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A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Derivatives of Group VI Metal Carbonyls. II. "Mixed" Ligand Complexes[1]

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The preparation, infrared spectra in the carbonyl stretching region, and phophorus-31 nmr spectra of nine "mixed" phophorus ligand derivatives of the group VI metal carbonyls are reported. In the two compounds which have phosphorus atoms in *cis* positions, the phosphorus–phosphorus spin–spin coupling constant is considerably smaller than for those corresponding situations with *trans* phosphorus atoms.

There has been considerable recent interest in the measurement of various heavy-atom nuclear spin–spin coupling constants in coordination compounds,[4–9] with the aim of assigning stereochemistry of isomers and investigating the bonding involved by nmr.

Phosphorus–phosphorus coupling constants have been calculated by Verkade and co-workers[10–12] from ^{1}H and ^{19}F nmr spectra of compounds which have identical phosphorus ligands in chemically equivalent positions. In order to measure ^{31}P–^{31}P couplings directly, the phosphorus atoms must be chemically different, such as in "mixed" ligand complexes.[13]

We have previously reported directly measured ^{31}P–^{31}P coupling constants in rhodium compounds containing three molecules of the same phosphorus ligand in different chemical environments[7] and also one compound containing two different phosphorus ligands in the same molecule.[9] This work reports eight new compounds of the type $LL'M(CO)_4$ where L and L′ are a tertiary phosphine and organophosphite or two different tertiary phosphines, and M is Cr, Mo, or W. The novel compound *trans*-$[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2][(C_2H_5O)_3P]Mo(CO)_3$ is also reported.

Experimental Section

Phosphorus-31 nmr measurements were made with a Varian Associates DP 60 nmr spectrometer at 24.3 MHz as described previously.[9] Chemical shifts (ppm *vs.* H_3PO_4) are accurate to ±0.5 ppm. Coupling constants are accurate to ±8 cps. The infrared spectra in the carbonyl stretching region of the disubstituted compounds were measured in cyclohexane solution with a Perkin-Elmer Model 621 double-beam spectrometer and calibrated by saturated water vapor lines at 1942.6, 1919.0, and 1889.6 cm^{-1}. Because of limited solubility of $[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2][(C_2H_5O)_3P]Mo(CO)_3$ in cyclohexane, its infrared spectrum was measured in CCl_4 with a Beckman IR-8 spectrometer and calibrated with the polystyrene absorption at 1601 cm^{-1}. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

1,2-Bis(diphenylphosphino)ethane was prepared as described previously.[14] Starting materials of the type $LM(CO)_5$ were prepared by the method of Magee and co-workers.[15]

1,2-Bis(diphenylphosphino)ethanemolybdenum Tetracarbonyl.—A mixture of $Mo(CO)_6$ (6.95 g, 28.7 mmoles) and $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$ (14.3 g, 28.7 mmoles) in 50 ml of diethylene glycol dimethyl ether (diglyme) was stirred magnetically in an N_2 atmosphere and heated at 115° for 3 hr. The white crystals which had formed after standing for 1 day were removed by filtration. Addition of methanol to the filtrate resulted in a second crop of crystals. The crude product (14.5 g) was twice washed briefly with 20 ml of $CHCl_3$ in order to remove excess ligand. The remaining pure product, mp 190–191° (lit.,[16a] 193–194°), weighed 8.0 g (46%). This procedure is similar to that of Dietsche[16b] and is more convenient than that originally reported.[16a]

trans-Tributylphosphinetriphenylphosphinemolybdenum tetracarbonyl was prepared as described previously.[9]

***trans*-Tributylphosphine(triphenyl phosphite)molybdenum Tetracarbonyl.**—A solution of $(C_6H_5O)_3PMo(CO)_5$ (5.5 g, 10 mmoles) in 30 ml of diglyme was stirred magnetically in an N_2 atmosphere and heated in an oil bath to about 160°. Tributylphosphine (2.0 g, 10 mmoles) was injected through a serum cap on a side arm of the flask and the heat was maintained for about 3 hr until the evolution of CO had ceased. After cooling, the solvent was removed at reduced pressure with a rotary evaporator and the residue was dissolved in CH_2Cl_2. Addition of methanol to the solution caused formation of white crystals, whose infrared spectrum indicated that only *trans* isomers of the symmetrical and unsymmetrical products [*i.e.*, $L_2Mo(CO)_4$, $L'_2Mo(CO)_4$, and $LL'Mo(CO)_4$] were present. The mixture was chromatographed on an alumina column with light petroleum ether (bp 30–60°) as the eluent. A faint yellow band eluted first and the product (0.5 g) from this band was identified by ^{31}P nmr and infrared spectra as *trans*-$((C_4H_9)_3P)_2Mo(CO)_4$. A grayish band was eluted next and the product (2.0 g, 27%) identified as *trans*-$[(C_6H_5O)_3P]((C_4H_9)_3P)Mo(CO)_4$. The last eluted component (0.5 g) was *trans*$[(C_6H_5O)_3P]_2Mo(CO)_4$.

***cis*- and *trans*-Dibutylphenylphosphinetriphenylphosphinemolybdenum Tetracarbonyl.**—A solution of $((C_6H_5)_3P)Mo(CO)_5$ (12.3 g, 24.8 mmoles) in 50 ml of diglyme was stirred magneti-

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TABLE I

PREPARATIVE DATA AND PHYSICAL PROPERTIES OF "MIXED" LIGAND DERIVATIVES OF GROUP VI METAL CARBONYLS

				Analytical data, %				
				Calcd		Found		Carbonyl str freq,[a]
Compound	Yield, %	Color	Mp, °C	C	H	C	H	cm^{-1}
trans-$((C_6H_5)_3P)((C_4H_9)_3P)Cr(CO)_4$	26	Yellow	140–142 dec	64.96	6.74	64.67	6.80	1886 vs
trans-$((C_6H_5)_3P)((C_4H_9)_3P)Mo(CO)_4$	41	Yellow	146–148 dec	60.71	6.30	60.16	6.46	1894 vs
trans-$((C_6H_5)_3P)((C_4H_9)_3P)W(CO)_4$	22	Yellow	155–158 dec	53.69	5.57	53.40	5.72	1887 vs
trans-$((C_6H_5)_3P)(C_6H_5(C_4H_9)_2P)Mo(CO)_4$	9	Yellow	150–153 dec	62.45	5.53	62.20	5.71	1898 vs
cis-$((C_6H_5)_3P)(C_6H_5(C_4H_9)_2P)Mo(CO)_4$	18	Colorless	133–135	62.45	5.53	62.38	5.77	2020 m 1924 s 1905 s 1893 s
trans-$[(C_6H_5O)_3P]((C_4H_9)_3P)Cr(CO)_4$	25	Colorless	49–50	60.35	6.26	60.44	6.50	1909 vs
trans-$[(C_6H_5O)_3P]((C_4H_9)_3P)Mo(CO)_4$	27	Colorless	49–50	56.67	5.88	56.87	6.02	1919 vs
trans-$[(C_6H_5O)_3P]((C_4H_9)_3P)W(CO)_4$	8	Colorless	67–68	50.51	5.24	50.70	5.51	1910 vs
trans-$[(C_6H_5O)_3P](C_6H_5(C_4H_9)_2P)Mo(CO)_4$	22	Colorless	70–72	58.38	5.17	58.56	5.17	1921 vs
trans-$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2[(C_2H_5O)_3P]Mo(CO)_3$	79	Yellow	117–118	56.46	5.28	57.03	5.50	1982 m 1958 m 1880 vs

[a] m, medium; s, strong; v, very.

cally in an N_2 atmosphere and heated in an oil bath to about 160°. $(C_4H_9)_2C_6H_5P$ (6.0 g, 24.7 mmoles) was injected into the mixture and the heat was maintained for 1 hr until the evolution of CO ceased. The solvent was removed at reduced pressure and the residue was treated with CH_2Cl_2. The insoluble portion (2 g) of the residue was separated by filtration and identified by its melting point and infrared spectrum as *trans*-$((C_6H_5)_3P)_2Mo(CO)_4$. Addition of CH_3OH to the CH_2Cl_2 solution caused formation of pale yellow crystals, whose infrared spectrum indicated the presence of *cis* and *trans* isomers. The sample was chromatographed on an alumina column with light petroleum ether (bp 30–60°) as the eluent. A yellow band was eluted first and the product (1.5 g, 9%) in this band was *trans*-$((C_4H_9)_2C_6H_5P)((C_6H_5)_3P)Mo(CO)_4$. A very pale gray band eluted next and the product (3.0 g, 18%) of this band was *cis*-$((C_4H_9)_2C_6H_5P)((C_6H_5)_3P)Mo(CO)_4$.

***trans*-(Triethyl phosphite)-1,2-bis(diphenylphosphino)ethanemolybdenum Tricarbonyl.**—A mixture of $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2Mo(CO)_4$ (1.1 g, 1.7 mmoles) and $(C_2H_5O)_3P$ (0.55 g, 3.3 mmoles) in 5 ml of *p*-xylene was heated under N_2 at reflux for 12 hr although CO evolution had essentially stopped after 3 hr. Removal of the *p*-xylene at 60° (1 torr) resulted in a viscous yellow liquid which would not crystallize. A solution in 10 ml of CH_2Cl_2 was allowed to evaporate slowly over a period of 1 week. The yellow crystals that resulted were recrystallized twice from a minimum amount of refluxing absolute methanol which was then cooled to −20° overnight. The light yellow crystals (1 g, 79%) were dried for 1 hr at 60° (1 torr).

Other Compounds.—The remaining compounds reported in Table I were prepared and isolated in a manner similar to that of $[(C_6H_5O)_3P]((C_6H_5)_3P)Mo(CO)_4$. Some physical properties and analytical data are given in Table I.

Results and Discussion

The assignment of stereochemistry of the disubstituted compounds is unambiguous from the infrared spectra of the carbonyl stretching region (Table I), since the *trans* compounds give rise to only one strong carbonyl stretching frequency as expected.[17]

The phosphorus-31 nmr results are listed in Table II. The spectra of the simple "mixed" ligand complexes are the expected pairs of doublets. Several points should be noted. First, the downfield coordination chemical shift[7] is largest for chromium and the smallest for tungsten as was noted previously.[9] Second, for the only *cis*–*trans* pair isolated, J_{PMoP} for the *trans* compound $((C_6H_5)_3P)(C_6H_5(C_4H_9)_2P)Mo(CO)_4$ is considerably larger than for the *cis* isomer. This agrees with the calculations of Verkade, *et al.*,[12] for molybdenum phosphine compounds. Unfortunately, a *cis*–*trans* pair was not isolated in the chromium case. The chromium compounds are the only ones that have been found to show reversal in the magnitude of J_{PCrP} for the *cis* and *trans* isomers.[12] Third, J_{PMP} increases in the *trans* series from Cr to Mo to W, with the first step being considerably larger than the second. Fourth, J_{PMP} is larger for phosphite–phosphine compounds. This fact is in agreement with Verkade's observation[12] that J_{PP} values are larger as the π-accepting abilities of the ligands increase.

TABLE II

PHOSPHORUS-31 NMR DATA FOR "MIXED" LIGAND COMPOUNDS

	Chem shift, ppm			
Compound	Free ligand	Compound	Coordn chem shift, ppm	$J_{P-P'}$, cps
trans-$((C_6H_5)_3P)((C_4H_9)_3P)$-$Cr(CO)_4$	6.0 32.3	−74.1 −43.3	−80.1 −75.6	25
trans-$((C_6H_5)_3P)((C_4H_9)_3P)$-$Mo(CO)_4$	6.0 32.3	−50.9 −22.0	−56.9 −54.3	50
trans-$((C_6H_5)_3P)((C_4H_9)_3P)$-$W(CO)_4$	6.0 32.3	−28.4 3.2	−34.4 −29.1	65
trans-$((C_6H_5)_3P)(C_6H_5$-$(C_4H_9)_2P)Mo(CO)_4$	6.0 26.2	−51.1 −27.9	−57.1 −54.1	49
cis-$((C_6H_5)_3P)(C_6H_5$-$(C_4H_9)_2P)Mo(CO)_4$	6.0 26.2	−38.3 −12.1	−44.3 −38.3	21
trans-$[(C_6H_5O)_3P]((C_4H_9)_3$-$P)Cr(CO)_4$	−128.0 32.3	−185.1 −38.2	−57.1 −70.5	30
trans-$[(C_6H_5O)_3P]$-$((C_4H_9)_3P)Mo(CO)_4$	−128.0 32.3	−165.0 −17.2	−37.0 −49.5	112
trans-$[(C_6H_5O)_3P]$-$((C_4H_9)_3P)W(CO)_4$	−128.0 32.3	−137.0 5.3	−9.0 −27.0	120
trans-$[(C_6H_5O)_3P](C_6H_5$-$((C_4H_9)_2P)Mo(CO)_4$	−128.0 26.2	−165.2 −23.1	−37.2 −49.3	112
trans-$[(C_2H_5O)_3P](C_6H_5)_2P$-$(CH_2)_2P(C_6H_5)_2Mo(CO)_3$	−139.0 13.2 13.2	−175.4 −53.8 (c) −64.5 (b)	−36.4 −67.0 −77.7	104

It is tempting to suggest that the larger coupling of the mutually *trans* phosphorus atoms is due partially to $d_\pi(P)d_\pi(M)d_\pi(P)$ bonding since the same metal orbital is bonded to both phosphorus atoms in this stereochemistry. It is known,[18] however, that *trans*

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P–Ir–H couplings are larger than *cis* P–Ir–H couplings, and since hydrogen cannot be involved in π bonding, this explanation loses much of its cogency.

The reaction of triethyl phosphite with 1,2-bis(diphenylphosphino)ethanemolybdenum tetracarbonyl produces the *trans* (meridional) complex. This product is somewhat unexpected, since dipyridylmolybdenum tetracarbonyl with phosphites yields exclusively the *cis* (facial) product.[18,19] The phosphine chelating ligand is expected to have a stronger *trans*-directing influence than dipyridyl, so the result might be rationalized by this observation. In addition, tertiary phosphines are described as "nonlabilizing" in molybdenum carbonyl derivatives, whereas dipyridyl is "labilizing."[20] Therefore, an entirely different mechanism might be operating.

The stereochemistry of $[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2][(C_2H_5O)_3P]Mo(CO)_3$ can be unambiguously assigned from the ^{31}P nmr spectrum (see Figure 1) which consists of two doublets and a singlet of equal intensities.

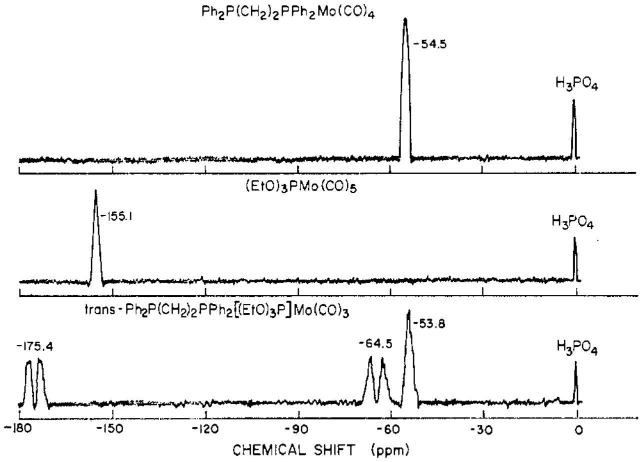

Figure 1.—The phosphorus-31 nmr spectra of several compounds.

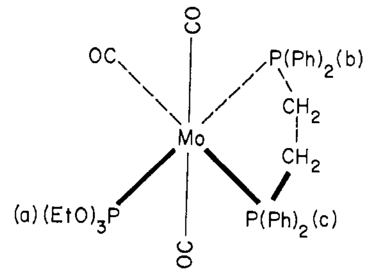

Figure 2.—The stereochemistry of *trans*-$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$-$[(C_6H_5O)_3P]Mo(CO)_3$.

The low-field doublet is due to the coordinated triethyl phosphite which is slightly downfield from the resonance in $(C_2H_5O)_3PMo(CO)_5$. It is the usual behavior of *trans*-disubstituted compounds[21] to have lower chemical shifts than the monosubstituted. The splitting is caused by coupling with the phosphorus b (see Figure 2) *trans* to the phosphite ligand. Coupling of phosphorus c with the phosphite is not clearly resolved and must be less than about 20 Hz, which is the approximate line width at half-height. The high-field doublet results from phosphorus b which is *trans* to the phosphite and split by it. No coupling with phosphorus c is observed. The singlet is due to phosphorus c which is *trans* to a carbonyl. Its chemical shift is upfield from phosphorus b and behaves like mono- and *cis*-disubstituted derivatives of group VI carbonyls.[21] No coupling with either of the phosphorus atoms *cis* to it is observed.

The preparative aspects of the "mixed" ligand complexes deserve some mention. All mixed ligand complexes of group VI metal carbonyls reported to date have had a chelating ligand (*e.g.*, a diphosphine, dipyridyl, *o*-phenanthroline) as the first of the groups attached to the metal in the reaction sequence.[18] With two points of attachment, the chelating ligand is less likely to be removed by substitution of the second attacking ligand than a monodentate ligand would be. We have found substitution to be a problem in the preparation of "mixed" bis-monodentate compounds. For example, the reaction of $LM(CO)_4$ with L′ can give the *cis* and *trans* isomers of $L_2M(CO)_4$, $L'_2M(CO)_4$, and $LL'M(CO)_4$. Although all of these isomers have not been isolated and identified from a specific reaction, the presence of many can be deduced from the very complex ^{31}P nmr spectrum of the reaction mixture. These complex reaction mixtures can be avoided by using the correct sequence of ligand attached to the metal: $(C_6H_5O)_3P$, $(C_6H_5)_3P$, $(C_4H_9)_2C_6H_5P$, $(C_4H_9)_3P$. Hence, *trans*-$((C_4H_9)_3P)((C_6H_5)_3P)Mo(CO)_4$ can be prepared from $((C_6H_5)_3P)Mo(CO)_5$ and $(C_4H_9)_3P$, but a complex mixture results from the reaction of $(C_6H_5)_3P$ with $((C_4H_9)_3P)Mo(CO)_5$.

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