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Transition Metal Complexes of a Constrained Phosphite Ester. III. Metal Carbonyl Complexes of 4-Methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane[1,2]

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The preparation and characterization of metal carbonyl complexes of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$, are described. Substitution products obtained from $Ni(CO)_4$ include compounds of the type $Ni[P(OCH_2)_3CCH_3]_x(CO)_{4-x}$ 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 $P(OCH_2)_3CCH_3$ is also reported. A study of the carbonyl infrared stretching frequencies implies that $P(OCH_2)_3CCH_3$ is equal to or greater than other phosphites in π-bonding ability. The proton n.m.r. spectra of the compounds are discussed with special attention given to the disubstituted complexes.

Introduction

Large numbers of complexes have been obtained by the reaction of metal carbonyls with tricovalent phosphorus ligands of the types PX_3,[3,4] $P(OR)_3$,[5,6] $P(NR_2)_3$,[7] and PR_3.[8,9] The phosphite ester 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane shown in Figure 1 and hereafter referred to as L, in contrast to trialkyl phosphites, exhibits low steric hindrance[10] and stronger σ- and π-bonding[11] abilities. In view of the apparent dependence[6,12-15] of the carbonyl infrared stretching frequency in partially substituted metal carbonyl complexes on the π-bonding ability of the ligand, it was of considerable interest to attempt the synthesis of such coordination complexes with L and to study their infrared absorptions in the carbonyl region. The proton n.m.r. spectra of these complexes are also herein reported and the unusual features of the phosphorus–phosphorus spin coupling discussed.

Experimental

The infrared spectra were obtained in Halocarbon oil and Nujol mulls and recorded on a Perkin-Elmer Model 21 double beam spectrometer using sodium chloride optics. In addition, the carbonyl region of the spectrum was observed for the compounds in chloroform solution and in Halocarbon oil mulls using a Beckman I.R.-7 spectrometer with sodium chloride optics. 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. Tetramethylsilane was used as an internal standard. Melting points were taken in capillaries and are uncorrected. Molecular weight determinations were made using a Mechrolab vapor pressure osmometer (Model 301 A). Measurements were made over a concentration range of 0.025–0.005 *M* on either benzene or chloroform solutions.

Carbon and hydrogen contents were determined by combustion. Nickel analyses were carried out by a standard procedure as the dimethylglyoxime complex.[16] Molybdenum[17] and tungsten[18] were determined gravimetrically as the 8-hydroxyquinoline complexes, chromium was determined spectrophotometrically using *s*-diphenylcarbazide,[19] iron was determined colorimetrically with 1,10-phenanthroline,[20] and phosphorus analyses were carried out by the Schöniger procedure.[21] Yields of monosubstituted compound were calculated on the basis of L and all others on the basis of metal carbonyl used.

Materials.—Nickel tetracarbonyl and iron pentacarbonyl were purchased from A. D. MacKay, Inc., chromium hexacarbonyl was purchased from the Diamond Alkali Corp., and molybdenum and tungsten hexacarbonyls were gifts from the Climax Molybdenum Co. The phosphite ligand, L, was prepared by a method described elsewhere.[22]

Mono-L-tricarbonylnickel—To a mixture of 4.0 g. (27 mmoles) of L in 50 ml. of chloroform, 5.0 ml. (37 mmoles) of nickel tetracarbonyl was 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°.

Anal. Calcd. for $C_8H_9O_6PNi$: C, 33.0; H, 3.1; P, 10.6; Ni, 20.2; mol. wt., 291. Found: C, 33.1; H, 3.2; P, 10.3; Ni, 20.3; mol. wt., 293.

Bis-L-dicarbonylnickel.—A mixture of 0.40 g. (1.4 mmoles) of $Ni(CO)_3L$, 0.20 g. (1.4 mmoles) of L, and 30 ml. of chloroform was refluxed 4 hr. under helium with magnetic stirring. From this reaction mixture 0.50 g. of crude $Ni(CO)_2L_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. Chromatography with a benzene–chloroform mixture (1:1) on an alumina column resulted in the isolation of 0.45 g. (79% yield) of $Ni(CO)_2L_2$. The first fractions contained the pure $Ni(CO)_2L_2$, while the latter ones yielded the impurity which was $Ni(CO)L_3$. The pure colorless crystals decomposed at 278°.

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[2] Presented in part at the Eighth International Conference on Coordination Chemistry, Vienna, Austria, Sept. 1964.

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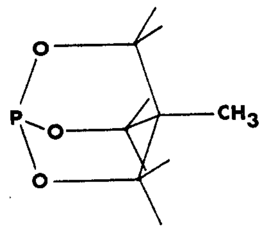

L

Figure 1.—Structure of 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, L.

Anal. Calcd. for $C_{12}H_{18}O_8P_2Ni$: C, 35.1; H, 4.4; P, 15.1; Ni, 14.3; mol. wt., 411. Found: C, 34.9; H, 4.6; P, 14.9; Ni, 14.4; mol. wt., 409.

Tris-L-monocarbonylnickel.—A mixture of 0.50 g. (1.7 mmoles) of $Ni(CO)_3L$, 1.0 g. (6.8 mmoles) of L, and 30 ml. of ethylbenzene was refluxed 6 hr. under helium with magnetic stirring. From this reaction mixture 0.80 g. of crude $Ni(CO)L_3$ was isolated in the same manner described for the isolation of $Ni(CO)_3L$. After several recrystallizations from chloroform, 0.65 g. (72% yield) of pure $Ni(CO)L_3$ decomposing at 328° was obtained.

Anal. Calcd. for $C_{16}H_{27}O_{10}P_3Ni$: C, 36.2; H, 5.1; P, 17.5; Ni, 11.1. Found: C, 36.1; H, 5.4; P, 17.2; Ni, 11.0.

Tetrakis-L-nickel.—A mixture of 0.30 g. (0.60 mmole) of $Ni(CO)_3L$, 0.20 g. (1.3 mmoles) of L, and 30 ml. of chlorobenzene was refluxed 18 hr. under helium with magnetic stirring. On cooling the reaction mixture a light yellow precipitate was obtained. Recrystallization from methylene chloride gave 0.35 g. (95% yield) of white crystals which decomposed at 365°.

Anal. Calcd. for $C_{20}H_{36}O_{12}P_4Ni$: C, 36.8; H, 5.5; P, 19.1; Ni, 9.0. Found: C, 37.0; H, 5.6; P, 18.9; Ni, 9.1.

Mono-L-tetracarbonyliron.—A mixture of 2.0 ml. (15 mmoles) of iron pentacarbonyl, 1.5 g. (10 mmoles) of L, 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 $Fe(CO)_4L$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. The very light yellow crystals decomposed at 179°.

Anal. Calcd. for $C_9H_9O_7PFe$: C, 34.2; H, 2.9; P, 9.8; Fe, 17.7; mol. wt., 316. Found: C, 34.4; H, 2.9; P, 9.7; Fe, 17.7; mol. wt., 318.

Bis-L-tricarbonyliron.—A mixture of 2.0 ml. (2.9 g., 15 mmoles) of iron pentacarbonyl, 4.5 g. (30 mmoles) of L, 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 $Fe(CO)_3L_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. The very light yellow crystals decomposed at 231°.

Anal. Calcd. for $C_{13}H_{18}O_9P_2Fe$: C, 35.8; H, 4.1; P, 14.2; Fe, 12.8; mol. wt., 436. Found: C, 35.7; H, 4.4; P, 14.0; Fe, 12.7; mol. wt., 441.

Mono-L-pentacarbonylchromium.—A mixture of 1.0 g. (4.5 mmoles) of chromium hexacarbonyl, 0.30 g. (2.0 mmoles) of L, and 200 ml. of chloroform was placed in a quartz tube. Irradiation with ultraviolet light (Hanovia lamp No. 654A) was carried out for 1.5 hr. with magnetic stirring. The solution was evaporated to one-tenth its volume under vacuum. From this solution 0.63 g. (93% yield) of $Cr(CO)_5L$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. The white crystals decomposed at 212°.

Anal. Calcd. for $C_{10}H_9O_8PCr$: C, 35.3; H, 2.7; P, 9.1; Cr, 15.3; mol. wt., 340. Found: C, 35.4; H, 2.8; P, 9.0; Cr, 15.3; mol. wt., 343.

Bis-L-tetracarbonylchromium.—A mixture of 1.1 g. (5.0 mmoles) of chromium hexacarbonyl, 1.9 g. (12 mmoles) of L, 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 $Cr(CO)_4L_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. The white crystals decomposed at 278°.

Anal. Calcd. for $C_{14}H_{18}O_{10}P_2Cr$: C, 36.5; H, 3.9; P, 13.5; Cr, 11.3; mol. wt., 460. Found: C, 36.7; H, 4.2; P, 13.3; Cr, 11.1; mol. wt., 461.

Mono-L-pentacarbonylmolybdenum.—A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 0.6 g. (4 mmoles) of L, 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 $Mo(CO)_5L$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. The white crystals decomposed at 197°.

Anal. Calcd. for $C_{10}H_9O_8PMo$: C, 31.3; H, 2.3; P, 8.1; Mo, 25.0; mol. wt., 384. Found: C, 31.3; H, 2.3; P, 7.8; Mo, 24.9; mol. wt., 381.

Bis-L-tetracarbonylmolybdenum.—A mixture of 1.3 g. (5.0 mmoles) of molybdenum hexacarbonyl, 1.9 g. (12 mmoles) of L, and 30 ml. of methylcyclohexane was refluxed for 24 hr. under helium with magnetic stirring. From this reaction mixture 1.3 g. of crude $Mo(CO)_4L_2$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. After recrystallization from acetone, 1.0 g. (40% yield) of pure $Mo(CO)_4L_2$ was obtained. The white crystals decomposed at 244°.

Anal. Calcd. for $C_{14}H_{18}O_{10}P_2Mo$: C, 33.4; H, 3.6; P, 12.3; Mo, 19.1; mol. wt., 504. Found: C, 33.4; H, 3.6; P, 12.0; Mo, 19.1; mol. wt., 499.

Mono-L-pentacarbonyltungsten.—A mixture of 1.8 g. (5.0 mmoles) of tungsten hexacarbonyl, 0.6 g. (4 mmoles) of L, 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 $W(CO)_5L$ was isolated in the same manner as described for the isolation of $Ni(CO)_3L$. The white crystals decomposed at 228°.

Anal. Calcd. for $C_{10}H_9O_8PW$: C, 25.4; H, 1.9; P, 6.6; W, 39.0; mol. wt., 472. Found: C, 25.5; H, 2.3; P, 6.4; W, 38.8; mol. wt., 466.

Bis-L-tetracarbonyltungsten.—A mixture of 1.8 g. (5.0 mmoles) of tungsten hexacarbonyl, 1.5 g. (10 mmoles) of L, and 200 ml. of ethylbenzene was placed in a quartz tube. Irradiation with ultraviolet light was carried out for 4 hr. with magnetic stirring. The solution was evaporated to one-tenth its volume under vacuum after filtering to remove some decomposition products. From this solution 2.5 g. of crude product was isolated in the same manner as described for $Ni(CO)_3L$. Recrystallization using chloroform and acetone gave 1.7 g. (58% yield) of pure white crystalline $W(CO)_4L_2$, which decomposed at 272°.

Anal. Calcd. for $C_{14}H_{18}O_{10}P_2W$: C, 28.4; H, 3.0; P, 10.4; W, 31.1; mol. wt., 592. Found: C, 28.4; H, 3.4; P, 10.1; W, 30.9; mol. wt., 581.

Both the solids and solutions of the above compounds are relatively stable to air and moisture. Some oxidation of the solids is observed after a few days standing in air. Solutions are stable for several hours to a day. Samples have been stored in a vacuum desiccator over Drierite for 3–5 months without noticeable decomposition.

Discussion

It is of interest that L is able to form NiL_4, analogous to $Ni(PCl_3)_4$, with $Ni(CO)_4$.[4] This is indicative of the relatively strong ability of L to participate in partial double bonding as has been postulated to account for the unusually strong field complexes formed with transition metals.[11] Since the complexes $Ni(L')_4$ where $L' = P(OCH_3)_3$,[5] $P(OCH_2CH_3)_3$,[5] or $P(OC_6H_5)_3$[23] have been reported, it is not unexpected that L behaves in a similar manner. As the conditions for the preparation of NiL_4 are less severe and the decomposition temperature unusually high (365°),[5,23,24] a lattice energy greater than that for similar complexes involving trialkyl phos-

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TABLE I

INFRARED SPECTRA OF 4-METHYL-2,6,7-TRIOXA-1-PHOSPHABICYCLO[2.2.2]OCTANE DERIVATIVES IN THE METAL CARBONYL REGION

Compound	CO stretching frequency, cm.$^{-1}$ Halocarbon oil			CHCl$_3$		
Ni(CO)$_3$L	2089 s		2003 vs	2090 s		2021 vs
Ni(CO)$_2$L$_2$	2044 s		1976 vs	2048 s		1994 vs
Ni(CO)L$_3$		1980 vs			1997 vs	
NiL$_4$		None			None	
Fe(CO)$_4$L	2063 s	1998 vs	1955 vs	2065 s	1996 vs	1965 vs
Fe(CO)$_3$L$_2$		1915 vs			1933 vs	
Cr(CO)$_5$L	2073 w	1980 sh	1945 vs	2082 w	1995 sh	1960 vs
Cr(CO)$_4$L$_2$	2035 vw	1957 sh	1918 vs	2040 vw	1975 sh	1930 vs
Mo(CO)$_5$L	2081 w	1981 sh	1945 vs	2085 w	2001 sh	1962 vs
Mo(CO)$_4$L$_2$	2038 vw	1960 sh	1927 vs	2049 vw	1984 sh	1940 vs
W(CO)$_5$L	2082 w	1975 sh	1935 vs	2084 w	1993 sh	1958 vs
W(CO)$_4$L$_2$	2040 vw	1955 sh	1913 vs	2045 vw	1981 sh	1931 vs

[a] vs, very strong; s, strong; w, weak; vw, very weak; sh, shoulder.

phites is implied. The borane complex of L also exhibits an unusually high melting point compared to other trialkyl phosphite boranes.[25]

Further support for the strong π-bonding ability of L is derived from the infrared spectra of these substituted compounds (Table I). The observed carbonyl stretching frequencies of L-substituted complexes are slightly less than those observed for PX$_3$ but greater than those found in analogous PR$_3$ complexes. In relation to carbonyl complexes containing the phosphites P(OCH$_3$)$_3$, P(OCH$_2$CH$_3$)$_3$, and P(OC$_6$H$_5$)$_3$, the carbonyl stretching frequencies are the same or slightly higher for complexes containing L. These results are in agreement with a previous study of phosphite complexes of Mn$_2$(CO)$_{10}$ by Angelici.[26] A preliminary study indicates that the trisubstituted complexes of hexacarbonyls can also form as should be expected if L participates in strong π-bonding. The disubstituted complexes of iron, chromium, molybdenum, and tungsten carbonyls all exhibit spectra characteristic of *trans* substitution.[15] No attempt to prepare the *cis* isomers has been made. Other features of the infrared spectra are the intense bands observed at approximately 1020, 860, 780, 770, and 650 cm.$^{-1}$ which are indicative of the presence of L in the complex.[27] Weaker absorption observed at approximately 3000, 2950, 1470, 1400, 1350, 1310, 1190, 1170, 950, 925, and 670 cm.$^{-1}$ may also be assigned to the ligand. The proton n.m.r. spectra of the monosubstituted carbonyl complexes should exhibit singlet methyl and doublet methylene resonances, the latter due to spin coupling with the phosphorus nucleus. Spectra of this type have been reported previously for the free ligand and for adducts of L with compounds of boron which behave as Lewis acids.[28] The same n.m.r. pattern is shown for all the monosubstituted carbonyls reported in this work, with J_{POCH} ranging from 3.9 c.p.s. in Ni(CO)$_3$L to 5.1 c.p.s. in Fe(CO)$_4$L compared with 1.8 c.p.s. for the free ligand (Table II).

TABLE II

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}[d]
L	CDCl$_3$	0.72	3.93[b]	1.8	. . .
Ni(CO)$_3$L	CDCl$_3$	0.78	4.14[b]	3.9	. . .
Ni(CO)$_2$L$_2$	CDCl$_3$	0.74	4.10[b]	4.0	0
Ni(CO)L$_3$	CDCl$_3$	0.70	4.06[c]	3.6	1
NiL$_4$	CH$_2$Cl$_2$	0.66	4.00[c]	3.8	15
Fe(CO)$_4$L	(CH$_3$)$_2$CO	0.90	4.48[b]	5.1	. . .
Fe(CO)$_3$L$_2$	(CH$_3$)$_2$CO	0.85	4.35[c]	5.0	>100
Cr(CO)$_5$L	(CH$_3$)$_2$CO	0.87	4.36[b]	4.1	. . .
Cr(CO)$_4$L$_2$	(CH$_3$)$_2$CO	0.83	4.24[c]	4.2	1
Mo(CO)$_5$L	(CH$_3$)$_2$CO	0.86	4.33[b]	4.1	. . .
Mo(CO)$_4$L$_2$	(CH$_3$)$_2$CO	0.82	4.21[c]	4.2	60
W(CO)$_5$L	(CH$_3$)$_2$CO	0.88	4.37[b]	4.1	. . .
W(CO)$_4$L$_2$	(CH$_3$)$_2$CO	0.82	4.23[c]	4.4	80

[a] Chemical shifts in p.p.m. downfield with respect to tetramethylsilane; J values in c.p.s. [b] Doublet. [c] Triplet. [d] Approximate values. See text.

The proton n.m.r. spectra of some disubstituted phosphine complexes wherein the ligands are *trans* to one another have been observed to exhibit a triplet instead of the expected doublet. This has been attributed to phosphorus–phosphorus coupling across the *trans* positions. For example, a 1:2:1 triplet has been observed for the *trans* complex PdI$_2$[P(CH$_3$)$_2$(C$_6$H$_5$)]$_2$, whereas only a doublet is observed for the *cis* isomer.[29] In *trans*-disubstituted metal carbonyl complexes of tris(dimethylamino)phosphine[7] and L (Figure 2) the proton n.m.r. spectra exhibit triplets of varying intensity ratios. In this work, a crude estimate of J_{PP} values has been made by treating these systems as a modified ten-line ABX$_2$ type in which $\delta_A = \delta_B$. Hence the system is designated as AA′X$_2$ wherein X$_2$ refers to the methylene hydrogens in L, A is the phosphorus atom in the same L molecule containing the X$_2$ hydrogens, and A′ is the phosphorus atom in a neighboring ligand molecule. Such a system can be shown[30] 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 III. The distance between

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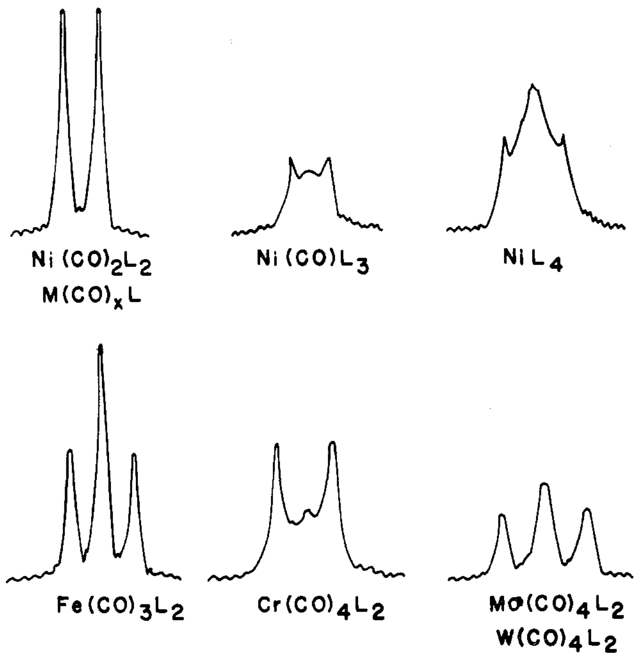

Figure 2.—Methylene n.m.r. absorptions of L-substituted metal carbonyl complexes. Line widths of the various spectra are not drawn to the same scale.

TABLE III

$AA'X_2$ N.M.R. SPECTRUM[a]

Positions with respect to mean δ_{X_2}	Relative intensities
$-\frac{1}{2}(J_{AA'} + Q)$	$1 - J_{AA'}/Q$
$-\frac{1}{2}J_{AX}$	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
$+\frac{1}{2}(J_{AA'} + Q)$	$1 - J_{AA'}/Q$

[a] Where $Q = (\frac{1}{4}J_{AX}^2 + J_{AA'}^2)^{1/2}$.

the outer peaks of the three-line spectra observed in this work is assigned to J_{AX} which ranges from 3.6 c.p.s. in $Ni(CO)L_3$ to 5.0 c.p.s. in $Fe(CO)_3L_2$. The central peak is assigned to the two lines $-\frac{1}{2}(Q - J_{AA'})$ and $+\frac{1}{2}(Q - J_{AA'})$. An estimate of the separation of these 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 work J_{PP}. From the values of J_{PP} listed in Table II 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 $J_{PP} \cong 1$ 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 $Fe(CO)_3L_2$, $Mo(CO)_4L_2$, and $W(CO)_4L_2$ where J_{PP} is large whereas those of $Ni(CO)L_3$ and $Cr(CO)_4L_2$ are broad and poorly defined.

A qualitative estimation of P–P coupling constants based on the above criterion gives the following order for disubstituted complexes: $Fe(CO)_3L_2 > W(CO)_4L_2 > Mo(CO)_4L_2 > Cr(CO)_4L_2 > Ni(CO)_2L_2$ (Figure 2). This order agrees with the order found for the tris(dimethylamino)phosphine complexes.[7] However, in all cases where P–P coupling is observed, the relative height of the center peak is slightly larger for L. This implies that the P–P coupling for any given carbonyl coordination compound will be greater wherein the ligand is L 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 the infrared spectrum conclusively indicates tetrahedral geometry for the compound $Ni(CO)_3L$, the data do not allow a distinction to be made between tetrahedral and square-planar geometry for the di- and trisubstituted nickel complexes. It is reasonable to assume that NiL_4 would be analogous to $Ni(PF_3)_4$ which has been shown to be tetrahedral.[31] This geometry also has been assumed in the analysis of the Raman spectrum of $Ni[P(OCH_3)_3]_4$ and the dipole moments of $Ni[P(OCH_3)_3](CO)_3$, $Ni[P(OCH_3)_3]_2(CO)_2$, and $Ni[P(OCH_3)_3]_3(CO)$.[32] Hence the assumption that the $Ni(CO)_{4-x}L_x$ system is tetrahedral does not seem unwarranted.

The results of the study of the mono- through tetrasubstituted complexes of L with $Ni(CO)_4$ are noteworthy. 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 2). From this we conclude that in a tetrahedral system increased substitution is accompanied by greater P–P coupling.

Although in all the complexes the methyl and methylene proton n.m.r. absorptions appear downfield with respect to the free ligand, increased substitution causes an upfield shift of these protons (Table II). Elsewhere[22] 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 L. In all cases, the donor–acceptor link can be assumed to be of the σ-type. The proton shifts in all of these complexes wherein π-bonding is probable do not correlate with their respective J_{POCH} values. The small variation of J_{POCH} from 4 c.p.s. in these compounds is not understood at present. It is apparent, however, that with respect to the correlation found for the σ-bonded compounds, the protons in the π-complexes all have abnormally high chemical shifts.

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