TABLE IV

Four-coordinate tetrahedral	$Co(LS)X_2$ (X = Cl, Br, I)	$Co(LE)X_2$ (X = Cl, Br, I, NCS)
		$Ni(LE)Br_2$
	$Ni(LS)I_2$	$Ni(LE)I_2$
	$Zn(LS)Cl_2$	$Zn(LE)Cl_2$
		$Hg_2(LE)Cl_4$
Four-coordinate square		$Ni(LE)_2(ClO_4)_2$
Five-coordinate	$Ni(LS)Cl_2$	$Ni(LE)Cl_2$
	$Ni(LS)Br_2$	
	$Ni(LS)(NCS)_2$	$Ni(LE)(NCS)_2$
Linear	$Hg(LS)Cl_2$	

with bidentate pyridine ligands requires some comment. Five-coordination with d^8 species is expected when the oxidation number of the central species is low (say 0 or 1), as a consequence of the decreasing separation of the nd and $(n + 1)$p orbitals.[26]

In the case of nickel(II), with a formal charge of +2, five-coordination will be favored with the more polarizable ligands, where the effective nuclear charge and therefore the 3d–4p separation may be reduced. In agreement many five-coordinate complexes of nickel(II) involve ligands with arsenic, phosphorus, sulfur, or selenium atoms as donors and are magnetically low spin. However a series of high-spin five-coordinate complexes are known (see ref 2 and references therein) which involve polydentate pyridine ligands. In these cases five-coordination must arise principally through the steric requirements of the ligand. The ligands under discussion here represent very simple examples of these polydentate pyridine ligands. They are sufficiently sterically crowded that six-coordination is inhibited, while their polarizability is small such that four-coordinate tetrahedral nickel(II) derivatives are only produced with the more polarizable counterions. Thus five-coordinate and high-spin complexes are produced by the exclusion of other less favorable stereochemistries. The existence of five-coordinate nickel complexes with LE and LS but not with azopyridine (LN) is probably due to the fact that while azopyridine cannot coordinate in a bidentate fashion to a single metal atom but can utilize its bridge atoms for coordination, the reverse is true for the LS and LE ligands.

Very recently Sacconi[27] discussed the spin state of five-coordinate nickel(II) and cobalt(II) complexes in terms of the electronegativity of the donor atoms as determined by Allred and Rochow.[28] Sacconi summed the electronegativities of the donor atoms and demonstrated the existence of a crossover point below which the complexes were low spin and above which they were high spin. For the tri- and tetradentate ligands he discussed the crossover came at about 13 (sum of donor atom electronegativities) for nickel(II). For the five-coordinate complexes discussed in this paper the sum exceeds 14 so that high-spin behavior is expected and is observed.

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Substituted Group VI Metal Carbonyl Complexes of Dimethyl Methylphosphonite and Bis(dimethylamino)methylphosphine

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The synthesis of substituted metal carbonyls of the types $M(CO)_{6-x}L_x$, where M = Cr, Mo, or W, where x = 1, 2, or 3 for L = $CH_3P(OCH_3)_2$, and where x = 1 or 2 for L = $CH_3P(N(CH_3)_2)_2$ are described. The infrared data in the CO stretching region and CO stretching force constants are discussed and an order is proposed for the π-acceptor strength of the ligands: $P(OCH_3)_3 \gtrsim CH_3P(OCH_3)_2 > (CH_3)_3P > CH_3P(N(CH_3)_2)_2 > P(N(CH_3)_2)_3$. The proton nmr data are also discussed for these complexes and tentative assignment is made for the sign of $^2J_{PH}$ (coupling of phosphorus to the methyl protons). In the di- and trisubstituted complexes, phosphorus–phosphorus coupling is observed in the proton nmr spectra with the absolute value of $^2J_{PP}$ being larger in the trans isomer than in the cis isomer for a given compound and larger in Mo and W compounds than in analogous Cr compounds. These spectral data are used to help interpret the nature of the metal–phosphorus bond.

Introduction

Many substituted metal carbonyl complexes of the types $M(CO)_{6-x}L_x$, where M = Cr, Mo, or W, x = 1, 2, or 3, and L = tertiary phosphorus ligands, have been prepared and studied before. In particular, complexes of $P(OCH_3)_3$,[1] $P(CH_3)_3$,[1,2] and $P(N(CH_3)_2)_3$[3] have been previously investigated using infrared tech-

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niques and their proton nmr spectra have been reported. However, no studies have been made on substituted metal carbonyls with ligands of the type CH_3PY_2 and $(CH_3)_2PY$, where Y = OCH_3 or $N(CH_3)_2$. In this work group VI hexacarbonyl complexes of dimethyl methylphosphonite, $CH_3P(OCH_3)_2$, and bis(dimethylamino)methylphosphine, $CH_3P(N(CH_3)_2)_2$, are reported. These complexes are of particular interest because of the potential value of their proton nmr spectra. Although the proton nmr spectra of metal complexes of $P(OCH_3)_3$[4] and $P(N(CH_3)_2)_3$[3] have been reported, the invariance of the chemical shifts and coupling constants has prevented interpretation in terms of phosphorus–metal bonding. Because of the closer proximity of the methyl protons to the phosphorus atom in the ligands used in this work, meaningful changes in the nmr spectra can be observed and correlated with infrared data to obtain information on the metal–phosphorus bond. Cotton and Kraihanzel[5] type force constant calculations have been combined with the proton nmr results, to help explain the stereochemistry and bonding in various substituted group VI metal carbonyls.

Experimental Section

The infrared spectra were obtained on a Perkin-Elmer Model 225 grating spectrophotometer. In all cases, hexane was used as a solvent with sodium chloride optics. Proton nmr spectra were taken in chloroform solutions on a Varian Associates Model A-56/60-D instrument with tetramethylsilane as an internal standard. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The n isomers of pentane, hexane, and octane were used where these solvents are involved.

Materials.—The molybdenum and tungsten hexacarbonyls were purchased from Pressure Chemical Co., and chromium hexacarbonyl was purchased from Strem Chemical Co. The ligands dimethyl methylphosphonite ($CH_3P(OCH_3)_2$) and bis(dimethylamino)methylphosphine ($CH_3P(N(CH_3)_2)_2$) were prepared according to previously described methods.[6] Molybdenum norbornadiene tetracarbonyl,[7] molybdenum mesitylene tricarbonyl,[8] tungsten mesitylene tricarbonyl,[8,9] and chromium cycloheptatriene tricarbonyl[7] were also prepared as described elsewhere. Acetonitrilepentacarbonyltungsten and *cis*-bis(acetonitrile)tetracarbonyltungsten were prepared using a modification of previously described methods.[10] These complexes were prepared by irradiation with ultraviolet light (Hanovia Lamp 654-A10) in a quartz tube for 2 and 5 hr for the mono- and disubstituted species, respectively. They were identified by their infrared spectra[10] with no further purification being performed.

(Dimethyl methylphosphonite)pentacarbonylchromium, $(CH_3)(CH_3O)_2PCr(CO)_5$.—A mixture of 2.1 g (9.5 mmol) of chromium hexacarbonyl and 1.0 g (9.2 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of octane was refluxed for 12 hr under nitrogen with magnetic stirring. The solution was then allowed to cool to room temperature and concentrated under vacuum to about 2 ml. Approximately 5 ml of pentane was added, and fractional crystallization of this solution in a Dry Ice–isopropyl alcohol bath gave first $Cr(CO)_6$ and $((CH_3)(CH_3O)_2P)_2Cr(CO)_4$ (both identified by their infrared spectra) and then the white, crystalline $(CH_3)(CH_3O)_2PCr(CO)_5$. The solvent was decanted, and allowing the solid (mp 6°) to come to room temperature left the yellow liquid product. Repeated fractional crystallizations gave the pure product, and any remaining solvent was removed under vacuum. *Anal.* Calcd for $C_8H_9PCrO_7$: C, 32.00; H, 3.00; P, 10.03. Found: C, 32.20; H, 3.15; P, 10.57.

(Bis(dimethylamino)methylphosphine)pentacarbonylchromium, $(CH_3)((CH_3)_2N)_2PCr(CO)_5$.—A mixture of 3.0 g (13 mmol) of chromium hexacarbonyl and 1.8 g (13 mmol) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of octane was refluxed for 15 hr under nitrogen with magnetic stirring. The resulting solution was concentrated under vacuum to about 2 ml of a brown liquid. Addition of about 5 ml of pentane and cooling to −78° yielded pale yellow crystals of $(CH_3)((CH_3)_2N)_2PCr(CO)_5$, mp 74–76°. The pentane was then decanted, and any remaining solvent was removed under vacuum. Vacuum sublimation at about 100° and 1 Torr produced pale yellow crystals of the complex. *Anal.* Calcd for $C_{10}H_{15}N_2PCrO_5$: C, 36.80; H, 4.60; P, 9.50. Found: C, 36.61; H, 4.73; P, 9.61.

***cis*-Bis(dimethyl methylphosphonite)tetracarbonylchromium, $((CH_3)(CH_3O)_2P)_2Cr(CO)_4$.**—A mixture of 5.0 g (9.1 mmol) of chromium hexacarbonyl and 2.1 g (20 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of octane was refluxed for 24 hr under nitrogen with magnetic stirring. The solution was concentrated to about 10 ml under vacuum, and cooling in a −78° bath caused precipitation of white, needlelike crystals of *cis*-$((CH_3)(CH_3O)_2P)_2Cr(CO)_4$, mp 75–76°. Recrystallization was achieved in pentane. *Anal.* Calcd for $C_{10}H_{18}P_2CrO_8$: C, 31.60; H, 4.74; P, 16.32. Found: C, 31.70; H, 4.87; P, 16.60. The trans isomer of $((CH_3)(CH_3O)_2P)_2Cr(CO)_4$ was observed after several recrystallizations of the cis isomer. It was not, however, produced directly from the reaction of the hexacarbonyl and ligand.

***trans*-Bis(bis(dimethylamino)methylphosphine)tetracarbonylchromium, $((CH_3)((CH_3)_2N)_2P)_2Cr(CO)_4$.**—A mixture of 5.0 g (9.1 mmol) of chromium hexacarbonyl and 2.5 g (19 mmol) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of octane was refluxed for 28 hr under nitrogen with magnetic stirring to give a brown solution. After cooling to room temperature, this solution was filtered, and the filtrate was further cooled in a −78° bath producing yellow crystals. The octane was decanted, and recrystallization from pentane gave yellow, needlelike crystals of *trans*-$((CH_3)((CH_3)_2N)_2P)_2Cr(CO)_4$, mp 88–90°. *Anal.* Calcd for $C_{14}H_{30}N_4P_2CrO_4$: C, 38.89; H, 6.95; P, 14.35. Found: C, 38.82; H, 6.89; P, 14.44.

Tris(dimethyl methylphosphonite)tricarbonylchromium, $((CH_3)(CH_3O)_2P)_3Cr(CO)_3$.—A mixture of 0.3 g (1.0 mmol) of chromium cycloheptatriene tricarbonyl and 0.4 g (3.7 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of methylcyclohexane was refluxed for 1 hr during which the initially dark red solution gradually turned to light yellow. This solution was then cooled to room temperature and filtered. The solvent was removed under vacuum and about 5 ml of octane was added to the oily residue. Upon cooling this solution in a −78° bath, the oily residue again formed. The solvent was decanted and the residue was again dissolved in octane and cooling at −20° for 2 hr produced the very pale yellow mixture of *fac*- and *mer*-$((CH_3)(CH_3O)_2P)_3Cr(CO)_3$, mp 152–155°. The product was recrystallized from pentane. *Anal.* Calcd for $C_{12}H_{27}P_3CrO_9$: C, 31.31; H, 5.88; P, 20.22. Found: C, 31.15; H, 5.88; P, 20.09.

(Dimethyl methylphosphonite)pentacarbonylmolybdenum, $(CH_3)(CH_3O)_2PMo(CO)_5$.—A mixture of 4.1 g (15 mmol) of molybdenum hexacarbonyl and 1.6 g (15 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of methylcyclohexane was refluxed for 4 hr under nitrogen with magnetic stirring. The clear to yellow liquid $(CH_3)(CH_3O)_2PMo(CO)_5$ was isolated in a manner completely analogous to the isolation of $(CH_3)(CH_3O)_2PCr(CO)_5$. *Anal.* Calcd for $C_8H_9PMoO_7$: C, 27.91; H, 2.62; P, 9.01. Found: C, 27.99; H, 2.88; P, 9.26.

(Bis(dimethylamino)methylphosphine)pentacarbonylmolybdenum, $(CH_3)((CH_3)_2N)_2PMo(CO)_5$.—A mixture of 2.5 g (9.3 mmol) of molybdenum hexacarbonyl and 1.2 g (9.2 mmol) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of methylcyclohexane was refluxed for 4 hr under nitrogen with magnetic stirring. The resulting black

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solution was cooled to room temperature, filtered, and concentrated under vacuum to about 2 ml of a brown liquid. The white, crystalline $(CH_3)((CH_3)_2N)_2PMo(CO)_5$, mp 45–47°, was isolated and purified in a manner completely analogous to the isolation of $(CH_3)((CH_3)_2N)_2PCr(CO)_5$. *Anal.* Calcd for $C_{10}H_{15}N_2PMoO_5$: C, 32.41; H, 4.05; P, 8.38. Found: C, 32.60; H, 4.21; P, 8.19.

cis-**Bis(dimethyl methylphosphonite)tetracarbonylmolybdenum,** $((CH_3)(CH_3O)_2P)_2Mo(CO)_4$.—A mixture of 1.0 g (3.3 mmol) of molybdenum norbornadiene tetracarbonyl and 1.0 g (9.2 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of hexane was refluxed for 1 hr. The cooled solution was filtered and the hexane was removed under vacuum leaving a yellow solid. Recrystallization from pentane gave white, needlelike crystals of *cis*-$((CH_3)(CH_3O)_2P)_2Mo(CO)_4$, mp 67–68°. *Anal.* Calcd for $C_{10}H_{18}P_2MoO_8$: C, 28.30; H, 4.25; P, 14.62. Found: C, 28.43; H, 4.36; P, 14.78.

trans-**Bis(bis(dimethylamino)methylphosphine)tetracarbonylmolybdenum,** $((CH_3)((CH_3)_2N)_2P)_2Mo(CO)_4$.—A mixture of 0.9 g (3.0 mmol) of molybdenum norbornadiene tetracarbonyl and 1.3 g (9.0 mmol) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of hexane was refluxed for 1 hr under nitrogen with magnetic stirring. In a manner identical with that used for the isolation of *cis*-$((CH_3)(CH_3O)_2P)_2Mo(CO)_4$, yellow, needlelike crystals of *trans*-$((CH_3)((CH_3)_2N)_2P)_2Mo(CO)_4$, mp 88–90°, were obtained. *Anal.* Calcd for $C_{14}H_{30}N_4P_2MoO_4$: C, 35.29; H, 6.30; P, 13.03. Found: C, 35.26; H, 6.37; P, 13.10.

fac-**Tris(dimethyl methylphosphonite)tricarbonylmolybdenum,** $((CH_3)(CH_3O)_2P)_3Mo(CO)_3$.—A mixture of 0.4 g (1.4 mmol) of molybdenum mesitylene tricarbonyl and 0.5 g (4.6 mmol) of $CH_3P(OCH_3)_2$ in 25 ml of hexane was refluxed for 0.75 hr under nitrogen with magnetic stirring. Cooling the clear solution to room temperature caused precipitation of white, needlelike crystals of *fac*-$((CH_3)(CH_3O)_2P)_3Mo(CO)_3$, mp 171–173°. *Anal.* Calcd for $C_{12}H_{27}P_3MoO_9$: C, 28.60; H, 5.36; P, 18.50. Found: C, 28.56; H, 5.30; P, 18.33.

(Dimethyl methylphosphonite)pentacarbonyltungsten, $(CH_3)(CH_3O)_2PW(CO)_5$.—A mixture of 3.0 g (8.4 mmol) of tungsten hexacarbonyl and 0.8 g (7.4 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of octane was refluxed for 72 hr under nitrogen with magnetic stirring. The pale yellow liquid, $(CH_3)(CH_3O)_2PW(CO)_5$, was isolated in a manner completely analogous to the isolation of $(CH_3)(CH_3O)_2PCr(CO)_5$. *Anal.* Calcd for $C_8H_9PWO_7$: C, 22.21; H, 2.09; P, 7.16. Found: C, 22.59; H, 2.14; P, 7.01.

(Bis(dimethylamino)methylphosphine)pentacarbonyltungsten, $(CH_3)((CH_3)_2N)_2PW(CO)_5$.—A mixture of 1.7 g of $(CH_3CN)W(CO)_5$ (4.6 mmol) and 0.6 g (4.5 mmol) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of hexane was refluxed for 4 hr under nitrogen with magnetic stirring. The solvent was removed under vacuum leaving a yellow solid that contained a mixture of $W(CO)_6$, $(CH_3)((CH_3)_2N)_2PW(CO)_5$, and *trans*-$((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$, which were identified in the infrared spectrum. Repeated attempts to purify the desired monosubstituted product failed.

cis-**Bis(dimethyl methylphosphonite)tetracarbonyltungsten,** $((CH_3)(CH_3O)_2P)_2W(CO)_4$.—A mixture of 2.0 g (5.2 mmol) of $(CH_3CN)_2W(CO)_4$ and 1.5 g (13 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of hexane was refluxed for 11 hr under nitrogen with magnetic stirring. The solvent was removed under vacuum, and the remaining solid yielded white crystals of *cis*-$((CH_3)(CH_3O)_2P)_2W(CO)_4$, mp 49–51°, when recrystallized from pentane. *Anal.* Calcd for $C_{10}H_{18}P_2WO_8$; C, 23.50; H, 3.52; P, 12.12. Found: C, 23.71; H, 3.42; P, 12.14.

trans-**Bis(bis(dimethylaminomethylphosphine))tetracarbonyltungsten,** $((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$.—A mixture of 3.1 g (7.8 mmol) of $(CH_3CN)_2W(CO)_4$ and 2.1 g (16 mmol) of $CH_3P(N(CH_3)_2)_2$ in 50 ml of hexane was refluxed for 9 hr under nitrogen with magnetic stirring. The yellow, crystalline *trans*-$((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$, mp 91–93°, was isolated in a manner completely analogous to the isolation of *cis*-$((CH_3)((CH_3)_2N)_2P)_2W(CO)_4$. *Anal.* Calcd for $C_{14}H_{30}N_4P_2WO_4$: C, 29.80; H, 5.32; P, 11.00. Found: C, 29.95; H, 5.19; P, 11.23.

fac-**Tris(dimethyl methylphosphonite)tricarbonyltungsten,** $((CH_3)(CH_3O)_2P)_3W(CO)_3$.—A mixture of 0.5 g (1.3 mmol) of tungsten mesitylene tricarbonyl and 0.5 g (5.6 mmol) of $CH_3P(OCH_3)_2$ in 50 ml of hexane was refluxed for 12 hr under nitrogen with magnetic stirring. This solution was cooled to room temperature and filtered, and the hexane was removed under vacuum. The remaining yellow solid was recrystallized from pentane giving white crystals of *fac*-$((CH_3)(CH_3O)_2P)_3W(CO)_3$. (See below.)

mer-**Tris(dimethyl methylphosphonite)tricarbonyltungsten,** $((CH_3)(CH_3O)_2P)_3W(CO)_3$.—*mer*-$((CH_3)(CH_3O)_2P)_3W(CO)_3$ was prepared in a manner completely analogous to the preparation of *fac*-$((CH_3)(CH_3O)_2P)_3W(CO)_3$ except that the reaction was refluxed for 6 hr in methylcyclohexane. When this reaction was stopped after 2 hr, infrared analysis of the product showed the presence of the fac isomer. An insufficient sample for either isomer prevented elemental analysis of the compounds; however, identification was accomplished through infrared and nmr spectral data.

Results and Discussion

The monosubstituted compounds $(CH_3)(CH_3O)_2PM(CO)_5$ (M = Cr, Mo, W) were prepared in good yields by refluxing equimolar mixtures of the hexacarbonyl and ligand in either methylcyclohexane or octane for various lengths of time depending on the metal employed. The ease with which the reactions took place decreased in the order Mo > Cr > W. These complexes are liquids at room temperature, as was observed by Poilblanc and Bigorgne[1] for similar complexes of $P(OCH_3)_3$. The isolation and purification of these compounds was most easily achieved by fractionally crystallizing a pentane solution in a Dry Ice–isopropanol slush bath, removing first the unreacted hexacarbonyl and the disubstituted complex and leaving behind the monosubstituted compound. Further cooling caused precipitation of white crystals of the monosubstituted complex which melted on warming to room temperature to give a pale yellow liquid.

The monosubstituted complexes of $CH_3P(N(CH_3)_2)_2$ were prepared in a similar manner; however, these compounds were observed to be crystalline solids, at room temperature, and were easily sublimed. The monosubstituted tungsten complex of $CH_3P(N(CH_3)_2)_2$ has not been isolated in a pure state. The infrared spectrum of the material obtained from the reaction of a 1:1 mixture of $W(CO)_6$ and $CH_3P(N(CH_3)_2)_2$ shows that the product is a mixture of unreacted hexacarbonyl and both the mono- and disubstituted compounds. Attempted purification by fractional crystallization has not freed the monosubstituted compound of these impurities. It may be that the monosubstituted compound is unstable and disproportionates to the disubstituted compound and the hexacarbonyl. It is interesting to note that when tris(dimethylamino)phosphine, $P(N(CH_3)_2)_3$, was allowed to react with $W(CO)_6$, only the disubstituted compound was observed although both mono- and disubstituted compounds of Cr and Mo were isolated.[3]

The disubstituted complexes of chromium for either $CH_3P(OCH_3)_2$ or $CH_3P(N(CH_3)_2)_2$ were prepared by refluxing the hexacarbonyl in octane, whereas, the molybdenum complexes were very easily prepared from molybdenum norbornadiene tetracarbonyl. Previously, disubstituted tungsten carbonyl complexes had

TABLE I
CO STRETCHING FREQUENCIES AND FORCE CONSTANTS[a]

	Freq, cm^{-1}				Force constants, mdyn/Å		
$ML(CO)_5$	$A_1^{(2)}$	$A_1^{(1)}$	B_1	E	k_1	k_2	k_i
$Cr[CH_3P(OCH_3)_2](CO)_5$	2071.0	1963.5	1987.0	1947.0	15.80	15.90	0.30
$Cr[CH_3P(N(CH_3)_2)_2](CO)_5$	2061.0	1948.5	(1974.0)[b]	1938.0	15.55	15.76	0.30
$Mo[CH_3P(OCH_3)_2](CO)_5$	2078.5	1967.0	1989.0	1953.0	15.85	16.01	0.30
$Mo[CH_3P(N(CH_3)_2)_2](CO)_5$	2070.5	1950.0	(1980.0)[b]	1946.0	15.56	15.89	0.30
$W[CH_3P(OCH_3)_2](CO)_5$	2077.0	1961.0	1983.0	1947.5	15.76	15.94	0.31
$W[CH_3P(N(CH_3)_2)_2](CO)_5$	2069.5	1946.0	(1972.0)[b]	1928.0	15.55	15.69	0.34
cis-$ML_2(CO)_4$	$A_1^{(2)}$	$A_1^{(1)}$	B_1	B_2	k_1	k_2	k_i
$Cr[CH_3P(OCH_3)_2]_2(CO)_4$	2022.0	1934.0	1911.5	1909.5	15.08	15.47	0.36
$Mo[CH_3P(OCH_3)_2]_2(CO)_4$	2031.5	1940.5	(1940.5)[b]	1921.0	15.20	15.81	0.30
$W[CH_3P(OCH_3)_2]_2(CO)_4$	2028.5	1943.0	1934.5	1912.5	15.10	15.77	0.33
trans-$ML_2(CO)_4$	A_{1g}	B_{1g}	E_u			k_2	k_i
$Cr[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	...[c]	...[c]	1883.0			15.00	(0.34)[d]
$Mo[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	...[c]	(1919.0)[b]	1894.0			15.17	(0.34)[d]
$W[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	...[c]	(1910.0)[b]	1886.0			15.05	(0.34)[d]
fac-$ML_3(CO)_3$	A_1	E				k_1	k_i
$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1960.0	1871.0				14.59	0.46
$Mo[CH_3P(OCH_3)_2]_3(CO)_3$	1970.0	1891.5				14.86	0.41
$W[CH_3P(OCH_3)_2]_3(CO)_3$	1966.0	1885.0				14.86	0.52
mer-$ML_3(CO)_3$	$A_1^{(2)}$	$A_1^{(1)}$	B_1		k_1	k_2	k_i
$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1972.0	1871.0	1887.0		14.38	14.92	(0.27)[d]
$W[CH_3P(OCH_3)_2]_3(CO)_3$	1984.0	1878.0	1899.0		14.53	15.10	(0.27)[d]

[a] Hexane solutions. [b] Tentative assignment. [c] Not observed. [d] Value of k_i is assumed after comparison with similar compounds: C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

been prepared either by direct reaction of the ligand with the hexacarbonyl or with a tungsten–diene complex, such as, tungsten cyclooctadiene tetracarbonyl[11] or tungsten norbornadiene tetracarbonyl.[2] These diene intermediates were prepared from $(CH_3CN)_3W(CO)_3$ according to the methods of King and Fronzaglia.[9] In the course of this work it was found that $(CH_3CN)_2W(CO)_4$ could be prepared easily and in good yields by irradiation of an acetonitrile solution of $W(CO)_6$ with ultraviolet light. This complex was then allowed to react directly with $CH_3P(OCH_3)_2$ or $CH_3P(N(CH_3)_2)_2$, producing the disubstituted compounds in almost quantitative yields.

The trisubstituted compounds of $CH_3P(OCH_3)_2$ were easily formed in good yields from either the metal mesitylene tricarbonyl complex or the metal cycloheptatriene tricarbonyl complex. $CH_3P(N(CH_3)_2)_2$ would not form a trisubstituted complex with any of the metals, regardless of the manner of preparation. When $CH_3P(N(CH_3)_2)_2$ was allowed to react with molybdenum mesitylene tricarbonyl, the disubstituted compound $((CH_3)((CH_3)_2N)_2P)_2Mo(CO)_4$ was obtained. This is similar to the reaction of $P(N(CH_3)_2)_3$ with molybdenum cycloheptatriene tricarbonyl where, again, only the disubstituted compound was isolated.[3]

Infrared Spectra.—Table I lists the infrared data for the carbonyl region of all the compounds studied in this work. The monosubstituted compounds exhibit the three infrared bands $A_1^{(2)}$, $A_1^{(1)}$, and E_1 for C_{4v} symmetry. An additional weak band is also observed which is assigned to the B_1 mode. This Raman-active band becomes weakly active in the infrared region due to the lower symmetry of the ligand which lowers the overall symmetry of the complex. The disubstituted compounds of $CH_3P(OCH_3)_2$ are primarily the cis isomers as is indicated by the four carbonyl stretching frequencies expected for C_{2v} symmetry. Indications of the trans isomers for Cr and W were observed in the infrared and in the nmr spectra; however, no trans isomer was observed for Mo. Both the cis and trans isomers have been reported for disubstituted complexes of chromium, molybdenum, and tungsten hexacarbonyls with the similar ligands $P(CH_3)_3$[1,2] and $P(OCH_3)_3$.[1,12] The disubstituted compounds of $CH_3P(N(CH_3)_2)_2$ are exclusively trans, as is shown by their infrared spectra which conform to D_{4h} symmetry. The same trans configuration is reported for the disubstituted complexes of $P(N(CH_3)_2)_3$,[3] although Verkade, *et al.*,[12] have been able to isolate the cis isomers of both $P(N(CH_3)_2)_3$ and $P(NCH_3C_6H_5)_3$ in the case of Mo. The $P(N(CH_3)_2)_3$ complex, however, readily isomerizes to the trans isomer in benzene solution at room temperature. Both fac and mer isomers were observed for the trisubstituted compounds of Cr and W; however, only the fac isomer was obtained for Mo. These isomers were identified by their infrared and nmr spectra. For all of the complexes reported the CO stretching vibrations occur at the highest frequencies for the Mo complexes with a given ligand, and for $CH_3P(OCH_3)_2$ with a given metal.

Substituted group VI hexacarbonyl complexes of tertiary nitrogen and phosphorus ligands have been the subject of many previous studies.[13] An integral part of most of these studies has been the interpretation of the carbonyl stretching frequencies and the stretching force constants in terms of the metal–ligand bond-

(11) A. C. Vandenbroucke, Jr., D. G. Hendricker, R. E. McCarley, and J. G. Verkade, *Inorg. Chem.*, **7**, 1825 (1968).

(12) F. B. Ogilvie, J. M. Jenkins, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 1916 (1970).

(13) See, for example, the review article by G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966).

ing.[14,15] Substitution of a CO group by another ligand of weaker π-acceptor capacity causes the frequencies of the remaining CO groups to shift to lower frequencies inasmuch as the weaker π-accepting capacity of the phosphorus ligands increases the available metal $d\pi$ electron density for back-donation to the CO $p\pi^*$ antibonding orbitals. Trends in such experimentally observable shifts may then be interpretable in terms of relative changes in the π-acceptor properties of the metal–ligand bond.

The method of Cotton and Kraihanzel[5] was used to calculate force constants from the frequencies given in Table I. The values of k_1 are for the CO stretching force constants of the CO groups trans to the ligands, k_2 for the CO stretching force constants cis to the ligands, and k_i for the interaction constant between the CO groups. The assignments of the bands shown in Table I are based on the assignments by Cotton[15] for similar compounds.

The CO groups in complexes with $CH_3P(N(CH_3)_2)_2$ as ligands have lower energy carbonyl stretching frequencies and, more importantly, smaller stretching force constants than corresponding complexes of $CH_3P(OCH_3)_2$. The values of their frequencies and force constants can be used to compare the relative π-acceptor strengths of these two ligands with other tertiary phosphorus ligands. $CH_3P(OCH_3)_2$ is comparable to $P(OCH_3)_3$[15] as a π acid, while $CH_3P(N(CH_3)_2)_2$ is weaker than $P(CH_3)_3$[15] but stronger than $P(N(CH_3)_2)_3$.[16] From this comparison, the π-acid strength is found to decrease in the order: $P(OCH_3)_3 \geqq CH_3P(OCH_3)_2 > P(CH_3)_3 > CH_3P(N(CH_3)_2)_2 > P(N(CH_3)_2)_3$. The position of $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$ in this order may be expected since it might be anticipated that a certain degree of $p\pi \rightarrow d\pi$ nitrogen to phosphorus π bonding exists. Support for this proposal comes from structural data available for the compound $F_2PN(CH_3)_2$[17] in which a short P–N bond length was observed along with a near-planar arrangement for the P, N, and C atoms. This suggestion of an sp^2 hybridization of N is consistent with the possibility of nitrogen to phosphorus π bonding. Thus, because of this potential $p\pi \rightarrow d\pi$ bonding, these nitrogen-containing ligands should be poorer π acceptors toward a metal carbonyl than, for example, $P(CH_3)_3$. Further support for this assumption comes from some force constant data of Nixon, *et al.*[18] For di- and trisubstituted molybdenum complexes of a variety of fluorophosphines they determined a π-accepting capacity of $ROPF_2 > R_2NPF_2 > RP(F)NR_2 > (R_2N)_2PF$. In the case of $P(OCH_3)_3$ and $CH_3P(OCH_3)_2$, although there may be some degree of oxygen to phosphorus $p\pi \rightarrow d\pi$ bonding, the important factor must be that the electronegativity of the oxygen creates a slight lowering of the energy of the phosphorus $d\pi$ orbital and an increase in its π-accepting capacity. In addition, with only one inductive methyl group on the oxygen, as opposed to the two on the nitrogen, the oxygen to phosphorus π bonding is expected to be somewhat less than the nitrogen to phosphorus π bonding.[19]

Proton Nmr.—For each ligand, the proton nmr spectrum consists of two doublets arising from the two types of protons coupled to the phosphorus (see Table II).

TABLE II
PROTON NMR DATA[a]

Compound	$\delta(CH_3)^b$	$^2J_{PH}{}^c$	$\delta(OCH_3)^b$ or $\delta(N(CH_3)_2)^b$	$^3J_{PH}{}^c$
$CH_3P(OCH_3)_2$	1.10	8.5	3.50	11.0
$Cr[(CH_3P(OCH_3)_2](CO)_5$	1.70	4.0	3.60	11.5
$Mo[(CH_3P(OCH_3)_2](CO)_5$	1.70	3.0	3.55	12.0
$W[(CH_3P(OCH_3)_2](CO)_5$	1.80	4.0	3.55	12.0
cis-$Cr[CH_3P(OCH_3)_2]_2(CO)_4$	1.70	3.5	3.60	11.5
cis-$Mo[CH_3P(OCH_3)_2]_2(CO)_4$	1.65	2.5	3.55	12.0
cis-$W[CH_3P(OCH_3)_2]_2(CO)_4$	1.85	4.0	3.55	12.0
fac-$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1.70	2.5	3.57	11.0
mer-$Cr[CH_3P(OCH_3)_2]_3(CO)_3$	1.65[d]	2.5	3.50[d]	11.0
	1.70[e]	2.5	3.57[e]	11.0
fac-$Mo[CH_3P(OCH_3)_2]_3(CO)_3$	1.65	1.0	3.55	11.0
fac-$W[CH_3P(OCH_3)_2]_3(CO)_3$	1.75	3.0	3.50	11.0
mer-$W[CH_3P(OCH_3)_2]_3(CO)_3$	1.75[d]	3.0	3.48[d]	11.0
	1.80[e]	3.5	3.53[e]	11.0
$CH_3P(O)(OCH_3)_2$	1.42	17.0	3.65	11.0
$CH_3P(N(CH_3)_2)_2$	1.05	8.0	2.60	9.0
$Cr[CH_3P(N(CH_3)_2)_2](CO)_5$	1.65	4.5	2.60	10.0
$Mo[CH_3P(N(CH_3)_2)_2](CO)_5$	1.65	3.8	2.60	10.5
$W[CH_3P(N(CH_3)_2)_2](CO)_5$	1.80	4.5	2.60	11.0
trans-$Cr[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	1.60	4.0	2.60	10.0
trans-$Mo[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	1.65	3.0	2.60	10.5
trans-$W[CH_3P(N(CH_3)_2)_2]_2(CO)_4$	1.80	4.0	2.60	10.5

[a] Chloroform solutions. [b] Chemical shifts are in ppm (±0.05) and are referenced to tetramethylsilane. [c] Coupling constants are in Hz (±0.5) and are given as the absolute value. See text for discussion of signs. [d] Apparent "doublet" for ligand cis to the two trans ligands. [e] Apparent "triplet" for the two ligands trans to each other.

The more shielded methyl group protons resonate at higher field than either the OCH_3 or the $N(CH_3)_2$ protons, and the $N(CH_3)_2$ protons appear at higher field than those of the OCH_3 group. When the ligands are complexed to the metals, there is a downfield shift for the CH_3 resonances due to the partial oxidation (as a result of donation of the lone pair of electrons) of the phosphorus. However, because of the greater distance from the phosphorus, for both the $N(CH_3)_2$ and the OCH_3 groups, their chemical shifts are relatively insensitive to complexation. A similar result is seen for the coupling constants. The absolute value of $^2J_{PH}$ (coupling to the methyl protons) is decreased upon complexation to less than half of its free-ligand value, while the absolute value of $^3J_{PH}$ (coupling to either the OCH_3 or the $N(CH_3)_2$ protons) remains unchanged or is slightly increased.

The spectra of the monosubstituted compounds consist of two doublets, while the spectra of the disubstituted and the fac-trisubstituted compounds consist of two resonances, each of which appears as a "triplet" with the center peak showing a wide variation in inten-

(14) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).
(15) F. A. Cotton, *ibid.*, **3**, 702 (1964).
(16) Calculated from the data of R. L. Keiter and J. G. Verkade, *ibid.*, **8**, 2115 (1969).
(17) E. D. Morris, Jr., and C. E. Nordman, *ibid.*, **8**, 1673 (1969).
(18) C. G. Barlow, J. F. Nixon, and M. Webster, *J. Chem. Soc. A*, 2216 (1968).
(19) Suggested by a referee.

sity from compound to compound. This apparent "triplet" is a result of both phosphorus–hydrogen coupling and phosphorus–phosphorus coupling, as has been previously observed in a variety of compounds.[3,12,20,21] The resonances which appear as "triplets" can be classed as $X_nAA'X'_n$[22] type spectra where X and A represent the protons and phosphorus, respectively, of one ligand and X′ and A′ represent the protons and phosphorus, respectively, of a second ligand cis or trans to the first. The subscript n may be equal to 3, 6, or 12 for the CH_3, OCH_3, or $N(CH_3)_2$ resonances, respectively. The center line of the observed "triplet" arises from the near coincidence of a large number of X lines and the spectrum may appear as a 1:2:1 triplet in the limiting case.[22] The intensity of the central peak is then dependent upon this coincidence of many other spectral lines and the value of $^2J_{PP}$ is a maximum when the central peak is most intense.[22,23] Using this qualitative approach, results similar to previous studies[3,12,21] can be achieved, namely, that $^2J_{PP}$ for trans compounds is larger than that for analogous cis compounds except perhaps for Cr and that coupling for trans compounds decreases as Mo > W ≫ Cr and for cis compounds as Cr > Mo > W. Unfortunately, the two ligands used in this study do not readily form the complexes of the same geometry so that comparisons of the effect of the ligand on $^2J_{PP}$ cannot be fully ascertained. One unique feature of these spectra, however, is that two resonances are observed for each complex (the CH_3 resonance and the OCH_3 or $N(CH_3)_2$ resonance) thus allowing for the possibility of two independent determinations of $^2J_{PP}$.

For the compound *mer*-$((CH_3)(CH_3O)_2P)_3W(CO)_3$, in addition to the two "triplets," both the CH_3 and the OCH_3 protons exhibited a "doublet" at approximately 0.05 ppm higher field (Figure 1A). These "doublets" can be attributed to the ligand which is uniquely trans to a CO group and cis to the other two ligands. These resonances represent one of the limiting cases of the $X_nAA'X'_n$ type spectrum where $^2J_{PP}$ is small for phosphorus atoms cis to one another while the slightly lower field "triplets" represent the X part of an $X_nAA'X'_n$ type spectrum wherein $^2J_{PP}$ is appreciable for two ligands trans to each other. The mer Cr compound exhibited a spectrum consisting of two sets of overlapping "doublets" (Figure 1C). In the OCH_3 proton resonance, where the phosphorus–hydrogen coupling is quite large, some indication of a very weak peak could be observed near the middle of this "doublet" grouping. However, it was impossible to assign this resonance unambiguously to the trans ligands or the cis ligands. Again the chemical shift difference between the two resonances is approximately 0.05 ppm, and, as expected, the chemical shifts and coupling constants for the cis Cr and W and the fac W compounds of $CH_3P(OCH_3)_2$ (Figure 1B) compare

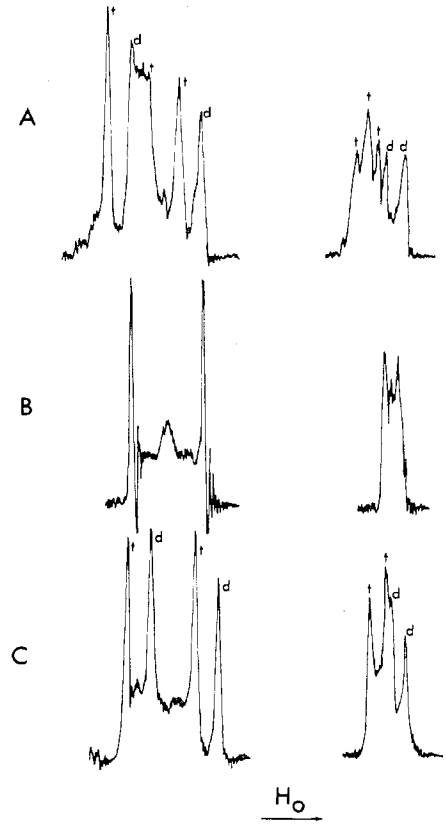

Figure 1.—Shapes of the proton nmr resonances of some trisubstituted complexes of $CH_3P(OCH_3)_2$ (L). A is *mer*-$W(CO)_3L_3$, B is *fac*-$W(CO)_3L_3$, and C is *mer*-$Cr(CO)_3L_3$. The methyl resonance is at higher field in all cases. Those resonances in the mer complexes labeled with the letter t are assigned to the two ligands trans to each other giving rise to a near "triplet" and those resonances labeled d refer to the "doublet" resulting from the ligand cis to the other two ligands (see text). In C, assignment of the central resonance in the "triplets" is not obvious and is, therefore, not labeled.

very well with the "doublet" parts of the corresponding mer complexes. Similar spectra have been observed by Shaw, *et al.*,[21] for the trisubstituted Cr compound of $C_6H_5P(OCH_3)_2$ and the analogous Mo compound of $(CH_3)_2PC_6H_5$.

The slight change in $^3J_{PH}$ for the P–OCH_3 system upon complexation is typical.[21] The relatively large change in $^2J_{PH}$ for the CH_3 group is of interest because it aids in the assignment of the sign of the P–C–H coupling. Manatt, *et al.*,[24] have suggested that the geminal coupling P–C–H ($^2J_{PH}$) in a variety of trivalent phosphorus compounds is positive and that $^2J_{PH}$ becomes more negative as the s character of the phosphorus bonding orbitals to carbon increases. Thus, $^2J_{PH}$ in $(CH_3)_3P$ is +2.66 Hz while $^2J_{PH}$ in $(CH_3)_4P^+$ and $(CH_3)_3P{=}O$ are −14.4 and −13.4 Hz, respectively.[24] In the latter two compounds, the hybridization around phosphorus is nearly pure sp^3 and consequently more s character should be in the PC bonds. In $CH_3P(OCH_3)_2$ and $CH_3P(N(CH_3)_2)_2$, the values of $^2J_{PH}$, 8.5 and 8.0 Hz (Table II), respectively, are proba-

(20) R. D. Bertrand, D. A. Allison, and J. G. Verkade, *J. Amer. Chem Soc.*, **92**, 71 (1970), and references therein.

(21) J. M. Jenkins, J. R. Moss, and B. L. Shaw, *J. Chem. Soc. A*, 2796 (1969).

(22) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

(23) R. K. Harris, *Inorg. Chem.*, **5**, 701 (1966).

(24) S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Amer. Chem. Soc.*, **88**, 2689 (1966).

bly positive (see later) while the value of 17.0 Hz for $^2J_{PH}$ in $CH_3P(O)(OCH_3)_2$ (Table II) is taken as negative. Therefore, it is assumed that as the phosphorus is oxidized, the s character of the PC bond increases, and the coupling becomes more negative. In the metal carbonyl complexes the phosphorus is partially oxidized because of donation of the lone pair. The result of this should be an increase in the s character of the PC bond, and the value of $^2J_{PH}$ for the complexed ligand should be more negative than for the free ligand. Since the absolute values of $^2J_{PH}$ in the complexes are less than those in the free ligands (Table II), this coupling in the ligand is very likely positive if the s-character effect is dominant. Although the $^2J_{PH}$ couplings could be either positive or negative in the complexes, some evidence can be cited for suggesting that they are negative. From the mono- to di- to trisubstituted compounds, the phosphorus atom is oxidized to a lesser extent because of the increased negative charge on the metal brought about by the increased substitution of the weakly basic CO groups by the more basic phosphorus ligands. Consequently, there should be less s character in the PC bonds and $^2J_{PH}$ should become more positive with increased substitution. Reference to Table II shows that the regular decrease in $^2J_{PH}$ from $|3|$ to $|1|$ Hz for the molybdenum complexes of $CH_3P(OCH_3)_2$ parallels the degree of substitution from mono- to trisubstitution. These values of $^2J_{PH}$, therefore, are probably increasing from -3 to -1. Similar trends can be noted (Table II) for the Cr and W compounds. It is of course consistent with this rationale that $^2J_{PH}$ for the trisubstituted compounds could be positive having passed through zero. The negative values were selected because the resulting incremental changes in $^2J_{PH}$ are rendered more consistent.

If it can be assumed that $^2J_{PH}$ in these complexes is a reflection of the extent of phosphorus to metal σ donation, then the methyl coupling constants give an indication of the strength of the σ bond. As the metal atom is varied for a given substitution and ligand, the $^2J_{PH}$ value consistently becomes more positive from tungsten to chromium to molybdenum although the overall change in $^2J_{PH}$ is relatively small. This trend could very well indicate that the σ interaction either is very nearly the same or is perhaps becoming slightly weaker in the same order.

It should be pointed out that in an $X_nAA'X'_n$ spectrum, the separation of the two most intense peaks (the outer peaks of the apparent "triplet") is given by $|J_{AX} + J_{AX'}|$.[22] If $J_{AX'}$ is considered to be very small or almost negligible compared to J_{AX}, then $J_{AX} \cong |J_{AX} + J_{AX'}|$ and $^2J_{PH}$ may be taken directly from the spectrum. The relatively large number of bonds (4) through which AX′ coupling takes place makes this assumption plausible for these complexes. Thus, the values reported in Table II for both $^2J_{PH}$ and $^3J_{PH}$ have been taken directly from the spectra.

Stereochemistry.—The observance of both cis and trans and fac and mer isomers for the disubstituted and trisubstituted complexes of $CH_3P(OCH_3)_2$, respectively, with the apparent predominance of the cis and fac isomers, is consistent with the proposed π-acceptor strength and σ-donor properties of the ligand as well as with the stereochemistry reported previously for complexes with similar ligands.[1,15] It was expected that no stable trisubstituted compounds would be formed with $CH_3P(N(CH_3)_2)_2$ since similar observations had been reported for $P(N(CH_3)_2)_3$.[3] If these nitrogen-containing phosphorus ligands are actually strong σ donors,[3] the increased charge on the metal would be too large to accommodate three such ligands. The suggestion[3] that electronic rather than steric effects are the primary cause for the lack of trisubstituted complexes with $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$[3] gains support from the fact that bulky $P(C_6H_5)_3$[1] forms stable fac complexes. Moreover, the ligands $FP(N(CH_3)_2)_2$, $CH_3P(F)(N(CH_3)_2)$, and $C_6H_5P(F)(N(C_2H_5)_2)$ all form fac complexes with molybdenum.[25] The stability of such complexes may result from an increase in π-acceptor character for the ligands over that of $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$ because of the electronegative fluorine atom. This increase in π acidity and corresponding decrease in σ basicity reduces the increased negative charge on the metal that must arise when three CO groups are replaced by three phosphorus ligands.

It is interesting that $CH_3P(N(CH_3)_2)_2$ was not found to form a stable (isolable) monosubstituted complex with tungsten (see Experimental Section), whereas, chromium and molybdenum readily afforded the monosubstituted complexes. Similarly no monosubstituted complex of $P(N(CH_3)_2)_3$[3] has been reported. This was not expected since monosubstituted tungsten complexes with various amine ligands, which should also be strong σ donors, are well known.[26,27] In order to explain this observation, an important role might be invoked for the metal to phosphorus π bond in stabilizing these compounds. Whether or not the σ bond is indeed the stronger bond, it *alone* is probably not sufficient in this system to stabilize a metal–phosphorus bond. Thus the π contribution to the synergic bonding mechanism must be sufficiently large before the phosphorus ligand will enter into a stable bond. This phenomenon is supported by the observed reactions of tungsten. For the group VI hexacarbonyls, the order of metal–CO π bonding is W > Cr > Mo.[5,28] Replacing a single CO group in $W(CO)_6$ by either $CH_3P(N(CH_3)_2)_2$ or $P(N(CH_3)_2)_3$ places a poor π-accepting ligand trans to and in direct competition with the strong π acid CO. Stable monosubstituted amine complexes of tungsten do form, however, because the increased basicity of the ligands over that of $CH_3P(N(CH_3)_2)_2$ or $P(N(CH_3)_2)_3$ and the resultant stronger σ interaction must be sufficient to provide for stable bond formation. Consistent with this argument are the observations that the most

(25) R. Schmutzler, *J. Chem. Soc.*, 5630 (1965).
(26) R. J. Angelici and M. D. Malone, B. V. M., *Inorg. Chem.*, **6**, 1731 (1967).
(27) W. Strohmeier and K. Gerlack, *Chem. Ber.*, **94**, 398 (1961).
(28) R. B. King, *Inorg. Nucl. Chem. Lett.*, **5**, 905 (1969).

stable disubstituted species of $CH_3P(N(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$[3,12] are the trans isomers, while amine-substituted compounds are of the cis geometry.[14] In these phosphorus-containing ligands, the trans isomer allows for the increase in metal–phosphorus π bonding necessary to stabilize the compounds, especially for the tungsten complex, by taking the ligand out of direct competition with a CO for the metal π-electron density. On the other hand, the cis isomer allows for maximum metal–CO π bonding in the case of the poor π-accepting amine ligands.

We are currently studying the coordination chemistry of $(CH_3)_2PN(CH_3)_2$ to determine what effect having only one $-N(CH_3)_2$ group on a phosphorus will have on the donor–acceptor properties of phosphorus.

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Complexing Tendency of Trifluoromethylsulfonate Ion As Measured Using Chromium(III)

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By using cation-exchange resins, a species which answers to the properties expected of $CrCF_3SO_3^{2+}$ can be separated from a solution in which Cr(III) has reached equilibrium in 9.1 *M* CF_3SO_3H. The rate constant for aquation of the complex at 25° and 1 *M* acid is $(7.6 \pm 0.2) \times 10^{-4}$ sec^{-1}, which is about tenfold slower than that of $CrClO_4^{2+}$ but in turn about tenfold more rapid than that of $CrNO_3^{2+}$. On the basis of the weak nucleophilic power for $CF_3SO_3^-$ thus indicated and its resistance to reducing agents, it shows great promise as an indifferent anion. Higher complexes of Cr(III) with $CF_3SO_3^-$ form at high acid concentration. The complex formed in 11.1 *N* acid is shown to aquate much less rapidly than the 1:1 complex referred to above.

Introduction

Perchlorate ion is widely used in research on metal and other cations in solution because of its weak tendency to form complexes. It is well suited to this use except for a serious limitation arising from the fact that it is strongly oxidizing. Because reduction reactions are often slow, the ion is compatible with many strongly reducing species under a wide range of conditions. It does, however, oxidize Ti(III), V(II), and Eu(II) rapidly enough even at room temperature severely to restrict its use in the presence of these species. With metal ions of the second- and third-row transition elements, interference by ClO_4^- acting as an oxidizing agent becomes quite common. More serious are the consequences of the great oxidizing capacity of ClO_4^- in dealing with perchlorate salts. Particularly when organic matter is present, these materials have proven to be extremely hazardous.

The description[1] of trifluoromethylsulfonic acid as a strong acid suggests that the anion may be a sufficiently weak nucleophile to replace ClO_4^- for many purposes. It appears to be indefinitely stable with respect to hydrolysis, at least under ordinary conditions,[1,2] and has the advantage over ClO_4^- that it is much more difficult to reduce. The present work was undertaken to gauge the nucleophilic power of $CF_3SO_3^-$. To do this, we chose Cr(III) as a representative of cations having a tendency to associate with oxygen bases. It is convenient for study because it is colored and also because its complexes are substitution inert. Moreover, the ClO_4^- complex has been described[3] and its rate of aquation measured. Taking advantage of the general conclusion[4] that the rates of formation of complexes of a given metal ion are nearly the same for different ligands of the same class and charge type, the relative affinities for a metal ion can then be assessed simply from the relative rates of aquation.

Experimental Section

Trifluoromethylsulfonic acid was supplied by courtesy of the 3M Corp. The acid as supplied was found by titration to be 11.2 *N* (pure anhydrous acid is 11.305 *N*). Some samples of the acid contained significant amounts of SO_4^{2-}. On redistilling the acid and rejecting the final one-eighth of liquid, it was found to be free of SO_4^{2-} as tested using Ba^{2+}. Formation of $CrSO_4^+$ is itself a test for the presence of SO_4^{2-}. Whereas, without untreated acid, in some cases there were complications arising from the formation of this species, no interference was observed for the distilled acid. The concentration of SO_4^{2-} in the purified acid (10 *M*) appears to be less than 10^{-3} *M*.

Cr(III) solution was made up by reducing chromium trioxide with hydrogen peroxide in CF_3SO_3H. Ten grams of Baker and

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