CF_3)_2I)$ but also produced dimeric complexed $Fe_2(CO)_6E(CF_3)_2I$ with $E(CF_3)_2$ and I bridges[61]. In still another example showing the effect of different substituent groups on P of a potential ligand, $P(CF_3)_2Cl$ and $Fe(CO)_5$ gave $Fe_2(CO)_6(P(CF_3)_2)_2$ and not the compound with bridging chloride[61]. Douglas and Ruff[62] showed that $Ni(CO)_4$ abstracted bromine from $Fe(CO)_4PF_2Br$ in refluxing hexane and produced $Fe_2(CO)_6(PF_2)_2$ instead of forming a mixed dinuclear complex. The ^{19}F-NMR spectrum of $Fe_2(CO)_6(PF_2)_2$ showed the fluorine atoms to reside in two non-equivalent environments as would be expected for a non-fluxional molecule with a folded P-Fe-P-Fe ring. The compound

 which also has been shown by ^1H-NMR and ^{31}P-NMR to have a dibridged structure with non-equivalent methylene protons was obtained as one of the products from the reaction of $Fe_3(CO)_{12}$ with

 [63]. The expected product 

was also obtained and has been prepared by the direct reaction of the free ligand with $Fe(CO)_5$ as well[44].

Several other reactions should be cited in which the integrity of phosphorus Lewis base is not retained. Kruck and Lang[64] observed that CoI_2 and PF_3 under pressure gave $(PF_3)_3Co(PF_2)_2Co(PF_3)_3$ which was characterized by ^{19}F-NMR and mass spectrometry. The cobalt carbonyl analog of this compound, $(CO)_3Co(PF_2)_2Co(CO)_3$, was made by Grobe and Stierand[65] by reacting $P(CF_3)_2I$ with $Hg(Co(CO)_4)_2$. Additional reactions of transition metal PF_3 complexes examined by Kruck, Sylvester and Kunaw[66] include the following:

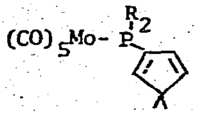


$$HCo(PF_3)_4 \xrightarrow{h\nu} (PF_3)_3Co(H)(PF_2)Co(PF_3)_3$$

$$HCo(PF_3)_4 + HIr(PF_3)_4 \rightarrow (PF_3)_3Co(H)(PF_2)Ir(PF_3)_3.$$

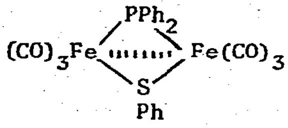
Other reactions of a related nature of various iron and cobalt organometallic complexes with pnictogen trihalides have been studied for some time. For example, $Na[Fe(h^5\text{-}Cp)(CO)_2]$ and $SbCl_3$ react to form $\{[Fe(h^5\text{-}Cp)(CO)_2]_3SbCl\}_2[FeCl_4]\cdot CH_2Cl_2$[67]. Although no experimentally based reaction mechanism has been proposed for this reaction, there are two possible and reasonable initial steps in the reaction. Either nucleophilic displacement of chloride from antimony will yield $Fe(h^5\text{-}Cp)(CO)_2(SbCl_2)$ or nucleophilic addition will yield $Na[Fe(h^5\text{-}Cp)(CO)_2SbCl_3]$. By either path, subsequent displacement of chloride must occur in order for the final product to be formed. Some additional reactions of pnictogen halides which lead to products which may be formed by a reaction of a coordinated pnictogen ligand in an intermediate step include: SbX_3(X-Cl,Br,I) with $[Fe(h^5\text{-}Cp)(CO)_2]_2$[68,69,70]; $AsCl_3$ with $Co_2(CO)_8$ to yield $Co_2(CO)_6As_2$[71]; formation of $Co_4(CO)_{12}Sb_4$ from cobalt(II) acetate, and $SbCl_3$ in methanol under carbon monoxide and hydrogen pressure[72].

In concluding this section, several reactions of organometallic reagents with coordinated halo-phosphine ligands will be mentioned[73]. Grignard reagents have been found to react with $Mo(CO)_5PR_2Cl$ to give relatively low yields of the complexes of tertiary phosphine ligands $Mo(CO)_5PR_2R'$, where R = Ph for R' = Me, Et, i-Pr and R = Me for R' = Me, Ph. An interesting side reaction of $Mo(CO)_5PPh_2Cl$ with EtMgBr led to formation of $(CO)_5MoPh_2P\text{-}PPh_2\text{-}Mo(CO)_5$[73] which could not be synthesized directly from $Mo(CO)_6$ and $Ph_2P\text{-}PPh_2$[74]. Reactions of $Mo(CO)_5PR_2Cl$, where R = Me,Ph, with NaC_5H_5 have yielded several complexes which have not been completely characterized. These substances have been tentatively identified from their IR and ^1H-NMR spectra as well as elemental analyses as

 and $[Mo(CO)_5PR_2]C_5H_4$.[19]

d. The E-Sulfur Bond

There appears to be only a single example of a reaction in this category. Job, McLean and Thompson[75] reacted Ph_2PSPh with $Fe(CO)_5$ and obtained

 in 75% yield instead of the expected $(CO)_4FePh_2PSPhFe(CO)$

Inasmuch as disulfides, as well as many biphosphines, undergo E-E cleavage upon reaction with the metal complexes[76], this result is not an unexpected one.

e. The E-Nitrogen Bond

In an earlier section, the reactions of coordinated halophosphine ligands with ammonia and amines to yield complexes of coordinated aminophosphine ligands was demonstrated. Here, a number of examples of the reverse reaction will be considered. Höfler and Schnitzler[58,77] have shown that anhydrous hydrogen halides as either the liquid or in hydrocarbon solutions readily displace the diethylamino moiety from phosphorus. Examples from their work are cited below.

$$MnCp(CO)_2(PPh(NEt_2)_2) + HX \rightarrow MnCp(CO)_2(PPhX_2) + \text{some } MnCp(CO)_2(PPhXNEt_2)$$

$$X = Cl, Br, I$$

$$\mathrm{MnCp(CO)_2(PPhFNEt_2)} + \mathrm{HCl/lig(25^\circ)} \xrightarrow{12\ \mathrm{hrs}} \left\{\begin{array}{c} 18\%\ \mathrm{MnCp(CO)_2(PPhF_2)} \\ + \\ 12\%\ \mathrm{MnCp(CO)_2(PPhFCl)} \\ + \\ 70\%\ \mathrm{MnCp(CO)_2(PPhCl_2)} \end{array}\right.$$

$$\xrightarrow{3\ \mathrm{hrs}} \left\{\begin{array}{c} 80\%\ \mathrm{MnCp(CO)_2(PPhFCl)} \\ + \\ 20\%\ \mathrm{MnCp(CO)_2(PPhCl_2)} \end{array}\right.$$

The largest yields of the $PPhF_2$ complex were obtained with HF although benzoyl fluoride and KHF_2 also were found to be acceptable. Höfler and Marre[78] obtained the following results:

$$\mathrm{Mo(CO)_5P(NMe_2)_3 + HX(\ell) \rightarrow Mo(CO)_5PX_3} \quad (\mathrm{X = Cl, Br})$$

$$\mathrm{Mo(CO)_5P(NMe_2)_3 + HCl/pentane \rightarrow Mo(CO)_5PCl_n(NMe_2)_{3-n}} \quad (n=1,2,3)$$

$$\underline{\mathrm{trans}}\mathrm{\text{-}Mo(CO)_4(P(NMe_2)_3)_2 + HCl(\ell) \rightarrow} \underline{\mathrm{trans}}\mathrm{\text{-}Mo(CO)_4(PCl_3)_2}$$

$$\mathrm{Mo(CO)_5P(NMe_2)_3 + HI/pentane} \xrightarrow{-20^\circ} \mathrm{Mo(CO)_5PI_2NMe_2}$$

$$\xrightarrow{-5^\circ} \mathrm{Mo(CO)_5PI_3 + Mo(CO)_5PI_2NMe_2}$$

The trend of reactivity of HX with the P-N bond was reported to be HI>HBr>HCl.

Douglas and Ruff[79] have reported some similar results from their work in addition to some notable differences. For example, $Fe(CO)_4PF_2NEt_2$ reacts with HCl or HBr to give $Fe(CO)_4PF_2X$ but HI gives $Fe(CO)_4I_2$. Further, $Fe(CO)_4PF(NEt_2)_2$ reacts with HCl only among the hydrogen halides to exchange halogen for the diethylamino group. Douglas and Ruff[80] also report $M(CO)_5PF_2(NEt_2)$, where M is Cr, Mo or W, to react with anhydrous HBr to yield $M(CO)_5PF_2Br$.

f. The E-E Bond (Bipnictogens and Cyclo(polypnictogens))

(i) Bipnictogens, R_4E_2: The reactions of biphosphines and biarsines with precursor metal complexes have been shown to form at least five types of metal complexes. In what seems to be the earliest report of a reaction in which the integrity of the ligand was maintained upon complexation, Burg and Mahler[81] obtained $(CO)_3NiP(CF_3)_2P(CF_3)_2Ni(CO)_3$ from the biphosphine and $Ni(CO)_4$. Subsequent work by Hayter and his coworkers as well as the work of others led to a number of other metal complexes in which both Lewis base sites of the biphosphines were attached to metals and in which the P-P bond was not cleaved. Among the known complexes are:

$(CO)_3NiPR_2PR_2Ni(CO)_3$, where R = Me[82,83], Ph[82], C_6H_{11} and Et[83];

$(CO)_4FePR_2PR_2Fe(CO)_3$, where R = Me[82,74,83], C_6H_{11} and Et[83];

$(CO)_5MPR_2PR_2M(CO)_5$, where M = Cr, Mo, W and R = Me, Et[74];

$(CO)_5WAsMe_2AsMe_2W(CO)_5$[74]; $(CO)_4(NO)VPPh_2PPh_2V(NO)(CO)_4$[84] and

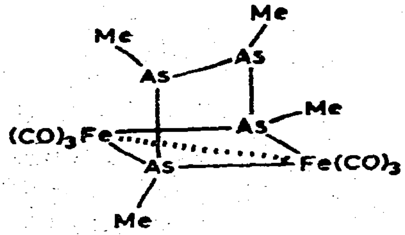
$(CO)_2(NO)CoPPh_2PPh_2Co(NO)(CO)_2$[84]; $X(ON)_2CoPPh_2PPh_2Co(NO)_2X$, where
X = Cl,Br[85]

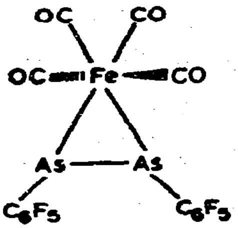
Very frequently, the direct reaction between a bipnictogen and a metal complex leads only to complexes containing bridging phosphido or arsenido ligands, R_2E, resulting from E-E bond cleavage. In a number of cases isolated complexes of the μ-biphosphine complexes have been found to undergo E-E bond cleavage upon heating. However, the exact mechanism whereby this reaction takes place and if the biphosphine complex is always formed first are not known. Complexes prepared either directly or upon rearrangement include the following: $(Ni(Cp)ER_2)_2$, where E = As,P and R = Me,Ph[86]; $[Ni(CO)_2(PPh_2)]_2$, R = Me,Ph[87]; $[Fe(CO)_3ER_2)_2$, where E = P with R = Me[74,82], Et[82] and E = As with R = Me[74]; $[Fe(CO)_3X(EMe_2)]_2$, where E = P for X = Br and E = As for X = Br or I[82]; $[Mn(CO)_4(ER_2)]_2$, where E = P for R = Ph[87] and E = As for R = Me[87] or R = CF_3[88]; $[Mn(CO)_3X(PPh_2)]_2$, where X = Cl,Br,I[84]; $[M(CO)_4ER_2]_2$, where M=Cr for E=P and R = Me[74,82,89] or Et[82], M = Mo or W for E = P with R = Me[82,89], Et or Ph[74] and for E = As with R = Me[82]; $[M(Cp)(CO)_2EMe_2]_2$, where M = Mo or W and E = P or As[86,89]; $[V(CO)_4EPh_2]_2$, where E=P or As.[84] Dobbie[90] has reported that $P_2(CF_3)_4$ reacts with $W(CO)_6$ to yield $[(CO)_4WP(CF_3)_2]_2$ in only 3% yield. Inasmuch as the major product is $W(CO)_5(P(CF_3)_2F)$, extensive ligand decomposition could possibly be involved. Another unique observation was made by Hayter and Williams[91] as they obtained the $[CpFe(CO)EMe_2Fe(CO)Cp]^+$ ion (E = As or P) as the ClO_4^- and Ph_4B^- salts from the reaction of $CpFe(CO)_2Br$ with E_2Me_4.

One of the most interesting studies on the reactions of biphosphines with metal carbonyls has been reported by Brockhaus, Staudinger and Vahrenkamp[89]. These investigators made $M(CO)_5PMe_2PMe_2$, where M = Cr,Mo,W by photochemical methods. A further photochemical reaction of each of these products with metal carbonyls in tetrahydrofuran led to $(CO)_5MPMe_2PMe_2M'(CO)_5$ where M and M' are the same or different group VI metals. Subsequent heating of these products in benzene at 190-250° led to decomposition to $(CO)_4M(PMe_2)_2M'(CO)_4$. In some cases the symmetrical bridged complexes with M = M' resulted. However, the compounds with M = Cr and M' = Mo or W and M = Mo and M' = W were also found and carefully characterized by ^1H-NMR, ^{31}P-NMR and mass spectrometry. The mechanism of conversion of a bridged biphosphine ligand is not known. However, one possible mode of decomposition could yield $(CO)_nM\dot{P}R_2$ radicals. Evidence for symmetrical cleavage of the P-P bond in P_2Ph_4 has been reported[92] and several of the P_2Me_4 complexes cited earlier have been shown to polymerize methyl methacrylate by a free radical pathway[93].

One additional reaction of organofluorine biphosphines and arsines should be mentioned. Both $As_2(CF_3)_4$ and $P_2(CF_3)_4$ react with $[CpFe(CO)_2]_2$ to yield the metal complexes $CpFe(CO)_2E(CF_3)_2$ which bear terminal pnictogenide ligands[88,94]. The basic chemistry of these ligands will be considered in more detail in a subsequent section. However, it is important to note that bridge formation does not always occur spontaneously upon cleavage of the E-E bond. While Cullen and Hayter[88] suggested that the electron withdrawing power of the CF_3 groups may be responsible for the lowering of the basicity of the coordinated $As(CF_3)_2$ group, this does not explain why $Mn_2(CO)_{10}$ and $Fe(CO)_2(NO)_2$ yield bridged complexes.

(ii) Cyclic(polypnictogens): Inasmuch as the ring systems of cyclopolyphosphines and arsines have as many potential Lewis base sites as pnictogen atoms, there is no wonder why coordination chemists were drawn to investigate the reactions of these catena compounds with metal carbonyls and metal halides. The most unusual type of result that has been found in these reactions has been the modification of ring size of the polypnictogen ligand upon complexation. For example, Ang, Shannon and West[95] report that $(PhP)_4$ reacts with $Mo(CO)_6$ or $W(CO)_6$ at temperatures greater than 120° to give $(PhP)_5M(CO)_5$. Fowles and Jenkins[96] presumably could not duplicate these results and obtained $(PhP)_4M(CO)_4$ instead. Quite interestingly, Maier and Daly[97] suggest that $(PhP)_4$ is in fact $(PhP)_5$. To further complicate the situation, Stone and his coworkers[98,99] found $(EtP)_5Mo(CO)_4$ to result from the direct reaction between $Mo(CO)_6$ and $(EtP)_4$. Displacement of acetonitrile from $(CH_3CN)_3W(CO)_3$ by $(EtP)_4$ formed $(EtP)_4W(CO)_4$[99]. A structural study of $(EtP)_5Mo(CO)_4$ has verified the suggestion of a 1,3-dihapta attachment mode for the $(EtP)_5$ ring[100]. Reactions of cyclo(organoarsines) with metal carbonyls lead to products in which As-As bonds are cleaved. For example, Elmes and West[101,102] report that $(RAs)_5$, where R is Me or Et and $(PhAs)_6$ all react with $Fe(CO)_5$ to yield complexes $(Fe(CO)_3)_2(AsR)_4$. The structure of the methyl analog has been determined and is shown below.





An equally fascinating complex $(Fe(CO)_4(AsC_6F_5)_2$ has been obtained from the reaction between $(C_6F_5As)_4$ and $Fe(CO)_5$[103]. As the structure shown above indicates, significant ligand decomposition has occurred to form a complex containing the $C_6F_5As\text{-}AsC_6F_5$ ligand in which the As-As bond distance of 2.39Å seems abnormally short. Even more extensive ligand decomposition which includes cleavage of As-C bonds occurs in the formation of $As_3Co(CO)_3$ from $Co_2(CO)_8$ and $(CH_3As)_5$[104].

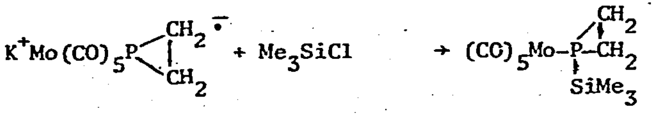
g. Terminal R_2E ligands

The compounds to be considered in this section contain coordinated tri-covalent pnictogen donor ligands. Owing to the tri-covalent nature of these ligands, the pnictogen ligand carries a non-bonded pair of electrons which can react with a Lewis acid. For the purposes of this review, whether or not the terminal phosphide ligand carries a charge is immaterial. As will become apparent below, complexes with a terminal R_2E ligand are not always isolable inasmuch as spontaneous reaction with a second molecule of complex is a commonplace process which results in formation of bridged complexes. For example, both $NaMn(CO)_5$[105] and $Me_3SnMn(CO)_5$[106] react with Ph_2PCl to yield $[(CO)_4MnPPh_2]_2$ and not the terminal phosphide complex $(CO)_5MnPPh_2$. Similarly, $Me_3SnCo(CO)_4$ gives $((CO)_3CoPPh_2)_2$[106]. In contrast, $(C_6F_5)_2ECl$, where E = P,As, reacts with $CpFe(CO)_2^-$ and $CpMo(CO)_3^-$ to yield terminal phosphide complexes $Cp(CO)_2FeE(C_6F_5)_2$ and $Cp(CO)_3MoE(C_6F_5)_2$[107]. Presumably, the basicity of a pnictogen atom is diminished by the C_6F_5 moiety and thereby inhibits bridge formation.

An alternative route to a terminal phosphide ligand is the nucleophilic displacement of an electronegative substance from a metal, typically a metal halide is chosen, by a diorganophosphide. In the early 1960's, Isslieb and his coworkers carried out a number of reactions between anhydrous transition metal halides and lithium and potassium dialkyl and diaryl phosphides[108,109,110]. Although the extent of bridge bonding was not demonstrated in these complexes, they were found to be sensitive to water and alcohols with formation of free or complexed Ph_2PH and reacted with methyl iodide to form quarternary phosphonium salts. Heiber and coworkers studied the reaction of $Re(CO)_5Cl$[111], $(Rh(CO)_2Cl)_2$[112], $[Ir(CO)_3Cl]_n$[112], $(Fe(NO)_2X]_2$[113], $[Co(NO)_2X]_2$[113] and $[Ni(NO)Br]_4$ with $KPPh_2$ and in no case obtained a complex with a free terminal phosphide ligand as bridge formation took place under the reaction conditions.

In an earlier section, the ability of various bases to abstract a proton from a coordinated secondary phosphine ligand was illustrated. The resulting anionic complexes are quite reactive and exhibit a varied chemistry as shown by the reactions cited below:

$$\begin{array}{llll} K^+(CO)_5MoP(C_6F_5)_2^- & + (C_6F_5)_2PCl & \rightarrow (CO)_5MoP(C_6F_5)_2P(C_6F_5)_2 & \text{(ref. 18)} \\ & + MeI & \rightarrow (CO)_5MoP(C_6F_5)_2Me & \\ K^+Mo(CO)_5PH_2^- & + Mo(CO)_5(PH_3) & \rightarrow (CO)_5MoPH_2Mo(CO)_5^- & \text{(ref. 19)} \\ & + MeCl & \rightarrow (CO)_5Mo(PH_2CH_3) & \\ & + Me_3SiCl & \rightarrow (CO)_5Mo(PH_2SiMe_3) & \\ & + CH_3COCl & \rightarrow (CO)_5Mo(PH_2\overset{O}{\overset{\|}{C}}CH_3) & \end{array}$$

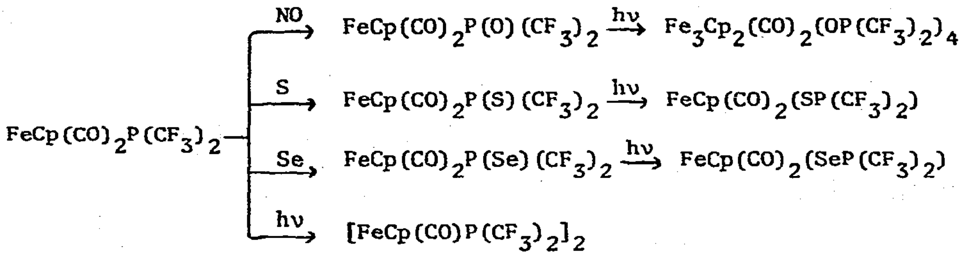


(ref. 21)

Although Treichel, Dean and Douglas[20] in their study of hydride abstractions did not isolate $FeCp(CO)_2PPh_2$, they did find that methyl iodide would react in solution to yield $[CpFe(CO)_2PPh_2Me]^+PF_6^-$. A similar type of reaction yielded $[FeCp(CO)_2PPhMe_2]^+PF_6^-$.

Among the isolable terminal pnictogenide ligand complexes, those with $E(CF_3)_2$ ligands seem to be most readily obtained. Cullen and Hayter[88] found that $FeCp(CO)_2As(CF_3)_2$ and $MoCp(CO)_3As(CF_3)_2$ dimerized only upon ultraviolet irradiation. On the other hand, $[MnAs(CF_3)_2(CO)_4]_2$ and $[Fe(As(CF_3)_2)(NO)]_2$ were formed directly in the reactions of $As_2(CF_3)_4$ with $Mn_2(CO)_{10}$ and $Fe(CO)_2(NO)_2$, respectively. No reactions of the terminal

$As(CF_3)_2$ group were reported. In contrast, two recent papers[94,114] have shown the terminal $P(CF_3)_2$ group in $CpFe(CO)_2P(CF_3)_2$ to have an extremely exciting chemistry which is summarized below. The reactions with nitric oxide, sulfur and selenium are exactly those found for tertiary



$$\mathrm{FeCp(CO)_2P(CF_3)_2} \xrightarrow{NO} \mathrm{FeCp(CO)_2P(O)(CF_3)_2} \xrightarrow{h\nu} \mathrm{Fe_3Cp_2(CO)_2(OP(CF_3)_2)_4}$$

$$\mathrm{FeCp(CO)_2P(CF_3)_2} \xrightarrow{S} \mathrm{FeCp(CO)_2P(S)(CF_3)_2} \xrightarrow{h\nu} \mathrm{FeCp(CO)_2(SP(CF_3)_2)}$$

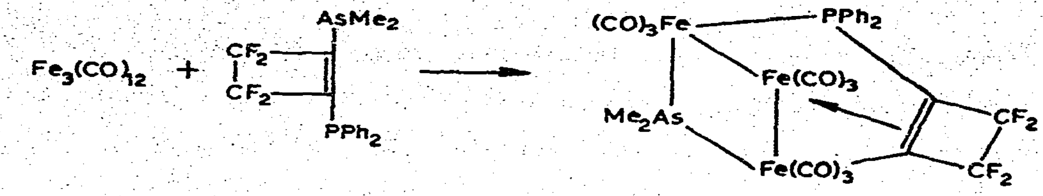
$$\mathrm{FeCp(CO)_2P(CF_3)_2} \xrightarrow{Se} \mathrm{FeCp(CO)_2P(Se)(CF_3)_2} \xrightarrow{h\nu} \mathrm{FeCp(CO)_2(SeP(CF_3)_2)}$$

$$\mathrm{FeCp(CO)_2P(CF_3)_2} \xrightarrow{h\nu} \mathrm{[FeCp(CO)P(CF_3)_2]_2}$$

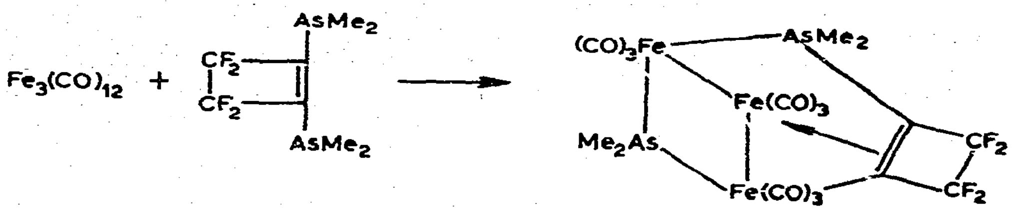
phosphines while the photodimerization reaction is similar to the many examples already cited.

h. The E-Carbon Bond

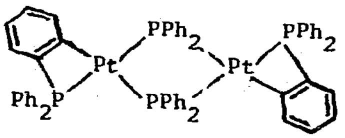
Our knowledge of the cleavage of P-C and As-C bonds is of relatively recent vintage. However, the first example of a complex in which as As-C bond was cleaved actually dates back to 1950. Nyholm[115] obtained a complex from the reaction between nickel(II) chloride and diars which in a subsequent report[116] was shown to have a structure resulting from two diars molecules having become linked with elimination of the elements of Me_3As to form the tridentate ligand bis-o-dimethylarsinophenyl(methyl arsine). Since that time, Cullen and his coworkers[117,118,119] have found that As-C bond cleavage is a quite general phenomenon in the reactions between a variety of arsenic donor ligands and iron carbonyls. Einstein and his coworkers[120,121,122] have characterized some of the substances obtained by Cullen and have reported an independent synthesis[123] involving As-C bond cleavage. Typical observations are given below.



(Refs. 119,122)



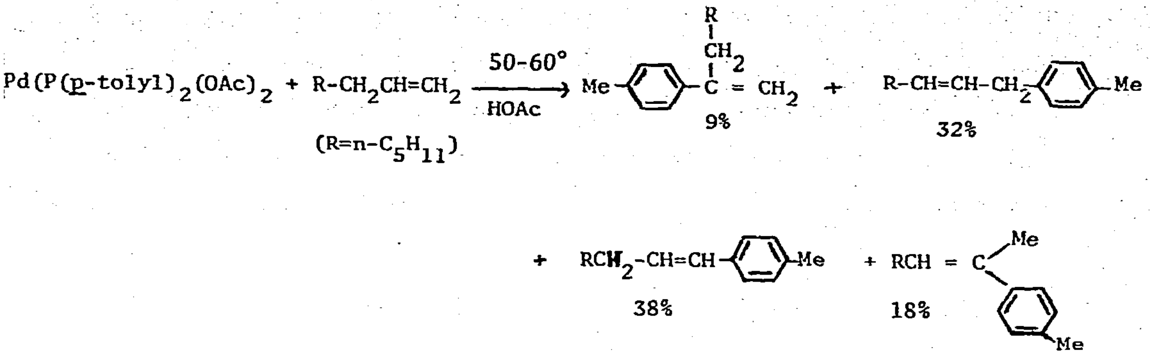
Slightly less spectacular have been the observations of cleavage of P-C bonds of triarylphosphines. Several years ago, Blake and Nyman[124] found Pt$(PPh_3)_2(C_2O_4)$ to decompose upon irradiation with formation of a complex to which they assigned the structure



$\cdot$ 1/2C_6H_6.

This compound decomposed upon treatment with aqueous potassium cyanide to yield PPh_3 and PPh_2H in a 1:1 ratio. More recently, both $IrH(CO)(PPh_3)_3$[125] and $Ru_3(CO)_9L_3$[126], where L is a tertiary phosphine or arsine, were found to be decomposed in refluxing decalin. An iridium complex $(Ph_3P)(CO)Ir(PPh_2)_2(CO)(PPh_3)$ was obtained in the first study and shown to have bridging Ph_2P groups.

Among the wide variety of products obtained in the second investigation are $Ru_2(CO)_6(R_2P)_2$ complexes with R = Ph or $\underline{m}$-MeC_6H_4. In each case, the cleavage of a P-C bond has occurred. Recently, a very interesting report on the utilization of the cleavage of the P-C bond in triaryl phosphines in organic synthesis has appeared[127,128]. The Japanese workers found that upon heating olefins at 50-60° in the presence of $Pd(P(\underline{p}\text{-tolyl})_3)_2(OAc)_2$ in acetic acid a variety of arylated olefins is obtained as shown in the following reaction:



Other olefins examined include styrene, hexa-1,5-diene, vinylacetate and ethyl acrylate. Several important factors regarding the chemistry need to be noted. First, the transfer of the aryl group from phosphorus to carbon is site specific with regard to the ring. Secondly, excess $P(\underline{p}\text{-tolyl})_3$, that is greater than two moles phosphine per metal atom, inhibits the arylation reaction. The authors propose a mechanism which involves a nucleophilic attack, presumably by solvent, at the coordinated triarylphosphine ligand with displacement of an aryl group onto the metal to form a Pd-C sigma bond. Migration of the aryl group to a pi-coordinated olefin ligand is thought to follow to yield an alkyl-palladium bond. Solvolysis of this intermediate, or of other intermediates obtained by rearrangements on the metal atom, would lead to the observed range of products.

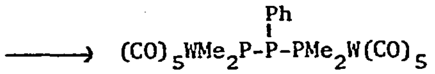
i. The E-Silicon, E-Germanium, and E-Tin Bonds

As has already been seen for so many other phosphorus and arsenic compounds reported thus far in this review, compounds containing bonds between phosphorus or arsenic and a group IV element have been found to react with metal complexes both with or without bond cleavage. For example, Abel and Sabherwal[129] obtained $[M(CO)_4PPh_2]_2$, where M is Mn or Re, in the reaction of $Ph_2P\text{-}SiMe_3$ with $M(CO)_5Br$. In a related study[130] copper salts were found to dissolve in $Ph_2P\text{-}SiMe_3$ and upon heating yielded Me_3SiX compounds, Ph_4P_2 and metal copper. Schumann and Kroth[131] reacted $(Me_3M)_3P$, where M is Ge or Sn, with $Mn(CO)_5Br$ and also found P-M cleavage to occur as they isolated $[(CO)_4MnP(MMe_3)_2]_2$ complexes. On the other hand, as Vahrenkamp has shown[42,13] metal carbonyl complexes containing stannylphosphine and stannyl arsine ligands to be preparable by photochemical procedures and serve as valuable sta materials for subsequent syntheses. Examples from his work are given below.

$$M(CO)_5EMe_2SnMe_3 + E'Me_2Cl \xrightarrow{-Me_3SnCl} M(CO)_5EMe_2E'Me_2 \qquad \text{(ref. 132)}$$

(M = Cr,W) (E,E' = P,As)

$W(CO)_5PPh(SnMe_3)_2$ + $2PMe_2Cl$ (Followed by $W(CO)_5(THF)$



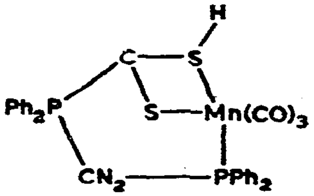
$$\longrightarrow (CO)_5WMe_2P\text{-}\overset{\overset{Ph}{|}}{P}\text{-}PMe_2W(CO)_5 \qquad \text{(ref. 42)}$$

$$W(CO)_5PPh(SnMe_3)_2 + 2AsMe_2Cl \rightarrow W(CO)_5PPh(AsMe_2)_2 \qquad \text{(ref. 42)}$$

2. Reactions Involving Cleavage of the M-E Bond

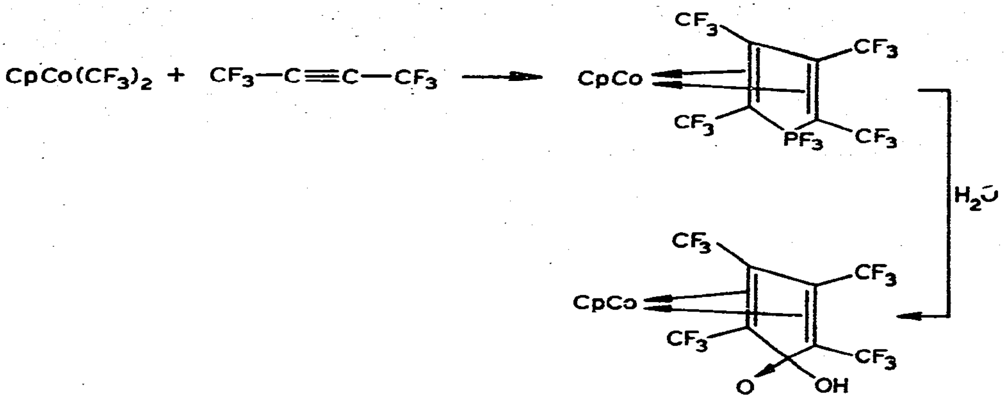
There are in fact a large number of reactions of complexes which fall into this category. For example, ligand exchange reactions, equilibrium processes and geometric isomerization may all involve dissociation of a pnictogen donor ligand from a metal. Inasmuch as these processes do not lead to any chemical modification of the ligand they will not be covered any further. However, there are several systems in which ligand modification does occur. Dobbie, Mason and Porter[114] have found that $FeCp(CO)_2P(G)(CF_3)_2$, where G = O, S or Se, all undergo ligand donor-atom rearrangement upon irradiation. For G = S or Se, the product is simply $CpFe(CO)_2GP(CF_3)_2$. The oxide derivative undergoes more extensive decomposition than the sulfide or selenide complexes, to yield a product analyzed as $Cp_2Fe_3(CO)_2[OP(CF_3)_2]$ which is paramagnetic and may contain a $Fe(OP(CF_3)_2)_2$ group as indicated by mass spectrometry. This type of rearrangement is of particular interest in relationship to an earlier observation by Griffiths and Burg[133]. They found that the structure $(CF_3)_2P(O)H$ was thermodynamically unstable relative to $(CF_3)_2POH$ whereas other phosphinous acid derivatives are known to prefer the phosphine oxide structure.

Einstein and his coinvestigators[134] have characterized the product of the reaction between cis-$Mn(CO)_3(Ph_2PCH_2PPh_2)H$ and CS_2. In this interesting complex, CS_2 is inserted between the metal and one of the phosphorus atoms. The reported structure as shown below also has a hydrogen atom which is thought to be attached to one of the sulfur atoms. Presumably, the carbon disulfide adducts of cis-$M(CO)_3(P\text{-}P)H$, where M is Re or Mn and P-P is $Ph_2PCH_2CH_2PPh_2$ and where M is Re and P-P is $Ph_2PCH_2PPh_2$ have similar structures.



Several reports have appeared regarding the catalytic oxidation of tertiary phosphines and arsines by nitrosyl complexes[85,135] and oxygen[136,137,138] in which an oxygen atom may possibly become positioned between the metal and phosphorus in an intermediate. Halpern and coworkers[136,137] in considering the catalytic oxidation of triphenylphosphine by $Pt(L)_3$ or PtL_4, where L is PPh_3, have postulated the formation of an $L_3Pt(O_2)$ complex which rearranges to $LPt(OL)_2$. Displacement of the oxidized ligand by unoxidized ligand leads to free $OPPh_3$. More recently, $Ru(NCS)(CO)(NO)(PPh_3)_2$ and $Ru(O_2)(NCS)(NO)(PPh_3)_2$[85] as well as $Rh(PPh_3)_3Cl$[138] have been shown to cause phosphine and arsine oxidation. However, as in the work of Halpern, no unequivocal evidence for the presence of an $M\text{-}O\text{-}PPh_3$ intermediate can be cited.

Recently, $CoCp(PF_3)_2$ has been shown to react with hexafluorobut-2-yne through an insertion type reaction to give a complex containing 1,1,1-trifluoro-2,3,4,5-tetrakistrifluoromethylphosphate as a pi-bonded ligand[139]. The product shown below is hydrolysable to the 1-hydroxy-1-oxide complex for which the molecular structure has been determined.



3. Reactions involving coordinated pnictogen acids, acid salts and esters

The reactions considered in the previous two sections all involve changes in a bond to the donor atom of a coordinated ligand. In this section, some reactions which involve the B-C bond of the P-B-C system are considered. These reactions fall into two categories: (1) where BC is OH, SH or O^- R_3NH^+; (2) where B-C is an organic ester group OR.

The hydrolyses of a number of coordinated halophosphine and haloarsine ligands delineated in an earlier section as well as some reactions of diorganophosphine oxides with metal complexes have provided routes to complexes of phosphinous acids (R_2POH), phosphorous acid ($P(OH)_3$), and in some cases quaternary salts ($R_2PO^-R_3\overset{+}{N}H$). Likewise, several complexes of thio analogs have also been made. Subsequent reactions of these coordinated ligands have led to new complexes. For example, Chatt and Heaton[40] noted that *cis*-$PtX_2(MR_2OH)(M'R'_3)$, where M and M' are P or As, R and R' are alkyl or aryl groups and X = Cl, Br, I, were obtained upon hydrolysis of the parent MR_2Cl complexes. Facile elimination of HX yielded bridging complexes

$(M'R'_3)XPt(R_2MO)_2PtX(M'R'_3)$. The reaction was found to be reversible upon treatment with concentrated hydrohalic acid.

Esterification reactions have been carried out with diazomethane on $Mo(CO)_5(PPh_2OH)$[39] and $Mn(CO)_4Br(PMe_2SH)$[140] to yield $Mo(CO)_5(PPh_2OCH_3)$ and $Mn(CO)_4Br(PMe_2SMe)$, respectively, and with $Et_3O^+BF_4^-$ on $Ba[Ni(PF_3)_3(PF_2O)]_2$ and $Ba[Fe(PF_3)_4(PF_2O)]_2$ to yield $Ni(PF_3)_3(PF_2OEt)$ and $Fe(PF_3)_4PF_2OEt)$[41]. Other types of esters have also been prepared. For example, Austin[37] reacted boron halides with platinum complexes containing cis-diphenylphosphinito ligands to prepare some incompletely characterized borate esters. A silicon ester $Mo(CO)_5Ph_2POSiMe_3$ and three diphosphoxane complexes $Mo(CO)_5PR_2OPR_2Mo(CO)_5$, where R=R'=Me, R=R'=Ph or R=Me and R'=Ph, were also made starting with $Mo(CO)_5PR_2OH$ or a quaternary amine salt.[39] Similar procedures were employed to make the complexes $W(CO)_5PMe_2OPMe_2W(CO)_5$ and $W(CO)_5PMe_2SPMe_2W(CO)_5$[42].

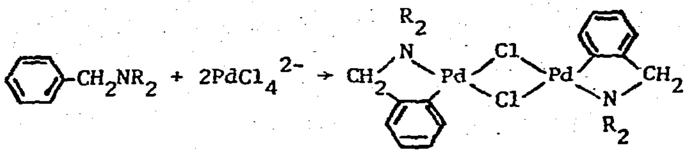
In contrast to the previously cited studies in which complexes of esters were prepared, there have been a number of reports of reactions in which alkyl elimination from a tertiary phosphite ester occurs upon complexation. All of the basic work in this area has been performed by Haines and his coworkers[141-144]. They found that whereas $FeCp(CO)_2I$ and $P(OR)_3$, where R is Me, Et, n-Bu reacted by CO displacement, the corresponding chloride complex gave an intermediate substance $[CpFe(CO)_2P(OR)_3]^+Cl^-$ which undergoes a Michaelis-Arbuzov type rearrangement eliminating RCl and forming $FeCp(CO)_2$-$P(O)(OR)_2$[141,142]. Some $FeCp(CO)(P(OR)_3)(P(O)(OR)_2)$ was also obtained in these reactions. Results of a similar nature, that is elimination of C_3H_5Cl, were obtained with $PPh(OC_3H_5)_2$ and $PPh_2(OC_3H_5)$. Reactions of several esters $P(OR)_3$ (R=Me,Et,i-Pr,n-Bu and C_3H_5) with $[MoCp(CO)_3]_2$ gave a variety of products which included $\{MoCp(CO)_2[P(OR)_3]_2\}\{MoCp(CO)_3\}$, $[MoCp(CO)_2P(OR)_3]_2$, $MoCp(CO)P(OR)_3P(O)(OR)_2$ and $MoCp(CO)_2P(OR)_3R$[143,144]. The last two compounds were reportedly obtained best in refluxing benzene. Exactly how the R group is transferred to the metal atom is not known, but certainly this is a most interesting reaction.

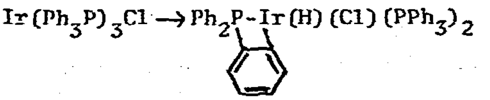
A related type of reaction, but one which probably results from clea of the P-O bond in an ester has been studied by two groups of workers. Levshina, Troitskaya and Shagidullin[145] and Pidcock and Waterhouse[146] have studied the reactions of $PdCl_4^{2-}$ and $PtCl_4^{2-}$ with trialkyl phosphites in an aqueous medium, respectively. Both groups of investigators noted that these reactions lead to complexes in which the phosphite esters have been partially hydrolyzed to yield P-coordinated dialkylphosphonate ligands. However, owing to the presence of water an alkoxy group is probably displaced by water from the coordinated ligand in an $S_N2(P)$ type reaction. As part of a recent study to be discussed in Section 3, we have obtained evidence that the exchange of alkoxy groups on a coordinated phosphorus donor ligand proceeds by inversion at phosphorus and thus must involve P-O bond cleavage.[50]

4. Reactions of Coordinated Pnictogen Ligands Remote from the Donor Site.

The question may be raised as to whether or not the reactions of coordinated ligands at functional sites two or more bonds removed from the donor atom ought to be included in this review. However, the extraordinary interest in phosphorus and arsenic donor ligands and the penchant of coordination chemists to synthesis new ligands have led to some rather remarkable discoveries which are worthy of mention. No attempt was made to cover exhaustively the reactions of coordinated ligands at sites remote from the pnictogen donor site. The examples chosen are merely meant to be illustrative of the range of reactions possible.

a. Metallation Reactions. Several years ago, Parshall[147] reviewed intramolecular aromatic substitution reactions in transition metal complexes. The general nature of the process is shown by several examples cited below.


(ref. 148)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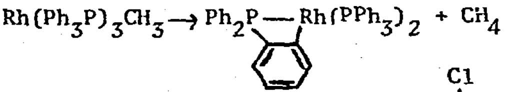
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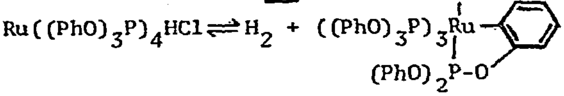
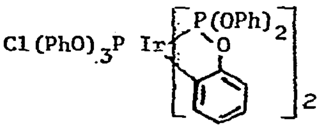
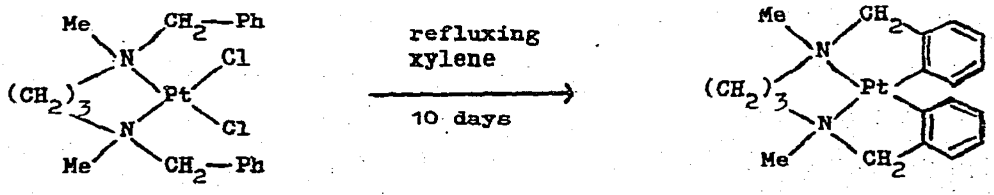

(ref. 151)

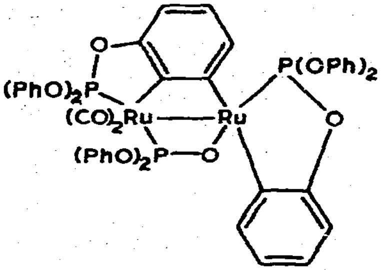
As is apparent from the selected early examples, the metallation of an aromatic ring attached to the donor atom of the coordinated ligand occurs exclusively in the ortho position. This led to the early application of the term o-metallation. Recent examples of studies in this area include a crystal structure determination of



which contains two o-metallated ligands[152], o-metallation of the naphthyl group in PMe_2(1-naphthyl) and PMePh(1-naphthyl)[153], and hydrogen exchange in $Ru(Ph_3P)_3Cl$ by way of o-metallated intermediates.[154] An extremely interesting reaction of a chelating N-donor ligand in which o-metallation is used to obtain a complex with a multidentate organometallic ligand is noted below.[155]

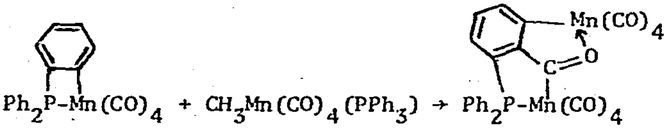


Bruce and coworkers[156] have recently characterized an unusual product obtained in the pyrolysis of $Ru_3(CO)_9[P(OPh)_3]_3$. The reported structure of the complex, as shown below, was found to contain, in addition to an o-metallated $P(OPh)_2(OC_6H_4)$ ligand, a $P(OPh)_2(OC_6H_3)$ ligand in which the dehydrogenated ring was attached through the o-position to one

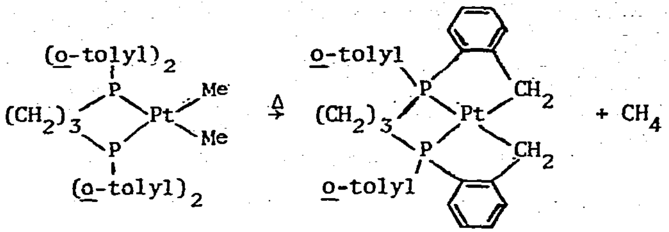


ruthenium atom and through the m-position to the other metal atom.

Recently, Kaesz and his coworkers[157] have found that the o-metallate complex $Ph_2\overline{P-C_6H_4-Mn}(CO)_4$ undergoes a rather unusual reaction with cis-$CH_3Mn(CO)_4(PPh_3)$. As is readily seen from the structure of the product shown below, both carbonyl insertion into the aryl-manganese bond and metallation in the position meta to phosphorus occur.

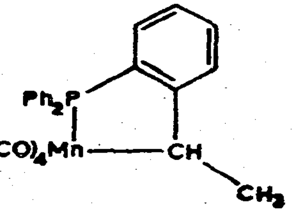


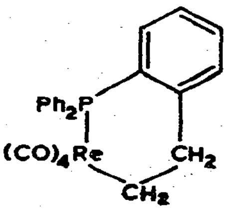
In addition to metallation in the ortho position of an aromatic ring, several examples of metal-carbon bond formation at o-methyl groups of o-tolyl phosphines have been reported[158,159]. Two truly unique examples of this general reaction can be cited. The double metallation of o-$Ph_2P-C_6H_4CH_2CH_2C_6H_4-PPh_2$-o by $RhCl_3\cdot 3H_2O$, $RhCl(PPh_3)_3$ or $[RhCl(1,5\text{-cyclooctadiene})]_2$ to give $RhCl(Ph_2PC_6H_4-CH{=}CH-C_6H_4PPh_2)$ in which the olefinic band is attached in the trans pi configuration to the metal was observed by Bennett and his coinvestigators[160]. Also unique is another double metallation reaction which has led to the formation of a quadridentate organometallic complex of platinum[155] according to the following reaction:



Neither the $PtCl_2$ complex with this same ligand nor the $PtMe_2$ complex with the analogous ligand with two methylene groups between the phosphorus atoms would undergo metallation.

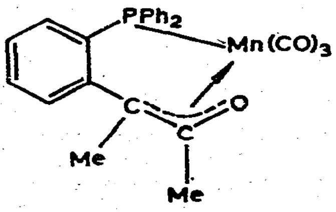
b. Reactions of unsaturated organic groups bound to the pnictogen. Several different types of reactions of coordinated pnictogen donor ligands fall into this category. One of the most popular ligands under investigation during the last few years is (o-vinylphenyl)diphenylphosphine (also called o-styryldiphenylphosphine, or SP). Bennett and Watt[161] have shown that this ligand reacts with $HMn(CO)_5$ to yield the isolable cis-$HMn(CO)_4(SP)$. Upon heating in cyclohexane under nitrogen, this complex rearranges to give a mixture of two chelate complexes containing σ-manganese-carbon bonds resulting from an internal hydrometallation of the olefinic bond. With manganese, the terminal addition of the hydrogen predominated whereas the analogous reaction of $HRe(CO)_5$ with (SP) gave predominantly terminal addition of the metal with the intermediate unchelated complex observable only by ^{1}H-NMR. The structures of the major products are:

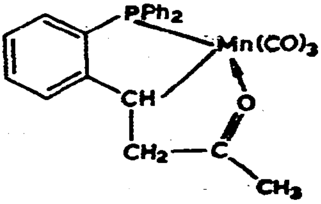




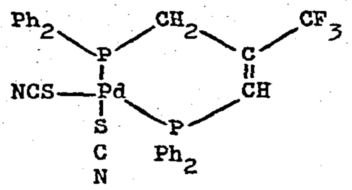
Quite recently, Brookes[162] has reported that hydrometallation reactions occur with a number of Pt(II) complexes, the formation of five-membered chelate rings being favored over six-membered rings. Another study by Brookes[163] has provided the interesting observation that $[Rh(Sp)_2]^+BPh_4^-$ in dichloromethane readily absorbs hydrogen gas at pressures less than one atmosphere to completely hydrogenate the Sp ligand to coordinated (o-ethylphenyl)-diphenylphosphine. Brookes offers the suggestion that hydrogenation may proceed through intermediates such as were noted earlier for the Mn, Re and Pt complexes.

An even more unusual type of rearrangement is involved in the reaction of Sp with $MeMn(CO)_5$[164]. The initial step in this reaction is expected to be formation of cis-$MeCOMn(CO)_4(Sp)$. However, subsequent isomerization occurs with formation of two complexes. Structural studies[165,16 have shown quite clearly that these two complexes arise from formation of a new bond (acyl migration) between the acetyl group and one or the other of the vinyl carbon atoms. The structures of the two complexes are shown below. The complex on the left is of particular interest because pi-oxpropenyl derivatives are considered to be intermediates in reduction of aldehydes and ketones by $HCo(CO)_4$[167].

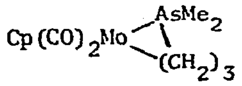
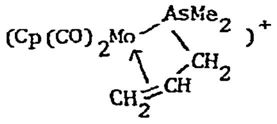




Although phosphinoacetylenes, such as $Ph_2P\text{-}C{\equiv}C\text{-}Me$, are incapable of forming chelate complexes like Sp does[168,169], Carty and Palenik and their coworkers have obtained a number of interesting complexes of the expected types with these ligands[170]. For example, an unprecedented example of net cleavage of an acetylenic triple bond in the reaction of MX_4^{2-} salts (where M = Pd or Pt and X = Cl or SCN) with $Ph_2PC{\equiv}CCF_3$ was discovered. The structure of one of these complexes was shown to be:

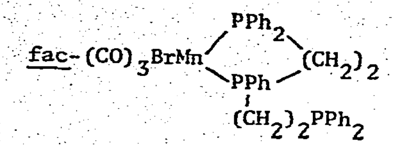


The exact mode of formation of the unusual chelating ligand found in this complex is not known. The authors obtained no evidence for σ-bonded complexes such as are found in methoxide ion attack on $PtCl_2(Ph_2PCH_2C{\equiv}CMe)_2$[171]

Another method of synthesis of chelating organometallic ligand systems was reported by Wainwright and Wild[172]. They found that $MoCp(CO)_2I(Me_2AsCH_2CH_2CH_2Cl)$ can be forced to undergo dehalogenation with Na/Hg in tetrahydrofuran to form  $Cp(CO)_2Mo\langle AsMe_2, (CH_2)_3\rangle$ Proton abstraction with $Ph_3C^+BF_4^-$ yielded a pi-olefin complex ion  $(Cp(CO)_2Mo\langle AsMe_2CH_2CH{=}CH_2\rangle)^+$ which upon treatment with cyanide ion gave $MoCp(CO)_2(CN)AsMe_2CH_2CH{=}CH_2$.

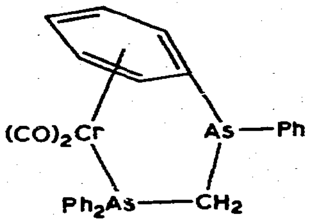
C. Additional Selected Reactions.

In general, many multidentate pnictogen donor ligands have the dual capability of forming either chelate or bridging complexes. Numerous examples of such behavior are known. Inasmuch as a chelation or bridge formation must be a stepwise procedure then one could consider these reactions as reactions of coordinated ligands. A fairly unusual example which illustrates this point is provided in a paper by Schneider, Coville and Butler[173]. They found that triphos$(Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2)$ and $Mn(CO)_5Br$ gave the simple chelated complex:



as a mixture of isomers, owing to the geometric isomerization which arises upon attachment of the medial P atom of the trident ligand to the metal. Subsequent reaction of the mixture with $Cr(CO)_5(THF)$ yielded two complexes which were separated. The molecular structure of one isomer has been reported and the $Cr(CO)_5$ is coordinated to the previously uncoordinated PPh_2 site.

An alternate and unexpected mode of attachment of dam ($Ph_2AsCH_2AsPh_2$ has been reported[174]. The complex $Cr(CO)_5$dam was found upon heating to eliminate three carbonyl groups and form the pi phenyl complex

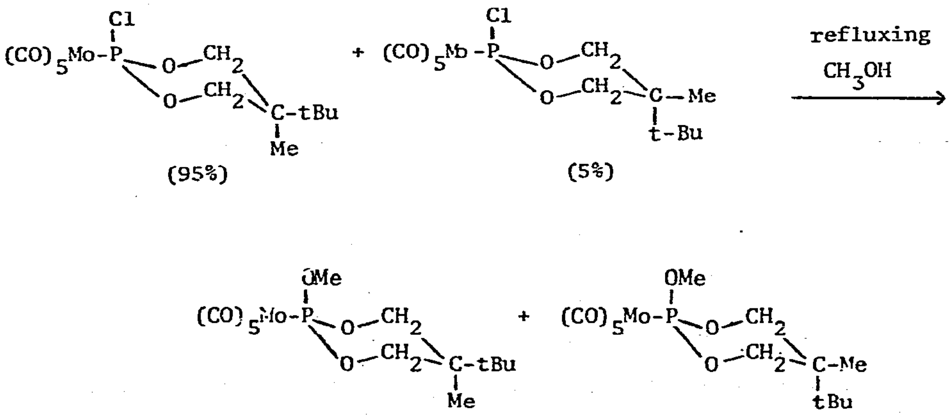


rather than a simple chelate structure. In another unexpected reaction, Nöth and Sze[174] found that the P-Sn bond of $M(CO)_5PPh_2SnMe_3$, where M = Cr, Mo or W, was not cleaved by BCl_3. Instead Sn-C bond cleavage occurred with formation of $M(CO)_5PPh_2SnMe_2Cl$.

In concluding this section, the fact that many other known and potential pnictogen donor ligands have reactive functions or different Lewis base sites remote from the pnictogen donor atom must be noted. For example, complexes of $Ph_2PCH_2CH_2X$, where X is -CN,[176] -NC,[177] and SMe[178] are known. Even quarternization of a remote tertiary phosphine site[179] has been observed. Surely, many other reactions, some predictable, but others not expected, will be found as long as there is interest in the chemistry of complexes of phosphorus and arsenic donor ligands.

C. Stereochemistry of E-A Bond Cleavage Reactions

In general, coordination chemists have focused their efforts primarily upon the types of reactions which coordinated pnictogen donor ligands can undergo and have not performed experiments to determine the stereochemistry of these reactions. Only a single study has been made thus far in which the stereochemistry of cleavage of an E-A bond has been ascertained.[50] The methanolysis of an equilibrium mixture containing 95% cis-5-t-butyl-2-chloro-5-methyl-2-pentacarbonylmolybdenum-1,3,2-dioxaphosphorinane and 5% of the trans isomer was found to yield an equilibrium mixture containing 86-88% trans-5-t-butyl-2-methoxy-5-methyl-2-pentacarbonylmolybdenum-1,3,2-dioxaphosphorinane when carried out in refluxing methanol over 1-2 days. The suggested structures of the substances are shown below.



Time (hrs)	Extent of Reaction (%)	%	%
1	77	24	76
6	92	44	56
17	100	59	41
48	100	86	14

However, closer examination of the reaction revealed that the ratio of methanolysis products formed was a function of the time of reaction. In particular, the major isomer obtained under long reflux times was the minor component under shorter reaction times as can be seen in the reaction diagram. This indicates that methanolysis of the P-Cl bond proceeds by inversion of configuration at phosphorus to yield the kinetically favored product with the 2-OMe and 5-Me groups cis on the heterocyclic ring. Continued contact with refluxing methanol causes this first-formed product to undergo isomerization, also by inversion of configuration at phosphorus, to the thermodynamically favored product in which the two large substituents $Mo(CO)_5$ and t-Bu both occupy equatorial positions on the ring. Based upon this observation, the methonalysis reaction was suggested to proceed by an S_N2-P mechanism by analogy to previous mechanistic studies of organophosphorus compounds.[180,181]

D. Reactivity of E-A Bonds of Coordinated Ligands

Of the four classes of reactions of a coordinated ligand E(A)(B-C)(D⁓Z) considered in this review, cleavage of the E-A bond is of particular interest because of the information that may be revealed regarding the nature of bonding to and by phosphorus. To obtain this information, a body of kinetic data showing the influence of various parameters, --*i.e.* metal, E, A, and the other groups on E, -- upon the rate of cleavage of the E-A bond is desirable. Unfortunately, kinetic data of this type has not been reported as yet and in fact only a few qualitative aspects of the relative rates of E-A bond cleavage are known.

Practically nothing is known regarding the effect of metals upon reactions of coordinated pnictogen donor ligands where A is a halogen. Chatt and Williams[27] report that Pt-PF_3 complexes are highly reactive towards water whereas all other fluoro-[28,31] and chlorophosphine ligands[35,43] are reported to be less reactive toward nucleophilic reagents than the uncomplexed ligands. Whether the Pt-PF_3 system is more reactive to nucleophiles than PF_3 has not been clarified. In general, of the various systems studied so far, E-F bonds do appear to be the most slow to react with nucleophiles and bromo and iodo compounds are the most reactive.

The reason(s) for this lowered reactivity is not completely clear. Nixon[28] was the first to suggest that $d\pi$-$d\pi$ back-bonding may reduce the susceptibility of phosphorus to nucleophilic attack by reducing the effective positive charge on phosphorus as seen by an incoming nucleophile. Alternatively, the partial population of phosphorus d orbitals could raise the activation energy necessary to form a five-coordinate intermediate in an S_N2-P mechanism.[43] Of course, other effects ought also to be considered in any further studies in this area, not the least of which is a steric effect imposed upon complex systems by the metal atom and the other spectator ligands on the metal.

With respect to the E atom of an E-halogen coordinated ligand, phosphorus donor complexes appear to be the most robust toward nucleophiles[30,49] and cleavage with bridge formation[59,60]. Also, as was shown in Sections B.1.f and B.1.h, P-P and P-C bonds appear to be considerably less readily cleaved than As-As or As-C bonds. The fact that most bonds to As are substantially less thermodynamically stable than bonds to phosphorus may account for the greater reactivity of the arsenic compounds.

Several examples from the literature show that the other organic groups attached to a coordinated phosphorus donor ligand can affect ligand reactivity. This effect seems to be predominately an electronic one with steric hindrance playing a lesser role. For example, $Mo(CO)_5PPh_2Cl$ reacts more rapidly with methanol than does $Mo(CO)_5PMe_2Cl$[43] and elimination of HX from various Ph_2PH complexes is much more facile than from dialkyl phosphine complexes.[4,7,8] Although the mechanisms of these two types of reactions are undoubtedly different, since one involves displacement of Cl^- and the other loss of H^+, the greater reactivity of the phenyl ligand may be traced to the greater electron withdrawing capacity of the phenyl group compared to that of alkyl substituents. In the first case the phenyl group may enhance the positive character of phosphorus to nucleophilic attack and in the second pair of complexes the phenyl group not only can stabilize the diorganophosphido residue but may weaken the P-H bond sufficiently to make Ph_2PH the more acidic ligand. We have already pointed out that $(CO)_5MoPPh_2(OH)$ is more acidic than $(CO)_5MoPMe_2OH$.[39] Also, the fact that $(CF_3)_2\ddot{E}$-M complexes, where E is P or As, do not readily dimerize has been attributed to a lowered basicity of $\ddot{E}$ caused by the strong electron withdrawing power of the trifluoromethyl groups on E.

E. Conclusion

Coordinated pnictogen donor ligands exhibit an extensive and varied chemistry. However, effectively all of the published work has been synthetic in nature. Profitable future studies should consider the reaction kinetics and mechanisms of these reactions. Comparisons between various classes of four-coordinate phosphorus compounds will be of particular interest. Finally, the possibility of development of new syntheses of organic compounds based on transfer of groups from a pnictogen donor ligand to unsaturated compounds such as has been shown with triaryl phosphine ligands[127,128] is worthy of examination.

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