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Transition Metal Complexes of a Constrained Phosphite Ester. V. Metal Carbonyl Complexes of 2,8,9-Trioxa-1-phosphaadamantane[1-4]

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The preparation and characterization of metal carbonyl complexes of 2,8,9-trioxa-1-phosphaadamantane, $P(OCH)_3(CH_2)_3$, are described. Substitution products obtained from $Ni(CO)_4$ include compounds of the type $Ni(CO)_{4-x}[P(OCH)_3(CH_2)_3]_x$ 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 $P(OCH)_3(CH_2)_3$ is also reported. A study of the carbonyl infrared stretching frequencies implies that $P(OCH)_3(CH_2)_3$ is equal to other phosphites in π-bonding ability. The proton nmr spectra of the compounds are discussed with special attention given to the disubstituted complexes. The proton nmr spectra of analogous disubstituted complexes of $P(OCH_2)_3CCH_3$ discussed previously by us (see ref 5) are more rigorously treated.

Introduction

In a previous paper,[5] we reported metal carbonyl complexes of a bicyclic phosphite ester, 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$. A strong π-bonding ability for $P(OCH_2)_3CCH_3$ was inferred from the carbonyl absorptions of these complexes in the infrared region. The nmr spectra exhibited some very unusual features of phosphorus–phosphorus spin coupling. Although 2,8,9-trioxa-1-phosphaadamantane (hereafter referred to as $P(OCH)_3(CH_2)_3$) and $P(OCH_2)_3CCH_3$ are constrained structures wherein the electron pair on the bridgehead phosphorus is readily available for donation, $P(OCH)_3(CH_2)_3$ is slightly more bulky as shown in Figure 1. The increased steric requirements for $P(OCH)_3(CH_2)_3$ could lead to ligand–ligand repulsion effects in metal carbonyl complexes resulting in reduced ligand properties. On the other hand, the basicity of $P(OCH)_3(CH_2)_3$ has been found to be somewhat greater than $P(OCH_2)_3CCH_3$ from its higher dipole moment and its lower tendency to dissociate from the boron moiety in the boron trimethyl adduct.[6] It was of interest, therefore, to compare the ligand characteristics of $P(OCH)_3(CH_2)_3$ with those observed for $P(OCH_2)_3CCH_3$ in the same series of carbonyl complexes. Of interest also was the possible comparison of phosphorus–phosphorus spin–spin coupling in complexes of these ligands.

Experimental Section

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 dichloromethane solutions and Halocarbon oil mulls using a Beckman IR-7 spectrometer with sodium chloride grating optics. Proton nmr spectra were obtained in approximately 15% deuteriochlorofom or methylene chloride solutions on Varian Associates HR-60 and A-60 spectrometers. In cases where compounds exhibited low solubility, saturated solutions were used. 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) where compound solubilities permitted. Measurements were made over a concentration range of 0.025–0.01 *M* on chloroform solutions.

Carbon and hydrogen contents were determined by combustion. Nickel analyses were carried out by a standard procedure as the dimethylglyoxime complex.[7] Molybdenum[8] and tungsten[9] were determined gravimetrically as the 8-hydroxyquinoline complexes, chromium was determined spectrophotometrically using *sym*-diphenylcarbazide,[10] and iron was determined colorimetrically with 1,10-phenanthroline.[11] Yields of monosubstituted compounds were calculated on the basis of $P(OCH)_3(CH_2)_3$ and all others on the basis of metal carbonyl used.

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 hexacarbonyl were gifts from the Climax Molybdenum Co. The phosphite ligand, $P(OCH)_3(CH_2)_3$ was prepared by a method described elsewhere.[12]

Two general methods were used in the preparation of the complexes of $P(OCH)_3(CH_2)_3$ (L) shown in Table I. In method A, a mixture of carbonyl, ligand, and 30 to 50 ml of solvent was brought to the desired temperature under a helium flush with magnetic stirring. After reaction for the indicated time interval, 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. In method B, a mixture of carbonyl, ligand, and 100 ml of solvent was placed in a quartz tube. Irradiation with ultraviolet light (200-w Hanovia Model 654A) was carried out for the time indicated under a flush of helium with magnetic stirring. After evaporation of the solution to one-tenth its volume under vacuum, the product was isolated in the same manner as described in method A. Table I lists the amount of carbonyls and ligand,

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[1] Contribution No. 1781 from the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission and the Chemistry Department of Iowa State University.

[3] Presented before the Division of Inorganic Chemistry, at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[4] From a dissertation submitted by D. G. Hendricker to the Graduate College of Iowa State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1965.

[5] J. G. Verkade, R. E. McCarley, D. G. Hendricker, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965).

[6] J. G. Verkade and C. W. Heitsch, *ibid.*, **2**, 512 (1963).

[7] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p 138.

[8] A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 508.

[9] Reference 8, p 567.

[10] Reference 8, p 791.

[11] D. E. Blair and H. Diehl, *Anal. Chem.*, **33**, 867 (1961).

[12] T. J. Huttemann, B. M. Foxman, C. R. Sperati, and J. G. Verkade, *Inorg. Chem.*, **4**, 950 (1965).

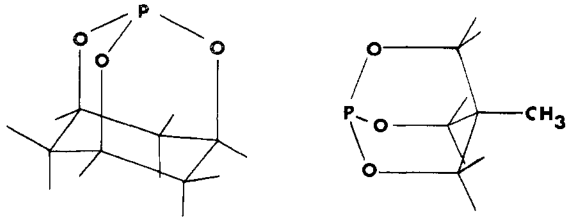

Figure 1.—Structures of 2,8,9-trioxa-1-phosphaadamantane, L, and 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, L′.

TABLE I

PREPARATION OF METAL CARBONYL COMPLEXES OF L

Compound	Amount of $M(CO)_x$ (or $M(CO)_{x-1}L)^a$	Amount of L, g	Reaction conditions temp, °C (time, hr)	Yield, %
$Ni(CO)_3L$	2.0 ml	2.3	15 (4)	91
$Ni(CO)_2L_2$	$(0.4\ g)^a$	0.2	45 (8)	99
$Ni(CO)L_3$	$(0.4\ g)^a$	0.4	58 (16)	89
NiL_4	$(0.4\ g)^a$	0.6	Reflux (18)	88
$Fe(CO)_4L$	2.0 ml	1.6	Reflux (4)	82
$Fe(CO)_3L_2$	1.5 ml	4.0	26 (6)	47
$Cr(CO)_5L$	1.1 g	0.8	100 (4)	85
$Cr(CO)_4L_2$	$(2.5\ g)^a$	1.8	26 (4)	57
$Mo(CO)_5L$	1.3 g	0.8	Reflux (4)	61
$Mo(CO)_4L_2$	1.3 g	1.8	Reflux (24)	61
$W(CO)_5L$	1.8 g	0.8	Reflux (24)	54
$W(CO)_4L_2$	1.8 g	1.8	26 (4)	55

[a] Amount enclosed with parentheses if reactant was $M(CO)_{x-1}L$.

TABLE II

ANALYTICAL DATA, MOLECULAR WEIGHTS, AND DECOMPOSITION TEMPERATURES

Compound	Carbon, %		Hydrogen, %		Metal, %		Mol wt		Decomposition temp, °C
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
$Ni(CO)_3P(OCH)_3(CH_2)_3$	35.6	35.6	3.0	3.3	19.4	19.3	303	301	142
$Ni(CO)_2[P(OCH)_3(CH_2)_3]_2$	38.6	38.2	4.1	4.3	13.5	13.6	435	437	225
$Ni(CO)[P(OCH)_3(CH_2)_3]_3$	40.2	39.9	4.8	4.7	10.4	10.2	. . .	. . .	305
$Ni[P(OCH)_3(CH_2)_3]_4$	41.2	40.9	5.2	5.4	8.5	8.6	. . .	. . .	>350
$Fe(CO)_4P(OCH)_3(CH_2)_3$	36.6	36.6	2.7	2.9	17.2	17.1	328	326	195
$Fe(CO)_3[P(OCH)_3(CH_2)_3]_2$	39.1	38.8	3.9	4.0	12.2	12.0	. . .	. . .	253
$Cr(CO)_5P(OCH)_3(CH_2)_3$	37.5	37.4	2.6	2.7	14.8	14.6	352	349	218
$Cr(CO)_4[P(OCH)_3(CH_2)_3]_2$	39.6	39.3	3.7	3.8	10.7	10.8	. . .	. . .	332
$Mo(CO)_5P(OCH)_3(CH_2)_3$	33.4	33.8	2.3	2.5	24.2	24.0	396	394	210
$Mo(CO)_4[P(OCH)_3(CH_2)_3]_2$	36.3	36.6	3.3	3.6	18.2	18.0	. . .	. . .	267
$W(CO)_5P(OCH)_3(CH_2)_3$	27.3	27.4	1.9	2.1	38.0	37.8	484	480	221
$W(CO)_4[P(OCH)_3(CH_2)_3]_2$	31.1	31.9	2.9	2.9	29.8	29.7	. . .	. . .	312

reaction temperature, reaction time, and per cent yield for the preparation of the compounds of $P(OCH)_3(CH_2)_3$. The solvents used in the preparations were chloroform for the nickel compounds, methylcyclohexane for $Mo(CO)_5L$, and ethylbenzene for the rest. Method A was used for all the preparations except the disubstituted iron, chromium, and tungsten compounds where method B was employed. Analytical data for the prepared compounds are given in Table II.

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

Discussion

Evidence to support the claim[12] that $P(OCH)_3(CH_2)_3$ is a fairly strong π-bonding ligand is derived from the infrared spectra of these substituted compounds in the carbonyl region (Table III). The observed carbonyl stretching frequencies are less than those noted for PX_3 (where X = F, Cl, Br) but greater than those found in analogous PR_3 and NR_3 complexes (R = alkyl).[13–18] Relative to trialkyl phosphites, the CO stretching frequencies for carbonyl compounds of $P(OCH)_3(CH_2)_3$ are less than those observed in analogous complexes of $P(OC_6H_5)_3$, but greater than those of $P(OCH_3)_3$ and $P(OC_2H_5)_3$.[8,11,13] Thus, assuming that π-bonding ability increases with the observed CO stretching frequency, it appears that $P(OCH)_3(CH_2)_3$ is a stronger π-bonding ligand than PR_3 and NR_3, weaker than PX_3, and about as strong as other phosphites.

The CO stretching frequencies observed for complexes of $P(OCH)_3(CH_2)_3$ are found to be slightly less than those of analogous complexes of $P(OCH_2)_3CCH_3$ in all cases.[5] This may indicate that $P(OCH_2)_3CCH_3$ is a better π-bonding ligand than $P(OCH)_3(CH_2)_3$. However, this effect may also be rationalized in terms of the difference in the basicities (σ^* values) of the ligands,[19] since it has been shown that $P(OCH)_3(CH_2)_3$ is a stronger base than $P(OCH_2)_3CCH_3$ toward boron Lewis acids.[6] The larger steric requirements of $P(OCH)_3(CH_2)_3$ may also account for its apparently weaker ligand properties in carbonyl complexes.

Although the infrared spectrum conclusively indicated 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 complexes.[13,20] The *trans*-disubstituted square-planar isomer is ruled out, however, since its spectrum would consist of a single infrared-active band. It is reasonable to assume that NiL_4 is analogous to $Ni(PF_3)_4$, which has been shown to be tetrahedral.[21] Hence, it would appear that in all probability all the members of the $Ni(CO)_{4-x}L_x$ system are tetrahedral. The disubstituted complexes of iron,

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(13) R. Poilblanc and M. Bigorgne, *Bull. Soc. Chim. France*, 1301 (1962).

(14) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 2323 (1959).

(15) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

(16) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

(17) F. A. Cotton and C. S. Kraihanzel, *ibid.*, **84**, 4432 (1962).

(18) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).

(19) M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964).

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 103.

(21) L. S. Woodward and J. R. Hall, *Nature*, **181**, 831 (1958).

TABLE III

INFRARED SPECTRA OF 2,8,9-TRIOXA-1-PHOSPHAADAMANTANE DERIVATIVES IN THE METAL CARBONYL REGION

Compound	C–O stretching frequency, cm^{-1}					
	CH_2Cl_2			Halocarbon oil		
$Ni(CO)_3L$	2086 s[a]	2018 vs[b]		2081 s	2003 vs	
$Ni(CO)_2L_2$	2044 s	1986 vs		2026 s	1970 vs	
$Ni(CO)L_3$		1979 vs			1961 vs	
NiL_4		None			None	
$Fe(CO)_4L$	2065 s	1993 vs	1962 vs	2062 s	1977 vs	1946 vs
$Fe(CO)_3L_2$		1926 vs			1916 vs	
$Cr(CO)_5L$	2077 s[c]	1995 sh[d]	1955 vs	2074 w	1985 sh	1943 vs
$Cr(CO)_4L_2$	2041 vw[e]	1983 sh	1923 vs	2037 vw	1970 sh	1911 vs
$Mo(CO)_5L$	2076 w	1995 sh	1955 vs	2075 w	1985 sh	1942 vs
$Mo(CO)_4L_2$	2042 vw	1984 sh	1923 vs	2038 vw	1977 sh	1912 vs
$W(CO)_5L$	2084 w	1991 sh	1953 vs	2082 w	1981 sh	1940 vs
$W(CO)_4L_2$	2041 vw	1984 sh	1923 vs	2037 vw	1980 sh	1913 vs

[a] Strong. [b] Very strong. [c] Weak. [d] Shoulder. [e] Very weak.

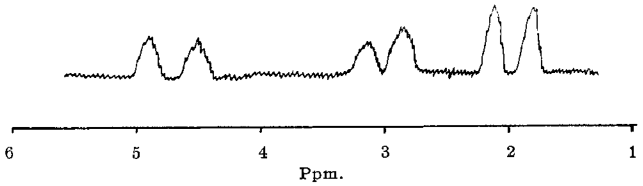

Figure 2.—Proton nmr spectrum of $Fe(CO)_4L$ in deuteriochloroform.

chromium, molybdenum, and tungsten all exhibit spectra characteristic of *trans* substitution.[17,22] Other features of the infrared spectra are the intense bands observed at approximately 1110, 949, 905, 850, 800, and 750 cm^{-1} which are indicative of the presence of $P(OCH)_3(CH_2)_3$ in the compound.[23] Weaker absorptions at 2980, 1430, 1310, 1210, 1040, 1060, 810, 730, and 720 cm^{-1} are also attributable to the ligand moiety.[23]

The proton nmr spectra of the monosubstituted carbonyl complexes of L exhibit three doublets attributable to the methine, axial, and equatorial protons as shown by the example in Figure 2. The doublet methine resonance is the result of spin coupling with the phosphorus nucleus while the axial and equatorial methylene doublets are due to geminal coupling. The broadening of all peaks is the result of unresolved fine structure from coupling within the nine-proton system. Spectra of this type were previously discussed in detail for adducts of $P(OCH)_3(CH_2)_3$ with boron compounds as well as for the free ligand.[24,25]

From Table IV it is seen that on coordination of $P(OCH)_3(CH_2)_3$ a downfield shift is observed for the methine protons while the axial and equatorial hydrogens remain constant or shift slightly upfield. The magnitude of the shift of the methine protons 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 such as for the chromium, molybdenum, and tungsten analogs appears to have no significant effect on the

TABLE IV

CHEMICAL SHIFTS AND COUPLING CONSTANTS FROM THE PROTON NMR SPECTRA OF 2,8,9-TRIOXA-1-PHOSPHAADAMANTANE DERIVATIVES[a]

Compound	Solvent	H_{ax}	H_{eq}	H_{CH}	J_{HCH}	J_{POCH}
L, $P(OCH)_3(CH_2)_3$	$CDCl_3$	1.89	3.04	4.34	14.0	6.3
$Ni(CO)_3L$	$CDCl_3$	1.85	3.02	4.54	14.2	11.6
$Ni(CO)_2L_2$	$CDCl_3$	1.80	2.95	4.49	13.8	11.8
$Ni(CO)L_3$	$CDCl_3$	1.76	2.88	4.41	13.5	b
NiL_4	CH_2Cl_2	1.74	2.84	4.37	12.9	b
$Fe(CO)_4L$	$CDCl_3$	1.90	3.00	4.75	14.5	14.7
$Fe(CO)_3L_2$	$CDCl_3$	1.79	2.92	4.57	14.0	b
$Cr(CO)_5L$	$CDCl_3$	1.88	3.00	4.59	13.8	12.6
$Cr(CO)_4L_2$	$CDCl_3$	1.79	2.98	4.50	13.6	b
$Mo(CO)_5L$	$CDCl_3$	1.89	3.01	4.60	14.2	12.7
$Mo(CO)_4L_2$	$CDCl_3$	1.79	2.99	4.51	14.1	b
$W(CO)_5L$	$CDCl_3$	1.95	3.05	4.63	14.1	12.8
$W(CO)_4L_2$	$CDCl_3$	1.88	3.01	4.49	14.0	b

[a] Chemical shifts in ppm downfield with respect to tetramethylsilane. J values in cps. [b] Broad single peaks.

proton chemical shifts. The value of J_{POCH}[26] is found to range from 11.6 cps in $Ni(CO)_3L$ to 14.7 cps in $Fe(CO)_4L$ compared with 6.3 cps in the free ligand. The value of $J_{H(gem)}$ is found to vary from 13.8 cps in $Cr(CO)_5L$ to 14.5 cps in $Fe(CO)_4L$ compared with 14.0 in the free ligand. It appears that J_{HCOP} approximately doubles on complexation and that within a complex it is slightly affected by the geometry in that the value for a trigonal bipyramid > octahedron > tetrahedron. On the other hand, $J_{H(gem)}$ appears to remain rather constant. Similar trends with respect to chemical shifts and coupling constants were observed for the monosubstituted carbonyl complexes of $P(OCH_2)_3CCH_3$.[5]

The proton nmr spectra of some disubstituted phosphine complexes wherein the ligands are *trans* to one another have been found to exhibit phosphorus–phosphorus coupling, while for the *cis* isomers of the compounds no P–P coupling was observed.[27] In *trans*-disubstituted metal carbonyl complexes of tris(dimethylamino)phosphine, the spectra are found to exhibit triplets of varying intensity ratios which have

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(22) T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, *J. Am. Chem. Soc.*, **83**, 3200 (1961).

(23) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 863 (1962).

(24) J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1964).

(25) J. G. Verkade and R. W. King, *ibid.*, **1**, 948 (1962).

(26) This coupling was taken to be the separation of the doublet common to all spectra. In all treatment of spectra of the disubstituted complexes, it is assumed that there is no direct coupling between the protons of one ligand and any nucleus of the other.

(27) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

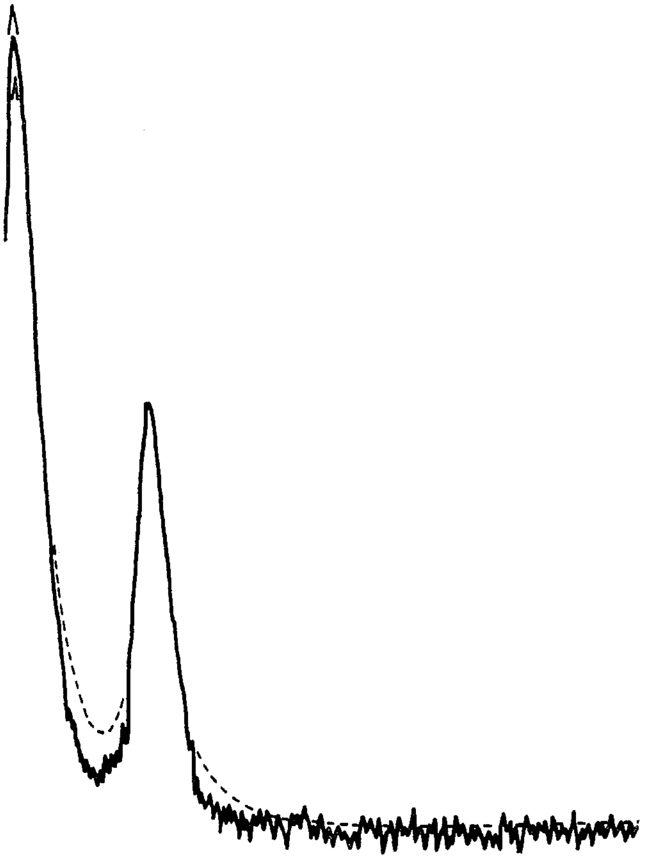

Figure 3.—Half the methylene proton resonance of *trans*-$Mo(CO)_4(P(OCH_2)_3CCH_2CH_3)_2$ is shown, the tallest peak being the center. The best computed fit (J_{PP} = 210 cps) is superimposable with the experimental curve except for the deviation (dotted line) near the base line. Using J_{PP} = 260 or 160 cps, the computed spectra differed from the best computed curve only in the higher and lower intensities for these values, respectively, of the middle peak.

been interpreted to indicate P–P coupling.[28] The nmr spectra of *trans*-disubstituted metal carbonyl complexes of $P(OCH_2)_3CCH_3$ were also found to exhibit P–P coupling as did those of the $Ni(CO)L'_3$ and NiL'_4 compounds.[5] Crude estimates of the values of J_{PP} were made for the disubstituted complexes of $P(OCH_2)_3CCH_3$ by treatment of the spectra as $X_2AA'X'_2$ systems. These spectra can be more correctly interpreted as $X_6AA'X'_6$ patterns. Since our original report[5,29] a computer program has been developed for the IBM 7074 for the synthesis and plotting of the envelope of the X_n portion of an $X_nAA'X'_n$ spectrum based on the treatment of Harris.[30] This treatment requires zero coupling between the groups of X nuclei and we have further assumed that $J_{AX'}$, the coupling between the protons of one ligand and the phosphorus nucleus of the other, is also zero. With the latter assumption J_{HCOP} was measured from the spectrum as the spacing of the doublet visible in all spectra and a line-width parameter was estimated from the width of the doublet peaks at half-height. These were used as input data for the program along with an estimated value for J_{PP}. Line shape was assumed to be a pure Lorentzian absorption mode without saturation. The computed envelope was compared visually with the observed spectrum and adjustments were made in the values of J_{PP} and the line width for best fit as shown in Figure 3. It is generally not possible to obtain an exact value of the line width from the observed spectrum because of distortion of the peaks of the main doublet attributable to contributions from the other 24 lines of the $X_6AA'X'_6$ spectrum. The revised values of J_{PP} for the disubstituted complexes of $P(OCH_2)_3CCH_3$ previously considered,[5] with estimated uncertainties, are given in Table V.

TABLE V

ESTIMATION OF J_{PP} IN DISUBSTITUTED[a] $P(OCH_2)_3CCH_3(L')$ COMPLEXES

Complex	J_{HCOP}, cps	Line width, cps	J_{PP}, cps
$Fe(CO)_3L'_2$	4.90	0.8–0.9	300[b]
$Mo(CO)_4L'_2$	4.20	0.7	210 ± 50
$W(CO)_4L'_2$	4.40	0.6	65 ± 10
$Cr(CO)_4L'_2$	4.11	0.6	9 ± 2
$Ni(CO)_2L'_2$	4.00	0.6	0

[a] We are engaged in a more rigorous treatment of complexes containing more than two ligands of this type. [b] See text.

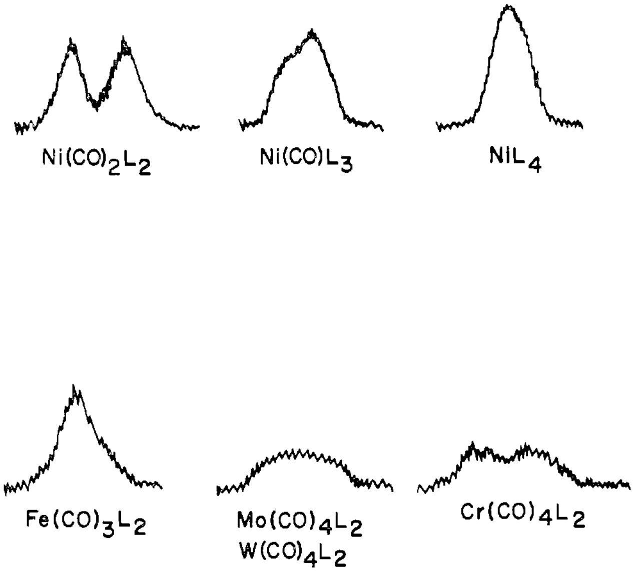

Figure 4.—Methine nmr absorptions of substituted metal carbonyl complexes of L. Line widths of various spectra are not drawn to the same scale. Due to the broadness of the methine peak in spectra of the molybdenum and tungsten complexes, the shapes for these peaks were very similar.

For the values of J_{HCOP} used, the calculated spectral envelopes are little affected by small changes in line width (±0.2 cps) when J_{PP} is greater than 200 cps. Also the effect on the calculated spectrum of increasing J_{PP} from 400 cps to infinity lies within the estimated error of comparison of the observed and calculated envelopes. Thus in the case of $Fe(CO)_3L'_2$ it is possible to set a lower limit of 200 cps for J_{PP} but no upper limit can be assigned. The visual comparison in the

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[28] R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

[29] An error in the expression for Q appeared in ref 5. The expression for Q is $Q = [J_{AX}^2 + J_{AA'}^2]^{1/2}$ and not $[{}^1/_4 J_{AX}^2 + J_{AA'}^2]^{1/2}$. Although the values of J_{PP} given in Table II of ref 5 would be affected, their relative order would not.

[30] R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

case of $Cr(CO)_4L'_2$ was made uncertain by an off-center peak (see ref 5, Figure 2) attributed to a small amount of impurity. The calculated spectra for this compound were observed to be markedly changed by varying J_{PP} in the range of 0–10 cps by as little as 1 cps.

We find as previously stated[5] that J_{PP} appears to follow the order $Fe(CO)_3L'_2 > Mo(CO)_4L'_2 > W(CO)_4L'_2 > Cr(CO)_4L'_2 > Ni(CO)_2L'_2$ for the disubstituted complexes, which is also the order suggested by inspection of the methine proton resonances of the corresponding $P(OCH)_3(CH_2)_3$ complexes shown in Figure 4. Owing to line broadening from coupling to the adjacent methylene protons, a rigorous treatment is more difficult. The increasing intensity at the center of the methine multiplet in the series of complexes of $P(OCH)_3(CH_2)_3$ is qualitatively similar to the behavior of the $X_6AA'X'_6$ system of the corresponding $P(OCH_2)_3CCH_3$ complexes as J_{PP} increases. This is also in the order of tetrahedral < octahedral < trigonal bipyramidal for the geometry of both series of complexes. It is found within the octahedral geometry that P–P coupling follows the order Mo > W > Cr. The shapes of the methine resonances for the tetrahedral nickel compounds are found to progress from a doublet to a relatively broad single peak from di- to tetrasubstitution.

The methine proton is observed to exhibit an upfield shift from the mono- to the disubstituted complexes. Indeed within the $Ni(CO)_{4-x}L_x$ system this upfield shift is observed to continue with the tri- and tetrasubstituted complexes. With respect to σ-bonded compounds of $P(OCH)_3(CH_2)_3$, it is found that these carbonyl compounds and others in which π-bonding is postulated have abnormally high-field proton chemical shifts.[31] Similar trends with respect to chemical shifts and P–P coupling were also observed for the analogous complexes of $P(OCH_2)_3CCH_3$.[5]

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Some Donor Properties of 1,4-Thioxane: Complexes with Transition Metal Halides

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Several complexes of 1,4-thioxane with transition metal halides have been prepared and their infrared spectra measured in the region 4000–265 cm^{-1}. By comparison with some analogous 1,4-dithiane and 1,4-dioxane complexes it is concluded that thioxane is sulfur-bonded rather than oxygen-bonded. Possible structures for these complexes are suggested on the basis of their far-infrared spectra. The magnetic susceptibilities and visible spectra of the copper complexes $CuCl_2 \cdot 2$thioxane, $CuBr_2 \cdot 2$thioxane, $CuCl_2 \cdot$dithiane, and $CuCl_2 \cdot$morpholine have been measured and are consistent with distorted octahedral structures.

Introduction

Several heterocyclic donor molecules of the type C_4H_8XY, such as 1,4-dioxane, 1,4-thioxane, 1,4-dithiane, and piperazine form a variety of complexes with transition and nontransition metal halides.[1–6] Infrared spectra measurements have shown[5,6] that the coordinated C_4H_8XY molecules invariably retain the "*chair*" conformation that is shown by the free ligands. Thus the infrared spectrum of 1,4-dioxane[7] and an X-ray analysis of 1,4-dithiane[8] show that these molecules have the "*chair*" rather than the "*boat*" conformation.

Of the above ligands 1,4-thioxane is particularly interesting since this molecule possesses oxygen and sulfur donor atoms in virtually identical, sterically unhindered positions. Several complexes of 1,4-thioxane with metal halides have therefore been prepared and their infrared spectra measured, and an attempt has been made to correlate the donor properties of 1,4-thioxane with the acceptor properties of the halides.

The relative affinities of ligand atoms for acceptor molecules and ions have been reviewed,[9] and it has been concluded that two types of acceptors exist: "class A, which form their most stable complexes with the first ligand atom of each group, *i.e.*, N, O, and F,

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