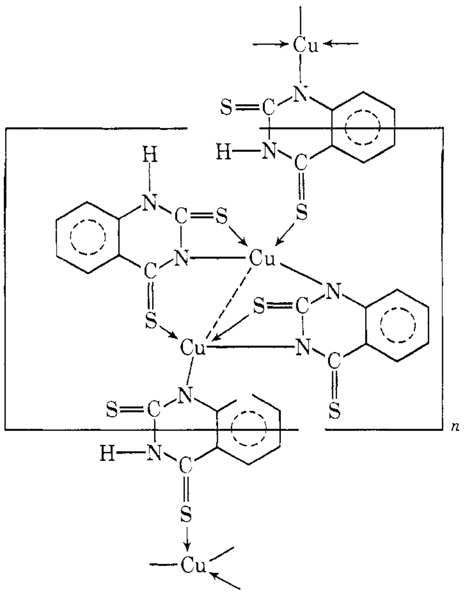

VII

Most of the Cd(II) and Hg(II) complexes mentioned in the literature are tetrahedral.[42] The complexes CdQ_2 and HgQ_2 are diamagnetic. Therefore, the tetrahedral arrangements of the ligand molecules around Cd(II) and Hg(II) are assigned to these complexes.

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Phosphorus-31–Phosphorus-31 Coupling in Metal Complexes Containing Two Different Phosphorus Ligands

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Phosphorus-31–phosphorus-31 coupling constants were determined from the ^{31}P resonance spectra of *trans*-$Fe(CO)_3LL'$, *cis* and *trans*-$Mo(CO)_4LL'$, and *cis*- and *trans*-$Mo(CO)_4LL''$ [$L = P(OCH_2)_3CR$, $L' = P(N(CH_3)_2)_3$, and $L'' = P(OCH_3)_3$] whose syntheses are reported for the first time. These couplings are found to lie between those found for the analogous complexes in which both ligands are identical. Evidence is presented suggesting that the signs of the *cis* and *trans* complexes are negative and positive, respectively. The CO stretching frequencies in the mixed complexes are found in every case to lie between those of the analogous compounds wherein both ligands are the same.

Introduction

Few bis-monodentate phosphorus mixed-ligand complexes have been prepared[2] although a considerable number of such compounds have been synthesized wherein one of the ligands is a chelate.[3] Mixed-ligand complexes are useful in that quite precise values of ^{31}P–^{31}P couplings can be obtained directly from the ^{31}P spectrum since the phosphorus atoms are chemically nonequivalent. We report here the preparation of *trans*-Fe-$(CO)_3LL'$, *cis*- and *trans*-$Mo(CO)_4LL'$, and *cis*- and *trans*-$Mo(CO)_4LL''$. Throughout this paper $L = P(OCH_2)_3CR$ [$R = C_2H_5$ or C_3H_7], $L' = P(N(CH_3)_2)_3$, and $L'' = P(OCH_3)_3$. Comparison of the ^{31}P–^{31}P couplings for these systems with those wherein both ligands are the same[4] reveals the strong possibility that coupling in the *trans* complexes is positive whereas in the *cis* systems it is negative. The magnitude of the couplings appear to be consistent with the hybridization and effective nuclear charge changes expected upon varying the ligands.

Experimental Section

Infrared spectra were obtained in the specified solvents on a Perkin-Elmer Model 21 and Beckman IR 12 spectrometers. Proton nmr spectra were observed in 10–20% solutions in $CDCl_3$ on a Varian A-60 instrument using tetramethylsilane as an internal standard. Phosphorus-31 nmr spectra were observed in saturated solutions in $CDCl_3$ on a Varian HR-60 instrument using phosphoric acid as an external standard. Molecular weights were determined from mass spectra recorded on an Atlas CH-4 single-focusing spectrometer at an energy of 70 eV. Microanalyses were run by Galbraith Laboratories, Knoxville, Tenn.

***cis*- and *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(N(CH_3)_2)_3]$.**—The monosubstituted complex $Mo(CO)_5[P(N(CH_3)_2)_3]$ was prepared as described by King.[5] A solution of methylcyclohexane (80 ml), $Mo(CO)_5[P(N(CH_3)_2)_3]$ (3.01 g, 7.5 mmol), and $P(OCH_2)_3C$-

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TABLE I

C–O STRETCHING FREQUENCIES AND ^{31}P–^{31}P COUPLING CONSTANTS OF *cis* COMPLEXES WITH IDENTICAL AND DIFFERENT PHOSPHORUS LIGANDS

Complex[a]	ν_{CO},[b] cm^{-1}				Solvent	$^2J_{PP}$, Hz
	B_2	B_1	$A_1{}^1$	$A_1{}^2$		
cis-$Mo(CO)_4L'_2$	1894 s		1908 sh	2012 m	$CHCl_3$	12.4 (±0.2)[c]
cis-$Mo(CO)_4LL'$	1913 s		1930 sh	2031 m	$CHCl_3$	39 (±3)
cis-$Mo(CO)_4L_2$	1937 s		1960 sh	2049 m	$CHCl_3$	50 (±10)[c]
cis-$Mo(CO)_4LL''$	1935 s	1944 sh	1961 m	2048 m	Cyclohexane	48 (±3)
cis-$Mo(CO)_4L''_2$	1921 s[d]	1926 sh[d]	1945 m[d]	2037 m[d]	Saturated hydrocarbon	−40.5 (±0.1)[c,e]

[a] L = $P(OCH_2)_3CR$ (R = C_2H_5, C_3H_7), L′ = $P(N(CH_3)_2)_3$, L″ = $P(OCH_3)_3$. [b] Deviation ±2 cm^{-1}. [c] Reference 4. [d] Reference 16. [e] Reference 16.

C_2H_5 (1.06 g, 6.5 mmol) was refluxed under nitrogen with magnetic stirring for 4 hr. The solution was filtered and then cooled to −20° whereupon a mixture of the *cis* and *trans* isomers precipitated. Dissolving the precipitate in a minimum of hot methylcyclohexane and cooling at 0° for 2 hr precipitated the *trans* compound. The filtrate when cooled to −20° precipitated the *cis* compound. *Anal.* Calcd for $C_{16}H_{29}MoN_3O_7P_2$: C, 36.03; H, 5.48; N, 7.88; P, 11.62. Found: *trans* compound: C, 35.90; H, 5.47; N, 7.84; P, 11.63; *cis* compound: C, 36.02; H, 5.44; N, 7.90; P, 11.64.

cis- **and** *trans*-$\mathbf{Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(OCH_3)_3]}$.—The monosubstituted complex $Mo(CO)_5[P(OCH_2)_3CC_2H_5]$ was prepared as described by Verkade, *et al.*[6] A solution of methylcyclohexane (125 ml), $Mo(CO)_5[P(OCH_2)_3CC_2H_5]$ (8.2 g, 20.6 mmol), and $P(OCH_3)_3$ (10.0 g, 80.6 mmol) was refluxed under nitrogen with magnetic stirring for 96 hr. The solvent was removed under reduced pressure leaving an oily residue which was eluted with benzene on a silica gel column. Six compounds were obtained of which four were identified by comparison of their nmr spectra with those of authentic samples described elsewhere. The products collected in order of their elution were *trans*-$Mo(CO)_4[P(OCH_3)_3]_2$,[4] *cis*-$Mo(CO)_4[P(OCH_3)_3]_2$,[4] *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(OCH_3)_3]$, $P(OCH_2)_3CC_2H_5$,[6] *cis*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(OCH_3)_3]$, and *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5]_2$.[6]

Mass spectra of both the *cis*- and *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(OCH_3)_3]$ showed the expected parent ion patterns from 490 to 498.

trans-$\mathbf{Fe(CO)_3[P(OCH_2)_3CC_3H_7][P(N(CH_3)_2)_3]}$.—The monosubstituted iron complex $Fe(CO)_4[P(N(CH_3)_2)_3]$ was prepared as described by King.[5] A solution of tetrahydrofuran (75 ml), $Fe(CO)_4[P(N(CH_3)_2)_3]$ (3.8 g, 11.5 mmol), and $P(OCH_2)_3CC_3H_7$ (2.1 g, 12.0 mmol) was irradiated with ultraviolet light (Hanovia 654 A lamp) for 36 hr. The solution was filtered and the filtrate was taken to dryness. The solid residue was eluted with a 20% ethyl acetate in petroleum ether (Skelly B) solution on a silica gel column. Preliminary thin layer chromatography showed the presence of seven compounds of which five were eluted from a silica gel column. Except for the desired product, the eluted compounds were identified by comparison of their nmr spectra with those of authentic samples described previously. The products obtained in order of their elution were unreacted $Fe(CO)_4[P(N(CH_3)_2)_3]$,[5] unreacted bicyclic phosphite,[6] the desired complex *trans*-$Fe(CO)_3[P(OCH_2)_3CC_3H_7][P(N(CH_3)_2)_3]$, $Fe(CO)_4[P(OCH_2)_3CC_3H_7]$,[6] and the oxide of the bicyclic phosphite.[7] A mass spectrum of $Fe(CO)_3[P(OCH_2)_3CC_3H_7][P(N(CH_3)_2)_3]$ showed a parent ion at 479.

Results and Discussion

As was observed earlier by Grim and coworkers,[2] synthesis of the desired bis mixed-ligand complex can be complicated by formation of several other products. Thus the preparation of *cis*- and *trans*-$Mo(CO)_4LL''$ [L = $P(OCH_2)_3CC_2H_5$, L″ = $P(OCH_3)_3$] involved the isolation of *cis*- and *trans*-$Mo(CO)_4L''_2$ and *trans*-$Mo(CO)_4L_2$ as well. Because the mixed-ligand fractions contained traces (<5%) of the compounds that were eluted immediately preceding or following the desired compounds, elemental analyses were not carried out.

The assignment of the stereochemistry of the mixed-ligand complexes is unambiguous from the infrared spectra in the carbonyl stretching region. The infrared spectra of *cis*-disubstituted tetracarbonyl metal molecules in this region are usually characterized by four absorptions which have been assigned by various workers to the B_2, B_1, $A_1{}^1$, and $A_1{}^2$ vibrational modes. These assignments have been verified by approximate force constant calculations for a number of carbonyl complexes having C_{2v} symmetry[8–11] and our frequency assignments given in Table I were based on the same spectral criteria. In several cases the B_1 mode was obscured because of overlap of the B_2 and $A_1{}^1$ modes. The single strong absorption in the *trans*-disubstituted tetracarbonylmolybdenum complexes allowed unambiguous assignment of this band to the E_u fundamental as given in Table II. The A_{1g} and B_{1g} fundamentals, occasionally found in spectra of D_{4h} symmetry,[8] were not observed in the compounds reported here. The infrared spectra of the *trans*-disubstituted tricarbonyliron compounds showed the expected single strong E′ absorption in the C–O stretching region.

TABLE II

C–O STRETCHING FREQUENCIES AND ^{31}P–^{31}P COUPLING CONSTANTS OF *trans* COMPLEXES WITH IDENTICAL AND DIFFERENT PHOSPHORUS LIGANDS

Complex[a]	ν_{CO},[b] cm^{-1}		$^2J_{PP}$, Hz
	E_u	Solvent	
trans-$Mo(CO)_4L'_2$	1885 s[e]	Halocarbon oil	+101 (±1)[c]
trans-$Mo(CO)_4LL'$	1910 s	$CHCl_3$	141 (±3)
trans-$Mo(CO)_4L_2$	1939 s	$CHCl_3$	210 (±30)[c]
trans-$Mo(CO)_4LL''$	1932 s	$CHCl_3$	185 (±3)
trans-$Mo(CO)_4L''_2$	1921 s[f]	Saturated hydrocarbon	+162 (±5)[c,d]
	E′		
trans-$Fe(CO)_3L'_2$	1870 s[e]	Halocarbon oil	+65 (±10)[c]
trans-$Fe(CO)_3LL'$	1899 s	Cyclohexane	183 (±1)
trans-$Fe(CO)_3L_2$	1926 s	CH_2Cl_2	300(±40)[c]

[a] L = $P(OCH_2)_3CR$ (R = C_2H_5, C_3H_7), L′ = $P(N(CH_3)_2)_3$, L″ = $P(OCH_3)_3$. [b] Deviation ±3 cm.$^{-1}$ [c] Reference 4. [d] Reference 16. [e] Reference 5. [f] Reference 11.

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TABLE III

NMR DATA FOR MIXED-LIGAND COMPLEXES

	L	$\delta(^1H)$,[a,b] ppm	$^3J_{PH}$,[c] Hz	$\delta(^{31}P)$,[d] ppm	L′ or L″	$\delta(^1H)$,[b] ppm	$^3J_{PH}$,[c] Hz	$\delta(^{31}P)$,[d] ppm
cis-$Mo(CO)_4LL''$	$P(OCH_2)_3CC_2H_5$	4.17	4.2	−139.6	$P(OCH_3)_3$	3.61	11.7	−164.3
trans-$Mo(CO)_4LL''$	$P(OCH_2)_3CC_2H_5$	4.21	4.3	−148.0	$P(OCH_3)_3$	3.61	11.7	−176.4
cis-$Mo(CO)_4LL'$	$P(OCH_2)_3CC_2H_5$	4.16	4.2	−138.0	$P(N(CH_3)_2)_3$	2.60	10.0	−145.0
trans-$Mo(CO)_4LL'$	$P(OCH_2)_3CC_2H_5$	4.22	4.2	−147.9	$P(N(CH_3)_2)_3$	2.62	10.2	−153.7
trans-$Fe(CO)_3LL'$	$P(OCH_2)_3CC_3H_7$	4.21	4.9	−168.4	$P(N(CH_3)_2)_3$	2.60	10.0	−164.3

[a] Methylene protons. [b] Downfield from tetramethylsilane (±0.01 ppm). [c] Deviation ±0.1 Hz. [d] Downfield from H_3PO_4 (±0.5 ppm).

Where both ligands are identical in the *cis*- and *trans*-disubstituted molybdenum complexes as well as the *trans*-disubstituted iron complexes, the stretching frequencies decrease in the series $P(OCH_2)_3CR > P(OCH_3)_3 > P(N(CH_3)_2)_3$. In other known carbonyl complexes which contain these ligands the same order is observed.[4,12] It has been suggested by Darensbourg and Brown[13] that if the ligand increases the charge on the metal, the M–C σ-bond strength decreases and hence lowers the carbonyl stretching frequency. Bigorgne[14] has concluded that the inductive effect of the ligand affects the M–C–O π bonds while others believe that the carbonyl frequency decreases as the π-bonding capacity of the ligand decreases.[8-10] Regardless of the mechanism which accounts for carbonyl stretching shifts, the order of the above ligands in their effect on ν(CO) is consistent with any of these points of view on basicity grounds. Thus there is chemical evidence that the lone-pair basicity on phosphorus in these ligands increases in the series $P(OCH_2)_3CR < P(OCH_3)_3 < P(N(CH_3)_2)_3$.[15] It is not surprising then that the mixed-ligand complexes $Mo(CO)_4LL'$, $Mo(CO)_4LL''$, and $Fe(CO)_3LL'$ are found to have values for ν(CO) which lie between those of the analogous complexes in which the ligands are identical (*i.e.*, $Mo(CO)_4L_2$, $Mo(CO)_4L'_2$; $Mo(CO)_4L_2$, $Mo(CO)_4L''_2$; and $Fe(CO)_3L_2$, $Fe(CO)_3L'_2$). Had solubility considerations allowed the use of the same solvent throughout this study, the carbonyl frequencies for the mixed-ligand systems might well have been more nearly the average of the values obtained for the nonmixed analogs as was observed previously.[2,3]

The nmr data other than the ^{31}P–^{31}P coupling values are given in Table III. The proton nmr spectra of the *cis*-molybdenum complexes and *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(OCH_3)_3]$ consist of two doublets (excluding the C_2H_5 proton resonances) whose intensity ratio allowed their unique assignment to the OCH_3, $N(CH_3)_2$, or OCH_2 groups each coupled over three bonds to a phosphorus atom. Although similar assignments could be made for the OCH_2 and $N(CH_3)_2$ proton resonances in the remaining two *trans* complexes, the doublets were significantly perturbed as shown in Figure 1.

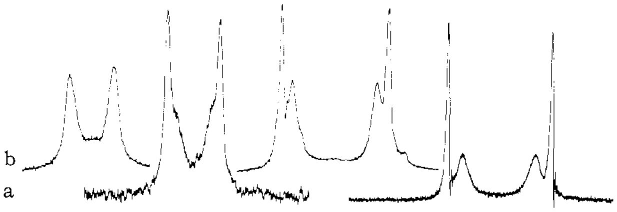

Figure 1.—Proton nmr spectra (not including the C_xH_{2x+1} chain): (a) *trans*-$Fe(CO)_3[P(N(CH_3)_2)_3][P(OCH_2)_3CC_3H_7]$; (b) *trans*-$Mo(CO)_4[P(N(CH_3)_2)_3][P(OCH_2)_3CC_2H_5]$.

The reason for the simple and perturbed doublets in the ^1H nmr traces of these compounds became clear upon observation of the ^{31}P resonance absorptions. The two *cis* compounds exhibited simple AX patterns consisting of two doublets (broadened by $^3J_{PH}$ coupling) in the ^{31}P region whereas that of the *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(OCH_3)_3]$, although showing some AB character, was very nearly an AX spectrum. The ^{31}P spectra of the other two *trans* compounds were distinct AB patterns similarly broadened by $^3J_{PH}$. The spin classification of the pertinent nuclei in the latter compounds (excluding the C_xH_{2x+1} protons) can be designated M_mABY_n where M and Y are the protons in $P(N(CH_3)_2)_3$ ($m = 18$) and $P(OCH_2)_3CR$ ($n = 6$), respectively, and A and B are the phosphorus nuclei in the aminophosphine and bicyclic phosphite. The amount of perturbation in the proton region depends on J_{AB} and the difference in chemical shift of the A and B nuclei ($\nu_A - \nu_B$). If $J_{AB} \ll (\nu_A - \nu_B)$, then no perturbation is observed as is the case for *trans*-$Mo(CO)_4[P(OCH_2)_3CC_2H_5][P(OCH_3)_3]$. If $J_{AB} \approx (\nu_A - \nu_B)$, then the perturbation is similar to that observed for the other two *trans* compounds (Figure 1). If $J_{AB} \gg (\nu_A - \nu_B)$, apparent triplets would be produced in the proton nmr spectrum. In the two M_mABY_n systems reported here the AB coupling ($^2J_{PP}$) results in $2m + 1$ pairs of lines in the M region and $2n + 1$ pairs in the Y portion of the spectrum even though J_{AY} and J_{BM} are zero. Hence the doublets in the proton spectra (Figure 1) reveal the envelopes of the $2m + 1$ and $2n + 1$ lines as a perturbation on the doublets.

In all of the complexes, $^2J_{PP}$ in the mixed-ligand complexes is intermediate in value between the values for the two analogous complexes in which both ligands are the same (Tables I and II). This might well be expected if the coupling contribution from each phosphorus is of the same sign. On the basis of the pres-

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ently available[16] sign data for transition metal complexes, it is very likely that the signs are negative in the *cis* mixed-ligand complexes and positive in the *trans* (Tables I and II). In the theory of Pople and Santry[17] the signs of coupling constants are dependent upon the inverse of the energy difference $(\epsilon_j - \epsilon_i)^{-1}$ and the product of coefficients of the s atomic orbitals of the coupling sites in the molecular orbitals Ψ_i (occupied) and Ψ_j (unoccupied). A tentative suggestion as to what molecular orbitals Ψ_i and Ψ_j might be responsible for the signs of $^{2}J_{\mathrm{PP}}$ recorded here for our complexes is given elsewhere.[4]

In the present absence of a detailed molecular orbital treatment for transition metal complexes, the trends in the magnitudes of $^{2}J_{\mathrm{PP}}$ can best be understood in terms of the s-orbital character of the bond connecting the coupling nuclei and their effective nuclear charges, both of which are parameters in the valence-bond treatment of the Fermi contact term.[18] This term, which is generally conceded to be the dominant coupling effect,[4,12,18–23] is expected to increase as the electronegativity of the organic substituents on the phosphorus ligands is augmented. Such a trend is clearly seen in the experimentally observed rise in the absolute magnitude of $^{2}J_{\mathrm{PP}}$ in the order $\mathrm{M[P(N(CH_3)_2)_3]_2} < \mathrm{M[P(N(CH_3)_2)_3][P(OCH_2)_3CR]} < \mathrm{M[P(OCH_2)_3CR]_2}$ where M is the metal carbonyl moiety in the *cis*-molybdenum, *trans*-molybdenum, or *trans*-iron complexes (Tables I and II). The similar order for the remaining series $\mathrm{M[P(OCH_3)_3]} < \mathrm{M[P(OCH_3)_3][P(OCH_2)_3CR]} < \mathrm{M[P(OCH_2)_3CR]_2}$ is reasonable only if $\mathrm{P(OCH_2)_3CR}$ is effectively more electronegative than $\mathrm{P(OCH_3)_3}$. Displacement studies on the $\mathrm{BH_3}$ adducts of these phosphites confirm this point inasmuch as the bicyclic phosphite is indeed the poorer Lewis base.[4,15]

The larger values of $^{2}J_{\mathrm{PP}}$ in the *trans*- than in the *cis*-molybdenum complexes may be attributable to the fact that the σ-bonding electrons of *trans*-phosphorus nuclei share the same p_σ-metal molecular orbital whereas those *cis* do not. Although larger *trans* than *cis* couplings are generally observed,[4,23] it should be pointed out that chromium complexes appear to be anomalous in that the opposite observation has been made[4,23] with all of the ligands studied.

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Force Constants of the Hexacarbonyls of Chromium, Molybdenum, and Tungsten from the Vibrational Spectra of Isotopic Species

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The vibrational spectra of $\mathrm{M(^{12}C^{16}O)_6}$, $\mathrm{M(^{13}C^{16}O)_6}$, and $\mathrm{M(^{12}C^{18}O)_6}$, with M = Cr, Mo, or W, have been observed. Infrared spectra are reported for the vapors and solutions (in $\mathrm{CCl_4}$ for Cr and Mo and in $\mathrm{CS_2}$ for W); Raman spectra are reported for the solutions and solids. From the results most of the fundamental vibrations have been assigned. Force constants, with standard deviations, have been calculated for a general quadratic valence force field. A set of stretch–stretch interaction constants is presented which can be transferred, with discretion, to other metal carbonyls. Mean amplitudes of vibration and shrinkage effects are calculated. It is shown that the CO, C′O′ force constants are best explained by a dipole–dipole interaction.

Introduction

The bonding in metal carbonyls has held the attention of numerous research chemists in recent years. Some very important clues to the nature of the bonding lie in the values of the force constants describing the bond strengths, the directional forces, and the interactions among the bonds and bond angles. Unfortunately, for metal carbonyls, as with most polyatomic molecules, there is not enough information in the vibrational spectrum of the normal molecular species to define the general quadratic potential constants. Therefore, in the past, one has resorted to various more or less arbitrary approximations[1,2] concerning some of the force constants in order to calculate values for the other force constants. Some chemists[3–5] have taken

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