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Metal carbonyl complexes of polycyclic phosphite esters

David George Hendricker
Iowa State University

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METAL CARBONYL COMPLEXES OF POLYCYCLIC PHOSPHITE ESTERS

by

David George Hendricker

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In Charge of Major Work

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Head of Major Department

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Dean of Graduate College

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INTRODUCTION

The discovery of nickel tetracarbonyl by Mond in 1890 (1) opened the field of zero-valent metal carbonyl chemistry. Investigation of the corrosion of nickel valves used in piping for a Solvay process plant led to the isolation of a colorless, mobile liquid with a boiling point of 42.4°C. Decomposition of this carbonyl offered a means by which extremely pure metallic nickel could be obtained (2). This process resulted in the construction of several large factories for the refining of nickel, even though the carbonyl was found to be dangerously toxic (3,4).

Recognizing the importance of such zero-valent compounds, Mond and his workers turned their efforts to synthesizing other metal carbonyls. After encountering considerable experimental difficulty, he and Quincke (5) reported their preparation of iron carbonyl on June 29, 1891. He was to learn later, however, that just two weeks previous, Berthelot (6), at a meeting in France, had reported his synthesis of $Fe(CO)_5$. This toxic, golden-yellow liquid which boils at 103°C. has been thoroughly investigated for use as an antiknock additive in gasolines, as attested to by the large number of patents issued for this purpose (7,8,9).

The discovery of the next carbonyl compound, that of molybdenum, was reported after a lapse of 19 years. Mond, Hirtz and Cowap (10) found that Mo$(CO)_6$ could be prepared and isolated only after great difficulty using an activated form of molybdenum metal obtained by hydrogen reduction of the oxychloride. The carbonylation proceeds in low yield only at relatively low temperatures in the presence of carbon monoxide at 200 atm. pressure. The white volatile crystals are soluble in benzene and hydrocarbons, but are insoluble in water.

The hexacarbonyls of chromium and tungsten were reported in 1926 (11) and 1928 (12), respectively. The method of preparation of these cases involved reacting the proper metal halide with a Grignard reagent in the presence of carbon monoxide under pressure. Similarily to molybdenum hexacarbonyl, these compounds are white volatile crystals and possess about the same solubilities. The relative volatility of the Group VI carbonyls is Cr $>$ Mo $>$ W. These compounds have been investigated as sources for dense adherent films of the pure metal, catalysts, lubricant additives, and anti-knock additives for gasoline. The history of the carbonyls of nickel, iron, chromium, molybdenum and tungsten and their development for commercial use is more completely covered in several review articles (2,13,14,15).

It is of interest that although nickel tetracarbonyl was available in research quantities in 1890, no complexes of this compound were reported until 1932. Hieber, who has published over 150 papers on metal carbonyls and their compounds, investigated the reaction of pyridine and orthophenanthroline with nickel tetracarbonyl and reported the following compounds: $Ni(CO)_2$<u>o</u>-phen, $Ni(CO)_2(py)_2$ and $Ni_2(CO)_4(py)_2$ (16). However, the first complexes of metal carbonyls reported were not those of nickel, but of iron. It was Hieber who reported the pyridine adducts of iron carbonyls having the formulas $Fe(CO)_4py$ and $Fe(CO)_3(py)_2$ in 1928 (17). In other papers published in the late twenties and early thirties, he and his coworkers, discussed complexes of iron carbonyls formed with orthophenanthroline (18), ethylenediamine (19), and ammonia (20). The first complexes of the Group VI carbonyls reported are of the following types: $M(CO)_4L_2$, $M(CO)_3L_3$ and $M(CO)_4L'$ where M = Cr, Mo, W; L = pyridine and L' = orthophenanthroline (21,22).

There are three general methods used for the preparation of metal carbonyl complexes. In the sealed tube method, the metal carbonyl and ligand are placed in a tube which is evacuated, sealed, and then heated to the desired temperature for a certain length of time. After cooling, the tube is opened, the evolved carbon monoxide removed, and the products extracted with solvents and purified by sublimation, recrystallization or chromatography. A typical example of this type of reaction is the preparation of $Fe(CO)_3[P(C_6H_5)_3]_2$ as reported by Cotton and Parish (23).

The second method involves a solvent for the reaction medium. The choice of solvent is determined by solubility of the carbonyl, ligand and product, boiling point, possible intermediate formation, and desired amount of substitution. The reaction mixture is then heated or refluxed. Thus, the choice of a high-boiling solvent to obtain higher substitution or for hard-to-react complexes is common. An example of this is the reaction of iron pentacarbonyl with triphenylphosphine using cyclohexanol as the solvent (24). Certain solvents form intermediates with carbonyls (25). Diethylene glycol dimethyl ether, diglyme, has been observed to yield a $Mo(CO)_3 \cdot$diglyme complex in which the diglyme molecule is very susceptible to replacement by other ligands (26).

It is also advantageous to use a solvent in which the ligand and carbonyl are soluble but in which the product is insoluble. The reactivity of metal carbonyl complexes toward air oxidation requires that reactions either be carried out *in vacuo* or under a flush of an inert gas. Reactions of the Group VI carbonyls are further complicated by their ability to sublime out of the reaction flask into the condenser. This results in a change in the concentration ratio of the carbonyl to ligand and makes the preparation of the lower substituted products somewhat more difficult. In many cases the sublimed carbonyl can be returned to the reaction flask by opening the system under a nitrogen flush and scraping the inside of the condenser with a spatula.

The third method of preparation involves the irradiation of a solution of carbonyl and ligand with ultraviolet light. Photochemical production of metal carbonyl complexes has come into general use only in the last few years. An advantage of this method is the relatively quick reaction time compared to the solvent and sealed-tube method. The relatively low temperature at which the reaction is carried out, usually room temperature, does not result in sublimation of the carbonyl out of the reaction mixture and facilitates the preparation of compounds which are difficult to prepare because of their instability at higher temperatures. The mechanism proposed for irradiation reactions is different from that proposed for those involving solvent systems. In a thermal displacement reaction the mechanism proposed is of the Sn2 type, while for irradiation an intermediate form of the Group VI carbonyl of the type $M(CO)_5$ (27) has been observed which has led to the proposal of an Sn1 mechanism. An interesting summary of the photochemical studies of metal carbonyls has been prepared by Strohmeier (28).

Nickel carbonyl complexes of trivalent phosphorus compounds have been quite widely investigated. The phosphine compounds have been the most extensively studied followed by the phosphites, phosphorus halides, and amino phosphines. The most recent interest in this field appears to be in the area of fluoro phosphorus complexes, most of which have been reported in the last few years (29,30,31). One of the movivations behind the wide study of trivalent phosphorus nickel carbonyl complexes was the discovery by Reppe in 1948 (32), that some of these compounds were good catalysts for organic polymerization reactions. Hence, many of the reported complexes are to be found in the patent literature (33-47). Typical polymerization studies are found in references 48, 49 and 50. Table 1 lists the trivalent phosphorus complexes

Table 1. Trivalent phosphorus complexes of nickel tetracarbonyl

---

$Ni(CO)_3PF_3$ (51)

$Ni(CO)_2(PF_3)_2$ (51,52)

$Ni(CO)(PF_3)_3$ (51,52)

$Ni(PF_3)_4$ (53,54)

$Ni(CO)_3PCl_3$ (51)

$Ni(CO)_2(PCl_3)_2$ (51)

$Ni(CO)(PCl_3)_3$ (51)

$Ni(PCl_3)_4$ (45,55)

$Ni(PBr_3)_4$ (54,55)

$Ni(PF_2Ph)_4^d$ (56)

$Ni(PF_2Me)_4$ (56)

$Ni(PCl_2Ph)_4$ (57,58)

$Ni(PCl_2Me)_4$ (58)

$Ni(CO)_2(P_2Cl_4)_2$ (30)

$Ni(CO)(P_2Cl_4)_3$ (30)

$Ni(P_2Cl_4)_4$ (30)

$2Ni(CO)_3P_2Cl_4$ (30)

$Ni(CO)_2(PF_2py)_2^a$ (31)

$Ni(CO)_2[PF_2N(Me)_2]_2^b$ (31)

$Ni(CO)_2[PF_2N(Et)_2]_2^c$ (31)

$Ni(PF_2py)_4$ (31)

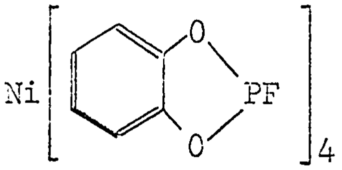
$Ni[PF_2N(Me)_2]_4$ (31)

$Ni[PF_2N(Et)_2]_4$ (31)

$Ni[PCl_2(OPh)]_4$ (57)

$Ni[PF_2(O\text{-}\underline{n}\text{-}Pr)]_4^e$ (29)

$Ni[PF_2(OPh)]_4$ (29)



(29)

---

^{a}py = NC_5H_5.

^{b}Me = CH_3.

^{c}Et = C_2H_5.

^{d}Ph = C_6H_5.

^{e}Pr = C_3H_7, $\underline{n}$ = normal.

Table 1. (Continued)

$Ni(CO)_3P(OMe)_3$ (51,59,60)

$Ni(CO)_2[P(OMe)_3]_2$ (51,59,60,61)

$Ni(CO)[P(OMe)_3]_3$ (51,59,60)

$Ni[P(OMe)_3]_4$ (51,59,62)

$Ni(CO)_3P(OEt)_3$ (50,51,59,63)

$Ni(CO)_2[P(OEt)_3]_2$ (51,59,63)

$Ni(CO)[P(OEt)_3]_3$ (51,57,59,63)

$Ni[P(OEt)_3]_4$ (51,59,62)

$Ni[P\{O(CH_2)_2(CH_2CH_3)(CH_2)_3CH_3\}_3]_4$ (39)

$Ni[P(O\text{-}\underline{n}\text{-}C_{10}H_{21})_3]_4$ (40)

$Ni[P(OCH_2CH_2Cl)_3]_4$ (40)

$Ni[P(OPh)_2(O\text{-}\underline{n}\text{-}C_{10}H_{21})]_4$ (40)

$Ni[P(OPh)_3]_3P(Ph)_3$ (39)

$Ni[P(OC_6H_4\underline{p}\text{-}CH_3)_3]_2[C_2H_4CN]_2$ (33)

$Ni(CO)_3P(O\text{-}\underline{n}\text{-}Bu)_3{}^f$ (59)

$Ni(CO)_2[P(O\text{-}\underline{n}\text{-}Bu)_3]_2$ (35,59)

$Ni(CO)[P(O\text{-}\underline{n}\text{-}Bu)_3]_3$ (59)

$Ni(CO)_3P(OPh)_3$ (49,51,63)

$Ni(CO)_2[P(OPh)_3]_2$ (35,42,49,51,61)

$Ni(CO)[P(OPh)_3]_3$ (49,51,57)

$Ni[P(OPh)_3]_4$ (39,40)

$Ni[P(OPh)_3]_2[P(OEt)_3]_2$ (39)

$Ni(CO)_2[P(OC_6H_4\underline{p}\text{-}F)_3]_2{}^g$ (57)

$Ni(CO)[P(OC_6H_4\underline{p}\text{-}F)_3]_3$ (57)

$Ni(CO)_2[P(OC_6H_4\underline{p}\text{-}NO_2)_3]_2$ (57)

$Ni(CO)[P(OC_6H_4\underline{p}\text{-}NO_2)_3]_3$ (57)

$Ni(CO)[P(OC_6H_4\underline{p}\text{-}OCH_3)_3]_3$ (57)

$Ni[P(OC_6H_4\underline{p}\text{-}OCH_3)_3]_4$ (39,40)

---

[f] $Bu = C_4H_9$.

[g] $\underline{p}$ = para.

Table 1. (Continued)

$\mathrm{Ni(CO)_3P(OC_6H_4\underline{p}\text{-}Cl)_3}$ (57)

$\mathrm{Ni(CO)_2[P(OC_6H_4\underline{p}\text{-}Cl)_3]_2}$ (57)

$\mathrm{Ni(CO)[P(OC_6H_4\underline{p}\text{-}Cl)_3]_3}$ (57)

$\mathrm{Ni(CO)_3PMe_3}$ (64)

$\mathrm{Ni(CO)_2(PMe_3)_2}$ (51,64)

$\mathrm{Ni(CO)(PMe_3)_3}$ (51)

$\mathrm{Ni(CO)_3PEt_3}$ (59,60,64)

$\mathrm{Ni(CO)_2(PEt_3)_2}$ (59,60,64)

$\mathrm{Ni(CO)(PEt_3)_3}$ (59)

$\mathrm{Ni(CO)_2[P(\underline{n}\text{-}Bu)_3]_2}$ (32,63)

$\mathrm{Ni(CO)_3P(Ph)_3}$ (32,50,51, 59,66)

$\mathrm{Ni(CO)_2[P(Ph)_3]_2}$ (32,50,51, 59,66)

$\mathrm{Ni(CO)[P(Ph)_3]_3}$ (59)

$\mathrm{Ni[P(Ph)_3]_4}$ (33,48)

$\mathrm{Ni[P(Ph)_3]_2}$ (33)

$\mathrm{Ni(CO)_3P(\underline{n}\text{-}C_7H_{15})_3}$ (32)

$\mathrm{Ni(CO)_2[P(Ph)_2Et]_2}$ (50)

$\mathrm{Ni(CO)_2[P(Ph)Et_2]_2}$ (50)

$\mathrm{Ni[P(OC_6H_4\underline{p}\text{-}CH_3)_3]_4}$ (39)

$\mathrm{Ni[P(OC_6H_4\underline{o}\text{-}CH_3)_3]_4}^h$ (33)

$\mathrm{Ni(CO)_3P(C_6H_4\underline{p}\text{-}CH_3)_3}$ (36)

$\mathrm{Ni(CO)_3P(CCPh)_3}$ (64)

$\mathrm{Ni(CO)_2[P(CCPh)_3]_2}$ (64)

$\mathrm{Ni(CO)_3P(Ph)_2\ CCC(CH_3)_2OH}$ (64)

$\mathrm{Ni(CO)_2[P(Ph)_2\ CCC(CH_3)_2OH]_2}$ (64)

$\mathrm{Ni(CO)_2C_2H_4(PMe_2)_2}$ (41)

$\mathrm{Ni[C_2H_4(PMe_2)_2]_2}$ (65)

$\mathrm{Ni(CO)_2C_2H_4(PEt_2)_2}$ (44,67,68)

$\mathrm{Ni[C_2H_4(PEt_2)_2]_2}$ (44,67,68

$\mathrm{Ni(CO)_2C_2H_4(PPh_2)_2}$ (41,67)

$\mathrm{Ni[C_2H_4(PPh_2)_2]_2}$ (65,67)

$\mathrm{Ni(CO)_2C_2H_4[P(C_2H_4CN)_2]_2}$ (50)

$\mathrm{Ni(CO)_2CH_2(PMe_2)_2}$ (41)

$\mathrm{Ni(CO)_2CH_2(PPh_2)_2}$ (41)

$\mathrm{Ni[CH_3C(CH_2PPh_2)_3]_2}$ (65)

---

[h] $\underline{o}$ = ortho.

Table 1. (Continued)

$Ni(CO)_2[PH_2(\underline{n}\text{-}C_8H_{17})]_2$	(50)	$Ni(CO)_2C_6H_4(PMe_2)_2$	(67)
$Ni(CO)_2[PH_2(C_2H_4CN)]_2$	(41, 50)	$Ni[C_6H_4(PMe_2)_2]_2$	(67)
$Ni(CO)_2[PH(C_2H_4CN)_2]_2$	(50)	$Ni(CO)_2C_6H_4(PEt_2)_2$	(44,67,68)
$Ni(CO)_2[P(C_2H_4CN)_3]_2$	(41,50, 69)	$Ni[C_6H_4(PEt_2)_2]_2$	(44,65,67)
$Ni[P(Ph)_3]_2C_8H_{12}$	(33)	$Ni(CO)_2C_6H_4(PPh_2)_2$	(67)
$Ni[P(Ph)_3]_2C_{14}H_{12}$	(33)	$Ni[C_6H_4(PPh_2)_2]_2$	(67)
$Ni(CO)_3P(CF_3)_3$	(64)	$Ni(CO)_3(PPh)_4$	(70)
$Ni(CO)_2[P(CF_3)_3]_2$	(64,71)	$2Ni(CO)_3P_2Ph_4$	(37,72)
$Ni(CO)[P(CF_3)_3]_3$	(71,73)	$2Ni(CO)_3P_2Me_4$	(72)
$2Ni(CO)_3P_2(CF_3)_4$	(73)	$Ni(CO)_2C_2H_4[P(CF_3)_2]_2$	(74)
$Ni(CO)_3P(NMe_2)_3$	(75)	$Ni[P(NH_2)_3]_4$	(53)
$Ni(CO)_2[P(NMe_2)_3]_2$	(75,76)	$Ni[P(NC_5H_{10})_3]_2$	(33)
$Ni(CO)_2[P(NMe_2)_2Cl]_2$	(75)	$Ni[P(NCO)_3]_4$	(77)
$Ni(CO)_2[P(NMe_2)_2CN]_2$	(75)	$Ni[P(NCS)_3]_4$	(77)

of nickel tetracarbonyl reported in the literature.

Most of the above compounds were prepared by refluxing the carbonyl and phosphorus ligand in a solvent such as ether, chloroform, or ethanol. Some sealed-tube reactions were also reported. In general, the degree of substitution may be controlled by keeping the reaction temperature within the following limits (51).

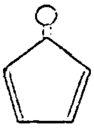
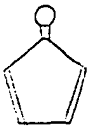
Monosubstitution	-30° to 10°C.
Disubstitution	30° to 50°C.
Trisubstitution	70° to 100°C.
Tetrasubstitution	Greater than 150°C.

The extreme difficulty in substituting all four CO groups to prepare tetrakis-phosphorus ligand-nickel(0) compounds has been circumvented by the reduction of nickel(+2) salts in the presence of the proper phosphorus ligand to give the desired product (40,48,62,65). Some compounds which could not be prepared directly from the carbonyl have been indirectly synthesized by making a substituted carbonyl complex whose ligand(s) are labile to replacement by the desired ligand(s) (54,58). The stability of the carbonyl complexes runs the gamut from those which must be rigorously protected from air, light and heat to those which are very stable. One major difficulty encountered by many investigators is that sometimes the complexes are obtained as oils containing mixtures of several substituted products which defy separation attempts (50). Thus, the study of ligands which give crystalline products is greatly preferred.

Trivalent phosphorus complexes of iron pentacarbonyl are relatively few. Table 2 lists those reported in the literature.

The triphenylphosphine complexes of iron pentacarbonyl were also studied by Rappe as possible catalysts but were found to be ineffective when compared with similar nickel compounds (32). The most likely reason behind the lack of study of trivalent phosphorus complexes of iron pentacarbonyl is their tendency to be oils or liquids. The experimental difficulties resulting from this are adequately described by Clark (78) in his preparation of the PF_3 complexes of $Fe(CO)_5$. Prior to this study, more than two substituents had not been reported for a mononuclear iron carbonyl compound. The preparation of the disubstituted derivatives from $Fe(CO)_5$ requires harsh conditions (23,24). Investigation has shown that though the preparation of complexes from $Fe(CO)_5$ is

Table 2. Trivalent phosphorus complexes of iron pentacarbonyl

$Fe(CO)_4PF_3$ (78)	$Fe(CO)(PF_3)_4$ (78)
$Fe(CO)_3(PF_3)_2$ (78)	$Fe(PF_3)_5$ (78,79)
$Fe(CO)_2(PF_3)_3$ (78)	
$Fe(CO)_3[P(OPh)_3]_2$[a] (35)	$Fe(CO)_2P(OPh)_3$  (56)
$Fe(CO)_4P(Ph)_3$ (23,24,32,80)	$[Fe(CO)_4]_2(PPh)_4$ (70)
$Fe(CO)_3(PPh_3)_2$ (23,24,31,36, 80,81,82,83)	$Fe_2(CO)_6(PPh_2)_2$ (84)
$Fe(CO)_3(PPh_3)(SbPh_3)$ (32)	$Fe_2(CO)_8P_2Ph_4$ (37,84)
$Fe(CO)_2PPh_3$  (56)	$Fe_2(CO)_6(PMe_2)_2$[b] (72,84)
$Fe(CO)_3C_2H_4(PPh_2)_2$ (82,85)	$Fe_2(CO)_8P_2Me_4$ (72,84)
$Fe(CO)_3C_2H_4[P(C_2H_4CN)_2]_2$ (85)	$Fe_2(CO)_6(PEt_2)_2$[c] (84)
$Fe(CO)_4P(NMe_2)_3$ (76)	$Fe(CO)_3[P(NMe_2)_3]_2$ (76)

[a] Ph = C_6H_5.

[b] Me = CH_3

[c] Et = C_2H_5

relatively difficult, the use of $Fe_3(CO)_{12}$ greatly facilitates these reactions (14).

Of the Group VI carbonyls, the trivalent phosphorus complexes of molybdenum have been the most widely investigated. $Mo(CO)_6$ is found to react with phosphorus ligands much more readily than either $Cr(CO)_6$ or $W(CO)_6$. Hence, investigators report complexes of molybdenum carbonyl and only some of chromium and tungsten. Table 3 lists the trivalent phosphorus complexes of molybdenum hexacarbonyl. The compounds of chromium and tungsten hexacarbonyls are given in Tables 4 and 5, respectively.

The replacement by a ligand of four of the six carbonyls of a Group VI compound through direct substitution has been the maximum obtained. The $M(PF_3)_6$ compounds where M = Cr, Mo or W were prepared by the reaction of PF_3 with $M(C_6H_5)_2$ under 100 atm. pressure (86,87). In general the monosubstituted products are prepared in solution at approximately 75°C., while the disubstituted products are obtained at temperatures in the range of 125° to 150°C. The trisubstituted products are usually synthesized by ligand displacement. Easily prepared complexes such as $M(CO)_3\cdot$ether or $M(CO)_3\cdot$cycloalkene are reacted with the desired ligand (L) to give

Table 3. Trivalent phosphorus complexes of molybdenum hexacarbonyl

---

Mo(CO)$_3$(PF$_3$)$_3$ (86,87)

Mo(PF$_3$)$_6$ (86,87)

Mo(CO)$_5$PCl$_3$ (88)

Mo(CO)$_4$(PCl$_3$)$_2$ (88)

Mo(CO)$_3$(PCl$_3$)$_3$ (88,89,90)

Mo(CO)$_2$(PCl$_3$)$_4$ (88)

Mo(CO)$_3$(PCl$_2$Ph)$_3$ (89)

Mo(CO)$_3$(PClPh$_2$)$_3$ (89)

Mo(CO)$_5$PBr$_2$Me (88)

Mo(CO)$_4$(PBr$_2$Me)$_2$ (88)

Mo(CO)$_3$(PBr$_2$Me)$_3$ (88)

Mo(CO)$_5$PCl$_2$OEt[a] (88)

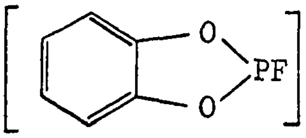
Mo(CO)$_4$(PCl$_2$OEt)$_2$ (88)

Mo(CO)$_3$(PCl$_2$OEt)$_3$ (88)

Mo(CO)$_2$(PCl$_2$OEt)$_4$ (88)

Mo(CO)$_3$(PF$_2$O-*n*-Pr)$_3$[b] (29)

Mo(CO)$_3$(PF$_2$OPh)$_3$[c] (29)

Mo(CO)$_3$  $_3$ (29)

Mo(CO)$_3$[PF$_2$N(Me)$_2$]$_3$[d] (31)

Mo(CO)$_3$(PF$_2$py)$_3$[e] (31)

Mo(CO)$_3$[PF$_2$N(Et)$_2$]$_3$ (31)

Mo(CO)$_5$P(OMe)$_3$ (88)

Mo(CO)$_4$[P(OMe)$_3$]$_2$ (88,90)

Mo(CO)$_3$[P(OMe)$_3$]$_3$ (88,90)

Mo(CO)$_3$[P(OEt)$_3$]$_3$ (88,90,91)

Mo(CO)$_2$[P(OEt)$_3$]$_4$ (90)

Mo(CO)$_5$P(OPh)$_3$ (88)

---

[a] Et = C$_2$H$_5$.

[b] Pr = C$_3$H$_7$, n = normal

[c] PH = C$_6$H$_5$.

[d] Me = CH$_3$.

[e] py = NC$_5$H$_5$.

Table 3 (Continued)

$Mo(CO)_2[P(OMe)_3]_4$ (88)

$Mo(CO)_5P(OEt)_3$ (88,90)

$Mo(CO)_4[P(OEt)_3]_2$ (88,90,91)

$Mo(CO)_5PMe_3$ (88)

$Mo(CO)_4(PMe_3)_2$ (88)

$Mo(CO)_3(PMe_3)_3$ (88,90)

$Mo(CO)_5PEt_3$ (88,91)

$Mo(CO)_4(PEt_3)_2$ (88,90,91)

$Mo(CO)_3(PEt_3)_3$ (88,90,91)

$Mo(CO)_5PPh_3$ (88,92,96)

$Mo(CO)_4(PPh_3)_2$ (88,90,91,99)

$Mo(CO)_3(PPh_3)_3$ (88,89,90, 91,93)

$Mo(CO)_3(PPh_3)(bipy)^f$ (100)

$Mo_2(CO)_8(PMe_2)_2$ (72,84)

$Mo_2(CO)_{10}P_2Me_4$ (72,84)

$Mo_2(CO)_8(PEt_2)_2$ (84)

$Mo_2(CO)_8(PPh)_2$ (72,84)

$Mo(CO)_4[P(OPh)_3]_2$ (88,90,92)

$Mo(CO)_3[P(OPh)_3]_3$ (88,90,92,93)

$Mo(CO)_4\ CH_2(PPh_2)_2$ (94)

$Mo(CO)_2[CH_2(PPh_2)_2]_2$ (94)

$Mo(CO)_4\ C_6H_4(PEt_2)_2$ (94)

$Mo(CO)_2[C_6H_4(PEt_2)_2]_2$ (94)

$Mo[C_6H_4(PEt_2)_2]_3$ (95)

$Mo(CO)_3PhP(C_2H_4PPh_2)_2$ (94)

$Mo[C_2H_4(PMe_2)_2]_3$ (95,97,98)

$Mo(CO)_4\ C_2H_4(PEt_2)_2$ (94)

$Mo(CO)_2[C_2H_4(PEt_2)_2]_2$ (94)

$Mo(CO)_4\ C_2H_4(PPh_2)_2$ (94,101)

$Mo(CO)_2[C_2H_4(PPh_2)_2]_2$ (94,101, 102)

$Mo[C_2H_4(PPh_2)_2]_3$ (95)

$Mo(CO)_2[(PEtPh)_2]_2$(94)

$Mo(CO)_3PhP(\underline{o}\text{-}C_6H_4PEt_2)_2^g$ (94)

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[f] bipy = $N_2C_{10}H_8$.

[g] $\underline{o}$ = ortho.

Table 3 (Continued)

$Mo_2(CO)_{10}\ P_2Ph_4$ (72,84)	$Mo(CO)_3MeC(CH_2PPh_2)_3$ (94)
$Mo(CO)_5(PPh)_5$ (70)	$Mo(CO)_4(PPh)_4$ (103)
$Mo(CO)_5P(NMe_2)_3$ (76)	$Mo(CO)_4[P(NMe_2)_3]_2$ (76)

Table 4. Trivalent phosphorus complexes of chromium hexacarbonyl

$Cr(CO)_3(PF_3)_3$ (86,87)

$Cr(PF_3)_6$ (86,87,104)

$Cr(CO)_3(PCl_2Ph)_3$[a] (89)

$Cr(CO)_3(PClPh_2)_3$ (89)

$Cr(CO)_5PCl_3$ (88)

$Cr(CO)_4(PCl_3)_2$ (88,89)

$Cr(CO)_3(PCl_3)_3$ (88)

$Cr(CO)_5P(OPh)_3$ (91,96)

$Cr(CO)_4[P(OPh)_3]_2$ (91,96,105)

$Cr(CO)_3[P(OPh)_3]_3$ (91)

$Cr(CO)_4[P(O\text{-}\underline{n}\text{-}Bu)_3]_2$[d] (91)

$Cr(CO)_3[P(O\text{-}\underline{n}\text{-}Bu)_3]_3$ (91,96)

$Cr(CO)_5P(NMe_2)_3$[b] (76)

$Cr(CO)_4[P(NMe_2)_3]_2$ (76)

$Cr(CO)_5P(NEt_2)_3$ [c] (96)

$Cr(CO)_5PEt_3$ (88)

$Cr(CO)_4(PEt_3)_2$ (88)

$Cr(CO)_3(PEt_3)_3$ (88)

$Cr(CO)_5PPh_3$ (91,96)

$Cr(CO)_4(PPh_3)_2$ (91,99)

$Cr(CO)_3(PPh_3)_3$ (89)

$Cr_2(CO)_8(PMe_2)_2$ (72,84)

$Cr_2(CO)_{10}P_2Me_4$ (72,84)

$Cr_2(CO)_8(PEt_2)_2$ (84)

$Cr_2(CO)_{10}$ P_2Et_4 (84)

$Cr_2(CO)_8(PPh_2)_2$ (72,84)

$Cr_2(CO)_{10}P_2Ph_4$ (72,84)

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[a] Ph = C_6H_5.

[b] Me = CH_3.

[c] Et = C_2H_5.

[d] Bu = C_4H_9, n̲ = normal.

Table 4 (Continued)

$Cr(CO)_3(PPh_3)_2NH_3$ (106)

$Cr(CO)_5P(n\text{-}Bu)_3$ (91)

$Cr(CO)_4(PEtPh)_2$ (94)

$Cr(CO)_2[(PEtPh)_2]_2$ (94)

$Cr(CO)_4C_6H_4(PEt_2)_2$ (94)

$Cr(CO)_2[C_6H_4(PEt_2)_2]_2$ (94)

$Cr(CO)_3PhP(C_2H_4PPh_2)_2$ (94)

$Cr(CO)_3PhP(o\text{-}C_6H_4PEt_2)_2$[e]

$Cr(CO)_4(PPh)_4$ (103)

$Cr[C_2H_4(PMe_2)_2]_3$ (97,98)

$Cr(CO)_4CH_2(PPh_2)_2$ (94)

$Cr(CO)_2[CH_2(PPh_2)_2]_2$ (94)

$Cr(CO)_4C_2H_4(PEt_2)_2$ (94)

$Cr(CO)_2[C_2H_4(PEt_2)_2]_2$ (94)

$Cr(CO)_4C_2H_4(PPh_2)_2$ (94,101)

$Cr(CO)_2[C_2H_4(PPh_2)_2]_2$ (94,101)

$Cr(CO)_3MeC(CH_2PPh_2)_3$ (94)

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[e] *o* = ortho.

Table 5. Trivalent phosphorus complexes of tungsten hexacarbonyl

$W(CO)_5PCl_3$ (88)

$W(CO)_4(PCl_3)_2$ (88)

$W(CO)_3(PCl_3)_3$ (89)

$W(CO)_3(PCl_2Ph)_3$[a] (89)

$W(CO)_3(PCl_2Ph)_3$ (89)

$W(CO)_5P(OPh)_3$ (91)

$W(CO)_4[P(OPh)_3]_2$ (91)

$W(CO)_3[P(OPh)_3]_3$ (91,107)

$W(CO)_4[P(NMe_2)_3]_2$[b] (76)

$W(CO)_5PEt_3$[c] (88,91)

$W(CO)_4(PEt_3)_2$ (88,91)

$W(CO)_3(PEt_3)_3$ (88,91)

$W(CO)_5PPh_3$ (91,92,95)

$W(CO)_4(PPh_3)_2$ (91,99)

$W(CO)_3(PPh_3)_3$ (89,91)

$W_2(CO)_8(PMe_2)_2$ (72,84)

$W_2(CO)_{10}P_2Me_4$ (72,84)

$W_2(CO)_8(PEt_2)_2$ (84)

$W(CO)_4CH_2(PPh_2)_2$ (94)

$W(CO)_2[CH_2(PPh_2)_2]_2$ (94)

$W[C_2H_4(PMe_2)_2]_3$ (97,98)

$W(CO)_4C_2H_4(PEt_2)_2$ (94)

$W(CO)_2[C_2H_4(PEt_2)_2]_2$ (94)

$W(CO)_4C_2H_4(PPh_2)_2$ (94,101)

$W(CO)_2[C_2H_4(PPh_2)_2]_2$ (94,101)

$W(CO)_4C_6H_4(PEt_2)_2$ (94)

$W(CO)_2[C_6H_4(PEt_2)_2]_2$ (94)

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[a] Ph = C_6H_5.

[b] Me = CH_3.

[c] Et = C_2H_5.

Table 5. (Continued)

$W_2(CO)_{10}P_2Et_4$ (84)	$W(CO)_3MeC(CH_2PPh_2)_3$ (94)
$W_2(CO)_8(PPh_2)_2$ (72,84)	$W(CO)_3PhP(C_2H_4PPh_2)_2$ (94)
$W_2(CO)_{10}P_2Ph_4$ (72,84)	$W(CO)_3PhP(\underline{o}\text{-}C_6H_4PPh_2)_2$[d] (94)
$W(CO)_5(PPh)_5$ (70)	$W(CO)_4(PPh)_4$ (103)

[d] $\underline{o}$ = ortho.

the product $M(CO)_3L_3$ (18,26,89,102).

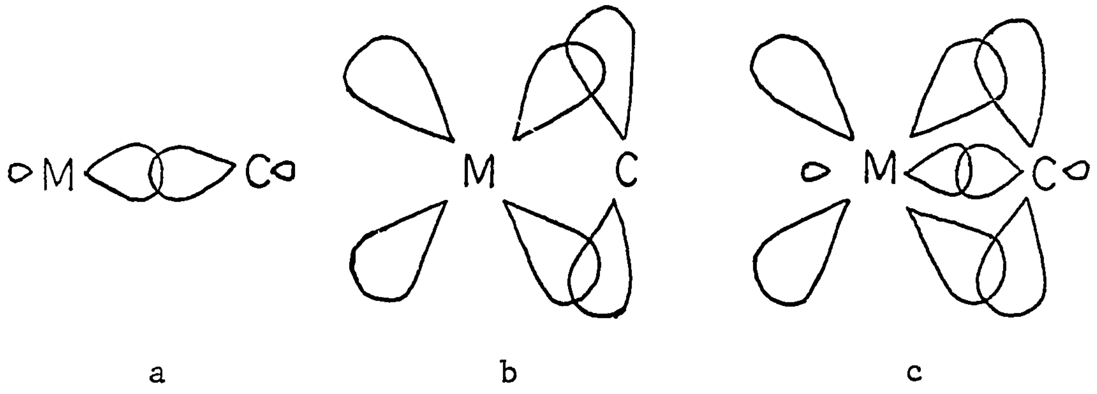
It is of interest to note that octahedral configuration will give rise to possible cis and trans isomers for the di- and trisubstituted species. Indeed, investigators have succeeded in isolating by crystallization and chromatography both isomers for several compounds (108). The rate of isomerization and relative stabilities of the cis and trans forms of some of these compounds have been studied (88). Since the Group VI carbonyls are crystalline in nature, their complexes are usually solids, which has greatly aided the investigation of these compounds. In general, the Group VI carbonyl compounds are found to be much more stable toward air, light, and heat than their iron and nickel analogs.

The question of type of bonding involved in metal carbonyls presented an interesting problem from the outset. Mond proposed that the structure of $Ni(CO)_4$ was Ni[-C(O)C(O)C(O)C(O)-] (2) since nickel was always in a +2 state in complexes. Similarily he proposed that the structure of $Fe(CO)_5$ was OC-Fe[-C(O)C(O)C(O)C(O)-] (2) in keeping with the +3 nature of iron. Since then, the structure of $Ni(CO)_4$ has been unequivocally established to be tetrahedral (109,110,111), and that of $Fe(CO)_5$ to be trigonal bipyramidal (23,111,112).

The first theoretical attempt to explain the bonding in metal carbonyls and their compounds was through the use of the "Effective Atomic Number", EAN, concept (113). It was observed that all known carbonyl compounds possessed an electronic configuration in which the central metal atom had completed its electron shell to the structure of that of the next inert gas by using electrons obtained through coordinate covalent bonding with the CO groups. It was postulated that any compound that could attain an EAN without existing as a charged species should be volatile, as indeed the carbonyls are (114). Structures for known carbonyls were postulated on the basis of EAN, and the absence of mononuclear carbonyls of odd atomic number metals was held as evidence in support of this treatment (115). Many of the structures postulated by this method were later shown to be erroneous, and some carbonyl compounds which do not fit the EAN scheme have been discovered (111). As a formalism, however, the EAN concept still retains considerable utility.

The tetrahedral geometry of $Ni(CO)_4$ presents an interesting challenge to interpretation of the bonding in the system. A structure might be proposed in which the CO groups are bonded to the central nickel atom through four *sigma*-

bonds; however, this would result in an extremely high charge density on the central atom. A study of the atomic orbitals shows that for the nickel d8 electronic configuration the nonbonding d orbitals are filled. These orbitals are of the proper symmetry to overlap the empty p antibonding orbitals on the CO groups (116) giving rise to *pi*-bonds. Such a *pi*-bond can then allow the central atom to reduce the charge density caused by electron donation through the *sigma*-bonds. This action is referred to as back donation or d-*pi* p-*pi*-bonding. A M-C *sigma*-bond, a, a M-C *pi*-bond, b, and the result of combining them, c, are shown below:



For the sp^3 tetrahedral geometry of $Ni(CO)_4$, it has been shown that only the dz^2 and dx^2-y^2 orbitals of the metal atom can overlap with the ligand orbitals to form *pi*-bonds (117). This leads to the conclusion that there are two strong *pi*-

bonds and two weak bonds of mostly sigma character in the $Ni(CO)_4$ structure. This hypothesis might be substantiated if the M-C and C-O bond orders in this compound could be determined exactly.

Probably the most widely studied physical property of carbonyls and their complexes is their infrared spectra. The carbonyl stretching frequency, observed in the region of 4.7 to 5.6 microns, has been used almost universally as a tool for estimating the bond order in these compounds (88,108, 109). By comparing the C-O stretching frequency observed for a metal carbonyl with those found for $C=O$ and $C\equiv O$ systems, it has been concluded that the C-O bond order in metal carbonyls is approximately two and one-half, $C\overset{\cdots}{=}O$ (111). It should be pointed out here that the expected M-C bond order when the bond order in the CO groups is two is also two, and when the C-O bond order is three a single M-C bond is expected. These two limiting cases, a and b, and the bond orders predicted for a metal carbonyl, c, from the infrared spectra, are shown below:

$M-C\equiv O$	$M=C=O$	$M\overset{\cdots}{-}C\overset{\cdots}{=}O$
a	b	c

From c we note that the average M-C bond order predicted from the infrared spectra is one and one-half, which would be expected for two strong pi-bonds and four sigma-bonds.

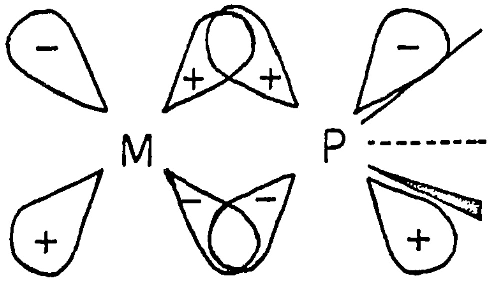
The carbonyl stretching frequency has been found to be sensitive to many factors, one of which is the charge density on the central atom. In the isoelectronic series $Ni(CO)_4$, $Co(CO)_4^-$, $Fe(CO)_4^=$, the frequencies observed are 2057, 1886, and 1786 cm^{-1}, respectively (118). Thus, as the negative charge on the central atom increases, the C-O stretching frequency decreases. This implies that the greater the negative charge on the central atom, the less the C-O bond order and consequently, an increase in the M-C bond order would be predicted. This is exactly what would be expected to happen through back donation of the excessive negative charge on the central atom through pi-bonding.

In a Raman study of this same isoelectronic series, Stammreich, Kawai, and Sala (109) measured both the C-O and M-C stretching frequencies and estimated bond orders from the calculated force constants. They concluded that the observed increase of the M-C force constant with the increase in electronic charge must be attributed to an increase in pi-bonding. Their estimations of the M-C bond orders in $Ni(CO)_4$,

$Co(CO)_4^-$, and $Fe(CO)_4^=$ were 1.33, 1.89, and 2.16, respectively (109).

The carbonyl stretching frequencies have been found to vary when other ligands are substituted for the carbonyls. In all cases, with the exception of NO (119), such substitution results in a decrease in the C-O stretching frequency. The amount of decrease depends upon the type of ligand and the number of carbonyls replaced. In general, the trivalent phosphorus complexes of carbonyls are found to have higher stretching frequencies than analogous substituted amine complexes (108,120). Among the trivalent phosphorus compounds, phosphorus halides are found to exhibit the highest C-O stretching frequency, followed by phosphites and then phosphines in carbonyl complexes of the same order of substitution (63,108). In some studies the M-C stretching frequencies have also been measured. Indeed the M-C stretching frequencies seem to be complementary to the C-O stretching frequencies in that a decrease in the C-O stretch is accompanied by a similar increase in the frequency of the M-C stretch (51). The interpretation of this behavior in terms of <u>pi</u>-bonding in these complexes will now be discussed.

The substituted ligand may be considered to donate a lone pair of electrons to the metal atom in a manner similar to CO. The metal may also donate some of the charge density back to the ligand by use of a pi-bond formed by the overlap of filled metal d orbitals with empty d orbitals of a trivalent phosphorus-containing ligand as shown below. Since



the phosphorus ligand is not quite as strong a pi-bonder as the replaced CO group, the remaining CO groups are forced to participate in slightly more pi-bonding to equalize the charge density on the metal atom. Thus, one would expect a slight increase in the M-C bond order which necessitates a slight decrease in the C-O bond order due to electron transfer from the metal to the antibonding pi-orbital of CO. Hence, a slight decrease in the C-O stretching frequency is predicted and indeed is observed.

If the ligand is a trivalent nitrogen, it is assumed that no empty d orbitals are energetically available for pi-bonding, and thus for these ligands no back donation is predicted.

In this case, the remaining CO groups are forced to participate in much more pi-bonding to equalize the charge density on the metal atom. Thus, one would expect a large increase in the M-C bond order complimented by a large decrease in the C-O bond order. Hence, a large decrease in the C-O stretching frequency is predicted and indeed is observed. Therefore, ligands of strong pi-bonding ability will be expected to reduce the C-O stretching frequency only slightly on substitution in a metal carbonyl, while ligands of little or no pi-bonding ability will be expected to reduce the C-O stretching frequency markedly.

The relative ability of ligands to pi-bond has been studied by Chatt and others (121,122) in the platinum and palladium halide complexes. From the trans effect they concluded that $PX_3 > P(OR)_3 > PR_3 > NR_3$ in pi-bonding ability (123). A similar spectrochemical series has been developed by Horrocks and Taylor (119) from a study of cobalt nitrosyl carbonyl complexes by infrared spectroscopy. In this study both the C-O and N-O stretching frequencies were used to determine the relative positions of the ligands. Many other studies of the C-O stretching frequencies in carbonyl complexes have led to the same relative order of pi-bonding ability (63,108).

In order to draw any quantitative conclusions from the carbonyl stretching frequencies, it is necessary to assign frequencies to their proper vibrational modes. For the system $Ni(CO)_{4-x}L_x$, the C-O stretching modes expected for both square planar and tetrahedral geometry and their activities are given in Table 6 (51,124,125).

Table 6. C-O stretching modes and activities for the system $Ni(CO)_{4-x}L_x$

Compound	Geometry	Symmetry	C-O stretching modes	Activity
$Ni(CO)_4$	Tetrahedral	T_d	A_1	R[a]
			F_1	R and IR[b]
	Square planar	D_{4h}	Eu	IR
			A_{1g}, B_{1g}	R
$Ni(CO)_3L$	Tetrahedral	C_{3v}	$2(A_1 + E)$	R and IR
	Square planar	C_{2v}	$3(2A_1 + E)$	R and IR
$Ni(CO)_2L_2$	Tetrahedral	C_{2v}	$2(A_1 + B_1)$	R and IR
	<u>cis</u>-Square planar	C_{2v}	$2(A_1 + B_1)$	R and IR
	<u>trans</u>-Square planar	D_{2h}	Ag	R
			B_{2u}	IR
$Ni(CO)L_3$	Tetrahedral	C_{3v}	A_1	R and IR
	Square planar	C_{2v}	A_1	R and IR

[a] R = Raman.

[b] IR = Infrared.

The symmetry types and activities of the C-O stretching modes for the trigonal bipyramidal system $Fe(CO)_{5-x}L_x$ are given in Table 7 (23,124,125).

Table 7. C-O stretching modes and activities for the trigonal bipyramidal system $Fe(CO)_{5-x}L_x$

Compound	Ligand configuration	Symmetry	C-O stretching modes	Activity
$Fe(CO)_5$		D_{3h}	E', A_2''	IR[a]
			$2A_1'$, E'	R[b]
$Fe(CO)_4L$	axial	C_{3v}	$2A_1$, E	R and IR
	equatorial	C_{2v}	$2A_1$,B_1,B_2	R and IR
$Fe(CO)_3L_2$	<u>trans</u>	D_{3h}	E'	R and IR
			A_1'	R
	<u>cis</u>	C_s	$2A'$, A''	R and IR
$Fe(CO)_2L_3$	<u>trans</u>	D_{3h}	A_2''	IR
			A'	R
	<u>cis</u>	C_s	$2A'$	R and IR
$Fe(CO)L_4$	axial	C_{3v}	A_1	R and IR
	equatorial	C_{2v}	A_1	R and IR

[a] IR = Infrared.

[b] R = Raman.

The symmetry types and activities of the C-O stretching modes for the octahedral system $M(CO)_{6-x}L_x$ are given in Table 8 (88,124,125).

Table 8. C-O stretching modes and activities for the octahedral system $M(CO)_{6-x}L_x$

Compound	Ligand configuration	Symmetry	C-O stretching modes	Activity
$Mo(CO)_6$		O_h	A_{1g}, E_g	R[a]
			F_{1u}	IR[b]
$Mo(CO)_5L$		C_{4v}	$2A_1$, E	R and IR
			B_1	R
$Mo(CO)_4L_2$	cis	C_{2v}	$2A_1$,B_1,B_2	R and IR
	trans	D_{4h}	Eu	IR
			A_{1g}, B_{1g}	R
$Mo(CO)_3L_3$	cis	C_{3v}	A_1, E	R and IR
	trans	C_{2v}	$2A_1$, B	R and IR
$Mo(CO)_2L_4$	cis	C_{2v}	A_1, B	R and IR
	trans	D_{4h}	A_{2u}	IR
			A_{1g}	R
$Mo(CO)L_5$		C_{4v}	A_1	R and IR

[a] R= Raman.

[b] IR = Infrared.

It is obvious that in many cases the number of observed carbonyl stretching frequencies is commensurate with only one geometry for a given compound. This is a major tool in distinguishing between a cis or trans isomer of compounds of the type $M(CO)_4L_2$. The cis isomer is expected to exhibit four bands which are both infrared and Raman active, while the trans isomer is expected to give rise to one infrared and two Raman active bands (126). However, the infrared spectrum of the trans isomer has been observed to give rise to one strong and two weak bands (92). The most reasonable interpretation of these weak bands is that they are the A_{1g} and B_{1g} fundamentals which gain a slight intensity since the three-fold symmetry of the ligand reduces the true molecular symmetry to C_1 (127). In a C_1 symmetry, the A_{1g} and B_{1g} modes become A' modes and are then infrared active (125). In order to make unambiguous assignments, it is necessary to obtain Raman spectra.

Cotton and Kraihanzel (108,127,128) have proposed a simple model for analyzing and assigning infrared frequencies of molecules of the type $M(CO)_{6-x}L_x$. Their theory involves qualitative and semiquantitative inferences as to the signs and relative magnitude of the C-O stretching force constants and the coefficients of quadratic interaction terms coupling the stretching motions of different CO groups. This method has been used to treat a large number of trivalent phosphorous, amine, and sulfur complexes of $M(CO)_6$ for which the infrared spectra are reported in the literature. In some cases incorrect assignments of frequencies have been eliminated by this treatment. Estimates of the absolute values of the C-O bond orders and attempts to semiquantitatively relate the relative _pi_-acceptor strength of various ligands have been made. This relative _pi_-acceptor strength order lists $PX_3 > P(OR)_3 > PR_3 \gg$ amines (108,127,128).

The relative _pi_-acceptor strength of PF_3 in complexes is shown to be greater than that of CO from calculations of the C-O force constants for the series $Ni(CO)_{4-x}(PF_3)_x$ where x = 1, 2, or 3 and $Mo(CO)_3(PF_3)_3$ (108). It is known that PF_3 will not form a complex with BF_3 (129) in spite of the fact that BF_3 is a good Lewis acid. Thus the lone pair of PF_3 must not be available for _sigma_-bonding; hence, the bonding in PF_3 carbonyl complexes must be considerably _pi_ in nature.

A Raman study of $Ni(PF_3)_4$ (130) has been interpreted to indicate that the force constant for the Ni-P bond is in the range expected for a single bond. This same study also concluded that the Ni-C bond in $Ni(CO)_4$ was in the range of a single bond. A more recent Raman study of $Ni(CO)_4$ (109) has confirmed the force constant value but the data is interpreted to indicate a M-C bond having a minimum order of 1.33. It is also relevant that a Raman study of the complex $Ni[P(OCH_3)_3]_4$ (51) resulted in a calculated value of 2.8 mdyn/Å for the M-P bond force constant which is quite similar to the value of 2.71 mdyn/Å reported for $Ni(PF_3)_4$ (130).

Further support for the strong _pi_-bonding ability of PF_3 is drawn from a comparison with $P(CH_3)_3$ in the complexes $Ni(CO)_3L$. From the C-O and M-C stretching frequencies observed for these complexes, Bigorgne and Zelwer (51) calculated the M-C bond orders to be 1.85 for the $P(CH_3)_3$ complex and 1.4 for the PF_3 compound. This can be interpreted to imply that PF_3 is a better _pi_-bonding ligand than $P(CH_3)_3$ because the M-C bond order is less for PF_3 than $P(CH_3)_3$.

Direct support from infrared evidence that a decrease in the C-O stretching frequency implies an increase in the M-C bond order can be drawn from a study of the $Ni(CO)_{4-x}L_x$ system by Bigorgne and Zelwer (51) where $x = 1, 2$ or 3 and $L = P(CH_3)_3$ or $P(OCH_3)_3$. They observed both the M-C and C-O stretching frequencies as a function of substitution and found that they were almost linear and complementary. From calculations of the force constants for the Ni-C and C-O bonds in these systems, they concluded that the Ni-C bond order is greater for a $P(CH_3)_3$ complex than its $P(OCH_3)_3$ analog. This may be interpreted to imply that $P(OCH_3)_3$ is a better pi-bonding ligand than $P(CH_3)_3$. However, Bigorgne and Zelwer (51) feel that the basicity of a ligand rather than its pi-bonding ability more adequately explains the infrared spectra and other physical properties of its carbonyl complexes.

In a study of several phosphine complexes of the type $Ni(CO)_{4-x}L_x$ where x = 1 or 2 and L = a phosphine ligand, Bigorgne (64) observed that a linear relationship between the C-O stretching frequency and sigma*, the Taft polar substituent constant, exists. It was also found that the analogous PF_3 derivatives follow this relationship. Thus it appears that the variation in the C-O stretching frequency may be attributed to the difference in inductive effects in the ligands. Therefore, the pi-bonding in the PX_3 and PR_3 complexes must be approximately the same and very weak or nonexistent. It is interesting to note, however, that no phosphites fall on this linear plot. Bigorgne (64) suggests that this descrepancy may be due to improper sigma* values.

In further support for the contention that the basicity of the ligand is the predominant influence, he cites the relative thermal stabilities of the monosubstituted carbonyl complexes. Here we find that as the basicity of the ligand increases so does the stability, e.g. $Ni(CO)_3P(CH_3)_3$ is much more stable than $Ni(CO)_3PF_3$ (51); $P(CH_3)_3$ is much more basic than PF_3. The relative ease of isolation of the different substituted carbonyl complexes of strongly basic ligands such as $P(CH_3)_3$ compared with the extreme difficulty encountered in attempts to isolate the different substituted products of PF_3 which is a weak base, has also been attributed to the difference in bacisities (51).

Poilblanc and Bigorgne (88) have conducted a similar study with the Group VI carbonyl derivatives of trivalent phosphorus compounds. Again they observe that a decrease in the C-O stretching frequency is accompanied by a similar increase in the M-C stretching frequency and that these changes became more pronounced as the ligand became less electronegative. Therefore, they concluded that the origin of the variation of the frequencies within the derivatives of the $M(CO)_{6-x}L_x$ system is essentially inductive and that the metal discharges any increase in charge due to ligand coordination by equal distribution via pi-bonds to the remaining CO groups. Confirmation of this conclusion from a study of amine substituted Group VI carbonyl complexes is claimed by Poilblanc (120).

Dipole moment studies have been employed in an attempt to estimate the M-L bond strength in carbonyl complexes (60, 67,94,131). If pi-bonding takes place, it might be expected that back donation would result in partial neutralization of the large dipole moment associated with single coordinate bonds. In order to make meaningful calculations it is first necessary to accurately estimate the M-CO moment, the $P-R_3$ moment, and the geometry of the compound. Chatt and Hart (67,131) have reported dipole moment studies of $Ni(CO)_4$ complexes of tertiary phosphines and arsines. From their data they were able to estimate that the Ni-P bond order was 1.4 to 1.7, thus indicating that pi-bonding is a major factor in the bonding in these compounds. A similar study (94) carried out using the same ligands with Group VI carbonyls led to the same conclusions as to pi-bonding.

Bigorgne and Messier (60) have reported the dipole moments of the following nickel carbonyl complexes: $Ni(CO)_3P(OCH_3)_3$, $Ni(CO)_2[P(OCH_3)_3]_2$, $Ni(CO)[P(OCH_3)_3]_3$,

$Ni(CO)_3P(C_2H_5)_3$, and $Ni(CO)_2[P(C_2H_5)_3]_2$. Their calculations substantiate the findings of Chatt and Hart (67,131) as to the relative Ni-P bond order. The results of studying the $P(OCH_3)_3$ derivatives as a function of substitution indicate that the charge on each ligand of the substituted derivatives decreases linearly with an increase in the degree of substitution. This is consistent with the interpretation given the bonding in metal carbonyl complexes from observation of the C-O stretching frequencies in the infrared spectra.

Some investigation of the kinetics and mechanism of reaction of metal carbonyls and their complexes has been carried out. Meriwether and Fiene (63) have studied the exchange rates of several complexes of the type $Ni(CO)_2L_2$ with L' where L and L' were different trivalent phosphorus ligands. The reaction was found to be first-order in complex and independent of the added phosphine. For the rate determining dissociation step they postulated the following mechanism: $Ni(CO)_2L_2 \rightleftarrows Ni(CO)_2L + L$. No direct spectroscopic or other evidence for the presence of a tricoordinate nickel species was observed indicating that its equilibrium concentration must be extremely low. The rates of dissociation were found to follow the order $PCl_3 \gg P(C_2H_4CN)_3 \sim P(C_6H_5)_3 > P(n\text{-}C_4H_9)_3$

$\gg P(OC_2H_5)_3 \sim P(OC_6H_5)_3$.

This series does not follow either the order of basicity or pi-bonding ability for these ligands. It would follow the order of basicity if the phosphites were located between PCl_3 and $P(C_2H_4CN)_3$. From this study they concluded that alkoxy and aryloxy phosphorus compounds appear to greatly increase the Ni-P bond strength. This is even observed in mixed carbonyl complexes where one of the two ligands is a phosphite. Since PCl_3 which is considered to be strongly pi-bonding exchanged at a rapid rate, they concluded that pi-bonding is relatively less important than previously thought. Considering the bulkiness of the ligands studied, it appears that the dissociation rate decreases with an increase in the size of the ligand.

In a study of the exchange rates of the carbonyl groups of $Ni(CO)_4$ and some of its mono- and disubstituted trivalent phosphorus complexes using radioactive carbon monoxide (132), the rate of CO exchange was found to decrease in the order $Ni(CO)_4 > Ni(CO)_3PR_3 > Ni(CO)_2(PR_3)_2$. The mechanism for exchange in $Ni(CO)_4$ was postulated to proceed as follows: $Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO$. The reason for choosing an Sn1 mechanism is that in the tetrahedral system only two orbitals are available to pi-bond whereas in an sp^2 type of intermediate three orbitals are available for pi-bonding (133). The rate of exchange of CO in $Ni(CO)_2(PR_3)_2$ complexes was found to decrease with increasing basicity of the PR_3 group. This behavior would be expected from *pi*-bonding arguments which predict a stronger M-C bond for a highly basic group, and a weaker M-C bond for the more weakly basic PR_3 ligands which would be expected to *pi*-bond more strongly.

The kinetics of the reaction of $Mn(CO)_5X$ where X = Cl, Br, or I with several trivalent phosphorus ligands (L) to yield $Mn(CO)_4XL$ has been studied by Angelici and Basolo (134). They observed that the rate of reaction decreased with increasing atomic number of X and was dependent neither on the nature of L nor its concentration. A mechanism involving a five coordinate intermediate resulting from the dissociation of a CO from $Mn(CO)_5X$ is postulated as the rate-determining step. A study of the C-O stretching frequencies of the compounds prepared by these reactions gave the order of $PCl_2(C_6H_5) \gg P(OCH_2)_3CCH_3 > P(OC_6H_5)_3 \gg P(O\text{-}\underline{n}\text{-}C_4H_9)_3 > Sb(C_6H_5)_3 \sim As(C_6H_5)_3 \sim P(C_6H_5)_3 > P(\underline{n}\text{-}C_4H_9)_3$ for *pi*-bonding ability.

In another study (135), they reported the rates of reaction of L' with $Mn(CO)_4LX$ to form $Mn(CO)_3LL'X$ where X = Cl, Br, or I with L and L' being trivalent phosphorus ligands.

The rates of reaction were found to be independent of the nature of L', to decrease with X in the order Cl > Br > I, and to decrease with L in the order $P(C_6H_5)_3 > As(C_6H_5)_3 > P(n\text{-}C_4H_9)_3 \sim PCl(C_6H_5)_2 > P(OC_6H_5)_3 \sim Sb(C_6H_5)_3 > PCl_2(C_6H_5) \sim P(O\text{-}\underline{n}\text{-}C_4H_9)_3 > P(OCH_2)_3CCH_3$. The reaction mechanism is postulated to involve a dissociation of one of the CO groups from $Mn(CO)_4LX$ to form a five coordinate intermediate which then reacts with L' to give $Mn(CO)_3LL'X$. The near-ultraviolet spectra of the complexes have been interpreted to indicate that phosphites are better <u>pi</u>-bonding ligands than phosphines.

The rates of isomerization of several trivalent phosphorus complexes in compounds of the type $Mn(CO)_3L_2Br$ have been studied by Angelici, Basolo and Poe (136). The <u>cis</u> and <u>trans</u> isomers of $Mn(CO)_3L_2Br$ have been reported where L = $PCl_2(C_6H_4)$, $P(OC_2H_5)_3$ and $P(\underline{n}\text{-}C_4H_9)_3$. The rate of isomerization was found to depend on the size of L, with the larger L isomerizing from the <u>cis</u> to the <u>trans</u> form most readily. The presence of excess L was found to measurably increase the rate of isomerization. The rate was also found to increase with increases in temperature. In general, the <u>cis</u> compound was prepared by reacting $Mn(CO)_5Br$ with the appropriate ligand at 37°C. The isomerization rates were then studied at temperatures from 40-70°C., by following the changes in the C-O stretching region of the infrared spectra. A study of cis-trans isomerization in the complexes $Mo(CO)_4[P(C_2H_5)_3]_2$ and $Mo(CO)_3[P(OC_2H_5)_3]_3$ has been reported by Poilblanc and Bigorgne (88). They conducted their studies at 45°C., and observed a transition from the cis to the trans form with a half life of about 15 hours.

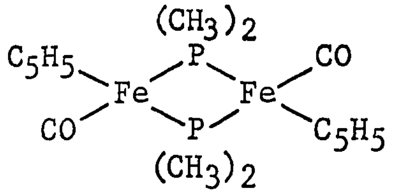
Nuclear magnetic resonance, n.m.r., studies of carbonyls and their complexes have been relatively few. The C^{13} and O^{17} n.m.r. spectra of iron and nickel carbonyl have been reported to exhibit single lines (137). An earlier study of the C^{13} spectrum of iron carbonyl by Cotton (138) was carried out in an attempt to substantiate the proposed trigonal bipyramidal structure. Only a single line was observed instead of the expected two in a 3:2 ratio for a trigonal bipyramidal structure. In the same paper, a study of the far infrared spectrum indicated D_{3h} symmetry. To explain the observed single line in the n.m.r. spectrum, rapid CO exchange or a chemical shift smaller than 40 c.p.s., which was the area covered by the single line, were postulated.

The first reported n.m.r. study of carbonyl complexes was that of the P^{31} spectra of eleven disubstituted complexes of $Ni(CO)_4$ in which the ligands were phosphines, phosphites and phosphorus halides (139). Also reported by Meriwether and Leto (139) was a similar study of trivalent phosphorus ligands for mono-, di-, tri- and tetrasubstituted $Ni(CO)_4$ complexes. The downfield shifts from free ligands to the $Ni(CO)_2L_2$ species were observed to increase in the order $P(OR)_3 > PR_3$, while the PCl_3 complex was observed to shift to higher field. By varying the number of substituted ligands from one to four an increase in phosphorus shielding was observed for the PCl_3 complexes, while a small decrease was noted for the $P(OC_2H_5)_3$ and PF_3 compounds.

A negative or downfield shift with respect to the free phosphine was interpreted to imply the formation of a donor bond from phosphorus to nickel which results in a decrease of electron density on the phosphorus. Thus, the formation of a *sigma*-bond is expected to result in a decrease in shielding, while d-*pi* d-*pi*-bonding should result in an increase in phosphorus shielding. For the eight PR_3 complexes studied they concluded that *pi*-bonding was either extremely small or constant and that the observed shifts within this group appear to be a function of basicity. When the ligand was a phosphite or phosphorus halide, the smaller negative shifts (or positive in the case of PCl_3) were attributed to the electronegativity of the O or X atoms attached to P and hence a low basicity. The data could also imply a weak sigma Ni-P bond, an increase in pi-bond contribution, or a change in phosphorus bond hydridization; however, Meriwether and Leto (139) feel that the electronegativity of the atom joined to the phosphorus contributes most to the observed shifts.

It is of interest to note that their data for PF_3 and PCl_3 complexes indicate an increase in electron shielding in the PCl_3 case and a decrease for the PF_3 case which would be expected if PF_3 is a stronger sigma-bonding ligand than PCl_3, and/or PCl_3 is a stronger pi-bonding ligand than PF_3. This is in direct opposition to the proposals concerning the relative sigma-and pi-bonding strengths of these ligands, as discussed earlier. Recently, Packer has reported the P^{31} and F^{19} n.m.r. spectrum for $Ni(CO)_2[P(CF_3)_3]_2$ (140).

Reports of the H^1 n.m.r. spectra of carbonyl complexes have been confined mostly to those containing cycloalkenes (141). Investigation of the hydrido metal carbonyls has also been carried out using n.m.r. techniques (142). The first report of a n.m.r. investigation of a carbonyl compound containing a phosphorus ligand was in 1962 by Davison, McFarlane, Pratt and Wilkinson (143) who worked with the complex $[HFe(CO)_3P(C_6H_5)_3]^{+2}$. A study of the compounds



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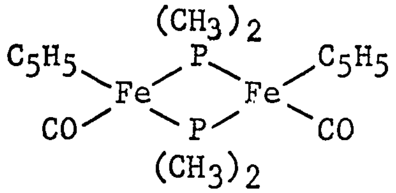


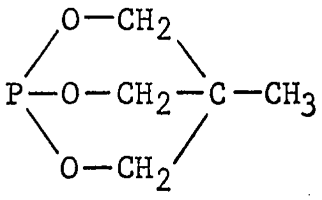
by Hayter (144) revealed that the n.m.r. spectra exhibited triplets for the methyl and cyclopentadienyl proton resonances instead of the expected doublets. This was attributed to phosphorus-phosphorus coupling. Crude estimates of the P-P coupling constants were made by treating the spectrum as an A_2X_2 type. In explanation of this phenomenon, the suggestion was advanced that the coupling effects could occur through the filled metal d orbitals and be aided by d-pi d-pi bonding. An extension of this work to include compounds of the type $[C_5H_5M(CO)_nP(CH_3)_2]_2$ where M = Mo, W (n=2) and M = Ni (n=0) (145) also resulted in observation of the same phenomenon.

A study of $P(CH_3)_2C_6H_5$ complexes of PdI_2, $IrCl_3$, $IrCl_4$ and $PtCl_2$ (146) led to the discovery that significant P-P coupling occurs only when the phosphorus ligands are in the trans positions. For the trans complexes $IrCl_4L_2$ and PdI_2L_2

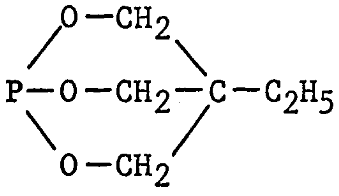
where L = $P(CH_3)_2C_6H_5$, the methylene resonances were found to be 1:2:1 triplets. For the cis compound $PtCl_2L_2$ only doublet methylene resonances were observed. The spectrum of $IrCl_3L_3$ exhibits a 1:2:1 triplet and a doublet with the ratio of triplet to doublet being 1:2. This would be expected since there is one pair of trans ligands and two pairs of cis ligands.

R. B. King (76) reported the first systematic H^1 n.m.r. study of a series of carbonyl complexes using tris(dimethylamino)phosphine, TDP, as the ligand. The free ligand and the complexes $Fe(CO)_4(TDP)$, $Cr(CO)_5(TDP)$, and $Mo(CO)_5(TDP)$ all exhibit doublet methylene resonances. Triplet methylene resonances attributed to P-P coupling are observed for the disubstituted trans complexes $Fe(CO)_3(TDP)_2$, $Cr(CO)_4(TDP)_2$, $Mo(CO)_4(TDP)_2$, and $W(CO)_4(TDP)_2$. For the complex $Ni(CO)_2(TDP)_2$ in which the geometry is tetrahedral, no P-P coupling was observed in the n.m.r. spectrum. The geometries of the complexes were established from their infrared spectra. The relative ratios of the triplet peaks were found to vary as a function of complex geometry and the metal atom. This implies a change in the amount of P-P coupling. Crude estimates of the P-P coupling constants were made from the shapes of the methyl resonances. These coupling constants were found to decrease in the order: $Fe(CO)_3(TDP)_2 \gg W(CO)_4(TDP)_2 \sim Mo(CO)_4(TDP)_2 > Cr(CO)_4(TDP)_2 \gg Ni(CO)_4(TDP)_2$.

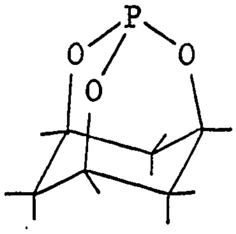
Although open chain phosphite complexes of nickel and the Group VI carbonyls appear to have been thoroughly investigated (see Tables 1, 3, 4 and 5), no mention is made in the literature of attempts to use cyclic phosphites as ligands. Indeed there are very few cyclic phosphites reported in the literature. Of these, 4-methyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane(I) (147), 4-ethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2]octane(II) (148), and 2,8,9-trioxa-1-phosphaadamantane (III) (149,150) would appear to be the most promising to investigate for several reasons.



I

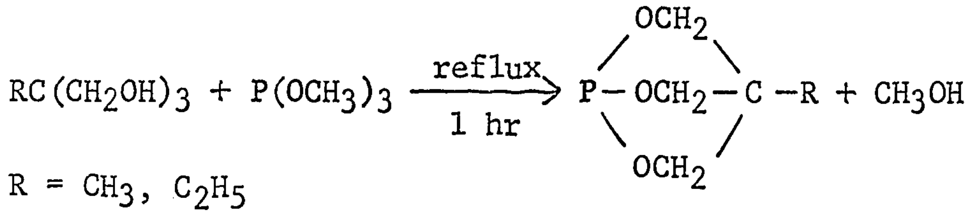


II

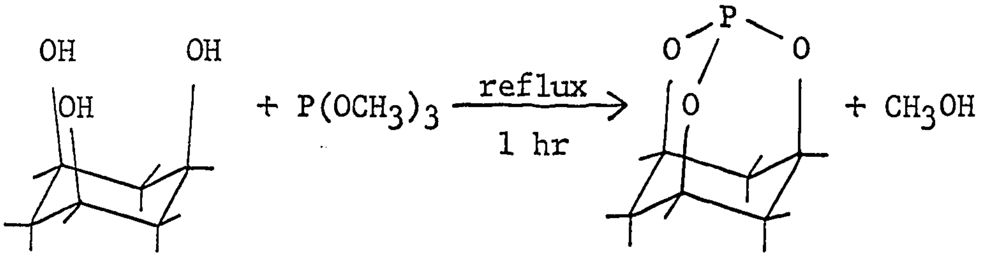


III

Since they are solids (I, m.p. = 98°; II, m.p. = 55°; III, m.p. = 208°) crystalline complexes might be expected instead of the oils so often encountered with open chain phosphites (63). The low steric requirements should make the cyclic phosphites more ideal for coordination than other phosphites. The high symmetry of these cyclic phosphites results in simplification of the infrared and n.m.r. spectra. Their preparation from the proper alcohol by refluxing with trimethylphosphite is facile.



(151)



(151)

Complexes of I have been reported with transition metal salts of Cu^{+1}, Ag^{+1}, Au^{+1}, Pd^{+2}, Pt^{+2}, and Rh^{+3} (152), while complexes of I, II, and III have been reported for Co^{+1}, Co^{+3}, Ni^{0}, and Ni^{+2}. It is of interest to note that in most cases the maximum coordination number of the metal in the complex is attained using only the phosphite ligand. The ligand field strength of I, II, and III has been shown to be approximately the same as that of the cyanide ion (153,154). The visible and UV spectra of a number of these compounds have been interpreted in terms of a significant amount of d-pi d-pi-bonding.

One to one complexes of I and III with $B(CH_3)_3$, BH_3, B_3H_7, and BF_3 have been prepared (155,156). The infrared spectra of these complexes when compared with that of the free ligand show little shift on coordination (157). Varying the strength of the Lewis acid acceptor does not appreciably influence the spectra. Ligand I was found to be a weaker base than trimethylamine toward BH_3 and $B(CH_3)_3$ by studying displacement reactions (155). Using the same procedure, ligand III was found to be a stronger base with respect to BH_3 than ligand I but still weaker than trimethylamine (156). The higher melting point of ligand III (208°) compared to I (98°), of the BH_3 complexes of III (247°) compared with I (199°), and the larger dipole moment of III (4.5D) compared to I (4.1D) also suggest that III is a stronger base than I (156).

The B^{11}, H^1, F^{19} and P^{31} n.m.r. spectra of complexes of I and III with BH_3, $B(CH_3)_3$, and BF_3 have been reported (158). Assignment of the doublets at approximately 2.9 ppm. to the equatorial and 1.9 ppm. to the axial protons in III has been made on the basis of a study of solvent shifts. A P^{31} and H^1 n.m.r. study of the ligands I and III as well as their phosphates and thiophosphates has also been carried out (159).

A recent study of the phosphonium salts of the type [R(I)]X and [R(III)]X, where R = $(C_6H_5)_3C$ or CH_3CH_2 and X = perchlorate or tetrafluroborate anion (151), has been made in which the structures of these compounds were confirmed by their n.m.r. spectra. A linear correlation between J_{POCH} and the downfield chemical shifts of the ligand protons was found. This effect was explained in terms of the decrease in s character of the phosphorus sigma-bond to the coordinating species, and hence an increase in the s character of the P-O links. This trend was observed to be limited to cases where no pi-bonding was possible.

EXPERIMENTAL

Materials

Carbonyls

Nickel tetracarbonyl   Nickel tetracarbonyl was supplied in a one pound lecture bottle cylinder by A. D. Mackay, Inc. Due to the extreme toxicity of the carbonyl (3,4), small amounts (2-7 ml.) were withdrawn from the cylinder by distillation on a vacuum line which was located inside a hood. From this small amount of carbonyl, which was kept cool by the use of liquid nitrogen, exact amounts were withdrawn with a syringe. Rubber gloves were worn for protection. All reactions involving nickel tetracarbonyl were carried out inside the hood.

Iron pentacarbonyl   Iron pentacarbonyl was supplied in a one pound can by A. D. Mackay, Inc. The proper amounts of carbonyl used in reactions were withdrawn from the can with a syringe. All handling of the carbonyl was carried out in a hood with the protection of rubber gloves. The reactions involving the use of iron pentacarbonyl were all vented into a hood.

Chromium hexacarbonyl   A 100 g. bottle of chromium hexacarbonyl was purchased from the Diamond Alkali Corporation. All reactions were vented to a hood.

Molybdenum hexacarbonyl The Climax Molybdenum Company is to be thanked for their gift of a research sample of molybdenum hexacarbonyl. All reactions were vented to a hood.

Tungsten hexacarbonyl The Climax Molybdenum Company is to be thanked for their gift of a research sample of tungsten hexacarbonyl. All reactions were vented to a hood.

Ligands

4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane(I) (151) A mixture of 120 g. (1.0 moles) of 2-hydroxymethyl-2-methyl-1,3-propanediol (Matheson) and 130 g. (1.05 moles) of trimethylphosphite (Eastman) was refluxed for one and one-half hours. The resulting methanol and excess trimethylphosphite were distilled from the reaction mixture. After extraction of the solids with several 100 ml. portions of diethylether, the product was recovered from the solution by removal of the solvent under vacuum. The white crystals were then sublimed onto a water-cooled cold finger at 0.02 mm. pressure and 50°C. The sublimation yielded 121 g. (82% yield) of I which melted at 98°C.

4-Ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane(II) (148) The procedure followed for this preparation was identical to that given for L with the exceptions that 135 g. (1.0 moles) of 2-ethyl-2-hydroxymethyl-1,3-propanediol (Matheson) was used as the alcohol and the sublimation temperature was 45°C. The sublimation yielded 150 g. (94% yield) of white crystalline II which melted at 55°C.

2,8,9-Trioxa-1-phosphaadamantane(III) (151) A mixture of 30 g. (0.23 moles) of cis-1,3,5-cyclohexanetriol and 125 g. (1.0 moles) of trimethylphosphite (Eastman) was refluxed for one and one-half hours. The resulting methanol and excess trimethylphosphite were distilled from the reaction mixture at 80°C. under vacuum. The white crystals were washed with heptane to remove any trace of trimethylphosphite and dried. Purification by sublimation at 80°C. under 0.02 mm. pressure gave 29 g. (79% yield) of white crystalline product which melted at 208°C.

The cis-triol was prepared by hydrogenating phloroglucinol-dihydrate. A mixture of 30 g. of a W-7 strength Raney nickel catalyst which had been prehydrogenated for 6 hours, 200 g. (1.2 moles) of phloroglucinol-dihydrate (Eastman), and 600 ml. of 95% ethanol were placed in a three-necked flask equipped with a stirrer, condenser and gas dispersion tube. The reaction temperature was maintained at 50°C. while hydrogen was bubbled through the slurry for 50 hours. The catalyst was then filtered off and the solution placed in a refrigerator for 12 hours.

The resulting crystals were filtered off and dried on a vacuum line for 8 hours at 80°C. The remaining solution was evaporated to one-half its volume, 50 ml. of water added, and the cooling-recovery cycle repeated. Four separate batches of crystals were obtained in this manner. The first two batches had melting points of 184° and 183°C., respectively, with the third being 180°C. and the fourth 160°C. A total of 47 g. (30% yield) of cis-1,3,5-cyclohexanetriol, m.p. 183-184°C., was isolated. This material then was used for the preparation of III as previously described.

Preparative Methods

Two general methods were used in the preparation of the complexes herein reported. One method involved the use of a refluxing solvent as the reaction medium while the ultraviolet light irradiation of a solution was the second method.

For the refluxing solvent method, a 50 ml. 24/40 standard taper flask was affixed to a Liebig condenser. By use of a T joint attached to the top of the condenser, a flush of helium was maintained over the reaction mixture. One side of the T was vented to a hood in order to allow the resulting carbon monoxide to escape harmlessly. The reaction flask was supported on a magnetic stirrer which drove a small Teflon coated stirring bar inside the flask. Heating of the reaction flask was accomplished by use of a 250 watt infrared heat lamp which was attached to a variable transformer for temperature control. In order to reduce temperature gradients, a tent of aluminum foil was made to enclose the heat lamp and reaction flask. In cases where cooling was necessary, a dish filled with ice water was placed under the flask.

For ultraviolet irradiation, a quartz tube 18 cm. long and 26 mm. in diameter was affixed to a 24/40 male standard taper joint. A Liebig condenser, T joint, and magnetic stirrer were added in a manner analogous to that used in the refluxing solvent method. Irradiation was carried out using a 200 watt Hanovia high pressure mercury vapor lamp (Model 654A) as the ultraviolet light source.

Complexes Prepared

Mono-I-tricarbonylnickel

To a mixture of 4.0 g. (27 mmoles) of I in 50 ml. of chloroform, 5.0 ml. (37 mmoles) of nickel tetracarbonyl were added. An exothermic reaction ensued. After stirring for 4 hr. at room temperature under helium flush, the solution was evaporated to one-fourth its volume under vacuum. Addition of 30 ml. of pentane to the concentrated solution resulted in the formation of white crystals which were filtered, washed with 20 ml. of pentane and dried under vacuum. The white crystalline product weighed 7.4 g. (94% yield) and decomposed at 128°C.

Mono-II-tricarbonylnickel

To a mixture of 1.1 g. (6.8 mmoles) of II in 30 ml. of chloroform, 1.0 ml. (7.5 mmoles) of nickel tetracarbonyl was added. The reaction temperature was maintained at 15°C. by means of an ice bath. After stirring for 4 hrs. under a helium flush, the solution was evaporated to dryness under vacuum. Recrystallization from pentane resulted in isolation of 1.9 g. (92% yield) of $Ni(CO)_3II$. The white crystals decomposed at 103°C.

Mono-III-tricarbonylnickel

To a mixture of 2.3 g. (14.3 mmoles) of III in 50 ml. of chloroform, 2.0 ml. (15 mmoles) of nickel tetracarbonyl were added. The reaction temperature was maintained at 15°C. by means of an ice bath. After stirring for 4 hrs. under a helium flush, 3.9 g. (91% yield) of $Ni(CO)_3III$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 142°C.

Bis-I-dicarbonylnickel

A mixture of 0.40 g. (1.4 mmole) of $Ni(CO)_3I$, 0.20 g. (1.4 mmole) of I, and 30 ml. of chloroform was refluxed 4 hr. under helium with magnetic stirring. From this reaction mixture 0.50 g. of crude $Ni(CO)_2I_2$ was isolated in the same manner described for the isolation of $Ni(CO)_3I$. Chromatography with a benzene chloroform mixture (1:1) on an alumina column resulted in the isolation of 0.45 g. (79% yield) of $Ni(CO)_2I_2$. The first fractions contained the pure $Ni(CO)_2I_2$, while the latter ones yielded the impurity which was $Ni(CO)I_3$. The pure colorless crystals decomposed at 258°C.

Bis-II-dicarbonylnickel

A mixture of 0.8 g. (2.6 mmoles) of $Ni(CO)_3II$, 0.42 g. (2.6 mmoles) of II and 30 ml. of chloroform was heated to 45°C. under a helium flush with magnetic stirring for 8 hrs. From the reaction mixture, 1.1 g. (96% yield) of $Ni(CO)_2II_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 178°C.

Bis-III-dicarbonylnickel

A mixture of 0.4 g. (1.3 mmoles) of $Ni(CO)_3III$, 0.21 g.

(1.3 mmoles) of III and 30 ml. of chloroform was heated to 45°C. under a helium flush with magnetic stirring for 8 hrs. From the reaction mixture 0.56 g. (99% yield) of $Ni(CO)_2III_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 225°C.

Tris-I-monocarbonylnickel

A mixture of 0.50 g. (1.7 mmole) of $Ni(CO)_3I$, 1.0 g. (6.8 mmole) of I and 30 ml. of ethylbenzene was refluxed 6 hr. under helium with magnetic stirring. From this reaction mixture 0.80 g. of crude $Ni(CO)I_3$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. After several recrystallizations from chloroform, 0.65 g. (72% yield) of pure $Ni(CO)I_3$ decomposing at 328°C was obtained.

Tris-II-monocarbonylnickel

A mixture of 0.8 g. (2.6 mmoles) of $Ni(CO)_3II$, 0.84 g. (5.2 mmoles) of II and 30 ml. of chloroform was refluxed under a flush of helium with magnetic stirring for 8 hrs. From the reaction mixture 1.3 g. (87% yield) of $Ni(CO)II_3$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 243°C.

Tris-III-monocarbonylnickel

A mixture of 0.4 g. (1.3 mmoles) of $Ni(CO)_3III$, 0.42 g.

(2.6 mmoles) of III and 30 ml. of chloroform was heated to 58°C. for 16 hrs. under a helium flush with magnetic stirring. From this reaction mixture 0.66 g. (89% yield) of white crystalline $Ni(CO)III_3$ melting at 305°C. was isolated in the same manner as described for the isolation of $Ni(CO)_3I$.

Tetrakis-I-nickel

A mixture of 0.30 g. (0.60 mmole) of $Ni(CO)_3I$, 0.30 g. (1.8 mmole) of I and 30 ml. of chlorobenzene was refluxed 18 hr. under helium with magnetic stirring. On cooling the reaction mixture a light yellow ppt. was obtained. Recrystallization from methylene chloride gave 0.35 g. (95% yield) of white crystals which decomposed at >350°C.

Tetrakis-II-nickel

A mixture of 0.7 g. (2.3 mmoles) of $Ni(CO)_3II$, 1.1 g. (6.9 mmoles) of II and 30 ml. of chlorobenzene was refluxed under helium with magnetic stirring for 24 hrs. From the reaction mixture, 1.5 g. (92% yield) of $NiII_4$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 275°C.

Tetrakis-III-nickel

A mixture of 0.4 g. (1.3 mmoles) of $Ni(CO)_3III$, 0.63 g. (3.9 mmoles) of III and 30 ml. of chloroform was heated to reflux for 18 hrs. under a flush of helium with stirring. On cooling the reaction mixture a white precipitate was obtained. Recrystallization from chloroform gave 0.8 g. (88% yield) of white crystalline $NiIII_4$ which decomposed at >350°C.

Tetrakis-trimethylphosphite-nickel

To a cool solution of 0.5 g. (2.1 mmoles) of $NiCl_2 \cdot 6H_2O$ in 10 ml. of 95% ethanol, 1.6 ml. (12 mmoles) of trimethylphosphite was added. The solution turned dark red-brown in color. Then 0.5 ml. (4.8 mmoles) of diethylamine was added dropwise causing the solution to turn to a yellow-green color. The addition of 60 ml. of water resulted in the formation of a white precipitate which was filtered under a stream of helium and washed with cold methanol. The precipitate was then dried and stored under vacuum. The 1.0 g. (86% yield) of white crystalline $Ni[P(OCH_3)_3]_4$ was found to melt at 174°C.

Tetrakis-triethylphosphite-nickel

To a cool solution of 0.5 g. (2.1 mmoles) of $NiCl_2 \cdot H_2O$ in 10 ml. of 95% ethanol, 1.9 ml. (11 mmoles) of triethylphosphite was added. The solution turned dark red-brown. Then 0.5 ml. (4.8 mmoles) of diethylamine was added dropwise causing the solution to turn to a yellow-green color. The addition of 60 ml. of water resulted in the formation of a white precipitate which was filtered under a stream of helium and washed with cold methanol. The precipitate was then dried and stored under vacuum. The 1.1 g. (72% yield) of white crystalling $Ni[P(OC_2H_5)_3]_4$ was found to melt at 107°C.

Mono-I-tetracarbonyliron

A mixture of 2.0 ml. (15 mmole) of iron pentacarbonyl, 1.5 g. (10 mmole) of I and 30 ml. of ethylbenzene was refluxed for 8 hr. under helium with magnetic stirring. From this reaction mixture 2.5 g. (79% yield) of $Fe(CO)_4I$ was isolated in the same manner described for the isolation of $Ni(CO)_3I$. The very light yellow crystals decomposed at 179°C.

Mono-II-tetracarbonyliron

A mixture of 2.0 ml. (15 mmoles) of iron pentacarbonyl, 1.6 g. (10 mmoles) of II and 30 ml. of ethylbenzene was refluxed for 4 hr. under helium with magnetic stirring. From this reaction mixture 2.9 g. (88% yield) of $Fe(CO)_4II$ was isolated in the same manner described for the isolation of $Ni(CO)_3I$. The very light yellow crystals decomposed at 122°C.

Mono-III-tetracarbonyliron

A mixture of 2.0 ml. (15 mmoles) of iron pentacarbonyl, 1.6 g. (10 mmoles) of III and 30 ml. of ethylbenzene was refluxed for 4 hr. under helium with magnetic stirring. From this reaction mixture 2.7 g. (82% yield) of $Fe(CO)_4III$ was isolated in the same manner described for the isolation of $Ni(CO)_3I$. The very light yellow crystals decomposed at 195°C.

Bis-I-tricarbonyliron

A mixture of 2.0 ml. (2.9 g., 15 mmole) of iron pentacarbonyl, 4.5 g. (30 mmole) of I and 30 ml. of ethylbenzene was refluxed for 15 hr. under helium with magnetic stirring. From this reaction mixture 4.2 g. (64% yield) of $Fe(CO)_3I_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The very light yellow crystals decomposed at 231°C.

Bis-II-tricarbonyliron

A mixture of 1.3 g. (3.9 mmoles) of $Fe(CO)_4II$, 1.4 g. (8.6 mmoles) of II and 100 ml. of ethylbenzene were placed in a quartz tube and irradiated with U.V. light for 4 hr. under helium with magnetic stirring. After the solution had been evaporated to 1/10 its volume under vacuum, 1.4 g. (77% yield) of $Fe(CO)_3II_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$.

Bis-III-tricarbonyliron

A mixture of 1.5 ml. (11 mmoles) of iron pentacarbonyl, 4.0 g. (25 mmoles) of III and 100 ml. of ethylbenzene was placed in a quartz tube and irradiated with U.V. light for 6 hours under helium with magnetic stirring. A precipitate which was observed to form on reaction was removed by filtering. The solution was evaporated to 1/10 its volume under vacuum and further crude product was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. Recrystallization from acetone gave 2.4 g. (47% yield) of pure $Fe(CO)_3III_2$. The very light yellow crystals decomposed at 253°C.

Mono-I-pentacarbonylchromium

A mixture of 1.0 g. (4.5 mmoles) of chromium hexacarbonyl, 0.30 g. (2.0 mmoles) of I and 100 ml. of chloroform was placed in a quartz tube and irradiated with U.V. light for one and one-half hours under helium with magnetic stirring. From the solution 0.63 g. (93% yield) of $Cr(CO)_5I$ was isolated in the same manner as described for the isolation of $Fe(CO)_3II_2$. The white crystals decomposed at 212°C.

Mono-II-pentacarbonylchromium

A mixture of 1.5 g. (6.8 mmoles) of chromium hexacarbonyl, 0.9 g. (5.6 mmoles) of II and 100 ml. of chloroform was placed in a quartz tube and irradiated with U.V. light for one and one-half hours under helium with magnetic stirring. From the solution 1.7 g. (86% yield) of $Cr(CO)_5II$ was isolated in the same manner as described for the isolation of $Fe(CO)_3II_2$. The white crystals decomposed at 163°C.

Mono-III-pentacarbonylchromium

A mixture of 1.1 g. (5 mmoles) of III and 30 ml. of ethylbenzene were heated to 100°C. for 4 hrs. under helium with magnetic stirring. A precipitate was observed to form as the reaction proceeded. From this reaction mixture 1.5 g. (85% yield) of $Cr(CO)_5III$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 218°C.

Bis-I-tetracarbonylchromium

A mixture of 1.1 g. (5.0 mmoles) of chromium hexacarbonyl, 1.9 g. (12 mmoles) of I and 30 ml. of ethylbenzene was refluxed for 20 hr. under helium with magnetic stirring. From this reaction mixture 2.2 g. (96% yield) of $Cr(CO)_4I_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 278°C.

Bis-II-tetracarbonylchromium

A mixture of 1.1 g. (5.0 mmoles) of chromium hexacarbonyl, 2.1 g. (13 mmoles) of II and 30 ml. of ethylbenzene was refluxed for 24 hrs. under helium with magnetic stirring.

From this reaction mixture 2.1 g. (86% yield) of $Cr(CO)_4II_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 214°C.

Bis-III-tetracarbonylchromium

A mixture of 2.5 g. (7.1 mmoles) of $Cr(CO)_5III$, 1.2 g. (7.5 mmoles) of III and 100 ml. of ethyl benzene was placed in a quartz tube and irradiated with U.V. light for four hours under helium with magnetic stirring. A precipitate, which was observed to form on reaction, was filtered off. Further crude $Cr(CO)_4III_2$ was isolated in the same manner as described for the isolation of $Fe(CO)_3III_2$. Recrystallization from acetone gave 2.7 g. (57% yield) of pure $Cr(CO)_4III_2$. The white crystals decomposed at 332°C.

Mono-I-pentacarbonylmolybdenum

A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 0.6 g. (4 mmoles) of I and 30 ml. of methylcyclohexane was refluxed for 4 hr. under helium with magnetic stirring. From this reaction mixture 1.1 g. (65% yield) of $Mo(CO)_5I$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 197°C.

Mono-II-pentacarbonylmolybdenum

A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 0.7 g. (4.3 mmoles) of II and 30 ml. of methylcyclohexane was refluxed for 4 hours under helium with magnetic stirring. From this reaction mixture 1.4 g. (82% yield) of $Mo(CO)_5II$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 158°C.

Mono-III-pentacarbonylmolybdenum

A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 0.8 g. (5.0 mmoles) of III and 30 ml. of methylcyclohexane was refluxed for 4 hr. under helium with magnetic stirring. A precipitate was observed to form as the reaction proceeded. Isolation of further product in the same manner as described for the isolation of $Ni(CO)_3I$ resulted in 1.2 g. (61% yield) of $Mo(CO)_5III$. The white crystals decomposed at 210°C.

Bis-I-tetracarbonylmolybdenum

A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 1.7 g. (12 mmoles) of I and 30 ml. of methylcyclohexane was refluxed for 24 hr. under helium with magnetic stirring. From this reaction mixture 1.3 g. of crude $Mo(CO)_4I_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. After recrystallization from acetone, 1.0 g.

(40% yield) of pure Mo$(CO)_4I_2$ was obtained. The white crystals decomposed at 244°C.

Bis-II-tetracarbonylmolybdenum

A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 2.0 g. (12 mmoles) of II and 30 ml. of ethylbenzene was refluxed for 24 hr. under helium with magnetic stirring. From this reaction mixture 1.9 g. (71% yield) of Mo$(CO)_4II_2$ was isolated in the same manner as described for the isolation of Ni$(CO)_3I$. The white crystals decomposed at 206°C.

Bis-III-tetracarbonylmolybdenum

A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 1.8 g. (11 mmoles) of III and 30 ml. of ethylbenzene was refluxed for 24 hr. under helium with magnetic stirring. As the reaction proceeded, a white precipitate was formed. More product was isolated from the solution in the same manner as described for the isolation of Ni$(CO)_3I$. A total of 1.6 g. (61% yield) of Mo$(CO)_4III_2$ was obtained. The white crystals decomposed at 267°C.

Mono-I-pentacarbonyltungsten

A mixture of 1.8 g. (5.0 mmoles) of tungsten hexacarbonyl, 0.6 g. (4.0 mmoles) of I and 30 ml. of ethylbenzene was refluxed for 16 hr. under helium with magnetic stirring. From this reaction mixture 1.2 g. (51% yield) of $W(CO)_5I$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 228°C.

Mono-II-pentacarbonyltungsten

A mixture of 1.8 g. (5.0 mmoles) of tungsten hexacarbonyl, 0.7 g. (4.0 mmoles) of II and 30 ml. of ethylbenzene was refluxed for 24 hr. under helium with magnetic stirring. From this reaction mixture 1.5 g. (76% yield) of $W(CO)_5II$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 167°C.

Mono-III-pentacarbonyltungsten

A mixture of 1.8 g. (5.0 mmoles) of tungsten hexacarbonyl, 0.8 g. (5.0 mmoles) of III and 30 ml. of ethylbenzene was refluxed for 24 hr. under helium with magnetic stirring. From this reaction mixture 1.3 g. (54% yield) of $W(CO)_5III$ was isolated in the same manner as described for the isolation of $Ni(CO)_3I$. The white crystals decomposed at 221°C.

Bis-I-tetracarbonyltungsten

A mixture of 1.8 g. (5.0 mmoles) tungsten hexacarbonyl, 2.5 g. (17 mmoles) of I and 100 ml. of ethylbenzene was placed in a quartz tube and irradiated with U.V. light for four hours under helium with magnetic stirring. From this reaction mixture 2.5 g. of crude product was isolated in the same manner as described for the isolation of $Fe(CO)_3III_2$. Recrystallization from chloroform and acetone gave 1.7 g. (58% yield) of pure white crystalline $W(CO)_4I_2$ which decomposed at 272°C.

Bis-II-tetracarbonyltungsten

A mixture of 1.0 g. (2.8 mmoles) tungsten hexacarbonyl, 1.4 g. (9.3 mmoles) of II and 100 ml. ethylbenzene was placed in a quartz tube and irradiated with U.V. light for 6 hr. under helium with magnetic stirring. From this reaction mixture 1.5 g. (85% yield) of $W(CO)_4II_2$ was isolated in the same manner as described for the isolation of $Fe(CO)_3II_2$. The white crystals decomposed at 210°C.

Bis-III-tetracarbonyltungsten

A mixture of 1.7 g. (4.7 mmoles) tungsten hexacarbonyl, 1.8 g. (11.2 mmoles) of III and 100 ml. of ethylbenzene was placed in a quartz tube and irradiated with U.V. light for four hours under helium with magnetic stirring. A precipitate was observed to form on reaction. Further product was isolated in the same manner as described for the isolation of $Fe(CO)_3III_2$. After recrystallization from acetone a total of 1.6 g. (55% yield) of $W(CO)_4III_2$ was obtained. The white crystals decomposed at 312°C.

Analysis of Compounds

Carbon-hydrogen

The carbon and hydrogen contents were determined by combustion. These determinations were performed by John Richard of the Analytical Service Group, Ames Laboratory, Ames, Iowa.

Nickel

Nickel analyses were carried out by a standard procedure as the dimethylglyoxime complex (160). A 100-200 mg. sample was decomposed by several evaporations to dryness with HNO_3 in a 25 ml. flask. The residue was then dissolved in water, diluted to approximately 40 ml., adjusted to a pH of 6-7 with NH_4OH and transferred to a 100 ml. beaker. After bringing the solution to the boiling point, a slight excess of 1% ethanolic dimethylglyoxime solution was slowly added. The solution was allowed to stand for one hour after the pH had been adjusted to 9 with NH_4OH. The solution was again brought to the boiling point, filtered through a medium frit crucible and the precipitate washed with hot water. After drying at 110°C. for one hour, the precipitate was washed with a 50% ethanol-water mixture to remove any excess dimethylglyoxime that might remain. Weighing followed drying at 110°C. for at least one hour. The weight of $Ni(C_4H_7O_2N_2)_2 \times 0.2032 =$

weight of nickel.

Iron

Iron was determined colorimetrically with 1,10-phenanthroline (161). A 5-40 mg. sample was evaporated to dryness with HNO_3 and then dissolved in 10 ml. of water. The solution was adjusted to a pH of approximately 5 with NH_4OH and brought to the boiling point after the addition of 2 ml. of 1% hydroxylamine hydrochloride solution. After transfer to a 100 ml. volumetric flask, 10 ml. of a buffer (83 g. sodium acetate and 57.5 g. glacial acetic acid diluted to one liter) and 10 ml. of 1,10-phenanthroline solution (1.2 g. 1,10-phenanthroline-monohydrate dissolved in one liter of water) were added. Following dilution to the mark, the solution was allowed to stand for 30 minutes before the transmittancy was measured at 515 millimicrons. A standard curve of transmittancy *vs*. iron concentration in mg./l. previously prepared using standard iron solutions (0.14 g. electrolytic iron in 20 ml. of HCl diluted to one liter; 100 ml. of this solution with 5 ml. HCl diluted to one liter) which had been treated as above was then used to obtain the amount of iron in the sample.

Chromium

The chromium content was determined spectrophotometrically using s-diphenylcarbazide (162). A 15 ml. sample of 0.2-0.5 ppm chromate solution obtained from the decomposition of a 0.02-0.05 g. sample by heating to dense fumes in 10 ml. 50% HNO_3 and 15 ml. $HClO_4$ was made 0.2N by the addition of 6N H_2SO_4. After the addition of 1 ml. of freshly prepared 0.25% solution of s-diphenylcarbazide in 50% acetone, the solution was transferred to a 100 ml. volumetric flask and diluted to the mark with water. The transmittancy was measured at 540 millimicrons. The concentration of chromium was then determined from a standard curve (transmittancy *vs.* chromium concentration in mg./l.) which had been prepared from standards made up from a 0.001N $K_2Cr_2O_7$ solution.

Molybdenum

Molybdenum was determined gravimetrically as the 8-hydroxyquinoline complex (162). An 80-100 mg. sample was dissolved in a mixture of 10 ml. 50% HNO_3 and 10 ml. $HClO_4$. The solution was boiled down to approximately 3 ml., cooled, and NaOH added until the solution became clear. After making the solution slightly acid, 5 ml. of 0.2N ammonium acetate was added. Upon dilution to 75 ml. and bringing to a boil, a 3% 8-hydroxyquinoline solution (1 g. 8-hydroxyquinoline and 2.5 ml. glacial acetic acid diluted to 25 ml. with water) was added until the supernatant became yellow in color. Following three minutes of boiling, the solution was filtered using a medium frit crucible and the precipitate washed with hot water. The precipitate, $MoO_2(C_9H_6ON)_2$, was weighed after at least one hour of drying at 135°C. The weight of precipitate x 0.231 = weight of molybdenum.

Tungsten

Tungsten was determined gravimetrically as the 8-hydroxyquinoline complex (162). An 80-100 mg. sample was dissolved in a mixture of 10 ml. 50% HNO_3 and 10 ml. $HClO_4$. The solution was boiled down to approximately 3 ml., cooled, and made slightly alkaline by the addition of NaOH. After reheating to boiling, a 4% ethanolic solution of 8-hydroxyquinoline was added to excess followed by the addition of dilute acetic acid until a precipitate was obtained. The precipitate was filtered onto a medium frit crucible, washed with hot water and dried at 120°C. for at least one hour. The tungsten was then weighed as $WO_2(C_9H_6ON)_2$. The weight of precipitate x 0.366 = weight of tungsten.

Phosphorus

Phosphorus analyses were carried out by the Schöniger procedure (163). A stock solution of quinolinium molybdate was first prepared by dissolving 150 g. MoO_3 and 30 g. NaOH in 500 ml. of boiling water. The solution was then filtered and 460 ml. of HCl with 1-2 drops of 100 vol. H_2O_2 were added to clear the greenish blue color. To this solution, 600 ml. of 50% HCl in which 28 ml. of distilled quinoline had been dissolved was added. The stock solution was then boiled and allowed to stand overnight before storing in a polyethylene bottle. A 15-20 mg. sample was wrapped in a piece of filter paper in such a manner that a strip of paper was left to act as a wick and folded in the platinum gauze attached to the combustion flask top. After adding 10 ml. of 0.5N NaOH and 8 ml. of saturated aqueous bromine, the flask was filled with oxygen. The wick was then lighted and the top put on the flask which was then immediately inverted. After the combustion had ceased, the flask was shaken for 10 minutes. The solution was then neutralized with 1N HCl and boiled to remove the bromine. After 70-90 mg. of citric acid and 15 ml. of quinolinium molybdate solution were added, the solution was boiled for a few minutes and then cooled. The solution was filtered through filter paper and the precipitate washed until the filtrate was neutral to litmus. The filter paper with its contents was transferred quantitatively to the original flask to which excess 0.1N NaOH was added. The solution was then backtitrated with 0.05N $HClO_4$ using phenophthalein as the indicator. One ml. of 0.1N NaOH = 0.119 mg. of phosphorus.

Melting points

Melting points were taken in capillaries and are uncorrected.

The analytical data for the compounds prepared in this work are listed in Table 9.

Infrared Spectra

In order to quickly characterize freshly prepared substances as to whether they were the desired product, a mixture of products or a different product than expected, a scan of the infrared spectrum in the range of 4.5-5.2 microns of the compounds in chloroform or methylene chloride solutions was made using either a Perkin-Elmer Model 21 or Beckman IR-5 spectrometer. Once a sample had been determined to be pure by this procedure, the infrared spectrum in the region of 5000 to 675 cm^{-1} was obtained in Halocarbon oil and Nujol

Table 9. Analytical data for prepared compounds

Compound	% Carbon		% Hydrogen		% Metal		% Phos.		Molecular weight	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
$Ni(CO)_3P(OCH_2)_3CCH_3$	33.0	33.1	3.1	3.2	20.2	20.3	10.6	10.3	291	293
$Ni(CO)_3P(OCH_2)_3CC_2H_5$	35.4	35.4	3.6	3.8	19.3	19.2	--	--	305	302
$Ni(CO)_3P(OCH)_3(CH_2)_3$	35.6	35.6	3.0	3.3	19.4	19.3	--	--	303	301
$Ni(CO)_2[P(OCH_2)_3CCH_3]_2$	35.1	34.9	4.4	4.6	14.3	14.4	15.1	14.9	411	409
$Ni(CO)_2[P(OCH_2)_3CC_2H_5]_2$	38.3	38.2	5.0	5.1	13.4	13.5	--	--	439	436
$Ni(CO)_2[P(OCH)_3(CH_2)_3]_2$	38.6	38.2	4.1	4.3	13.5	13.6	--	--	435	437
$Ni(CO)[P(OCH_2)_3CCH_3]_3$	36.2	36.1	5.1	5.4	11.1	11.0	17.5	17.2	---	---
$Ni(CO)[P(OCH_2)_3CC_2H_5]_3$	39.7	39.6	5.8	5.6	10.3	10.4	--	--	573	570
$Ni(CO)[P(OCH)_3(CH_2)_3]_3$	40.2	39.9	4.8	4.7	10.4	10.2	--	--	---	---
$Ni[P(OCH_2)_3CCH_3]_4$	36.8	37.0	5.5	5.6	9.0	9.1	19.1	18.9	---	---
$Ni[P(OCH_2)_3CC_2H_5]_4$	40.6	40.7	6.2	6.3	8.4	8.6	--	--	707	700
$Ni[P(OCH)_3(CH_2)_3]_4$	41.2	40.9	5.2	5.4	8.5	8.6	--	--	---	---
$Ni[P(OCH_3)_3]_4$	26.0	26.0	6.3	6.5	8.15	8.14	--	--	555	549
$Ni[P(OC_2H_5)_3]_4$	39.2	39.8	8.3	8.2	10.6	10.6	--	--	723	721

Table 9. (Continued)

Compound	% Carbon		% Hydrogen		% Metal		% Phos.		Molecular weight	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
$Fe(CO)_4P(OCH_2)_3CCH_3$	34.2	34.4	2.9	2.9	17.7	17.7	9.8	9.7	316	318
$Fe(CO)_4P(OCH_2)_3CC_2H_5$	36.4	36.7	3.4	3.6	17.0	16.9	--	--	330	328
$Fe(CO)_4P(OCH)_3(CH_2)_3$	36.6	36.6	2.7	2.9	17.2	17.1	--	--	328	326
$Fe(CO)_3[P(OCH_2)_3CCH_3]_2$	35.8	35.7	4.1	4.4	12.8	12.7	14.2	14.0	436	441
$Fe(CO)_3[P(OCH_2)_3CC_2H_5]_2$	38.8	38.7	4.7	4.9	12.1	12.0	--	--	464	463
$Fe(CO)_3[P(OCH)_3(CH_2)_3]_2$	39.1	38.8	3.9	4.0	12.2	12.0	--	--	---	---
$Cr(CO)_5P(OCH_2)_3CCH_3$	35.3	35.4	2.7	2.8	15.3	15.3	9.1	9.0	340	343
$Cr(CO)_5P(OCH_2)_3CC_2H_5$	37.3	37.4	3.1	3.4	14.7	14.6	--	--	354	352
$Cr(CO)_5P(OCH)_3(CH_2)_3$	37.5	37.4	2.6	2.7	14.8	14.6	--	--	352	349
$Cr(CO)_4[P(OCH_2)_3CCH_3]_2$	36.5	36.7	3.9	4.2	11.3	11.1	13.5	13.2	460	461
$Cr(CO)_4[P(OCH_2)_3CC_2H_5]_2$	39.4	39.3	4.5	4.7	10.6	10.5	--	--	488	482
$Cr(CO)_4[P(OCH)_3(CH_2)_3]_2$	39.6	39.3	3.7	3.8	10.7	10.8	--	--	---	---

Table 9. (Continued)

Compound	% Carbon		% Hydrogen		% Metal		% Phos.		Molecular weight	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
$Mo(CO)_5P(OCH_2)_3CCH_3$	31.3	31.3	2.3	2.3	25.0	24.9	8.1	7.9	384	381
$Mo(CO)_5P(OCH_2)_3CC_2H_5$	33.2	33.2	2.8	2.9	24.1	24.0	--	--	398	396
$Mo(CO)_5P(OCH)_3(CH_2)_3$	33.4	33.8	2.3	2.5	24.2	24.0	--	--	396	394
$Mo(CO)_4[P(OCH_2)_3CCH_3]_2$	33.4	33.4	3.6	3.6	19.1	19.1	12.3	12.0	504	499
$Mo(CO)_4[P(OCH_2)_3CC_2H_5]_2$	36.1	36.2	4.1	4.2	18.0	17.8	--	--	532	529
$Mo(CO)_4[P(OCH)_3(CH_2)_3]_2$	36.3	36.6	3.3	3.6	18.2	18.0	--	--	---	---
$W(CO)_5P(OCH_2)_3CCH_3$	25.4	25.5	1.9	2.3	39.0	38.8	6.6	6.4	472	466
$W(CO)_5P(OCH_2)_3CC_2H_5$	27.2	27.6	2.3	2.7	37.9	37.6	--	--	486	481
$W(CO)_5P(OCH)_3(CH_2)_3$	27.3	27.4	1.9	2.1	38.0	37.8	--	--	484	480
$W(CO)_4[P(OCH_2)_3CCH_3]_2$	28.4	28.4	3.0	3.4	31.1	30.9	10.4	10.1	592	581
$W(CO)_4[P(OCH_2)_3CC_2H_5]_2$	31.0	31.3	3.6	3.8	29.7	29.5	--	--	620	615
$W(CO)_4[P(OCH)_3(CH_2)_3]_2$	31.1	31.9	2.9	2.9	29.8	29.7	--	--	---	---

mulls and recorded on a Perkin-Elmer Model 21 double beam spectrometer using sodium chloride optics. In addition, the carbonyl region (2200-1900 cm^{-1}) of the spectrum was observed for the compounds in chloroform or methylene chloride solutions and in Halocarbon oil mulls using a Beckman IR-7 spectrometer with sodium chloride prism-grating optics. The far infrared spectra from 800 to 50 cm^{-1} were obtained from Nujol mulls of compounds smeared on polyethylene film windows and recorded on a Beckman IR-11 grating spectrometer.

Since mulls of the ligands could not be prepared, it was necessary to develop new techniques in order to prepare the samples for spectral study*. A saturated solution of ligand in acetone was prepared and then poured over polyethylene powder. The acetone was then allowed to evaporate resulting in the formation of a homogeneous mixture of ligand and crystals and polyethylene powder. This mixture was pressed between two heated metal plates to form a film. In cases where the ligand exhibited extreme volatility, the mixture was placed between two thin polyethylene films prior to heat

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*These new techniques were developed by Miss Evelyn Conrad of the Spectrochemistry Service Group of Ames Laboratory, Ames, Iowa.

pressing. The films thus formed were used to obtain spectra.

Nuclear Magnetic Resonance Spectra

The proton n.m.r. spectra were obtained in approximately 15% chloroform, methylene chloride or acetone solutions on a Varian Associates Model HR-60 spectrometer using a 60 mc. sweep. Tetramethylsilane was used as an internal standard for all proton work. The n.m.r. spectra of disubstituted complexes of III were obtained in saturated solutions due to their very low solubility. The H^1 n.m.r. spectra of $Ni[P(OCH_3)_3]_4$ and $Ni[P(OC_2H_5)_3]_4$ were observed in 30-40% benzene solutions.

The P^{31} n.m.r. spectra were observed in saturated acetone or chloroform solutions on a Varian Associates Model HR-60 spectrometer using a 24.3 mc. sweep. Aqueous 85% H_3PO_4 was used as an external standard for all P^{31} work. Solutions for both the H^1 and P^{31} work were prepared immediately before use.

Molecular Weight Determinations

Molecular weight determinations were made using a Mechrolab vapor pressure osmometer (Model 301A). Standard curves (ΔR vs. molar concentration, where ΔR = bridge imbalance) for each solvent were prepared using solutions of known concentrations (0.005-0.03M) of benzil as a standard. Reagent grade chloroform was used as obtained. Benzene was dried and stored over sodium wire before use. The solvent system used was allowed to equilibrate overnight before use. Solutions (0.012-0.027M) of carbonyl complexes were prepared just prior to use by weighing a known amount of complex into a volumetric flask and diluting to the mark.

The solutions used for the molecular weight determinations of $Ni[P(OCH_3)_3]_4$ and $Ni[P(OC_2H_5)_3]_4$ were prepared by weighing the complexes under a nitrogen atmosphere, using benzene which had been scrupulously dried, and making up the solutions under a flush of nitrogen. Determinations were immediately performed on these freshly prepared solutions which were 0.009 to 0.027M in concentration. All readings were made after allowing exactly two minutes for a solution drop to equilibrate. The two minute wait was determined using a stop watch. The manufacturers specifications indicate that the instrument should be expected to give a precision of ± 1% on molecular weights of 700 or less.

DISCUSSION

Infrared Spectra

The geometries of the prepared compounds may be inferred, in some cases, from the C-O stretching frequencies observed in the infrared spectra. Tables 10, 11, and 12 list the infrared spectra in the metal carbonyl region of the derivatives of I, II and III, respectively.

For the nickel complexes, only the monosubstituted derivative can be conclusively assigned as possessing a tetrahedral configuration (Table 6). The data do not allow a distinction to be made between tetrahedral and square planar geometry for the di- and trisubstituted complexes. It is reasonable to assume that the NiL_4 complexes where L = I, II or III, would be analogous to $Ni(PF_3)_4$ (130) and $Ni[P(OCH_3)_3]_4$ (51) which have been shown to be tetrahedral. Nickel tetracarbonyl is also known to possess tetrahedral geometry (109, 110). Hence, the assumption that the $Ni(CO)_{4-x}L_x$ systems are tetrahedral does not seem unwarranted.

For the monosubstituted iron compounds, the data indicate that they possess a trigonal bipyramidal structure with the ligand in an axial position (Table 7). The single strong frequency observed for the $Fe(CO)_3L_2$ species implies that the

Table 10. Infrared spectra of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2] octane derivatives in the metal carbonyl region

Compound	C-O stretching frequency (cm.$^{-1}$)					
		CH_2Cl_2			Halocarbon oil	
$Ni(CO)_3I$	2090(s)[a]	2021(vs)[b]		2089(s)	2003(vs)	
$Ni(CO)_2I_2$	2048(s)	1994(vs)		2044(s)	1976(vs)	
$Ni(CO)I_3$		1997(vs)			1980(vs)	
NiI_4		none			none	
$Fe(CO)_4I$	2065(s)	1996(vs)	1965(vs)	2063(s)	1998(vs)	1955(vs)
$Fe(CO)_3I_2$		1933(vs)			1915(vs)	
$Cr(CO)_5I$	2082(w)[c]	1995(sh)[d]	1960(vs)	2073(w)	1980(sh)	1945(vs)
$Cr(CO)_4I_2$	2040(vw)[e]	1975(sh)	1930(vs)	2035(vw)	1957(sh)	1918(vs)
$Mo(CO)_5I$	2085(w)	2001(sh)	1962(vs)	2081(w)	1981(sh)	1945(vs)
$Mo(CO)_4I_2$	2049(vw)	1984(sh)	1940(vs)	2038(vw)	1960(sh)	1927(vs)
$W(CO)_5I$	2084(w)	1993(sh)	1958(vs)	2082(w)	1975(sh)	1935(vs)
$W(CO)_4I_2$	2045(vw)	1981(sh)	1931(vs)	2040(vw)	1955(sh)	1913(vs)

[a] s - strong.

[b] vs - very strong.

[c] w - weak.

[d] sh - shoulder.

[e] vw - very weak.

Table 11. Infrared spectra of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane derivatives in the metal carbonyl region

Compound	C-O stretching frequency (cm.$^{-1}$)					
	CH_2Cl_2			Halocarbon oil		
$Ni(CO)_3II$	2088(s)[a]	2019(vs)[b]		2086(s)	2015(vs)	
$Ni(CO)_2II_2$	2042(s)	1989(vs)		2029(s)	1965(vs)	
$Ni(CO)II_3$		1987(vs)			1957(vs)	
$NiII_4$		none			none	
$Fe(CO)_4II$	2064(s)	1997(vs)	1958(vs)	2061(s)	1994(vs)	1955(vs)
$Fe(CO)_3II_2$		1926(vs)			1920(vs)	
$Cr(CO)_5II$	2082(w)[c]	1998(sh)[d]	1956(vs)	2075(w)	1998(sh)	1950(vs)
$Cr(CO)_4II_2$	2040(vw)[e]	1975(sh)	1926(vs)	2037(vw)	1969)sh)	1918(vs)
$Mo(CO)_5II$	2084(w)	1997(sh)	1958(vs)	2081 (w)	1990(sh)	1950(vs)
$Mo(CO)_4II_2$	2046(vw)	1990(sh)	1932(vs)	2043(vs)	1980(sh)	1933(vs)
$W(CO)_5II$	2084(w)	1998(sh)	1954(vs)	2081(w)	1987(sh)	1941(vs)
$W(CO)_4II_2$	2041(vw)	1985(sh)	1925(vs)	2037(vw)	1978(sh)	1920(vs)

[a] s = strong.

[b] vs = very strong.

[c] w = weak.

[d] sh = shoulder

[e] vw = very weak.

Table 12. Infrared spectra of 2,8,9-trioxa-1-phosphaadamantane derivatives in the metal carbonyl region

Compound	C-O stretching frequency (cm.$^{-1}$) CH$_2$Cl$_2$			Halocarbon oil		
Ni(CO)$_3$III	2086(s)[a]		2018(vs)[b]	2081(s)		2003(vs)
Ni(CO)$_2$III$_2$	2044(s)		1986(vs)	2026(s)		1970(vs)
Ni(CO)III$_3$		1979(vs)			1961(vs)	
NiIII$_4$		none			none	
Fe(CO)$_4$III	2065(s)	1993(vs)	1962(vs)	2062(s)	1977(vs)	1946(vs)
Fe(CO)$_3$III$_2$		1926(vs)			1916(vs)	
Cr(CO)$_5$III	2077(s)[c]	1995(sh)[d]	1955(vs)	2074(w)	1985(sh)	1943(vs)
Cr(CO)$_4$III$_2$	2041(vw)[e]	1983(sh)	1923(vs)	2037(vw)	1970(sh)	1911(vs)
Mo(CO)$_5$III	2076(w)	1995(sh)	1955(vs)	2075(w)	1985(sh)	1942(vs)
Mo(CO)$_4$III$_2$	2042(vw)	1984(sh)	1923(vs)	2038(vw)	1977(sh)	1912(vs)
W(CO)$_5$III	2084(w)	1991(sh)	1953(vs)	2082(w)	1981(sh)	1940(vs)
W(CO)$_4$III$_2$	2041(vw)	1984(sh)	1923(vs)	2037(vw)	1980(sh)	1913(vs)

[a] s = strong.

[b] vs = very strong.

[c] w = weak.

[d] sh = shoulder.

[e] vw = very weak.

ligands are trans to each other. These assignments are in agreement with those made for the compounds $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3[P(C_6H_5)_3]_2$ (23). The trigonal bipyramidal geometry is in agreement with that established for $Fe(CO)_5$ (111, 112).

The three observed C-O stretching frequencies for the $M(CO)_5L$ complexes are in accord with an octahedral configuration (Table 8). The disubstituted species $M(CO)_4L_2$ would be expected to exhibit four infrared active bands for a cis configuration and one for a trans arrangement. However, three bands are observed (Figure 1). The appearance of the two weak bands may be explained as resulting from a symmetry reduction of the molecule. Since the ligand has a three-fold symmetry, the molecular symmetry is reduced from D_{4h} to C_1. Then the A_{1g} and B_{1g} modes which were only Raman active become A' modes and are infrared active (125,127). The very weak intensity of these bands indicates that the distortion from true D_{4h} symmetry is not extreme. Similar spectra for trans $M(CO)_4L_2$ where L = phosphites and phosphines have been observed by Magee, et al. (92), Cotton and Kraihanzel (127), and Poilblanc and Bigorgne (88). With the aid of Raman spectra, the structure can be unequivocally established.

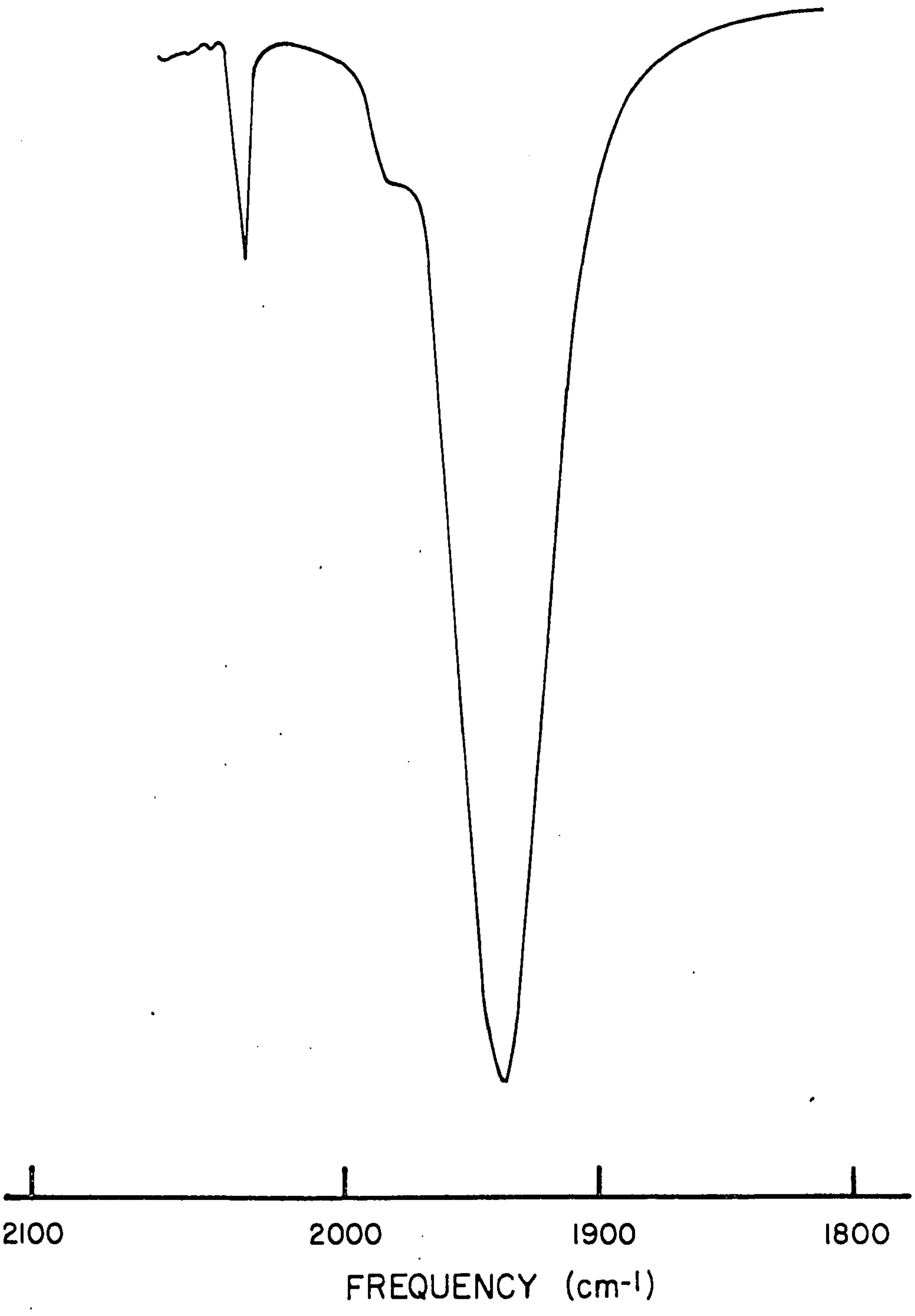

Figure 1. Carbonyl region of the infrared spectra of trans-$M(CO)_4L_2$ complexes where L = I, II or III and M = Cr, Mo, or W

Evidence to support the claim that the polycyclic phosphites I, II, and III are strong pi-bonding ligands may be derived from the infrared spectra of their carbonyl compounds. As pointed out in the introduction, analogous carbonyl compounds which have substituted ligands of differing pi-bonding ability exhibit different C-O stretching frequencies. It was found that as the pi-bonding ability of the ligand increased, the higher was the observed C-O stretching frequency (108, 119). Thus, the data in Table 13 imply that the polycyclic phosphites are better pi-bonding ligands than phosphines and amines but slightly weaker than phosphorus halides. In relation to trialkyl and triaryl phosphites, the polycyclic

Table 13. C-O stretching frequencies of selected compounds[a]

Ligand	A_1 mode of $Ni(CO)_3L$	E mode of $Mo(CO)_5L$	Eu mode of trans-$Mo(CO)_4L_2$
PCl_3	2103	1987	1996
I	2090	1962	1940
II	2088	1958	1932
III	2086	1955	1923
$P(OC_6H_5)_3$	2084	1960	1938
$P(OCH_3)_3$	2079	1950	1921
$P(C_6H_5)_3$	2074	1951	1902
$P(CH_3)_3$	2063	1943	1893
$N(C_2H_5)_3$		1936	1856

[a] All frequencies in $cm.^{-1}$.

phosphites appear to be equal to or slightly better in pi-bonding ability. These findings are in accord with the reported pi-bond order derived from a study by Angelici and Basolo (134) of $Mn(CO)_4XL$ compounds where X = Cl, Br, and I and L = phosphorus-containing ligand.

Calculation of the C-O stretching force constants and stretch-stretch interaction constants from the infrared spectra of the $Ni(CO)_{4-x}L_x$ and $M(CO)_{6-x}L_x$ series where M = Cr, Mo, or W and L = I or III using the method of Cotton and Kraihanzel (127) has been carried out. The secular equations used for the analysis of the $Ni(CO)_{4-x}L_x$ system (108) are given in Table 14 while those used for the $M(CO)_{6-x}L_x$ system (127) are given in Table 15.

Table 14. Secular equations for the C-O stretching modes of the $Ni(CO)_{4-x}L_x$ system (108)

$Ni(CO)_4$	$\lambda_{A_1} = \mu\,(k + 3k_i)^a$
	$\lambda_{T_2} = \mu\,k$
$Ni(CO)_3L$	$\lambda_A = \mu\,(k + 2k_i)$
	$\lambda_E = \mu\,(k - k_i)$
$Ni(CO)_2L_2$	$\lambda_{A_1} = \mu\,(k + k_i)$
	$\lambda_{B_1} = \mu\,(k - k_i)$
$Ni(CO)L_3$	$\lambda = \mu\,k$

$^a\mu = 0.14583$, $\lambda = (5.889\text{x}10^{-2})\,\nu^2$, k = force constant in dyne cm^{-1}, ν = frequency in cm^{-1}.

Table 15. Secular equations for the C-O stretching modes of the $M(CO)_{6-x}L_x$ system (127)

$M(CO)_6$	$\lambda_{A_{1g}} = \mu (k + 6k_i)$[a] $\lambda_{E_g} = \mu k$ $\lambda_{T_{1u}} = \mu (k - 2k_i)$
$M(CO)_5L$	$\begin{matrix} \lambda_{A_1'} \\ \lambda_{A_1''} \end{matrix} \begin{vmatrix} \mu k_i - \lambda & 2\mu k_i \\ 2\mu k_i & \mu (k_2 + 4k_i) - \lambda \end{vmatrix} = 0$ $\lambda_{B_1} = \mu k_2$ $\lambda_E = \mu (k_2 - 2k_i)$
trans-$M(CO)_4L_2$	$\lambda_{A_{1g}} = \mu (k + 4k_i)$ $\lambda_{B_{1g}} = \mu k$ $\lambda_{E_u} = \mu (k - 2k_i)$

[a] $\mu = 0.14583$, $\lambda = (5.889 \times 10^{-2})\nu^2$, k = force constant in dynes cm^{-1}, ν = frequency in cm^{-1}.

From the values obtained for the force constants of the complexes of I and III (Table 16), it can be semiquantitatively shown by comparison with the data of Cotton (108) that the relative *pi*-acceptor strength order should be $PX_3 > I \sim P(OC_6H_5)_3 \sim III > P(OCH_3)_3 > PR_3 >$ amine. All calculations were carried out on a hand calculator since a computer program was not available. The values obtained for the $M(CO)_5L$ complexes are not entirely consistent with all four secular

Table 16. Force constants calculated for $Ni(CO)_{4-x}L_x$ and $M(CO)_{6-x}L_x$ complexes of I and III

Compound	Ligand	K values[a]		
$Ni(CO)_3L$	I	$K = 16.88$	$K_i = 0.39$	
	III	$K = 16.64$	$K_i = 0.43$	
$Ni(CO)_2L_2$	I	$K = 16.50$	$K_i = 0.44$	
	III	$K = 16.40$	$K_i = 0.47$	
$Ni(CO)L_3$	I	$K = 16.10$		
	III	$K = 15.82$		
$Cr(CO)_5L$	I	$K_1 = 15.7$	$K_2 = 16.07$	$K_i = 0.28$
	III	$K_1 = 15.7$	$K_2 = 16.04$	$K_i = 0.31$
$Mo(CO)_5L$	I	$K_1 = 16.0$	$K_2 = 16.16$	$K_i = 0.30$
	III	$K_1 = 15.8$	$K_2 = 16.09$	$K_i = 0.32$
$W(CO)_5L$	I	$K_1 = 15.7$	$K_2 = 16.04$	$K_i = 0.28$
	III	$K_1 = 15.6$	$K_2 = 16.01$	$K_i = 0.30$
$Cr(CO)_4L_2$	I	$K = 15.63$	$K_i = 0.29$	
	III	$K = 15.56$	$K_i = 0.31$	
$Mo(CO)_4L_2$	I	$K = 15.78$	$K_i = 0.29$	
	III	$K = 15.57$	$K_i = 0.31$	
$W(CO)_4L_2$	I	$K = 15.67$	$K_i = 0.30$	
	III	$K = 15.56$	$K_i = 0.31$	

[a] K values in mdynes/Å.

equations since successive approximations were not made. The values obtained for the other compounds are consistent with all the secular equations. It is still instructive to note that these semiquantitative estimates substantiate the conclusions drawn as to the pi-bonding ability of I and III from a cursory examination of the C-O stretching frequencies.

The C-O stretching frequencies observed for the complexes of III are found to be slightly less than those for the analogous complexes of I in all cases. This may indicate that I is a slightly better pi-bonding ligand than III. However, one may also rationalize this effect as resulting from a difference in the basicity of the two ligands. Bigorgne (64) has suggested that the shifts observed for the C-O stretching frequencies of analogous carbonyl compounds of various ligands can be attributed to the difference in the basicity of the ligands instead of differences in their pi-bonding ability. Angelici has found that in a series of $Mn(CO)_3Br_2L$ complexes where L=substituted pyridines and anilines of varying basicity that as the basicity of L increased, the C-O stretching frequency was found to decrease[1]. Since it has been shown that

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[1] R. J. Angelici, Department of Chemistry, Iowa State University, Ames, Iowa. Infrared studies of analine and pyridine derivatives of manganese pentacarbonyl bromide. Private communication. 1964.

III is a stronger base than I toward boron Lewis acids (156), one can speculate that the variance in C-O stretching frequencies of analogous compounds may be due to the difference in basicity of the two ligands. Indeed, the two ligands may be of equal pi-bonding ability, with the stronger basicity of III resulting in the observed shift of the C-O stretching frequencies.

Other features of the infrared spectra of the compounds of I are the intense bands observed at approximately 1020, 860, 780, 770, and 650 cm^{-1} which are indicative of the presence of I in the complex (157). Weaker absorptions observed at 3000, 2950, 1470, 1400, 1350, 1310, 1190, 1170, 950, 925, and 670 cm^{-1} may also be assigned to the ligand (157). Similarly for the complexes of II, intense bands were observed at approximately 1160, 1030, 960, 940, 850, 810, 790, 770, and 740 cm^{-1}. Weak absorptions found at 3000, 2950, 1470, 1400, 1190, and 720 cm^{-1} may also be assigned to this ligand. The complexes of III exhibited intense bands at approximately 1110, 940, 905, 850, 800 and 750 cm^{-1} and weaker bands at 2980, 1430, 1310, 1210, 1060, 1040, 810, 730, and 720 cm^{-1} that are attributable to the ligand moiety (157).

The far infrared spectra of the ligands I, II and III and some of their complexes were also observed. Table 17

Table 17. Far infrared frequencies of the ligands $P(OCH_2)_3CCH_3$, $P(OCH_2)_3CC_2H_5$ and $P(OCH)_3(CH_2)_3$[a]

$P(OCH_3)_2CCH_3$	$P(OCH_2)_3CC_2H_5$	$P(OCH)_3(CH_2)_3$
653(s)[b]	644(s)	648(w)[c]
638(w)	628(w)	613(m)[d]
		585(w)
	521(w)	521(s)
505(w)	505(w)	506(s)
495(w)	494(w)	478(m)
461(m)	462(m)	464(w)
		435(s)
402(w)	409(w)	410(m)
		392 387 (s)
	359(m)	371 364 (w)
344(s)	342(m)	330(s)
	315(m)	
265(m)	278(m)	291(w)

[a] All frequencies in cm^{-1}.

[b] s = strong.

[c] w = weak.

[d] m = medium.

lists the frequencies and their intensities observed in the infrared spectra from 700-100 cm^{-1} of the ligands I, II and III. Aside from ligand frequencies, the far infrared spectra of carbonyl complexes of these ligands would be expected to exhibit M-C stretching modes at 370-500 cm^{-1}, the M-C-O bending modes at 500-625 cm^{-1}, and M-P stretching modes at 175-225 cm^{-1} (51,88,109,112,130). Due to the overlap of free ligand frequencies in the M-C stretch and M-C-O bending areas, assignment of a number of these modes observed could not be made with certainty.

New frequencies occurring at approximately 200 cm^{-1} were observed for all the complexes. This corresponds to the M-P stretching mode area as observed in the Raman for $Ni(PF_3)_4$ (130) and $Ni[P(OCH_3)_3]_4$ (51). Poilblanc and Bigorgne (88) have also reported bands in this region for the complexes $Mo(CO)_5PCl_2(OC_2H_5)$ and $Mo(CO)_5P(OCH_3)_3$. Table 18 lists the frequencies observed other than those attributed to the ligand and their tentative assignments for carbonyl complexes of II.

The M-C-O bending frequencies were strong but hard to distinguish from a very strong ligand band at 644 cm^{-1} which appears to shift to slightly lower energy on coordination. The assignments are in good agreement with those made by Poilblanc and Bigorgne (88) for their $Mo(CO)_{6-x}L_x$ compounds.

In a study of the $Ni(CO)_{4-x}[P(OCH_3)_3]_x$ system Bigorgne and Zelwer (51) observed a definite linear increase of the M-C stretching frequency from 385-500 cm^{-1} on increased substitution. Since the system $Ni(CO)_{4-x}(II)_x$ has been considered to

Table 18. Far infrared frequencies of metal carbonyl complexes of II[a]

Compound	M-C-O	M-C	M-P
$Ni(CO)_3II$	650 534	382 380	211
$Ni(CO)_2II_2$	654 534	383 376	208 203
$Ni(CO)II_3$	536	387	214 201
$NiII_4$	---	---	215
$Fe(CO)_5II$	630 616 590	389	214
$Fe(CO)_3II_2$	601 591	385	194
$Cr(CO)_5II$	595 587	386	213 196
$Cr(CO)_4II_2$	632 591	388	227
$Mo(CO)_5II$	604 575	376	213 187
$Mo(CO)_4II_2$	598 577	384	216
$W(CO)_5II$	595 588	384	214 183
$W(CO)_4II_2$	600 589	384	215

[a] All frequencies in cm^{-1}.

be fairly analogous, the constant value observed for the frequency attributed to the M-C stretching mode might raise doubts as to the validity of this assignment. However, in all spectra this frequency is a distinct, new band of medium intensity. All other bands in the region of 350-500 cm^{-1} were attributable to ligand bands. None of these absorptions were observed to shift frequency on increased substitution. The consistency of the M-C stretching frequency is hard to rationalize due to the observed change of the C-O stretching mode on increased substitution.

A far infrared study of a series of $Mo(CO)_{6-x}L_x$ compounds resulted in the assignment of frequencies in the range of 380-416 cm^{-1} to the M-C stretching mode (88). The values observed for the Group VI metal carbonyl complexes of II are in good agreement. Theoretically the number of M-C modes should be the same as the number of C-O stretching modes (Table 8). For all the $M(CO)_5II$ cases, a very broad band was observed which could easily encompass the three theoretically predicted frequencies. The trans-$M(CO)_4(II)_2$ cases should exhibit one M-C mode which indeed is what was found.

The frequency assigned to the M-P stretching mode was found to be relatively constant for all the compounds studied. The far infrared spectra of complexes of the type MX_4 and MX_2L_2 have been observed and the M-X stretching mode assigned (124,164). In these cases it was found that within a group, e.g. Zn, Cd, Hg, as the atomic weight of the metal increased, the M-X stretching frequency decreased when X was the same for all complexes. Hence, one would expect the M-P stretching frequency to decrease in the order Cr > Mo > W for the carbonyl complexes of II. This is not the case, however. The consistency of the observed frequency may indicate that the M-P bond strength increases in analogous carbonyl complexes of II as one goes down the Group VI metals. The observation of two M-P bands for the $M(CO)_5II$ complexes is puzzling, but in agreement with the number reported by Poilblanc and Bigorgne (88). The consistency of the Ni-P frequency for the series $Ni(CO)_{4-x}(II)_x$ suggests that the Ni-P bond is of approximately the same strength in these cases.

It should be pointed out that the peaks observed in the 200 cm^{-1} region were very broad; approximately 15 cm^{-1} at half-height. This, coupled with the accurace of the instrument in this region of $\pm$ 2 cm^{-1}, means that there is room for considerable error in the measurements. Considering the difficulty encountered in assigning the M-C and M-C-O modes due to complication of the region by ligand frequencies, the degree of confidence that should be placed in the band assignments in the far infrared spectra is open to question.

Nuclear Magnetic Resonance Spectra

The proton n.m.r. spectra observed for the monosubstituted carbonyls of I exhibit singlet methyl and doublet methylene resonances, the latter due to spin coupling with the phosphorus nucleus (Figure 2). Spectra of this type have been previously reported for I (159) and adducts of I with compounds of boron which behave as Lewis acids (158). On complexation, a downfield shift for both the methyl and methylene protons with respect to the free ligand is observed (Table 19). This can be interpreted to imply that the electron density about the protons is being decreased. The formation of a donor bond from the ligand to the metal would lead one to predict such a shift.

The magnitude of the downfield shift appears to be affected by the geometry of the complex in that trigonal bipyramidal > octahedral > tetrahedral. Varying the metal atom in the same geometry does not appear to produce any shift. The value of J_{POCH} is found to range from 3.9 c.p.s. in $Ni(CO)_3I$ to 5.1 c.p.s. in $Fe(CO)_4I$ compared with 1.8 c.p.s. for the free ligand (Table 19). It appears that J_{POCH} may also be influenced by geometry in that trigonal bipyramidal > octahedral > tetrahedral. Varying the metal atom while retaining the same geometry does not appear to influence J_{POCH}.

The proton n.m.r. spectra of some disubstituted phosphine complexes wherein the ligands are <u>trans</u> to one another

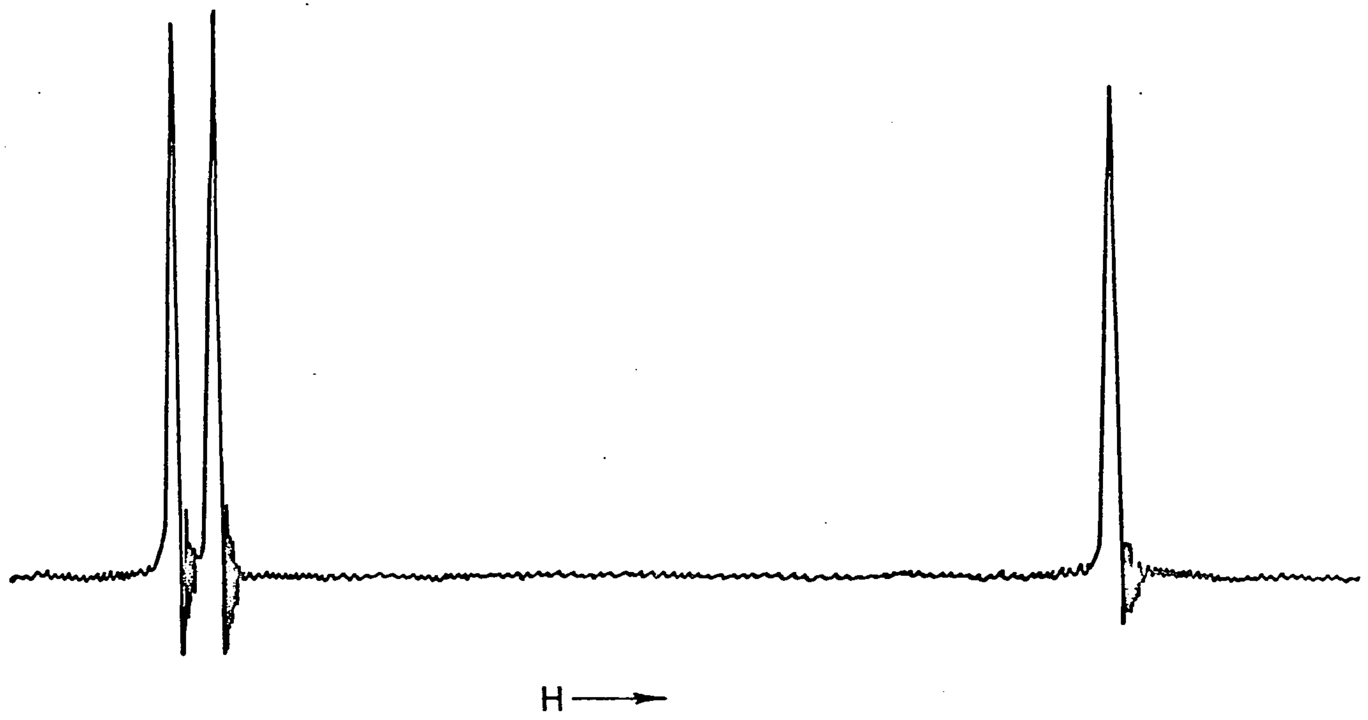


Figure 2. The proton n.m.r. spectrum of a monosubstituted carbonyl complex of I

Table 19. Chemical shifts and coupling constants from the proton n.m.r. spectra of 4-methyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane derivatives[a]

Compound	Solvent	Methyl	Methylene	J_{POCH}	J_{PP}[b]
I, $P(OCH_2)_3CCH_3$	$CDCl_3$	0.72	3.93[c]	1.8	--
$Ni(CO)_3I$	$CDCl_3$	0.78	4.14[c]	3.9	--
$Ni(CO)_2I_2$	$CDCl_3$	0.74	4.10[c]	4.0	0
$Ni(CO)I_3$	$CDCl_3$	0.70	4.06[d]	3.6	9
NiI_4	CH_2Cl_2	0.66	4.00[d]	3.8	62
$Fe(CO)_4I$	$(CH_3)_2CO$	0.90	4.48[c]	5.1	--
$Fe(CO)_3I_2$	$(CH_3)_2CO$	0.85	4.35[d]	5.0	>400
$Cr(CO)_5I$	$(CH_3)_2CO$	0.87	4.36[c]	4.1	--
$Cr(CO)_4I_2$	$(CH_3)_2CO$	0.83	4.24[d]	4.2	19
$Mo(CO)_5I$	$(CH_3)_2CO$	0.86	4.33[c]	4.1	--
$Mo(CO)_4I_2$	$(CH_3)_2CO$	0.82	4.21[d]	4.2	253
$W(CO)_5I$	$(CH_3)_2CO$	0.88	4.37[c]	4.1	--
$W(CO)_4I_2$	$(CH_3)_2CO$	0.82	4.23[d]	4.4	321

[a] Chemical shifts in p.p.m. downfield with respect to tetramethylsilane; J values in c.p.s.

[b] Approximate values. See text.

[c] Doublet.

[d] Triplet.

have been found to exhibit phosphorus-phosphorus coupling across the trans position. For example a 1:2:1 triplet has been observed for the trans complex $PdI_2[P(CH_3)_2(C_6H_5)]_2$, whereas the expected doublet is observed for the cis isomer (146). In trans disubstituted metal carbonyl complexes of tris(dimethylamino)phosphine the spectra are found to exhibit triplets of varying intensity ratios which has been interpreted to indicate P-P coupling (76). The methylene resonances observed for the disubstituted complexes of I are shown in Figure 3. The fact that triplets, instead of the expected doublets, are found suggests that P-P coupling is taking place.

Crude estimates of the J_{PP} values can be made by treating these systems as a modified 10 line ABX_2 type (165) in which $\delta_A = \delta_B$. Hence the system is designated $AA'X_2$ wherein X_2 refers to the methylene hydrogens in I, A is the phosphorus atom in the same I molecule containing the X_2 hydrogens, and A' is the phosphorus atom in a neighboring ligand molecule. By assuming $J_{A'X} = 0$ such a system can be shown to exhibit a maximum of six lines symmetrically grouped around the mean chemical shift of the methylene protons. The positions and relative intensities are shown in Table 20. The distance

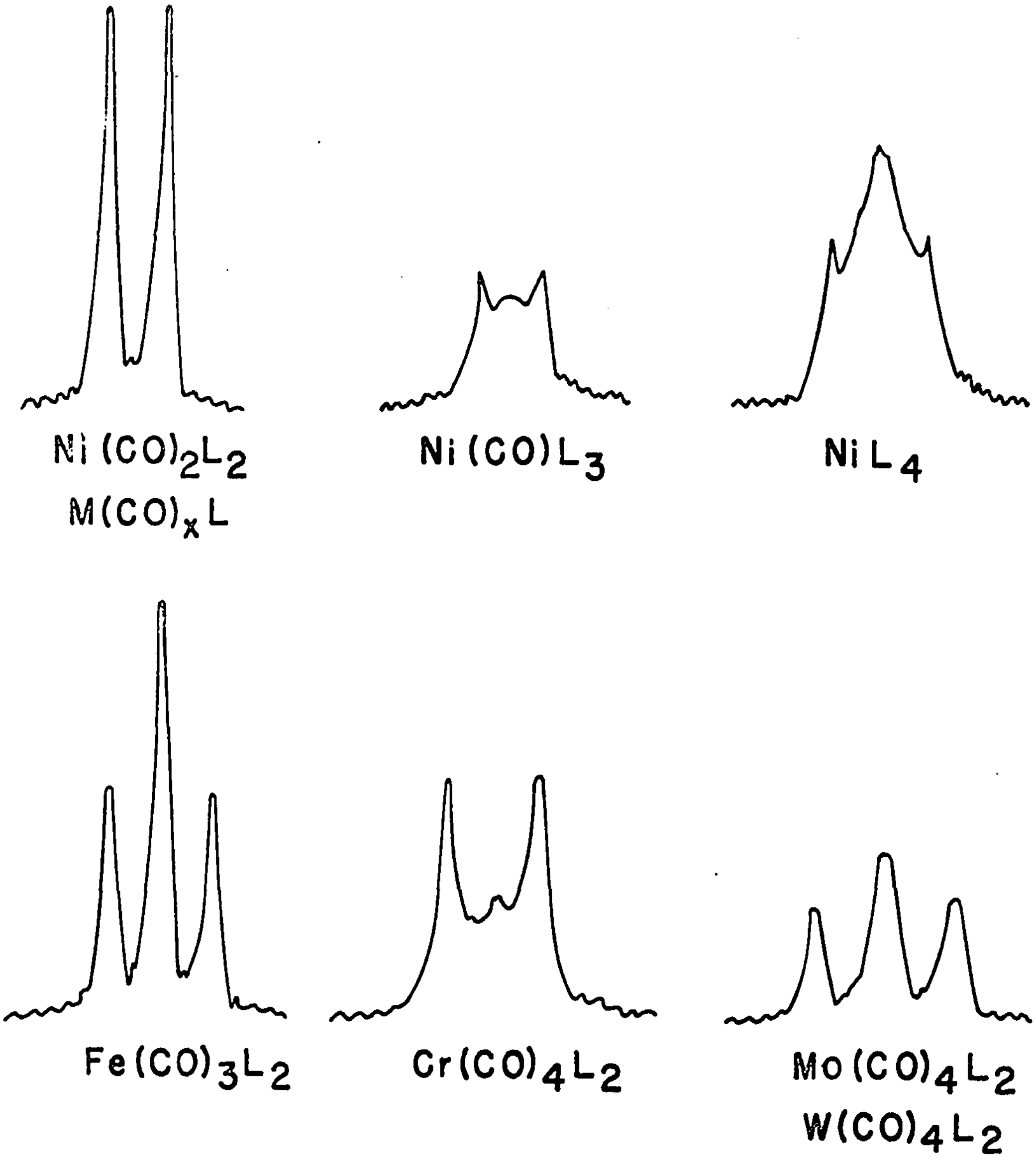


Figure 3. Methylene n.m.r. absorptions of substituted metal carbonyl complexes of L where L = I or II. Line widths of various spectra are not drawn to the same scale

Table 20. $AA'X_2$ n.m.r. spectrum

Positions with respect to mean δ_{x_2}	Relative intensity
$-\frac{1}{2}(J_{AA'} + Q)$	$1 - JAA'/Q$
$-\frac{1}{2} J_{AX}$	2
$-\frac{1}{2}(Q - J_{AA'})$	$1 + J_{AA'}/Q$
$+\frac{1}{2}(Q - J_{AA'})$	$1 + J_{AA'}/Q$
$+\frac{1}{2} J_{AX}$	2
$+\frac{1}{2}(J_{AA'} + Q)$	$1 - J_{AA'}/Q$
Where $Q = (J_{AX}^2 + J_{AA'}^2)^{\frac{1}{2}}$	

between the outer peaks of the three-line spectra shown in Figure 3 is assigned to J_{AX} which ranges from 3.6 c.p.s. in $Ni(CO)_2I_2$ to 5.0 c.p.s. in $Fe(CO)_3I_2$. The central peak is assigned to the two lines $-\frac{1}{2}(Q-J_{AA'})$ and $+\frac{1}{2}(Q-J_{AA'})$. It can be shown that if $J_{AA'} = 0$, the intensity of these two lines approaches zero. If $J_{AA'}$ is very, very large, these two lines coalesce and gain a total relative intensity of four. This situation would give a 1:2:1 triplet.

An estimate of the separation of the center pair of lines was obtained from the difference of the line width at half-height of the central and outer peaks. Where the peaks were ill-defined, the outer pair was assumed to be gaussian in order to resolve the central peak system. Solution of the equation $Q-J_{AA'}$ = separation of central peaks (c.p.s.) then affords an estimate of $J_{AA'}$ or in this case J_{PP}. From the values of J_{POCH} listed in Table 19, it can easily be shown that when J_{PP} = 10 c.p.s., the intensities of the outermost peaks of the theoretical six-line spectrum are too small to be observed, and when J_{PP} = 1 c.p.s. these intensities although appreciable are included in the observed "three-line" spectra. It is therefore reasonable that the spectra are quite well resolved for $Fe(CO)_3I_2$, $Mo(CO)_4I_2$, and $W(CO)_4I_2$ where J_{PP} is large whereas those of $Ni(CO)I_3$ and $Cr(CO)_4I_2$ are broad and poorly defined.

Estimates of the P-P coupling constants based on the above criterion gives the following order for disubstituted complexes: $Fe(CO)_3I_2 > W(CO)_4I_2 > Cr(CO)_4I_2 > Ni(CO)_2I_2$. This order agrees with that found for the tris(dimethylamino) phosphine complexes (76). However, in all cases where P-P coupling is observed, the relative height of the center peak is slightly larger for I. This implies that the P-P coupling for analogous carbonyl complexes will be greater wherein the ligand is I than those wherein the ligand is tris(dimethylamino)phosphine. It also appears that the P-P coupling constant in these compounds is a function of their geometry in that the value for a trigonal bipyramid > octahedral > tetrahedral complex.

Although in all complexes the methyl and methylene proton n.m.r. absorptions appear downfield with respect to the free ligand, increased substitution causes an upfield shift in these protons (Table 19). The apparent influence of geometry on the magnitude of the chemical shifts and J_{POCH} is the same for the disubstituted compounds as observed in the monosubstituted cases. This shift can be interpreted to indicate that an orderly increase in electron density about the protons follows with increased substitution.

The results of the study of the mono- through tetrasubstituted complexes of I with $Ni(CO)_4$ are noteworthy. The shifts observed for the methyl and methylene protons on increased substitution are extremely systematic. In the disubstituted complex, no P-P coupling was observed since the methylene proton n.m.r. absorptions appeared as a doublet. The trisubstituted complex yields a triplet of approximate 1:0.9:1 ratio while the tetrasubstituted complex exhibits a 1:2:1 triplet (Figure 3). From this we conclude that in a tetrahedral system increased substitution is accompanied by greater P-P coupling.

Elsewhere it has been shown that a direct proportionality exists between the amount of coupling (J_{POCH}) and the chemical shifts of the protons in a number of adducts and phosphonium salts of I and III (151). In all these cases the donor acceptor link can be assumed to be of the sigma type. The proton shifts in complexes wherein pi-bonding is probable such as the phosphate of I and III, do not correlate with their respective J_{POCH} values. It is apparent, that with respect to the correlation found for the sigma-bonded compounds, the protons in the pi-bonded complexes all have abnormally high - field shifts (151). A comparison of the chemical shifts and coupling constants observed for the carbonyl complexes indicates some degree of pi-bonding is taking place.

The proton n.m.r. spectra of the monosubstituted carbonyl complexes of II exhibit a complex 6 line group attributable to the ethyl resonances and a doublet methylene resonance due to spin coupling with the phosphorus nucleus (Figure 4). The same trends for the chemical shifts and coupling constants are observed for the complexes of II as previously discussed for complexes of I (Table 21). The disubstituted

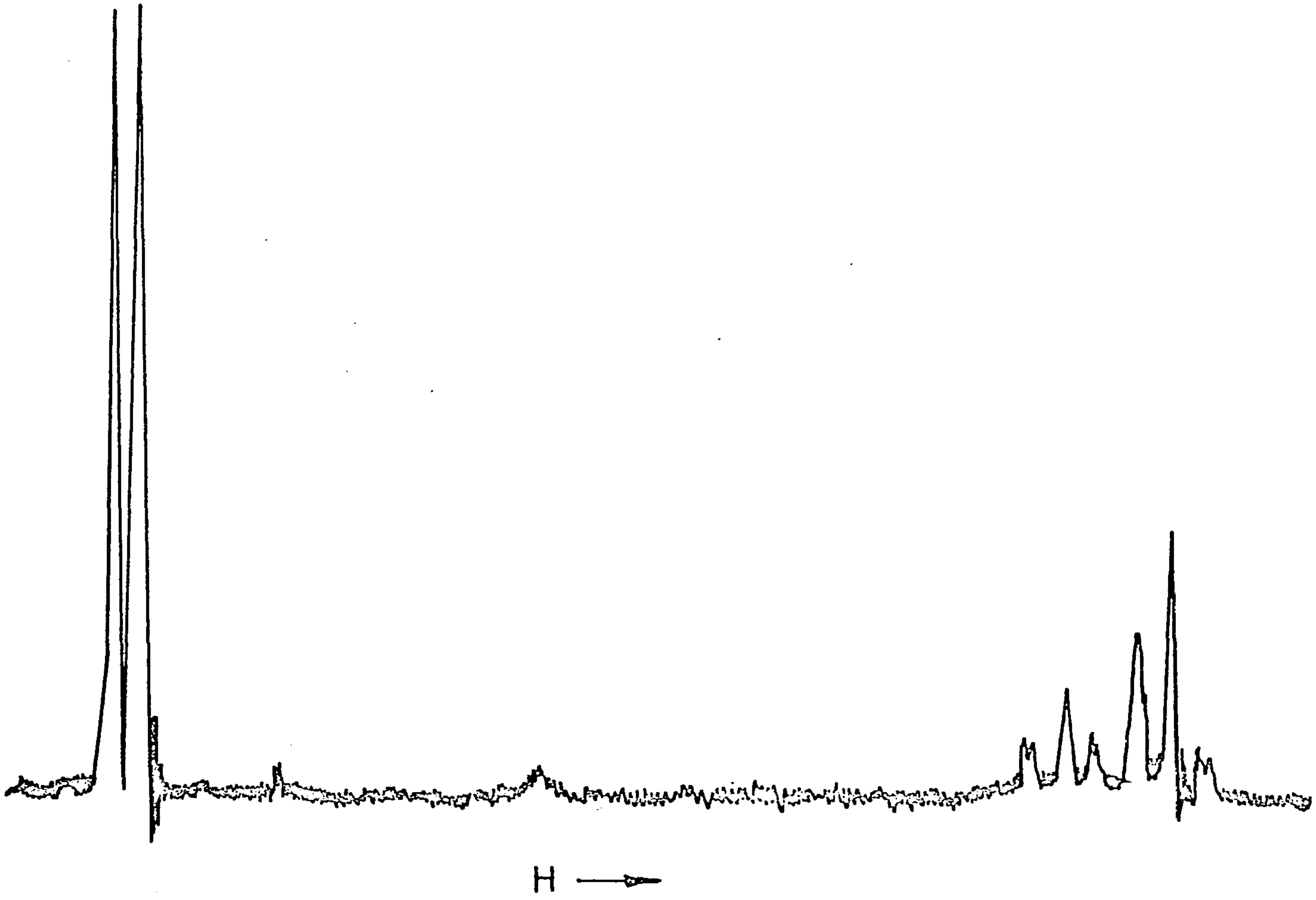


Figure 4. The proton n.m.r. spectrum of a monosubstituted carbonyl complex of II

Table 21. Chemical shifts and coupling constants from the proton n.m.r. spectra of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane derivatives[a]

Compound	Solvent	Methyl	Ethyl[b]	J_{POCH}	J_{PP}[c]
II, $P(OCH_2)_2CC_2H_5$	$CDCl_3$	3.96	0.92	1.6	--
$Ni(CO)_3II$	$CDCl_3$	4.18	1.01	4.0	--
$Ni(CO)_2II_2$	$CDCl_3$	4.15	0.97	4.0	0
$Ni(CO)II_3$	$CDCl_3$	4.09	0.95	4.0	8
$NiII_4$	$CDCl_3$	4.04	0.93	3.9	59
$Fe(CO)_4II$	$CDCl_3$	4.43	1.08	5.3	--
$Fe(CO)_3II_2$	$CDCl_3$	4.30	1.04	5.1	>400
$Cr(CO)_5II$	$CDCl_3$	4.24	1.02	4.3	--
$Cr(CO)_4II_2$	$CDCl_3$	4.20	0.98	4.3	20
$Mo(CO)_5II$	$CDCl_3$	4.20	1.01	4.2	--
$Mo(CO)_4II_2$	$CDCl_3$	4.16	0.95	4.3	247
$W(CO)_5II$	$CDCl_3$	4.25	1.02	4.4	--
$W(CO)_4II_2$	$CDCl_3$	4.19	0.96	4.4	314

[a] Chemical shifts in p.p.m. downfield with respect to tetramethylsilane; J values in c.p.s.

[b] Center of 6 line group.

[c] Approximate values. See text.

complexes exhibit methylene resonances that are nearly identical to those shown in Figure 3. The disubstituted complexes of II may also be considered as an $AA'X_2$ type, hence, the equations in Table 20 can be used to make estimates of J_{PP}. Here again there is a great similarity with the values obtained for the complexes of I (Tables 19 and 21). Such agreement in chemical shifts and coupling constants are expected due to the great similarity between ligands I and II. Extending the "tail" of the ligand by one CH_2 group would not be expected to affect the coordinating end of the molecule appreciably. Also, such an addition would not be expected to alter the cage structure in any manner, hence, the values and trends observed for the methylene protons would be expected to be nearly identical for ligands I and II.

The proton n.m.r. spectra of the monosubstituted carbonyl complexes of III exhibit three doublets attributable to the methine, axial, and equatorial protons (Figure 5). The doublet methine resonance is the result of spin coupling with the phosphorus nucleus while the axial and equatorial doublets are due to geminal proton coupling. The broadness of the peaks is the result of coupling between the methine and axial or methine and equatorial protons. Spectra of this type have

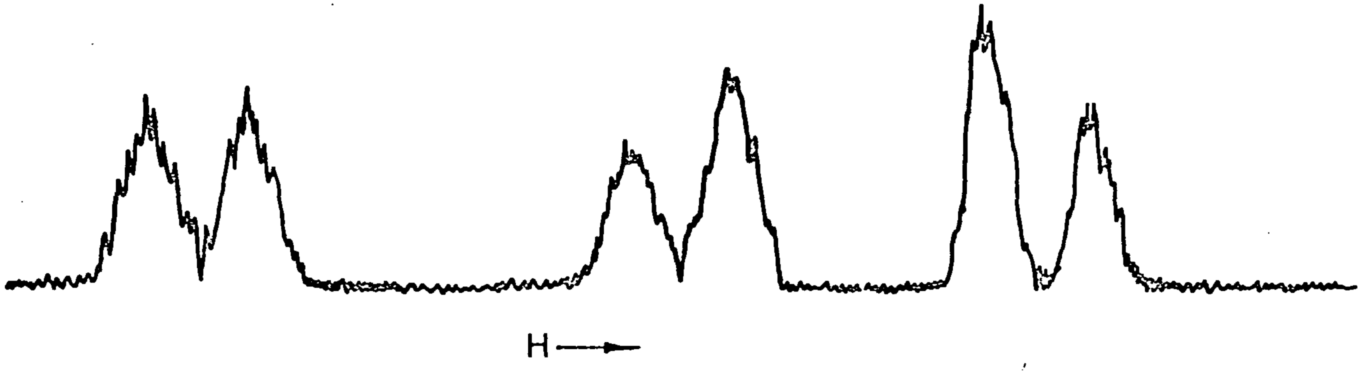


Figure 5. The proton n.m.r. spectrum of a monosubstituted carbonyl complex of III

been previously reported for adducts of III with boron compounds which act as Lewis acids (158) as well as for the free ligand (159).

On complexation, a downfield shift is observed for the methine protons while the axial and equatorial hydrogens remain constant or shift slightly upfield (Table 22). The magnitude of the shift of the methine proton appears to be a function of the geometry of the complex with trigonal bipyramid > octahedral > tetrahedral. Varying the metal atom in a complex of similar geometry appears to have no effect as evidenced by the chromium, molybdenum and tungsten complexes. The J_{POCH} is found to range from 11.6 c.p.s. in $Ni(CO)_3III$ to 14.7 c.p.s. in $Fe(CO)_4III$ compared to 6.3 c.p.s. in the free ligand. The J_{HH} is found to vary from 13.8 c.p.s. in $Cr(CO)_5III$ to 14.5 c.p.s. in $Fe(CO)_4III$ compared with 14.0 in the free ligand. It appears that J_{POCH} is slightly affected by the geometry of the complex in that the value for a trigonal bipyramid > octahedral > tetrahedral. On the other hand, J_{HH} appears to remain rather constant for the monosubstituted complexes.

The spectra of the trans disubstituted complexes are observed to give broad peaks for the methine protons

Table 22. Chemical shifts and coupling constants from the proton n.m.r. spectra of 2,8,9-trioxa-1-phospha-adamantane derivatives[a]

Compound	Solvent	H_{ax}	H_{eq}	H_{CH}	J_{HH}	J_{POCH}
III, $P(OCH)_3(CH_2)_3$	$CDCl_3$	1.89	3.04	4.34	14.0	6.3
$Ni(CO)_3III$	$CDCl_3$	1.85	3.02	4.54	14.2	11.6
$Ni(CO)_2III_2$	$CDCl_3$	1.80	2.95	4.49	13.8	11.8
$Ni(CO)III_3$	$CDCl_3$	1.76	2.88	4.41	13.5	b
$NiIII_4$	CH_2Cl_2	1.74	2.84	4.37	12.9	b
$Fe(CO)_4III$	$CDCl_3$	1.90	3.00	4.75	14.5	14.7
$Fe(CO)_3III_2$	$CDCl_3$	1.79	2.92	4.57	14.0	b
$Cr(CO)_5III$	$CDCl_3$	1.88	3.00	4.59	13.8	12.6
$Cr(CO)_4III_2$	$CDCl_3$	1.79	2.98	4.50	13.6	b
$Mo(CO)_5III$	$CDCl_3$	1.89	3.01	4.60	14.2	12.7
$Mo(CO)_4III_2$	$CDCl_3$	1.79	2.99	4.51	14.1	b
$W(CO)_5III$	$CDCl_3$	1.95	3.05	4.63	14.1	12.8
$W(CO)_4III_2$	$CDCl_3$	1.88	3.01	4.49	14.0	b

[a] Chemical shifts in p.p.m. downfield with respect to tetramethylsilane. J values in c.p.s.

[b] Broad single peaks.

(Figure 6). This is again attributable to P-P coupling. In order to gain some insight as to the make-up of this broad peak, a theoretical treatment for an AA'X system was carried out by modifying an ABX treatment (166) with the assumptions that $\delta_A = \delta_B$ and $J_{BX} = 0$. This results in a five-line AA'X system wherein X refers to the methine proton, A is the phosphorus atom in the same ligand molecule containing the X hydrogen and A' is the phosphorus atom in a neighboring ligand molecule. The positions and relative intensities are shown in Table 23. For the case where $J_{AA'} = 0$, the $-D_+-D_-$ and $+D_++D_-$ lines are found to have the same position as the $-\frac{1}{2}J_{AX}$ and $+\frac{1}{2}J_{AX}$ lines, respectively. The peaks assigned as $-D_+-D_-$ and $+D_+-D_-$ which coincide at all times because $D_+ = D_-$, are then found to have no intensity since $\theta_+ = 0^o$ and $\theta_- = 90^o$. If one considers $J_{AA'}$ = very, very large, $\theta_+ = 90^o$ and $\theta_- = 0^o$. Then the lines $-D_+-D_-$ and $+D_+-D_-$ have no intensity and the center line formed by the coincidence $-D_++D_-$ and $+D_+-D_-$ is 2. The case where $J_{AA'}$ = intermediate would give rise to a broadened spectra since the $-D_+-D_-$ and $+D_++D_-$ peaks now would move out away from $-\frac{1}{2}J_{AX}$ and $+\frac{1}{2}J_{AX}$ and possess some intensity.

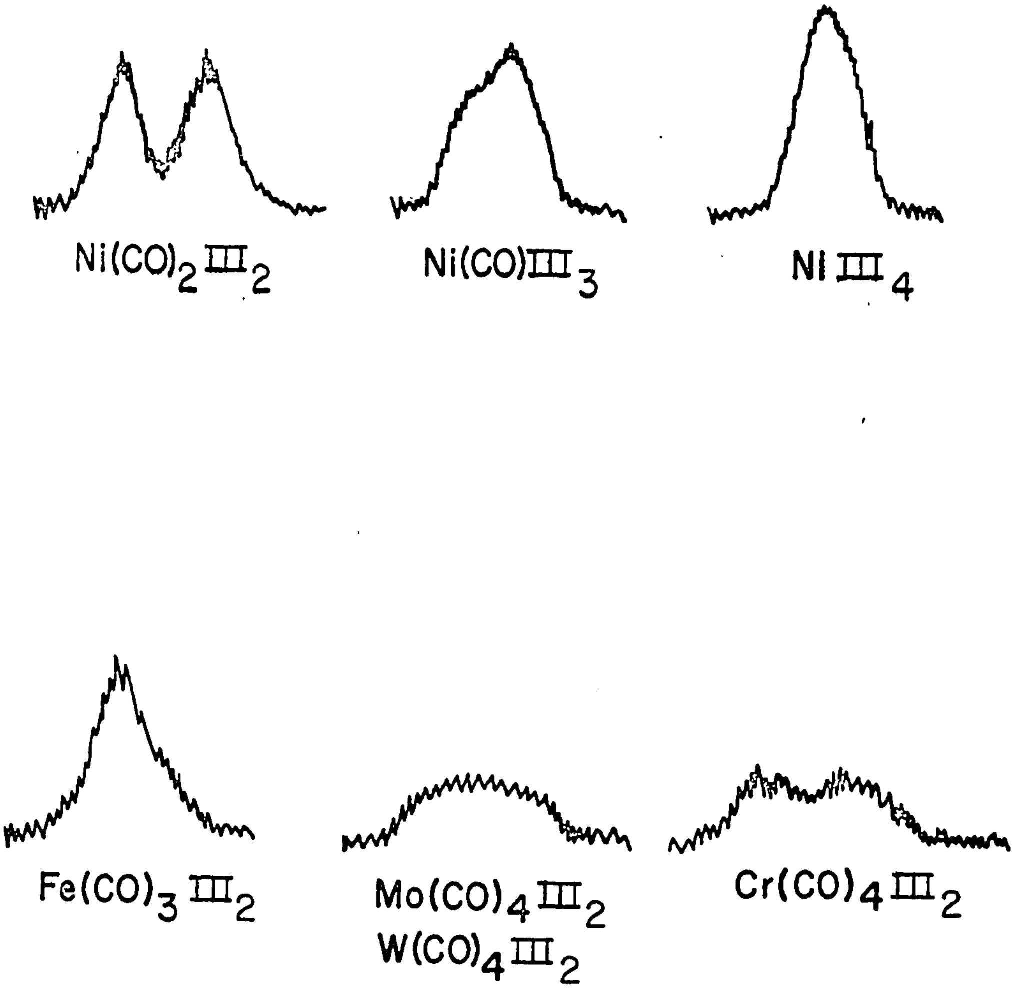


Figure 6. Methine n.m.r. absorptions of substituted metal carbonyl complexes of III. Line widths of various spectra are not drawn to the same scale

Table 23. AA'X n.m.r. spectrum

Position with respect to mean δ_X	Relative intensity
$-D_+ - D_-$	$\sin^2(\theta_+ - \theta_-)$
$-\frac{1}{2}J_{AX}$	1
$-D_+ + D_-$	$\cos^2(\theta_+ - \theta_-)$
$+D_+ - D_-$	$\cos^2(\theta_+ - \theta_-)$
$+\frac{1}{2}J_{AX}$	1
$+D_+ + D_-$	$\sin^2(\theta_+ - \theta_-)$

where $D_+ = D_- = \frac{1}{2}(\frac{1}{4}J_{AX}^2 + J_{AA'}^2)^{\frac{1}{2}}$

$$\sin 2\theta_+ = \sin 2\theta_- = J_{AA'}/2D_+$$

$$\cos 2\theta_+ = J_{AX}/4D_+$$

$$\cos 2\theta_- = -J_{AX}/4D_-$$

Visual estimation of the P-P coupling from Figure 6 gives the order $Fe(CO)_3III_2 > W(CO)_4III_2 \sim Mo(CO)_4III_2 > Cr(CO)_4III_2 > Ni(CO)_2III_2$. This is also in the order of trigonal bipyramidal > octahedral > tetrahedral for the geometry of the complexes. It is again found that within the octahedral geometry, the P-P coupling follows the order W > Mo > Cr. For the intermediate cases, W and Mo, the peak widths at half-height are found to be broader than for the extreme cases where J_{PP} is very large or very small. Indeed this is what is predicted from the theoretical analysis. Due to the broadening of the spectra into a relatively ill-defined peak, no crude calculations as to the amount of J_{PP} could be made.

In the $Ni(CO)_{4-x}(III)_x$ system, a systematic upfield shift of the methine proton with respect to $Ni(CO)_3III$ is observed on increased substitution. The shapes of the methine resonances are found to progress from a doublet to a single peak from di- to tetrasubstitution. Thus, increasing substitution is accompanied by a greater P-P coupling constant in a manner similar to that observed for the analogous complexes of I and II.

The proton n.m.r. spectra of the complexes $Ni[P(OCH_3)_3]_4$ and $Ni[P(OC_2H_5)_3]_4$ were investigated for two reasons. It was of interest to see if these compounds exhibit P-P coupling similar to the NiL_4 complexes where L = I, II, or III. If such coupling was observed, a comparison of the magnitudes observed as a function of the difference in bonding ability would be instructive. Secondly, Vinal and Reynolds (62) have reported that in benzene solutions the $Ni[P(OC_2H_5)_3]_4$ complex is dissociated from 10-30% as indicated by the following equation:

$$\mathrm{Ni}[\mathrm{P}(\mathrm{OC_2H_5})_3]_4 \Longleftrightarrow \mathrm{Ni}[\mathrm{P}(\mathrm{OC_2H_5})_3]_3 + \mathrm{P}(\mathrm{OC_2H_5})_3 \,.$$

If the positions of the free ligand and complex resonances are substantially different, the dissociation should be observable by n.m.r. techniques assuming that the exchange rate is not faster than the relaxation time. Calculation of the amount of dissociation might be possible by comparing the intensities of the resonances attributable to the free ligand and complexes.

The existence of a tricoordinated Ni(0) species has been postulated by Meriwether and Fiene (63) to explain the mechanism of L exchange of $\mathrm{Ni(CO)_2L_2}$ species where L = phosphites or phosphines. They did not observe any spectroscopic or other direct evidence to support the presence of such a species. A study of the CO exchange in $\mathrm{Ni(CO)_4}$ by Wojcicki and Basolo (132) also led to the conclusion that a tricoordinate Ni(0) species, $\mathrm{Ni(CO)_3}$, was an intermediate in the exchange. However, no direct evidence for this species was reported by them.

The n.m.r. spectra of $\mathrm{P(OC_2H_5)_3}$ and $\mathrm{Ni[P(OC_2H_5)_3]_4}$ are shown in Figure 7. The broad peaks appearing between the five-line group assigned to the methylene protons of the

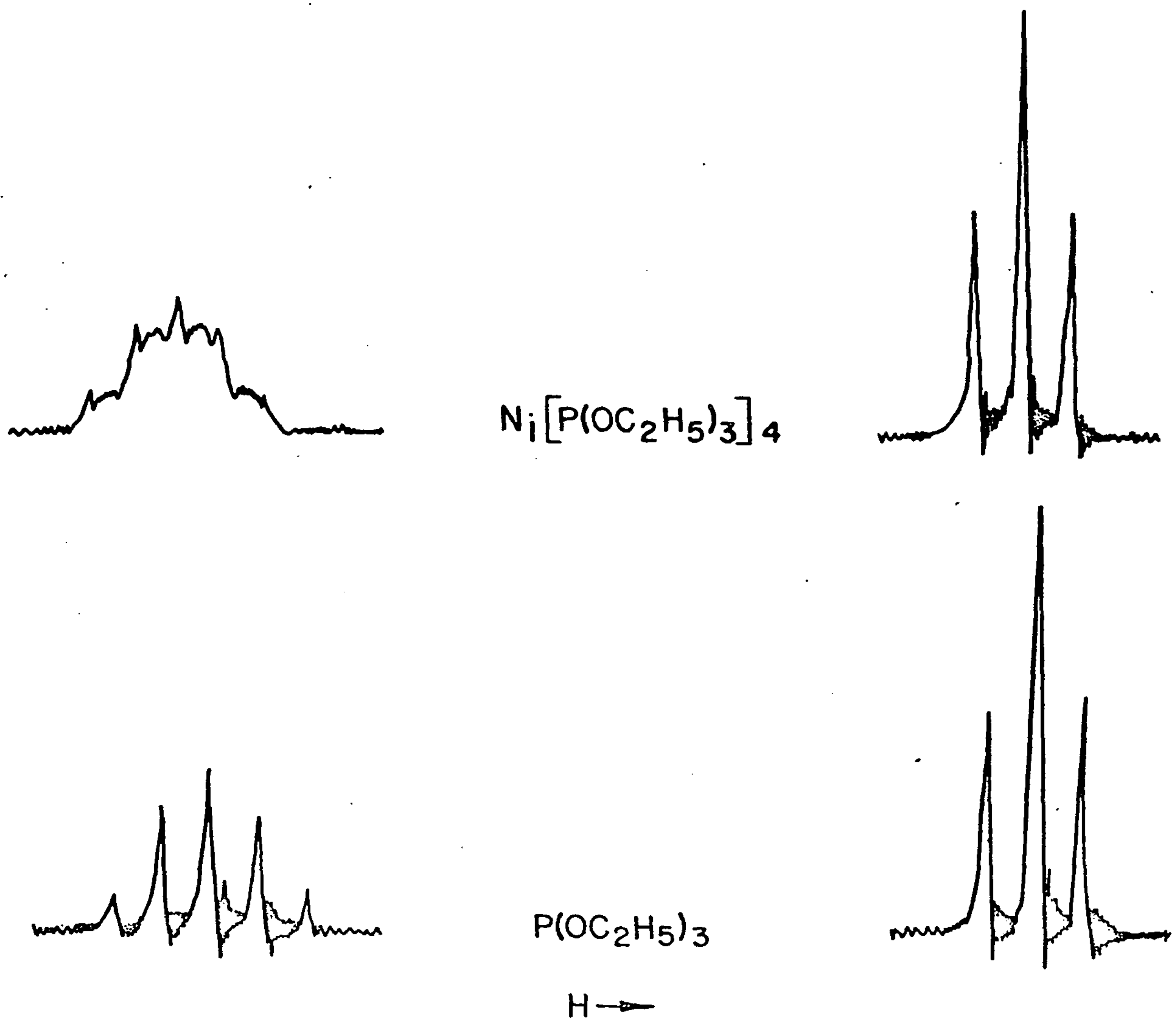


Figure 7. The proton n.m.r. spectra of $P(OC_2H_5)_3$ and $Ni[P(OC_2H_5)_3]_4$

$Ni[P(OC_2H_5)_3]_4$ complex are attributable to P-P coupling. The lack of any resonances in the spectrum that could be assigned to the free ligand casts doubt on the postulated equilibrium. A 10-30% dissociation would result in a concentration of free ligand that would be readily observable in the n.m.r. spectrum. Fast exchange may explain why only one species was observed. Table 24 lists the chemical shifts and coupling constants observed for $P(OCH_3)_3$, $P(OC_2H_5)_3$ and their NiL_4 complexes. The n.m.r. spectrum of $Ni[P(OCH_3)_3]_4$ also exhibits

Table 24. Chemical shifts and coupling constants from the proton n.m.r. spectra of alkyl phosphites and their NiL_4 complexes[a]

Compound	Solvent	Methyl	Methylene	J_{HH}	J_{POCH}	J_{PP}[b]
$P(OCH_3)_3$	C_6H_6	3.30			10.6	
$Ni[P(OCH_3)_3]_4$	C_6H_6	3.62			10.3	11
$P(OC_2H_5)_3$	C_6H_6	3.80	1.12	7.0	7.3	
$Ni[P(OC_2H_5)_3]_4$	C_6H_6	4.13	1.26	7.0	6.7	19

[a] Chemical shifts in p.p.m. downfield with respect to tetramethylsilane; J values in c.p.s.

[b] Approximate values. See text.

P-P coupling. Enlargements of the methyl resonance of Ni$[P(OCH_3)_3]_4$ and methylene resonance of Ni$[P(OC_2H_5)_3]_4$ which clearly show P-P coupling are found in Figure 8.

By assuming that the spectrum of Ni$[P(OCH_3)_3]_4$ may be treated as an AA'X_3 system, a crude estimate of the value of J_{PP} can be made. Modification of an $X_3AA'X'_3$ treatment (167) with the assumptions that $J_{XX'}$ and $J_{AX'} = 0$ resulted in a 14-line spectra wherein the X_3 refers to the methyl protons, A is the phosphorus atom in the same ligand molecule containing the X_3 hydrogens, and A' is the phosphorus atom in a neighboring ligand molecule. The positions and relative intensities of the lines are shown in Table 25.

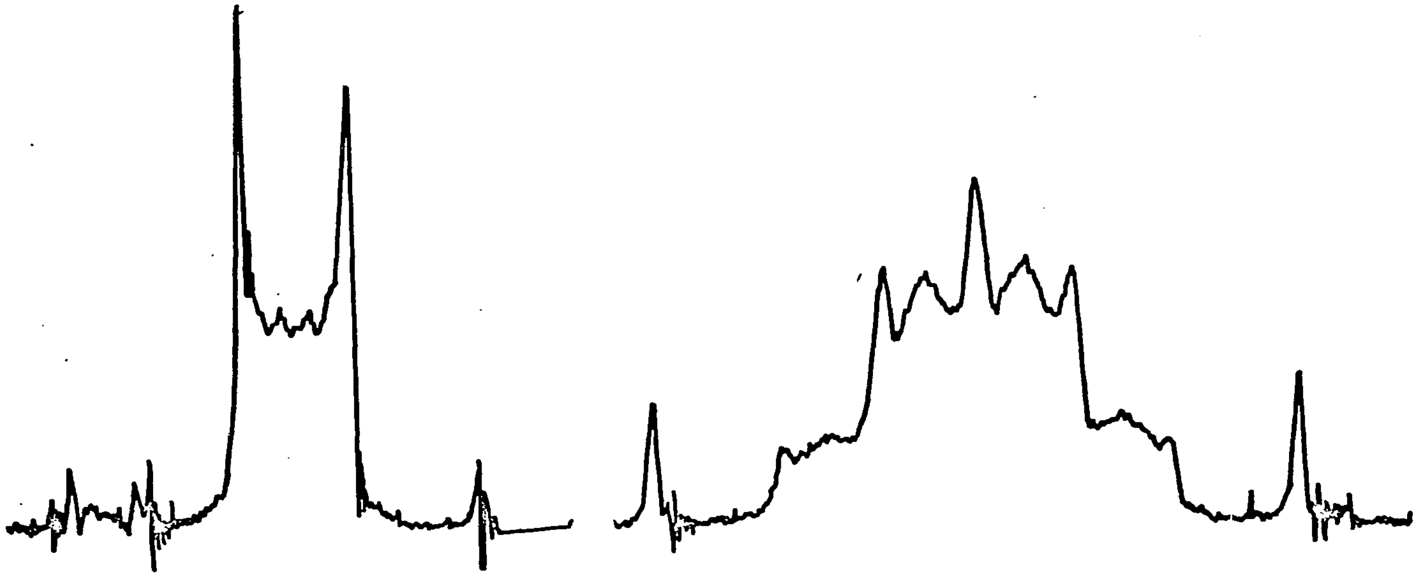
Table 25. AA'X_3 n.m.r. spectrum

Position with respect to mean δx_3	Relative intensities
$\pm \frac{1}{2} J_{AX}$	16
$\pm \frac{1}{2} (A - J_{AA'})$	$5(1 + \sin 2\theta_A)$
$\pm \frac{1}{2} (A + J_{AA'})$	$5(1 - \sin 2\theta_A)$
$\pm \frac{1}{2} (B - A)$	$5\cos^2(\theta_A - \theta_B)$
$\pm \frac{1}{2} (B + A)$	$5\sin^2(\theta_A - \theta_B)$
$\pm \frac{1}{2} (C - B)$	$\cos^2(\theta_B - \theta_C)$
$\pm \frac{1}{2} (C + B)$	$\sin^2(\theta_B - \theta_C)$

where $A = (J_{AX}^2 + J_{AA'}^2)^{\frac{1}{2}}$ $\qquad \sin 2\theta_A = J_{AA'}/A$

$B = (4J_{AX}^2 + J_{AA'}^2)^{\frac{1}{2}}$ $\qquad \sin 2\theta_B = J_{AA'}/B$

$C = (9J_{AX}^2 + J_{AA'}^2)^{\frac{1}{2}}$ $\qquad \sin 2\theta_C = J_{AA'}/C$



$Ni[P(OCH_3)_3]_4$ $Ni[P(OC_2H_5)_3]_4$

Figure 8. Enlarged portions of the proton n.m.r. spectra of $Ni[P(OCH_3)_3]_4$ and $Ni[P(OC_2H_5)_3]_4$

The spectrum for this type of system will always be roughly a doublet because the two lines at $\pm \frac{1}{2}J_{AX}$, which are independent of $J_{AA'}$, account for one-half the intensity of the methyl group. The lines at $\pm \frac{1}{2}(B+A)$ and $\pm \frac{1}{2}(C+B)$ have zero intensity when the ratio $J_{AA'}/(J_{AX} + J_{AA'})$ is either zero or infinity. The more intense pair of the two lines, $\pm \frac{1}{2}(A+B)$, has been shown by Anet (167) to exhibit a maximum intensity of 0.1. The intensity of the lines at $\pm \frac{1}{2}(C-B)$ will also be of negligible intensity. It can be seen from inspection that the two lines $\pm \frac{1}{2}(A+J_{AA'})$ will be found outside the main doublet at $\pm \frac{1}{2}J_{AX}$. As $J_{AA'}$ increases, these lines will decrease rapidly in intensity while moving farther away from the main doublet. Hence, one would expect to observe a strong doublet within which is contained another pair of doublets. The methyl resonance for $Ni[P(OCH_3)_3]_4$ exhibits a center pair of distinct doublets which are attributable to the $\pm \frac{1}{2}(A - J_{AA'})$ lines. A value of J_{PP} of 19 c.p.s. was calculated using the formula: Separation of two center peaks = $(J_{AX}^2 + J_{AA'}^2)^{\frac{1}{2}} - J_{AA'}$. On close inspection of the spectrum, what appear to be shoulders on the two main peaks attributed to $\pm \frac{1}{2}J_{AX}$ are observed. These shoulders are at the position expected for the $\pm \frac{1}{2}(B-A)$ lines and, hence, are tentatively assigned as such.

For the $Ni[P(OC_2H_5)_3]_4$ complex whose methylene resonance which exhibits P-P coupling is shown in Figure 8, a value of 11 c.p.s. for J_{PP} was obtained by treating the spectrum as an $AA'X_2$ system. The notation and method of calculation was the same as previously described for the complexes of $P(OCH_2)_3CCH_3$ and $P(OCH_2)_3CC_2H_5$. Comparing the results obtained for the NiL_4 complexes studied indicates that varying the ligand in analogous systems results in changes in the value of J_{PP}. It is also of interest that J_{POCH} is observed to decrease on coordination for the trialkyl phosphites while the polycyclic phosphites exhibit an increase for analogous complexes (Tables 19, 21, 22, and 24).

Since it appears that P-P coupling occurs only when the ligands are in the trans position, conjecture that the mechanism involved might make use of pi-orbital overlap does not seem unreasonable. Indeed, support for this argument can be derived from the n.m.r. spectra observed for the compound $(CH_3)_3CP(O)(F)N(CH_3)_2$ which was found to exist in two, presumably rotational, isomeric forms. Schmutzler and Reddy[1]

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[1] R. Schmutzler and G. S. Reddy, E. I. duPont de Nemours and Company, Wilmington, Delaware. An n.m.r. study of some tertiary butyl-phosphorus compounds. Private communication. 1965.

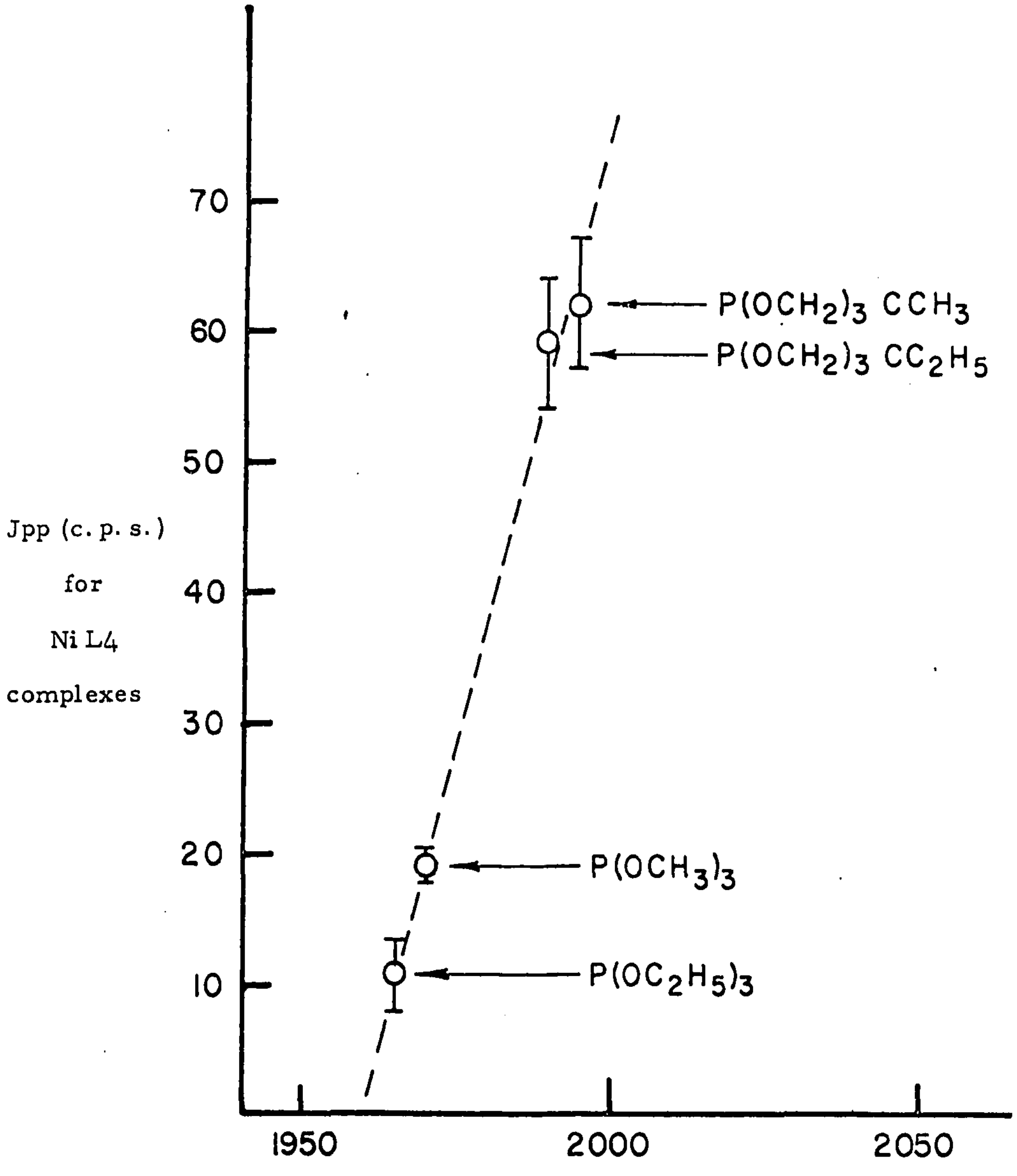
have reported that the $N(CH_3)_2$ resonances for a mixture of these isomers exhibit a doublet of doublets and a singlet. The doublet of doublets is explained as resulting from coupling of the methyl protons with the phosphorus and with the fluorine, while the singlet represents the isomer where no H-P or H-F coupling takes place.

If one constructs models of the isomers, in one case the lone pair of the nitrogen and the phosphorus are arranged so *pi*-orbital overlap is feasible while for the other isomer orbital overlap is unlikely. Hence, the mechanism of coupling may involve the use of d-*pi* p-*pi*-bonding between the phosphorus and nitrogen. Investigation of the P^{31} spectra also indicated two isomers, one wherein coupling with the $N(CH_3)_2$ protons was observed and one wherein no coupling of this type was found.

The observed P-P coupling in carbonyl complexes appears to be a function of geometry in that trigonal bipyramid > octahedral > tetrahedral. In the tetrahedral compound $Ni(CO)_2L_2$, the two ligands would not be expected to use the same orbital for *pi*-bonding. No P-P coupling is observed for this case. For the trigonal bipyramidal compounds of the type $Fe(CO)_3L_2$ and the octahedral $M(CO)_4L_2$ compounds, the two trans ligands can use the same orbital for pi-overlap. In these cases P-P coupling is observed.

It is also found that the P-P coupling can be related to the pi-bonding ability of the ligand. A comparison of the methylene resonances of the carbonyl compounds of I and tris (dimethylamino)phosphine (76) indicates that the center peak is slightly larger for I. The C-O stretching frequencies of these compounds indicate that I is a better pi-bonding ligand than tris(dimethylamino)phosphine. Since the height and sharpness of the center peak is directly proportional to the amount of P-P coupling, it appears that the stronger pi-bonding ligand exhibits the greatest P-P coupling.

Further support for this argument can be derived from the J_{PP} values calculated for the NiL_4 system wherein L = I, II, $P(OCH_3)_3$ or $P(OC_2H_5)_3$. The relative pi-bonding ability of these ligands has been established from the C-O stretching frequency of substituted carbonyl complexes. Figure 9 shows a plot of J_{PP} versus the relative pi-bond strength of L where the relative pi-bonding strength was assumed to be proportional to the symmetric C-O stretching frequency in the $Ni(CO)_2L_2$ complexes. A direct linear relationship between J_{PP} and relative pi-bonding ability is noted. Since it has



Relative π-Bonding Strength of L

from

Frequency in $cm.^{-1}$ of $Ni(Co)_2L_2$ complexes

Figure 9. Correlation of Jpp with pi-bonding ability

been suggested that P-P coupling takes place by use of _pi_-orbital overlap, the observation that ligands which make better use of _pi_-orbital overlap in bonding exhibit more coupling supports this argument.

The P^{31} n.m.r. spectra of several complexes are reported in Table 26. Lack of adequate solubility prevented spectra of the other complexes from being obtained. The chemical shifts observed for the complexes are denoted as δ P-M while those for the free ligands are given as δ P. The value δ P-M - δ P, the magnitude and sign of the resonance shift on complexation, listed for each complex has been previously found useful in the interpretation of P^{31} data of nickel carbonyl-phosphine complexes (139).

Correlation of the chemical shifts observed in the P^{31} spectra of compounds has been attempted by many (139, 168, 169,170). Relationships of the P^{31} shifts to bond angle, degree of substitution, electronegativity of substituents, and types of groups substituted on the phosphorus have been shown. No quantitative correlation between the chemical shift and the nature of the atom or group attached to the phosphorus has been demonstrated even though the P^{31} chemical shifts of over 1,000 phosphorus compounds have been reported

Table 26. Chemical shifts from the P^{31} n.m.r. spectra of metal carbonyl complexes of phosphites

Compound	δ_{P-M}	Ligand	δ_P	$\delta_{P-M} - \delta_P$
$Ni(CO)_3II$	-128.0	$P(OCH_2)_3CC_2H_5$	-92.8	-35.2
$Ni(CO)_2II_2$	-129.3	$P(OCH_2)_3CC_2H_5$	-92.8	-36.5
$Ni(CO)II_3$	-129.4	$P(OCH_2)_3CC_2H_5$	-92.8	-36.6
$NiII_4$	-128.8	$P(OCH_2)_3CC_2H_5$	-92.8	-36.0
$Ni(CO)_3I$	-126.2	$P(OCH_2)_3CCH_3$	-91.5	-34.7
$Ni(CO)_3III$	-156	$P(OCH)_3(CH_2)_3$	-137	-19
$Ni[P(OCH_3)_3]_4$	-163.2	$P(OCH_3)_3$	-140	-23
$Ni[P(OC_2H_5)_3]_4$	-158.5	$P(OC_2H_5)_3$	-140	-19
$Fe(CO)_4II$	-136	$P(OCH_2)_3CC_2H_5$	-92.8	-43
$Cr(CO)_5II$	-162	$P(OCH_2)_3CC_2H_5$	-92.8	-69
$Mo(CO)_5II$	-136	$P(OCH_2)_3CC_2H_5$	-92.8	-43
$W(CO)_5II$	-114	$P(OCH_2)_3CC_2H_5$	-92.8	-21

in the literature (171,172,173).

Theoretical equations for the electron shielding of atoms in a compound have been derived by Ramsey (174,175,176, 177). By considering only the 3p electrons Saika and Slichter (178) have shown that the chemical shift is primarily effected by the second order paramagnetic term in the Ramsey equation (175). In this treatment, the closed electron shell and the s electrons have been shown to give little effect (178). However, the use of any of the d orbitals for pi-bonding will result in a change in dependence of the chemical shift on the second order paramagnetic term. Thus, the anisotropy of the phosphorus appears to be an important influence on the chemical shift.

The factors that must be considered when attempting to interpret P^{31} chemical shifts are: 1) second order paramagnetic contribution, 2) inductive effects of groups attached to the phosphorus, 3) number of substituents on the phosphorus, 4) bond angles about the phosphorus, 5) possible back donation to the phosphorus through pi-bonding, 6) aromatic ring currents, and 7) steric effects. A study of the P^{31} n.m.r. spectra of several nickel carbonyl-phosphine complexes has been made by Meriwether and Leto (139). They concluded that additional factors that should be considered when attempting to correlate chemical shifts of complexes are: 1) paramagnetic contribution from the diamagnetic complex, 2) sigma- and possible pi-bonding between the nickel and phosphorus, 3) bond rehybridization and change in bond angles of the phosphorus on complex formation, 4) change in number of substituents about the phosphorus, and 5) steric effects.

In Table 26 it is found that the $Ni(CO)_{4-x}(II)_x$ series exhibits a constant δ P-M value on increased substitution. This is in agreement with the constant δ P-M values observed for the system $Ni(CO)_{4-x}[P(OC_2H_5)_3]_x$ (139) which can be interpreted to indicate that the electron density about the phosphorus does not change. Hence, the same M-P bond for the series would be predicted. This is in agreement with the constant value observed for the M-P stretching frequency in the far infrared spectra.

With respect to other phosphites, the δ P-M - δ P value for analogous nickel carbonyl complexes of II are the most negative. The $Ni(CO)_3L$ complexes of I, II and III exhibit δ P-M - δ P values that decrease in that order. It is interesting to note that for the NiL_4 systems, as the pi-bonding ability of the ligand increases, the δ P-M - δ P value decreases: -19, $P(OC_2H_5)_3$; -23, $P(OCH_3)_3$; -36, $P(OCH_2)_3CC_2H_5$. Meriwether and Leto (139) have concluded from their data that as the δ P-M - δ P value becomes more negative, the pi-bonding ability of the ligand decreases. If such were the case, the ligand II would appear to be a poorer pi-bonding ligand than trialkyl phosphites which is contrary to the inferences drawn from the infrared data.

The monosubstituted complexes of the Group VI carbonyls of II are found to exhibit decreasing δ P-M - δ P values going down the group from Cr to W. Thus as the metal atom becomes more polarizable, the electron density about the phosphorus appears to increase. It was predicted from the far infrared spectra that the metal-phosphorus bond strength appeared to increase proceeding down the Group IV complexes. The observed P^{31} shifts can also be interpreted to indicate a stronger metal-phosphorus bond from Cr to W. In going across the period from Cr to Ni, a decrease in the δ P-M - δ P value is also found. This decrease accompanies a slight decrease in the polarizability of the metal atom. It should be noted here, however, that the geometries of the complexes also are different. Thus the decrease in δ P-M - δ P values might be ascribed to the change in geometry of the complexes.

Molecular Weight Determinations

Vinal and Reynolds' (62) postulated equilibrium for $Ni[P(OC_2H_5)_3]_4$ in benzene solutions was based on cryoscopic molecular weight data obtained over a concentration range of 0.043 to 0.014 Molar. Since no evidence for this dissociation was observed in the n.m.r. spectra of $Ni[P(OC_2H_5)_3]_4$ or $Ni[P(OCH_3)_3]_4$, a reexamination of the molecular weight using a vapor pressure osmometer was undertaken. The results thus obtained indicate monomeric behavior over a 0.023 to 0.006 Molar concentration range (Table 27).

Table 27. Molecular weight determinations of $Ni[P(OCH_3)_3]_4$ and $Ni[P(OC_2H_5)_3]_4$ in benzene using vapor pressure lowering techniques

	Solution concentration (g/ml.)	Observed molarity	Calculated molecular wt.
$Ni[P(OCH_3)_3]_4$	0.02020	0.0370	545
	0.01010	0.0182	553
	0.00505	0.0092	549
		average = 549 ± 4 theoretical = 555	
$Ni[P(OC_2H_5)_3]_4$	0.01696	0.0234	725
	0.01523	0.0212	719
	0.00848	0.0118	718
	0.00762	0.0105	725
	0.00424	0.0059	718
		average = 721 ± 4 theoretical = 723	

As was pointed out in the experimental portion, these compounds are sensitive to air oxidation and must be handled under an inert atmosphere. Molecular weight determinations made ignoring this precaution resulted in a range of values from 410 to 635 (theoretical 723) for $Ni[P(OC_2H_5)_3]_4$. If solutions were allowed to stand exposed to the air a quasi linear decrease of molecular weight with time was found. These solutions were observed to exhibit a light green coloration suggestive of nickel(II) ion, hence, the variation of the values found for the molecular weight might be explained by the following equation:

$$2Ni[P(OC_2H_5)_3]_4 + O_2 \longrightarrow 2NiO + 8P(OC_2H_5)_3.$$

Due to the lack of evidence for dissociation of $Ni[P(OC_2H_5)_3]_4$ or $Ni[P(OCH_3)_3]_4$ in benzene solution from the n.m.r. spectra and the excellent agreement of the theoretical molecular weights with those determined by osmometric methods, it must be concluded that these compounds exhibit monomeric behavior in benzene solutions. The molecular weights of all the complexes of I and II indicate that they are monomers as expected (Table 9). Selected compounds of III also appear to be monomeric (Table 9). Poor solubility prevented the molecular weight determination of all the complexes of III.

SUMMARY

The preparation and characterization of metal carbonyl complexes of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$, 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CC_2H_5$, and 2,8,9-trioxa-1-phosphaadamantane, $P(OCH)_3(CH_2)_3$, have been described. Substitution products obtained from $Ni(CO)_4$ include compounds of the type $Ni(CO)_{4-x}(Ligand)_x$ where x = 1, 2, 3, or 4. Synthesis of the mono- and disubstituted complexes of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with these ligands has also been reported. A comparison of the carbonyl infrared stretching frequencies of compounds prepared in this work with analogous compounds (23, 88,108) implied that these ligands are equal to or greater than other phosphites in *pi*-bonding ability. Calculation of the force and interaction constants for the C-O modes using the method of Cotton and Kraihanzel (127) have led to the same conclusion. The spectra indicated that the $Ni(CO)_3$(Ligand) complexes are tetrahedral and that the disubstituted complexes of the carbonyls other than nickel are of a *trans* configuration. The far infrared spectra of the ligands and selected complexes were observed. Attempts to assign the M-C, M-C-O, and M-P modes in the compounds and correlate the

observed frequencies with bonding were made.

The proton n.m.r. spectra of all the prepared compounds were observed. Trends in the chemical shifts as a function of the degree of substitution and complex geometry were noted. The magnitude of the chemical shifts and J_{POCH} indicate that some pi-bonding is taking place in these complexes. The proton spectra of the disubstituted complexes exhibited varying degrees of P-P coupling. Crude attempts to calculate the magnitude of this coupling which appears to be a function of the complex geometry, metal atom and pi-bonding ability of the ligand were made. The P^{31} spectra of selected complexes were reported and attempts to correlate the observed shifts made. The P^{31} resonance appeared to be unaffected by the degree of substitution but strongly influenced by the polarizability of the metal atom or the geometry of the complex.

The proton n.m.r. spectra of the complexes $Ni[P(OCH_3)_3]_4$ and $Ni[P(OC_2H_5)_3]_4$ were found to exhibit P-P coupling. Crude calculations as to the magnitude of this coupling lent support to the postulate that P-P coupling is affected by the pi-bonding ability of the ligand. No evidence to support the dissociation of these compounds in benzene proposed by others was observed by n.m.r. techniques. The molecular weight determinations of these complexes in benzene solutions using a vapor pressure osmometer indicated monomeric behaviour over a concentration range of 0.006 to 0.023 Molar. Hence, the complexes $Ni[P(OCH_3)_3]_4$ and $Ni[P(OC_2H_5)_3]_4$ appear to be monomeric in benzene.

SUGGESTIONS FOR FUTURE WORK

The ease with which the NiL_4 complexes where L = I, II, or III can be prepared from $Ni(CO)_4$ might indicate the possibility of the preparation of higher substituted complexes of the carbonyls of iron, chromium, molybdenum and tungsten. Since the complex $Mo(CO)_2[P(OCH_3)_3]_4$ has been reported in the literature (88), analogous compounds with the polycyclic ligands would also be expected to exist. Evidence of the existence of $M(CO)_3L_3$ species has been observed in the infrared spectra. An extremely insoluble material possessing properties which are vastly different from the $Fe(CO)_3L_2$ species was obtained from some iron carbonyl reactions in which a large excess of ligand was used. The possibility that compounds similar to $M(PF_3)_6$ (86,87) the $Fe(CO)_{5-x}(PF_3)_x$ series where x = 3, 4 or 5 (78) could be prepared using analogous reactions with polycyclic phosphites as ligands should be investigated.

There are two general areas of work in the field of carbonyl chemistry which have not been investigated using polycyclic ligands. Complexes of the dinuclear carbonyls of the cobalt, iron and manganese groups should provide some very interesting compounds. The second area, that of cycloalkene carbonyl chemistry, should also be of interest. Studies of the ability of the polycyclic ligands to replace all of the carbonyls of $M(CO)_3$cycloalkene complexes should be undertaken. Since it has been found that the polycyclic ligands are relatively strong pi-bonding ligands, perhaps the displacement of the cycloalkene ligand may be attained in some complexes.

As was pointed out in the introduction, numerous patents concerning the ability of complexes of the type $Ni(CO)_{4-x}L_x$ to act as catalysts have been issued (33-47). The fact that this series of complexes wherein L is a polycyclic phosphite exhibit much greater thermal stabilities than analogous complexes may make them much more useful as catalysts in high temperature processes. Studies of the abilities of these compounds to act as organic polymerization catalysts should be undertaken.

Reports of the far infrared spectra of carbonyl complexes are almost nonexistent. A systematic study of a large series of such complexes should be undertaken in order to clear up doubt that exists about the assignment of the M-C, M-P and M-C-O modes. An accurate determination of these frequencies and proper interpretation should lead to a better understanding of the bond strengths and bond orders of these compounds.

The phenomena of P-P coupling which was observed for several of the disubstituted complexes deserves extensive study. The apparent relation between orbital overlap, pi-bonding ability of the ligand and the observed coupling leads to conjecture about the relation between bonding in the complex and this effect. Since the reports in the literature of P-P coupling are few (76), a study of a large number of complexes should be undertaken in order to elucidate the phenomenon. Some specific areas that should be of interest are the study of PF_3 complexes wherein the F^{19} spectra would be expected to exhibit P-P coupling, and studies of several cis and trans isomers to further establish the dependency of P-P coupling on geometry.

Our ignorance is again revealed by the P^{31} spectral data. Even though the spectra of many phosphorus compounds and a few of their complexes are reported in the literature (168-173), no theory has been developed which adequately explains the meaning of the observed shifts in terms of bonding (171). Due to a rather inadequate amount of P^{31} data on complexes (139), a large number of complexes should be systematically investigated in order to form a basis for understanding the observed shifts.

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VITA

David George Hendricker

Born October 14, 1938 Aurora, Illinois

Married Sara Lynn Ague June 19, 1965 Denison, Texas

Education

East Aurora High School Aurora, Illinois 1952-1956

Northern Illinois University Dekalb, Illinois
1956-1960 B.S. 1960

Iowa State University Ames, Iowa 1960-1965
M.S. 1963 Ph.D. 1965

Employment

Ohio University Athens, Ohio Assistant Professor of
Chemistry September 1965