directly from preformed ion pairs. However, the previous view[2] of a common five-coordinate intermediate $[(NH_3)_4(NH_2)Co]^{2+}$ accommodates the new and more discriminating data reported herein. It needs reemphasis that this intermediate is short-lived to the extent that it does not survive to completely equilibrate with the bulk solution. The small but consistent dependence on leaving group indicates Y^{m-} capture from an inherited ion atmosphere.[2,5-8] The mixed-anion competition experiments suggest that the presence of multicharged ions such as CO_3^{2-} or PO_4^{3-} do not exclude N_3^- from this atmosphere. This difficulty may be overcome if the five-coordinate intermediate is considered to be in free-ion and ion-pair forms where anion capture from the "ion pair" is highly efficient. Support for this view will be presented in a subsequent publication.

Acknowledgment. The authors are grateful to the ANU Microanalytical Service for elemental analyses.

Registry No. Co, 7440-48-4; $[(NH_3)_5CoNCS]^{2+}CO_3^{2-}$, 90342-60-2; $[(NH_3)_5CoNCS]^{2+}SO_4^{2-}$, 15739-27-2; $[(NH_3)_5CoNCS]^{2+}PO_4^{3-}$, 90342-61-3; $[(NH_3)_6Co]^{3+}CO_3^{2-}$, 90342-62-4; $[(NH_3)_6Co]^{3+}SO_4^{2-}$, 67119-18-0; $[(NH_3)_6Co]^{3+}PO_4^{3-}$, 55494-92-3; $[Co(NH_3)_5Cl]^{2+}$, 14970-14-0; $[Co(NH_3)_5I]^{2+}$, 15392-08-2; $[Co(NH_3)_5NO_3]^{2+}$, 15077-47-1; $[Co(NH_3)_5SO_4]^+$, 18661-07-9; $[Co(NH_3)_5OSMe_2]^{3+}$, 44915-85-7; ClO_4^-, 14797-73-0; N_3^-, 14343-69-2; OAc^-, 71-50-1; NCS^-, 302-04-5; NO_2^-, 14797-65-0; $NH_2SO_3^-$, 15853-39-1; NO_3^-, 14797-55-8; CO_3^{2-}, 3812-32-6; SO_4^{2-}, 14808-79-8; $S_2O_3^{2-}$, 14383-50-7; PO_4^{3-}, 14265-44-2.

Supplementary Material Available: Table II, giving spectrophotometric ion-pair constant data (3 pages). Ordering information is given on any current masthead page.

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Poly(tertiary phosphines and arsines). 21. Metal Carbonyl Complexes of Bis(dimethylphosphino)methane[1,2]

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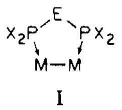
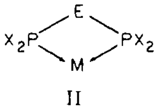
This paper reports a variety of metal carbonyl complexes of the highly basic small-bite bidentate bis(tertiary phosphine) $(CH_3)_2PCH_2P(CH_3)_2$ (abbreviated as dmpm). Thus, displacement of the coordinated norbornadiene in $C_7H_8M(CO)_4$ (M = Cr, Mo, W) with dmpm gives the corresponding pale yellow mononuclear chelates $(dmpm)M(CO)_4$. Similarly, displacement of the coordinated cycloheptatriene in $C_7H_8M(CO)_3$ (M = Cr, Mo, W) with dmpm gives the corresponding yellow binuclear complexes *fac*-$(dmpm)_3M_2(CO)_6$ shown by their NMR spectra to contain one bridging and two chelating dmpm ligands. The chromium complex *fac*-$(dmpm)_3Cr_2(CO)_6$ is unstable in solution, being converted ultimately to yellow *mer*-$(dmpm)_2Cr(CO)_3$ in which one of the dmpm ligands is monodentate with an uncomplexed $P(CH_3)_2$ unit. The phosphorus-31 NMR spectrum of *mer*-$(dmpm)_2Cr(CO)_3$ is compared with that of *fac*-$(dmpm)_2W(CO)_3$, one of the products obtained by the photolysis of $W(CO)_6$ with dmpm. The acetonitrile complexes *fac*-$(CH_3CN)_3M(CO)_3$ (M = Mo, W) react with dmpm in boiling acetonitrile to give *fac*-$(dmpm)_3M(CO)_3$ containing three monodentate dmpm ligands. Thermal reactions of $M_2(CO)_{10}$ (M = Mn, Re) with dmpm under various conditions give binuclear complexes of the type $(dmpm)_nM_2(CO)_{10-2n}$ (M = Mn, n = 1 and 2; M = Re, n = 2) containing five-membered bimetallic chelate rings. The orange to red binuclear iron carbonyl complexes $(dmpm)_nFe_2(CO)_{9-2n}$ are obtained from the reaction of dmpm with $Fe_2(CO)_9$ at room temperature (n = 1) and by the photolysis of dmpm with $Fe(CO)_5$ (n = 2). Reactions of dmpm with the cyclopentadienyl metal carbonyls $C_5H_5Mn(CO)_3$ and $[C_5H_5Fe(CO)_2]_2$ give yellow pyrophoric $(dmpm)Mn(CO)(C_5H_5)$ and green $(dmpm)Fe_2(CO)_2(C_5H_5)_2$, respectively. The nickel carbonyls $Ni(CO)_4$ and $[C_5H_5NiCO]_2$ react with dmpm to give white air-sensitive $(dmpm)Ni(CO)_2$ and yellow relatively air-stable $(dmpm)_3Ni_2(CO)_2$.

Introduction

Small-bite bidentate trivalent phosphorus ligands are of interest because of the possibility of stabilizing binuclear transition-metal complexes through the formation of five-membered chelate rings (I) as well as mononuclear transition-metal complexes through the formation of four-membered chelate rings (II). Previous work from this laboratory has involved the study of metal carbonyl complexes of the small-bite bidentate ligands $CH_3N(PX_2)_2$ (X = F[3], OCH_3[4]) in which the two donor phosphorus atoms are bridged by a single nitrogen atom. This paper reports a survey of the metal carbonyl coordination chemistry of the small-bite bis(tertiary phosphine) $(CH_3)_2PCH_2P(CH_3)_2$ (abbreviated as dmpm) in which each phosphorus atom is bonded only to carbon atoms. This ligand, which is the simplest possible bis(tertiary phosphine), is also of interest in being highly basic and sterically undemanding and frequently exhibits well-defined proton CH_2 and CH_3 NMR resonances in its metal carbonyl complexes. Also the volatilities of mononuclear metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ are generally sufficient for purification by vacuum sublimation and observation of their mass spectra.



I



II

Experimental Section

Microanalyses (Table I) were performed by Atlantic Microanalytical Laboratory, Atlanta, GA, and Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting and decomposition points (Table I) were determined in capillaries and are uncorrected. Infrared spectra (Table II) were taken in the ν(CO) region in the indicated solvents and recorded on a Perkin-Elmer Model 297 spectrometer. Proton NMR spectra (Table III) were recorded on a Varian EM-390 spectrometer operating at a nominal frequency of 90 MHz. Chemical

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[2] Presented in part at the 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983; see Abstracts, No. INOR 35.

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Table I. Metal Carbonyl Complexes of Bis(dimethylphosphino)methane

complex[a]	color	mp, °C	subl temp, °C, (*P*, mm)	anal. calcd (found) % C	anal. calcd (found) % H	mol wt[b]
$(dmpm)Cr(CO)_4$	pale yellow	154-155	120 (0.1)	36.0 (36.3)	4.7 (5.0)	300 300 (M^+)
$(dmpm)Mo(CO)_4$	pale yellow	140 dec	120 (0.01)	31.4 (31.1)	4.1 (4.2)	344 344 (M^+)
$(dmpm)W(CO)_4$	pale yellow	168-170	120 (0.01)	25.0 (24.8)	3.2 (3.3)	432 432 (M^+)
fac-$(dmpm)_3Cr_2(CO)_6$	yellow	123-125	not volatile	37.1 (37.9)	6.2 (6.3)	680 *c*
fac-$(dmpm)_3Mo_2(CO)_6$	yellow	163 dec	not volatile	32.8 (32.9)	5.5 (5.5)	768 753 ($C_2H_4Cl_2$)
fac-$(dmpm)_3W_2(CO)_6$	yellow	168-169	not volatile	26.7 (26.4)	4.5 (4.4)	944 *c*
mer-$(dmpm)_2Cr(CO)_3$	waxy yellow	74-76	80 (0.1)	38.2 (38.3)	6.9 (7.0)	408 408 (M^+)
fac-$(dmpm)_3Mo(CO)_3$	yellow	70-73	90 (0.1)	36.7 (35.6)	7.1 (6.6)	575 588 (benzene)
fac-$(dmpm)_3W(CO)_3$	yellow	86-87	110 dec (0.1)	32.0 (31.2)	6.2 (6.0)	664 676 (benzene)
$(dmpm)Mn_2(CO)_8$	yellow	>300	160 (0.005)	33.2 (33.5)	3.0 (3.1)	470 470 (M^+)
$(dmpm)_2Mn_2(CO)_6$	yellow	>300	160 (0.005)	34.9 (34.9)	5.1 (5.1)	550 550 (M^+)
$(dmpm)Mn(CO)Cp$	yellow	110	90 (0.005)	46.5 (44.4)	6.7 (6.8)	284 284 (M^+)
$(dmpm)_2Re_2(CO)_6$	pale yellow	>300		23.6 (23.5)	3.5 (3.5)	
$(dmpm)Fe_2(CO)_7$	yellow-orange	159-160 dec		32.5 (32.0)	3.2 (3.4)	444 460 ($C_2H_4Cl_2$)
$(dmpm)_2Fe_2(CO)_5$	red	143 dec	not volatile	34.4 (34.1)	5.3 (4.9)	524 506 ($C_2H_4Cl_2$)
$(dmpm)Fe_2(CO)_2Cp_2$	green	>300	not volatile	47.0 (47.0)	5.5 (5.6)	434 420 (toluene)
$(dmpm)Ni(CO)_2$	white	126-129 dec	80 dec (0.1)	33.5 (33.4)	5.6 (5.8)	251 256 (benzene)
$(dmpm)_3Ni_2(CO)_2$	yellow	161-163 dec	120 (0.1)	35.1 (35.4)	7.2 (7.4)	582 590 (benzene)

[a] dmpm = $(CH_3)_2PCH_2P(CH_3)_2$; Cp = η^5-cyclopentadienyl. [b] M^+ indicates molecular weights determined by observation of the molecular ion in the mass spectrometer; the remaining reported molecular weights were determined by vapor pressure osmometry in the indicated solvents. [c] The instability of this compound in solution prevented reliable molecular weight data from being obtained by osmometry. The volatility of this compound was insufficient for molecular weight determination by mass spectrometry.

shifts (δ) are reported downfield from internal tetramethylsilane. Phosphorus-31 NMR spectra (Table III) were recorded on a JEOL FX-90Q spectrometer operating in the pulsed Fourier transform mode at a nominal frequency of 36.27 MHz with proton noise decoupling. Chemical shifts (δ) are reported downfield from external 85% H_3PO_4.

The metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ appear to be significantly more air sensitive than analogous metal carbonyl complexes of most other tertiary phosphines. Therefore, all manipulations were performed under nitrogen by using Schlenkware[5] where appropriate. All solvents used in this work were redistilled under nitrogen over appropriate drying agents immediately before use. Ultraviolet irradiations were performed with a medium-pressure Englehard-Hanovia 450-W mercury-vapor lamp through a water-cooled Pyrex well.

The metal carbonyls $M(CO)_6$ (M = Cr, Mo, W), $RC_5H_4Mn(CO)_3$ (R = H, CH_3), $Re_2(CO)_{10}$, $Fe(CO)_5$, and $Ni(CO)_4$ were obtained from standard, commercial sources and were converted to *nor*-$C_7H_8M(CO)_4$ (M = Cr,[6] Mo[6], W[7]), $C_7H_8M(CO)_3$ (M = Cr,[6] Mo,[6] W[7]), $Mn_2(CO)_{10}$,[8] $Fe_2(CO)_9$,[9] $[C_5H_5Fe(CO)_2]_2$,[6] and $[C_5H_5NiCO]_2$[6] by using the standard cited procedures. The reported reaction[10] of $Cl_2AlCH_2AlCl_2$[11] with PCl_3 was used to prepare $Cl_2PCH_2PCl_2$, which was then methylated with commercial methyllithium or methylmagnesium bromide to give $(CH_3)_2PCH_2P(CH_3)_2$, bp 30 °C (6 mm) (lit.[12] bp 48 °C (10.5 mm)). The purities of all samples of $(CH_3)_2PCH_2P(CH_3)_2$ were checked by proton NMR spectroscopy and gas chromatography/mass spectrometry before use.

Preparation of $(dmpm)Cr(CO)_4$. A mixture of 1.0 g (3.9 mmol) of (norbornadiene)tetracarbonylchromium, 1.2 g (8.8 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 100 mL of degassed diethyl ether was boiled under reflux for 40 h. Removal of the diethyl ether under vacuum gave 0.93 g (79% yield) of pale yellow $(dmpm)Cr(CO)_4$. The analytical sample was purified by sublimation at 120 °C (0.1 mm).

Preparation of $(dmpm)Mo(CO)_4$. A solution of 1.5 g (5 mmol) of (norbornadiene)tetracarbonylmolybdenum in 50 mL of diethyl ether was treated with 1.36 g (10 mmol) of $(CH_3)_2PCH_2(CH_3)_2$. A pale yellow precipitate formed immediately. After the mixture was stirred overnight, this precipitate was filtered, washed with pentane, and dried under vacuum to give 1.7 g (99% yield) of $(dmpm)Mo(CO)_4$. The analytical sample was purified by sublimation at 120 °C (0.01 mm).

Preparation of $(dmpm)W(CO)_4$. A solution of 0.6 g (1.5 mmol) of (norbornadiene)tetracarbonyltungsten in 50 mL of hexane was treated with 0.5 g (3.7 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$. A pale yellow precipitate formed after stirring at room temperature for approximately 1 h. This precipitate was filtered, washed with pentane, and dried under vacuum to give 0.5 g (77% yield) of $(dmpm)W(CO)_4$.

Preparation of *fac*-$(dmpm)_3Cr_2(CO)_6$. A mixture of 2.0 g (8.8 mmol) of (cycloheptatriene)tricarbonylchromium, 2.4 g (18 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 200 mL of hexane was stirred for 3 h at room temperature. The resulting yellow precipitate was filtered,

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Table II. Infrared ν(CO) Frequencies of Metal Carbonyl Complexes of Bis(dimethylphosphino)methane and Related Compounds

complex	solvent	ν(CO), cm^{-1}
(dmpm)Cr(CO)$_4$	CH$_2$Cl$_2$	2000 m, 1905 m, 1875 s
(dmpm)Mo(CO)$_4$	CH$_2$Cl$_2$	2000 m, 1890 s, 1870 m
(dmpm)W(CO)$_4$	CH$_2$Cl$_2$	2010 m, 1887 s, 1865 m
fac-(dmpm)$_3$Cr$_2$(CO)$_6$	CH$_2$Cl$_2$	1920 m, 1825 vs
fac-(dmpm)$_3$Mo$_2$(CO)$_6$	CH$_2$Cl$_2$	1920 s, 1820 vs
fac-(dmpm)$_3$W$_2$(CO)$_6$	CH$_2$Cl$_2$	1930 s, 1830 vs
fac-(dmpm)$_3$Mo(CO)$_3$	CH$_2$Cl$_2$	1929 s, 1826 s
fac-(dmpm)$_3$W(CO)$_3$	CH$_2$Cl$_2$	1924 s, 1823 s
fac-(dmpm)$_2$W(CO)$_3$	Et$_2$O	1935 s, 1840 vs
mer-(dmpm)$_2$Cr(CO)$_3$	hexane	1935 m, 1890 s, 1835 vs
mer-[MeN(PF$_2$)$_2$]$_2$Cr(CO)$_3$^{a}	hexane	2031 m, 1972 s, 1948 vs
(dmpm)Mn$_2$(CO)$_8$	CH$_2$Cl$_2$	2054 m, 1984 s, 1961 s, 1937 m, 1912 m
(dppm)Mn$_2$(CO)$_8$^{b}	hexane	2060 s, 2000 m, 1997 s, 1952 m, 1925 s
(dmpm)$_2$Mn$_2$(CO)$_6$	CH$_2$Cl$_2$	1980 w, 1906 s, 1894 s, 1850 m
(dppm)$_2$Mn$_2$(CO)$_6$^{b}	CH$_2$Cl$_2$	1994 w, 1923 sh, 1912 s, 1866 m
(dmpm)$_2$Re$_2$(CO)$_6$	CH$_2$Cl$_2$	1939 m, 1906 s, 1851 m
(dppe)$_2$Re$_2$(CO)$_6$^{c}	*c*-C$_6$H$_{12}$	1950 s, 1930 s, 1870 s
(dmpm)Fe$_2$(CO)$_7$	CH$_2$Cl$_2$	2044 s, 1988 s, 1972 s, 1937 s, 1745 m^{d}
(dppm)Fe$_2$(CO)$_7$^{e}	MeC$_6$H$_{11}$	2050 s, 2005 s, 1992 s, 1965 s, 1950 s, 1935 m, 1770 m^{d}
(dmpm)$_2$Fe$_2$(CO)$_5$	CH$_2$Cl$_2$	1941 m, 1890 s, 1865 s, 1840 m, 1670 w^{d}
{MeN[P(OMe)$_2$]$_2$}$_2$Fe$_2$(CO)$_5$^{f}	KBr	1990 m, 1939 s, 1908 s, 1890 s, 1711 m^{d}
(dmpm)Mn(CO)Cp	CH$_2$Cl$_2$	1808 s
(dppm)Mn(CO)Cp^{g}	CS$_2$	1854 s
(dmpm)Fe$_2$(CO)$_2$Cp$_2$^{h}	CH$_2$Cl$_2$	1666 s^{d}
(dppm)Fe$_2$(CO)$_2$Cp$_2$^{h}	*c*-C$_6$H$_{12}$	1590 s^{d}
(dmpm)Ni(CO)$_2$	CH$_2$Cl$_2$	1991 s, 1927 s
(dmpe)Ni(CO)$_2$^{i}	C$_2$H$_4$Cl$_2$	1994 s, 1929 s
(dmpm)$_3$Ni$_2$(CO)$_2$	hexane	1919 s, 1908 s
[MeN(PF$_2$)$_2$]$_3$Ni$_2$(CO)$_2$^{j}	hexane	2070 s, 2055 s

[a] Data from: King, R. B.; Lee, T. W. *Inorg. Chem.* **1982,** *21,* 319. [b] Data from: Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975,** *28,* 1673. [c] Data from: Freni, M.; Giusto, D.; Romiti, P. *J. Inorg. Nucl. Chem.* **1967,** *29,* 761. dppe = (C$_6$H$_5$)$_2$PCH$_2$CH$_2$P(C$_6$H$_5$)$_2$. [d] Bridging ν(CO). [e] Data from: Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974,** *96,* 4422. [f] Data from: Brown, G. M.; Finholt, J. E.; King, R. B.; Bibber, J. W.; Kim, J. H. *Inorg. Chem.* **1982,** *21,* 3790. [g] Data from: Hayter, R. G.; Williams, L. F. *J. Inorg. Nucl. Chem.* **1964,** *26,* 1977. [h] Data from: Haines, R. J.; du Preez, A. L. *J. Organomet. Chem.* **1970,** *21,* 181. [i] Data from: Booth, G.; Chatt, J. *J. Chem. Soc.* **1965,** 3238. dmpe = (CH$_3$)$_2$PCH$_2$CH$_2$P(CH$_3$)$_2$. [j] Data from: King, R. B.; Gimeno, J. *Inorg. Chem.* **1978,** *17,* 2390.

Table III. NMR Spectra of Metal Carbonyl Complexes of Bis(dimethylphosphino)methane

	proton NMR spectrum, δ((CH$_3$)$_4$Si)^{a}				phosphorus-31 NMR spectrum, δ(H$_3$PO$_4$)^{a}	
complex	solvent	CH$_2$	CH$_3$	C$_5$H$_5$	solvent	resonances
dmpm	CDCl$_3$	1.40 t (0.7)	1.08 t (15)		neat	−56.5
(dmpm)Cr(CO)$_4$	CDCl$_3$	3.12 t (10)	1.57 t (4)		CH$_2$Cl$_2$	+4.0
(dmpm)Mo(CO)$_4$	CDCl$_3$	3.20 t (8)	1.60 d (7)		CH$_2$Cl$_2$	−28.0
(dmpm)W(CO)$_4$	CDCl$_3$	3.73 t (9)	1.83 d (8)		THF	−57.4
(dmpm)Mn(CO)Cp	CDCl$_3$	3.4 br	1.5 br	4.12 s	THF	+34.0 br
fac-(dmpm)$_3$Mo(CO)$_3$	C$_6$D$_6$	~1.73 br	1.37 d (5), 0.87 d (4)		C$_6$H$_6$	−8.7 qn (10), −61.5 qn (10)
fac-(dmpm)$_3$W(CO)$_3$	C$_6$D$_6$	1.89 t (3)	1.47 d (5), 0.83 d (4)		C$_6$H$_6$	−29.6 qn (10), −61.3 qn (10)
fac-(dmpm)$_3$Mo$_2$(CO)$_6$	CH$_2$Cl$_2$	3.1 m, 2.52 t (5)	1.77 d (5), 1.60 d (7), 1.47 d (6)		CH$_2$Cl$_2$	+2.0 br, −27.7 d (27)
fac-(dmpm)$_3$W$_2$(CO)$_6$	CDCl$_3$	3.45 t (10), 2.7 m	1.83 d (6), 1.67 d (8), 1.50 d (6)		THF	−19.0 br, −55.3 d (22)
mer-(dmpm)$_2$Cr(CO)$_3$	CDCl$_3$	3.20 t (9), 1.78 td (6, 3)	1.53 t (6), 1.43 t (6), 1.10 t (3)		Et$_2$O	+35.4 dt (54, 28), +22.6 dd (43, 28), +2.5 d dd (43, 28, 10), −59.8 dd (54, 10)
fac-(dmpm)$_2$W(CO)$_3$	CH$_2$Cl$_2$	3.60 t (10), 2.04 dd (6, 3)	1.70 d (8), 1.63 d (6), 1.20 d (3)		CH$_2$Cl$_2$	−24.8 dt (39, 27), −55.9 d (27), −58.2 d (39)
(dmpm)Mn$_2$(CO)$_8$	CDCl$_3$	2.67 t (10)	1.63 t (3)		CH$_2$Cl$_2$	+32.2 br
(dmpm)$_2$Mn$_2$(CO)$_6$	CDCl$_3$	2.37 br	1.53		THF	+31.9
(dmpm)$_2$Re$_2$(CO)$_6$	CDCl$_3$	2.87 dt (9, 5)	1.71		CDCl$_3$	−37.0
(dmpm)Fe$_2$(CO)$_7$	CH$_2$Cl$_2$	2.03 t (11)	1.62 t (4)		CH$_2$Cl$_2$	+42.8
(dmpm)$_2$Fe$_2$(CO)$_5$	CDCl$_3$	2.0 m	1.58		THF	+47.9
(dmpm)Fe$_2$(CO)$_2$Cp$_2$	CDCl$_3$	1.77	1.27	4.45 s	THF	+71.2
(dmpm)$_3$Ni$_2$(CO)$_2$	C$_6$D$_6$	1.33 br	1.15		C$_6$H$_6$	+12.4
(dmpm)Ni(CO)$_2$	C$_6$H$_6$	1.40 t (7)	1.1		C$_6$H$_6$	−15.1

[a] d = doublet, t = triplet, m = multiplet, br = broad, dd = double doublet, td = triplet of doublets, qn = nonbinomial quintet, with all peaks of comparable relative intensities (within a factor of 2); coupling constants in Hz given in parentheses.

washed with pentane, and dried under vacuum to give 1.89 g (63% yield) of *fac*-(dmpm)$_3$Cr$_2$(CO)$_6$. The analytical sample was purified by dissolving in a minimum of dichloromethane and precipitating immediately with heptane at −40 °C. The complex *fac*-(dmpm)$_3$Cr$_2$(CO)$_6$ is insoluble in hexane, diethyl ether, and benzene but dissolves in dichloromethane to give air-sensitive solutions that decompose at room temperature even in the absence of oxygen to give *mer*-(dmpm)$_2$Cr(CO)$_3$ as the ultimate product. Because of the instability of *fac*-(dmpm)$_3$Cr$_2$(CO)$_6$ in solution, reliable NMR and osmometric molecular weight data could not be obtained.

Preparation of *mer*-(dmpm)$_2$Cr(CO)$_3$. A mixture of 3.0 g (13 mmol) of (cycloheptatriene)tricarbonylchromium, 5.4 g (40 mmol) of (CH$_3$)$_2$PCH$_2$P(CH$_3$)$_2$, and 125 mL of deoxygenated hexane was boiled under reflux for 20 h. During this time the original red color of C$_7$H$_8$Cr(CO)$_3$ turned yellow. After completion of the reaction period, the hexane was removed under a vacuum. The resulting yellow liquid was taken up in 30 mL of a 1:1 mixture of pentane/diethyl ether. The resulting solution was cooled overnight in a −78 °C bath. The yellow highly air-sensitive precipitate was filtered, washed with cold pentane, and dried to give 1.7 g (28% yield) of *mer*-$(dmpm)_2Cr(CO)_3$. The analytical sample was purified by sublimation at 80 °C (0.1 mm) to give a waxy yellow solid, but this sublimation was relatively inefficient (only 30% recovery of the crude material as pure product).

Preparation of *fac*-$(dmpm)_3Mo_2(CO)_6$. A solution of 3.54 g (13 mmol) of (cycloheptatriene)tricarbonylmolybdenum in 250 mL of hexane was treated with 4.8 g (35 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$. A yellow precipitate appeared immediately. This precipitate was filtered, washed with hexane, and dried under vacuum (50 °C (0.1 mm)) to give 4.4 g (88% yield) of *fac*-$(dmpm)_3Mo_2(CO)_6$. The analytical sample was purified by recrystallization from a mixture of dichloromethane/hexane.

Preparation of *fac*-$(dmpm)_3W_2(CO)_6$. A solution of 0.8 g (2.2 mmol) of (cycloheptatriene)tricarbonyltungsten in 100 mL of diethyl ether was treated with 0.5 g (3.7 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$ at room temperature. The original red color of $C_7H_8W(CO)_3$ became yellow in about 5 min, and a pale yellow solid separated. This solid was filtered, washed with pentane, and dried under vacuum to give 0.6 g (58% yield) of *fac*-$(dmpm)_3W_2(CO)_6$. The analytical sample was obtained by recrystallization from a mixture of tetrahydrofuran/hexane followed by chromatography on a Florisil column using a mixture of diethyl ether/dichloromethane as the eluent.

Reaction of *fac*-$(CH_3CN)_3Mo(CO)_3$ with $(CH_3)_2PCH_2P(CH_3)_2$. A mixture of 1.32 g (5 mmol) of $Mo(CO)_6$ and 75 mL of acetonitrile was boiled under reflux for 24 h to generate *fac*-$(CH_3CN)_3Mo(CO)_3$.[13] This solution was treated with 2.3 g (16 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$. The reaction mixture was then boiled under reflux for an additional 6 h. Acetonitrile was then removed under vacuum. The resulting yellow viscous liquid was chromatographed on an alumina column using a 3:1 mixture of pentane/tetrahydrofuran as the eluent. The resulting yellow solution was concentrated under vacuum and stored at −20 °C for 2 days. The resulting solid was filtered, washed with cold pentane, and dried under vacuum (50 °C (0.1 mm)) to give 1.97 g (67% yield) of pale yellow air-sensitive *fac*-$(dmpm)_3Mo(CO)_3$. The analytical sample was obtained by recrystallization from a mixture of tetrahydrofuran/pentane. This complex sublimes at 90 °C (0.1 mm) with decomposition and release of $(CH_3)_2PCH_2P(CH_3)_2$.

Reaction of *fac*-$(CH_3CN)_3W(CO)_3$ with $(CH_3)_2PCH_2P(CH_3)_2$. A mixture of 2.0 g (5.7 mmol) of $W(CO)_6$ and 75 mL of acetonitrile was boiled under reflux for 4 days to generate *fac*-$(CH_3CN)_3W(CO)_3$.[13] This solution was treated with 2.5 g (18 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$. The reaction mixture was then boiled under reflux for an additional 6 h. Chromatography by a procedure analogous to that described above for the isolation of *fac*-$(dmpm)_3Mo(CO)_3$ gave 3.2 g (83% yield) of yellow air-sensitive *fac*-$(dmpm)_3W(CO)_3$. The complex sublimes at 110 °C (0.1 mm) with decomposition and release of $(CH_3)_2PCH_2P(CH_3)_2$.

Reaction of $Cr(CO)_6$ with $(CH_3)_2PCH_2P(CH_3)_2$. A mixture of 2.2 g (10 mmol) of $Cr(CO)_6$, 1.4 g (10 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 90 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 12 h. Removal of the tetrahydrofuran from the filtered reaction mixture under vacuum gave a yellow-brown solid. Vacuum sublimation of this solid at 125 °C (0.025 mm) gave a yellow sublimate shown by its infrared spectrum in the $\nu(CO)$ region (CH_2Cl_2 solution) to contain a mixture of $(dmpm)Cr(CO)_4$ (2000 m, 1911 m, 1877 s cm^{-1}) and an $LCr(CO)_5$ derivative (2060 w (A_1), 1940 s (E) cm^{-1}).

Pure $(dmpm)Cr(CO)_4$ could be separated from this mixture by chromatography. Thus, a concentrated dichloromethane solution of this yellow residue was chromatographed on a 50 × 2 cm Florisil column. The first yellow band was eluted with diethyl ether. Evaporation of the diethyl ether under vacuum followed by sublimation of the residue at 120 °C (0.1 mm), washing the sublimate twice with cold pentane, and drying under vacuum gave 1.5 g (50% yield) of pure $(dmpm)Cr(CO)_4$ as indicated by melting point, C and H analyses, infrared spectrum, proton and phosphorus-31 NMR spectra, and mass spectrum.

Reaction of $Mo(CO)_6$ with $(CH_3)_2PCH_2P(CH_3)_2$. A mixture of 1.0 g (3.8 mmol) of $Mo(CO)_6$, 1.0 g (7.6 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 10 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 24 h in a 2 × 10 cm quartz tube. Removal of tetrahydrofuran at 25 °C (25 mm) followed by sublimation of the yellow residue at 115–120 °C (0.1 mm) gave 0.78 g (60% yield) of $(dmpm)Mo(CO)_4$, identified by comparison of its infrared and NMR spectra with those of authentic material obtained from (norbornadiene)tetracarbonylmolybdenum and $(CH_3)_2PCH_2P(CH_3)_2$ as described above.

Reaction of $W(CO)_6$ with $(CH_3)_2PCH_2P(CH_3)_2$. A mixture of 3.52 g (10 mmol) of $W(CO)_6$, 2.8 g (21 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 200 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 36 h. Tetrahydrofuran was removed under vacuum from the resulting reaction mixture. The resulting viscous yellow-brown liquid was taken up in 30 mL of a 1:1 mixture of pentane/diethyl ether. Cooling the resulting solution to −78 °C precipitated 3.5 g of a yellow solid that was shown by its elemental analyses (C, H), mass spectrum, infrared $\nu(CO)$ spectrum, and proton and phosphorus-31 NMR spectra to be a 1:1 mixture of $(dmpm)W(CO)_4$ and *fac*-$(dmpm)_2W(CO)_3$. Attempts to separate the components of this mixture by chromatography on Florisil using diethyl ether as a solvent and/or sublimation at 130 °C (0.1 mm) were unsuccessful as shown by the analytical data. Anal. Calcd for $C_{22}H_{42}O_7P_6W_2$ (i.e., $(dmpm)W(CO)_4$/*fac*-$(dmpm)_2W(CO)_3$)= C, 27.2; H, 4.3. Found (on an original sample crystallized from pentane): C, 25.6; H, 4.3. Found (after chromatography): C, 26.1; H, 4.5. Found (after sublimation): C, 25.8; H, 4.3. Found (after both chromatography and sublimation): C, 27.0; H, 4.8.

The infrared and NMR spectra of *fac*-$(dmpm)_2W(CO)_3$ listed in Tables II and III, respectively, are obtained from the spectra of this 1:1 $(dmpm)W(CO)_4$/*fac*-$(dmpm)_2W(CO)_3$ mixture after subtracting the spectra obtained separately on a pure sample of $(dmpm)W(CO)_4$ prepared from *nor*-$C_7H_8W(CO)_4$ and dmpm as described above.

Preparation of $(dmpm)Mn_2(CO)_8$. A mixture of 2.0 g (5.1 mmol) of $Mn_2(CO)_{10}$, 0.7 g (5.1 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 50 mL of toluene was boiled for 16 h under reflux. The reaction mixture was filtered through Celite. Removal of toluene from the filtrate under vacuum followed by addition of pentane and cooling gave 2.1 g (88% yield) of yellow solid $(dmpm)Mn_2(CO)_8$. The analytical sample was obtained by chromatographing a concentrated dichloromethane solution of this crude product on a Florisil column, eluting the first yellow band with a 1:1 mixture of diethyl ether/dichloromethane, evaporating the eluate under vacuum, and drying the yellow solid residue at 50 °C (0.1 mm).

Preparation of $(dmpm)_2Mn_2(CO)_6$. A mixture of 0.8 g (2.1 mmol) of $Mn_2(CO)_{10}$, 0.55 g (4.0 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 30 mL of xylene was boiled for 16 h under reflux. Xylene was removed under vacuum. The yellow residue was extracted under nitrogen with boiling diethyl ether in a Soxhlet apparatus. Removal of the diethyl ether from the extract under vacuum gave 0.55 g (48% yield) of yellow $(dmpm)_2Mn_2(CO)_6$. The analytical sample was purified by chromatography followed by sublimation at 160 °C (0.005 mm). This compound is very air sensitive in solution.

Preparation of $(dmpm)_2Re_2(CO)_6$. A mixture of 1.0 g (1.5 mmol) of $Re_2(CO)_{10}$, 0.52 g (3.8 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 30 mL of xylene was boiled under reflux for 24 h. Removal of xylene under vacuum followed by addition of heptane and cooling overnight at −20 °C gave 0.93 g (76% yield) of pale yellow $(dmpm)_2Re_2(CO)_6$. The analytical sample was obtained by chromatography of a concentrated dichloromethane solution on Florisil, eluting the yellow band with 1:1 diethyl ether/dichloromethane, evaporating the eluate under vacuum, and crystallizing the residue from a mixture of heptane/dichloromethane.

No evidence for the formation of $(dmpm)Re_2(CO)_8$ from the reaction of $Re_2(CO)_{10}$ with dmpm was obtained even when a corresponding $Re_2(CO)_{10}$/dmpm ratio was used.

Preparation of $(dmpm)Mn(CO)(C_5H_5)$. A mixture of 2.03 g (10 mmol) of $C_5H_5Mn(CO)_3$, 2.8 g (21 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 300 mL of hexane was exposed to ultraviolet irradiation for 3 h. Hexane was then removed under vacuum. Crystallization of the residue from a mixture of tetrahydrofuran/pentane at −78 °C gave 1.5 g (53% yield) of yellow pyrophoric $(dmpm)Mn(CO)(C_5H_5)$. The analytical sample was obtained by sublimation at 90 °C (0.005 mm). Attempted chromatography of $(dmpm)Mn(CO)(C_5H_5)$ on Florisil led to complete decomposition.

Preparation of $(dmpm)Fe_2(CO)_7$. A mixture of 10 g (27.4 mmol) of $Fe_2(CO)_9$, 3.7 g (27.2 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 250 mL of diethyl ether was stirred for 16 h. The yellow-orange $Fe_2(CO)_9$

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[13] Tate, D. P.; Augl, J. M.; Knipple, W. R. *Inorg. Chem.* **1962**, *1*, 433.

dissolved, and a new orange solid separated. Filtration of this solid followed by washing with pentane and diethyl ether gave 3.5 g (29% yield) of $(dmpm)Fe_2(CO)_7$. A concentrated tetrahydrofuran solution of this crude product was chromatographed on a Florisil column. The yellow band was eluted with 2:1 diethyl ether/tetrahydrofuran. The eluate was concentrated under vacuum and cooled to −78 °C. Supernatant liquid was removed from the yellow-orange precipitate by centrifugation. The solid was washed several times with pentane and dried at 50 °C (0.1 mm) to give pure $(dmpm)Fe_2(CO)_7$ as a yellow-orange air-sensitive solid.

Preparation of $(dmpm)_2Fe_2(CO)_5$. A solution of 3.92 g (20 mmol) of $Fe(CO)_5$ and 2.72 g (20 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$ in 300 mL of deoxygenated tetrahydrofuran was exposed to ultraviolet irradiation for 10 h. The red solid that precipitated was filtered and washed with pentane. This solid was dissolved in tetrahydrofuran. The resulting tetrahydrofuran solution was filtered through Celite. Concentration of the filtrate under vacuum followed by addition of heptane and cooling to −78 °C resulted in the slow precipitation of a red solid. This solid was isolated by filtration, washed with pentane, and dried at 50 °C (0.1 mm) to give 2.1 g (40% yield) of $(dmpm)_2Fe_2(CO)_5$. The crude product was placed in a Soxhlet extraction apparatus. Soxhlet extraction with boiling diethyl ether under nitrogen gave a very air-sensitive red solution from which pure $(dmpm)_2Fe_2(CO)_5$ separated upon concentration under vacuum. The pure product was washed with pentane and dried at 50 °C (0.1 mm) for 6 h.

This product is very air sensitive, particularly in solution. Solutions in dichloromethane are so unstable that dichloromethane must be avoided as a solvent during the isolation of pure $(dmpm)_2Fe_2(CO)_5$.

Preparation of $(dmpm)Fe_2(CO)_2(C_5H_5)_2$. A mixture of 3.54 g (10 mmol) of $[C_5H_5Fe(CO)_2]_2$, 1.36 g (10 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 100 mL of toluene was boiled under reflux for 16 h. Cooling the resulting mixture to −78 °C precipitated 3.1 g (71% yield) of solid $(dmpm)Fe_2(CO)_2(C_5H_5)_2$. The analytical sample was purified by recrystallization from a mixture of dichloromethane/methylcyclohexane.

Reaction of $Ni(CO)_4$ with $(CH_3)_2PCH_2P(CH_3)_2$. A mixture of 4.0 g (23 mmol) of $Ni(CO)_4$, 3.5 g (26 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 50 mL of hexane was stirred overnight at room temperature. The resulting white precipitate was filtered, washed with pentane, and dried under vacuum to give 5.4 g (92% yield) of analytically pure $(dmpm)Ni(CO)_2$. Sublimation of this compound at 75 °C (0.1 mm) gave a white sublimate shown by its infrared and phosphorus-31 NMR spectra to be a mixture of unchanged $(dmpm)Ni(CO)_2$ and a second product exhibiting a strong bridging $\nu(CO)$ frequency at 1712 cm^{-1} and a phosphorus-31 NMR resonance at δ − 49.3 in CH_2Cl_2 solution. Because of its air sensitivity this second product has not been separated from $(dmpm)Ni(CO)_2$ and therefore has not been identified.

Reaction of $[C_5H_5NiCO]_2$ with $(CH_3)_2PCH_2P(CH_3)_2$. A mixture of 1.0 g (3.3 mmol) of $[C_5H_5NiCO]_2$, 1.8 g (13.2 mmol) of $(CH_3)_2PCH_2P(CH_3)_2$, and 50 mL of tetrahydrofuran was boiled under reflux for 24 h. The filtered reaction mixture was concentrated at 25 °C (25 mm) and then chromatographed on alumina. The first yellow band was eluted with a 2:1 mixture of hexane/tetrahydrofuran. Concentration of the eluate and storage at −20 °C for 4 days gave large dull yellow crystals. These were filtered, washed with pentane, and dried at 26 °C (0.1 mm) for 24 h to give 0.4 g (21% yield) of fairly air-stable $(dmpm)_3Ni_2(CO)_2$.

Mass Spectra. The mass spectra listed below were obtained on the Finnegan 4023 combined gas chromatograph/mass spectrometer located in the University of Georgia chemistry department. Relative intensities of the ions are given in parentheses after the ion formula. For the metal complexes only the major metal-containing ions are reported.

A. $Cl_2PCH_2PCl_2$: $CH_2P_2Cl_4^+$ (27), $CH_2P_2Cl_3^+$ (20), PCl_3^+ (11), $CH_2PCl_2^+$ (100), PCl_2^+ (70), CH_2PCl^+ (45), $CHPCl^+$ (31), CHP_2^+ (27), CP_2^+ (20), PCl^+ (40), CH_2P^+ (76).

B. $(CH_3)_2PCH_2P(CH_3)_2$: $(CH_3)_2PCH_2P(CH_3)_2^+$ (63), $(CH_3)_2PCH_2PCH_3^+$ (27), $(CH_3)_3P^+$ (50), $(CH_3)_2PCH_2^+$ (100), $(CH_3)_2P^+$ (27), $C_2H_4P^+$ (22), $C_2H_2P^+$ (22), CH_4P^+ (36), CH_2P^+ (37).

C. $(dmpm)Cr(CO)_4$: $(CH_3)_2PCH_2P(CH_3)_2Cr(CO)_n^+$ [n = 4 (55), 3 (16), 2 (8), 1 (38), 0 (100)], $C_4H_{11}P_2Cr^+$ (15), $C_4H_{10}P_2Cr^+$ (24), $(CH_3)_3PCr^+$ (70), $(CH_3)_2PCH_2Cr^+$ (33), $(CH_3)_2PCr^+$ (51), $C_2H_5PCr^+$ (41), Cr^+ (98).

D. $(dmpm)Mo(CO)_4$: $(CH_3)_2PCH_2P(CH_3)_2Mo(CO)_n^+$ [n = 4 (47), 3 (20), 2 (39), 1 (100), 0 (81)].

E. $(dmpm)W(CO)_4$: $(CH_3)_2PCH_2P(CH_3)_2W(CO)_n^+$ [n = 4 (100), 3 (21), 2 (18), 1 (33), 0 (42)], $C_5H_{12}P_2W^+$ (33).

F. *mer*-$(dmpm)_2Cr(CO)_3$: $[(CH_3)_2PCH_2P(CH_3)_2]_2Cr(CO)_n^+$ [n = 3 (7), 2 (7), 0 (35)], $(CH_3)_2PCH_2P(CH_3)_2CrCH_2P(CH_3)_2^+$ (20), $(CH_3)_2PCH_2P(CH_3)_2CrCH_3^+$ (11), $(CH_3)_2PCH_2P(CH_3)_2Cr^+$ (100), $(CH_3)_3PCr^+$ (42).

G. *fac*-$(dmpm)_3Mo(CO)_3$: $[(CH_3)_2PCH_2P(CH_3)_2]_2Mo(CO)_n^+$ [n = 3 (1), 2 (6), 1 (4), 0 (1)].

H. *fac*-$(dmpm)_3W(CO)_3$: $[(CH_3)_2PCH_2P(CH_3)_2]_2W(CO)_n^+$ [n = 3 (1), 2 (8), 1 (1), 0 (1)].

I. $(dmpm)W(CO)_4$/*fac*-$(dmpm)_2W(CO)_3$: $[(CH_3)_2PCH_2P(CH_3)_2]_2W(CO)_n^+$ [n = 3 (1), 2 (42), 1 (10), 0 (8)], $(CH_3)_2PCH_2P(CH_3)_2W(CO)_n^+$ [n = 4 (100), 3 (50), 2 (50), 1 (89), 0 (63)], $C_5H_{12}P_2W^+$ (53).

J. $(dmpm)Mn(CO)(C_5H_5)$: $(CH_3)_2PCH_2P(CH_3)_2Mn(CO)(C_5H_5)^+$ (32), $(CH_3)_2PCH_2P(CH_3)_2MnC_5H_5^+$ (100), $C_5H_5MnCH_2P(CH_3)_2^+$ (45), $C_5H_5MnP(CH_3)_2^+$ (23), $C_5H_5MnCH_2PCH_3^+$ (26), $C_5H_5Mn^+$ (83), Mn^+ (77).

K. $(dmpm)Mn_2(CO)_8$: $(CH_3)_2PCH_2P(CH_3)_2Mn_2(CO)_n^+$ [n = 8 (1), 5 (2), 4 (24), 3 (23), 2 (3), 1 (15), 0 (32)], $(CH_3)_2PCH_2P(CH_3)_2Mn(CO)_n^+$ [n = 3 (12), 2 (7), 1 (19), 0 (100)], $(CH_3)_3PMn^+$ (57).

L. $(dmpm)_2Mn_2(CO)_6$: $[(CH_3)_2PCH_2P(CH_3)_2]_2Mn_2(CO)_n^+$ [n = 6 (6), 3 (42), 2 (12), 0 (78)], $(CH_3)_2PCH_2P(CH_3)_2MnCH_3^+$ (88), $(CH_3)_2PCH_2P(CH_3)_2Mn^+$ (82), $(CH_3)_3PMn^+$ (100).

Results and Discussion

A. General Comments. The small size and high basicity of $(CH_3)_2PCH_2P(CH_3)_2$ lead to metal carbonyl complexes having a relatively electron-rich and sterically unencumbered central metal atom compared with analogous metal carbonyl complexes of other trivalent phosphorus ligands such as even $(C_6H_5)_2PCH_2P(C_6H_5)_2$.[14] This is most obviously reflected in an increased air sensitivity of metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$. Thus, rigorous exclusion of air using Schlenk tube techniques is necessary for handling most of the metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ even though they have the favored 18-electron rare-gas electronic configuration and several strongly π-accepting carbonyl groups to remove electron density from the metal atoms. Furthermore, the complex $(dmpm)Mn(CO)(C_5H_5)$, which has only one carbonyl group, was found to be pyrophoric in contrast to other $C_5H_5Mn(CO)L_2$ derivatives.[15] Reactions of $(CH_3)_2PCH_2P(CH_3)_2$ with $Co_2(CO)_8$ and with $C_5H_5Co(CO)_2$ gave products that have proven to be too air sensitive for definitive identification and full characterization; therefore, they are not reported in this paper.

The high basicity of $(CH_3)_2PCH_2P(CH_3)_2$ relative to $(C_6H_5)_2PCH_2P(C_6H_5)_2$ is also reflected in the infrared $\nu(CO)$ frequencies of analogous complexes of these two ligands (Table II). In all cases for which comparisons can be made, metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ have $\nu(CO)$ frequencies that are lower than the corresponding $\nu(CO)$ frequencies of analogous metal carbonyl complexes of $(C_6H_5)_2PCH_2P(C_6H_5)_2$, as illustrated by complexes of the types $(diphos)Mn_2(CO)_8$, $(diphos)_2Mn_2(CO)_6$, $(diphos)Fe_2(CO)_7$, $(diphos)Mn(CO)(C_5H_5)$, and $(diphos)Fe_2(CO)_2(C_5H_5)_2$ (diphos = dmpm, dppm) in Table II. This lowering of $\nu(CO)$ frequencies in metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ compared with analogous metal carbonyl complexes of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ relates to increased $d\pi$–$p\pi^*$ backbonding to carbonyl groups in the $(CH_3)_2PCH_2P(CH_3)_2$ metal carbonyl complexes because of a higher electron density on the metal atom arising from the higher net basicity of $(CH_3)_2PCH_2P(CH_3)_2$ relative to $(C_6H_5)_2PCH_2P(C_6H_5)_2$.

In general, the metal carbonyl complexes of $(CH_3)_2PCH_2P(CH_3)_2$ appear to be more soluble in organic solvents than analogous complexes of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (dppm), which

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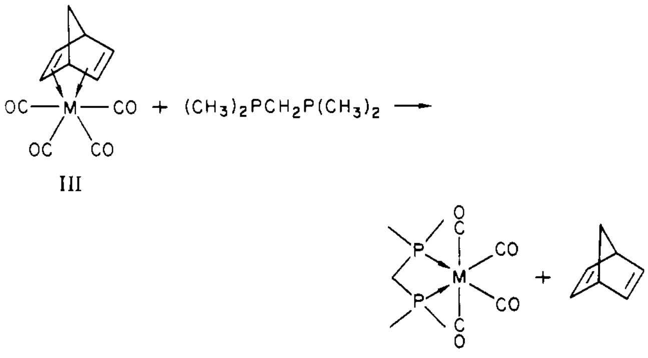
(14) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99.

(15) Hayter, R. G.; Williams, L. F. *J. Inorg. Nucl. Chem.* **1964**, *26*, 1977.

have been studied in some detail.[14] This coupled with the availability of both CH_2 and CH_3 groups as proton NMR probes in $(CH_3)_2PCH_2P(CH_3)_2$ complexes makes these complexes more amenable to NMR characterization than analogous complexes of $(C_6H_5)_2PCH_2P(C_6H_5)_2$. In some cases not only the phosphorus-31 but also the proton NMR spectra are diagnostic of different bonding modes of the $(CH_3)_2PCH_2P(CH_3)_2$ ligand or the symmetry of the complex as illustrated by several of the group 6 metal carbonyl complexes discussed below. In general, phosphorus-31 NMR chemical shifts of $(CH_3)_2PCH_2P(CH_3)_2$ ligands in bimetallic chelate rings I are 30–40 ppm downfield from those in four-membered monometallic chelate rings II as illustrated most clearly in the NMR spectra of the complexes *fac*-$(dmpm)_3M_2(CO)_6$ (M = Mo, W) (Table III).

The low molecular weight of the $(CH_3)_2PCH_2P(CH_3)_2$ ligand makes all of the mononuclear metal carbonyl complexes and some of the binuclear metal carbonyl complexes (e.g., $(dmpm)Mn_2(CO)_8$ and $(dmpm)_2Mn_2(CO)_6$) sufficiently volatile to obtain the mass spectra by conventional electron-impact methods. The metal carbonyl derivatives exhibit the expected[16] generally stepwise loss of carbonyl groups from their parent molecular ions. Other types of fragmentation processes do not appear to compete effectively with this carbonyl loss. The mass spectrum of the free ligand $(CH_3)_2PCH_2P(CH_3)_2$ exhibits the ions $(CH_3)_2PCH_2PCH_3^+$, $(CH_3)_2PCH_2^+$, and $(CH_3)_2P^+$, arising from various types of phosphorus–carbon bond cleavages, as well as a strong ion $(CH_3)_3P^+$, which necessarily must involve hydrogen or methyl transfer. Related to the latter is the observation of the relatively intense ions $(CH_3)_3PM^+$ (M = Cr, Mn) in the mass spectra of the first-row transition-metal derivatives $(dmpm)Cr(CO)_4$, *mer*-$(dmpm)_2Cr(CO)_3$, and $(dmpm)_nMn_2(CO)_{10-2n}$ (n = 1, 2).

B. Chromium, Molybdenum, and Tungsten Complexes. Reactions of the norbornadiene metal tetracarbonyl complexes (III; M = Cr, Mo, W) with $(CH_3)_2PCH_2P(CH_3)_2$ proceed in the expected manner according to the following scheme with complete displacement of the norbornadiene ligand to give the biligate monometallic complexes $(dmpm)M(CO)_4$ (IV; M = Cr, Mo, W):

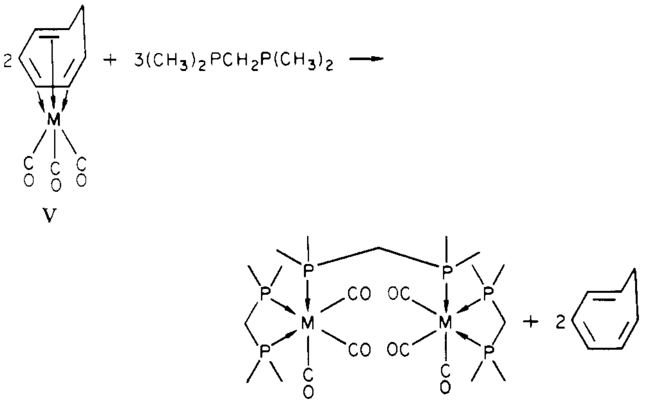


III

IV

The infrared spectra of these complexes in the ν(CO) region (Table II) exhibits the expected pattern for *cis*-$L_2M(CO)_4$ derivatives. The phosphorus-31 NMR spectra of these complexes (Table III) exhibit single resonances at relatively high fields apparently because of the effect of the four-membered chelate ring. In fact, the resonance of the coordinated phosphorus atoms in $(dmpm)W(CO)_4$ is shifted upfield (δ −57.4) from the free ligand (δ −56.5) in contrast to the usual downfield shifts of trivalent phosphorus resonances upon coordination with transition metals.[17] The CH_2 proton resonances in $(dmpm)M(CO)_4$ (IV; M = Cr, Mo, W) are triplets in accord with the (real) coupling of the CH_2 protons with the equivalently situated phosphorus atoms. The CH_3 proton resonance in $(dmpm)Cr(CO)_4$ is also a triplet arising from "virtual" coupling[18,19] involving the combined effects of $|^2J(P-H)|$ and a high $|^2J(P-P)|$. However, the CH_3 proton resonances in $(dmpm)M(CO)_4$ (IV; M = Mo, W), are doublets since $|^2J(P-P)|$ becomes smaller upon descending the periodic table from Cr to Mo and W so that $|^2J(P-H)|$ is the only coupling constant affecting these methyl resonances. This effect is well-known in phosphine metal carbonyl complexes having apparently been first observed[20] in tris(dimethylamino)phosphine complexes of Cr, Mo, and W carbonyls of the type *trans*-$L_2M(CO)_4$.

Reactions of the cycloheptatriene metal tricarbonyl complexes $C_7H_8M(CO)_3$ (V; M = Mo, W) with $(CH_3)_2PCH_2P(CH_3)_2$ also involve complete displacement of the cycloheptatriene ligand to give products of the stoichiometry $(dmpm)_3M_2(CO)_6$ according to



V

VI

The indicated structure VI for the $(dmpm)_3M_2(CO)_6$ products is based on the following spectroscopic evidence:

(1) The infrared spectra in the ν(CO) region (Table II) exhibit the two bands expected for *fac*-$L_3M(CO)_3$ rather than *mer*-$L_3M(CO)_3$ stereochemistry of each metal atom.

(2) The phosphorus-31 NMR spectrum of the molybdenum complex $(dmpm)_3Mo_2(CO)_6$ (Table III) exhibits resonances at δ +2.0 and −27.7. The resonance at δ −27.7 may be assigned to the four phosphorus atoms in the two four-membered chelate rings on the basis of the similarity of its chemical shift to the δ −28.0 phosphorus-31 resonance in $(dmpm)Mo(CO)_4$. The splitting of this resonance into a doublet under proton decoupling conditions may be attributed to coupling of each of these chelate-ring phosphorus atoms with the bridging phosphorus atom bonded to the same metal. The remaining somewhat broad resonance at δ +2.0 is assigned to the two equivalent phosphorus atoms in the bridging $(CH_3)_2PCH_2P(CH_3)_2$ ligand. The interpretation of the phosphorus-31 NMR spectrum of $(dmpm)_3W_2(CO)_6$ is exactly analogous with the resonances at δ −19.0 and −55.3 corresponding to the bridging and chelating phosphorus atoms, respectively.

(3) The proton NMR spectra of $(dmpm)_3M_2(CO)_6$ (VI; M = Mo, W) exhibit three methyl doublets of equal relative intensities. One of three methyl doublets can be assigned to the four equivalent methyl groups of the bridging $(CH_3)_2PCH_2P(CH_3)_2$ ligand. The other two methyl doublets are assigned to the eight methyl groups of the two chelating $(CH_3)_2PCH_2P(CH_3)_2$ ligands, which are split into two sets of four equivalent methyl groups since in *fac*-$(dmpm)_3M_2(CO)_6$ (VI) unlike $(dmpm)M(CO)_4$ (IV) the two sides of the four-mem-

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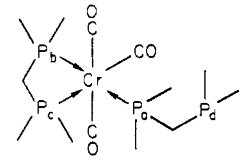
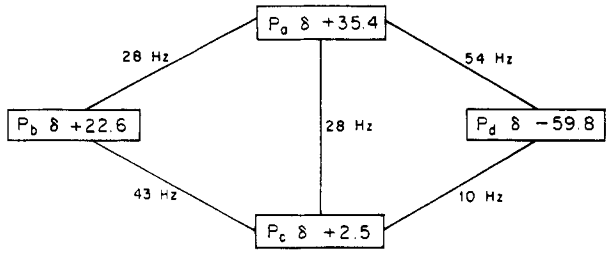
[16] King, R. B. *Top. Curr. Chem.* **1970**, *14*, 92.
[17] Grim, S. O.; Keiter, R. L.; McFarlane, W. *Inorg. Chem.* **1967**, *6*, 1133.
[18] Musher, J. I.; Corey, E. J. *Tetrahedron* **1962**, *18*, 791.
[19] Shaw, B. L.; Jenkins, J. M. *J. Chem. Soc.* **1966**, 770.
[20] King, R. B. *Inorg. Chem.* **1963**, *2*, 936.

bered chelate rings are nonequivalent because of the asymmetry of the other ligands around the metal atom.

The initial product from the reaction of the chromium complex $C_7H_8Cr(CO)_3$ (V; M = Cr) with $(CH_3)_2PCH_2P(CH_3)_2$ is the corresponding *fac*-(dmpm)$_3$Cr$_2$(CO)$_6$, which, like its Mo and W analogues, is precipitated from the hexane reaction solvent as rapidly as it is formed. This Cr complex is characterized by elemental analyses and by the typical *fac*-L$_3$M(CO)$_3$ pattern of ν(CO) frequencies in its infrared spectrum. However, *fac*-(dmpm)$_3$Cr$_2$(CO)$_6$, unlike its Mo and W analogues, decomposes so rapidly in solution that reliable proton and phosphorus-31 NMR spectra cannot be obtained. The ultimate product of the decomposition of *fac*-(dmpm)$_3$Cr$_2$(CO)$_6$ in solution appears to be *mer*-(dmpm)$_2$Cr(CO)$_3$ (VII), which can also be obtained directly from the reaction of $C_7H_8Cr(CO)_3$ (V; M = Cr) with $(CH_3)_2PCH_2P(CH_3)_2$ when conducted under conditions where *fac*-(dmpm)$_3$Cr$_2$(CO)$_6$ is not precipitated out of solution as rapidly as it is formed.



VII



VII-NMR

Structure VII for *mer*-(dmpm)$_2$Cr(CO)$_3$ was initially surprising since the formation of a metal complex with an *uncomplexed* highly basic compact $(CH_3)_2P$ unit was unexpected. However, the following spectroscopic properties of *mer*-(dmpm)$_2$Cr(CO)$_3$ clearly support structure VII:

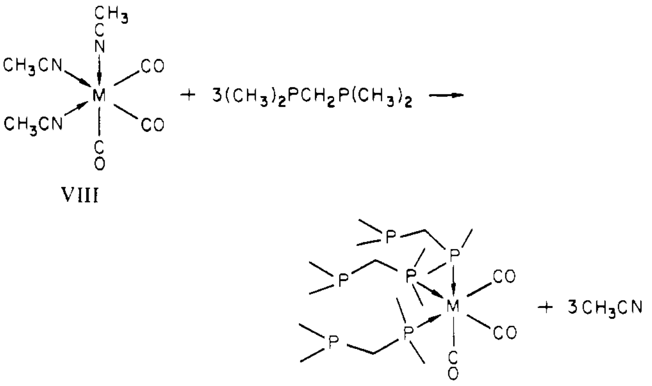
(1) The ions (dmpm)$_2$Cr(CO)$_n^+$ (n = 3, 2, 0) are observed in the mass spectrum of *mer*-(dmpm)$_2$Cr(CO)$_3$, thereby providing a more reliable indication of its stoichiometry than the microanalytical data.

(2) The infrared spectrum of *mer*-(dmpm)$_2$Cr(CO)$_3$ (Table II) exhibits three rather than only two ν(CO) frequencies. Furthermore, the relative positions and intensities of these three frequencies are in accord with those previously found[21,22] for other *mer*-L$_3$M(CO)$_3$ complexes.

(3) The phosphorus-31 NMR spectrum of *mer*-(dmpm)$_2$Cr(CO)$_3$ (Table III) exhibits four distinct resonances that are multiplets centered at δ +35.4, +22.6, +2.5, and −59.8. The resonances centered at δ −59.8 and +2.5 can be assigned to the uncomplexed phosphorus atom (H_d in VII) and the chelate phosphorus atom trans to CO (H_c in VII), respectively, on the basis of the similarities of these chemical shifts to the phosphorus-31 chemical shifts of free $(CH_3)_2PCH_2P(CH_3)_2$ (δ −56.5) and (dmpm)Cr(CO)$_4$ (IV; M = Cr) (δ +4.0), respectively. The multiplicities of these four phosphorus-31 NMR resonances are consistent with the coupling constants depicted in VII-NMR. The remaining assignments are made so that the only unobserved phosphorus–phosphorus constant is the one involving the most remote pair of phosphorus atoms, namely $^4J(P_b–P_d)$.

(4) The proton CH_3 resonances of *mer*-(dmpm)$_2$Cr(CO)$_3$ centered at δ 1.53, 1.43, and 1.10, respectively (Table III), may be assigned to the $(CH_3)_2P$ groups in the chelating $(CH_3)_2PCH_2P(CH_3)_2$ ligand, the coordinated $(CH_3)_2P$ group in the monodentate $(CH_3)_2PCH_2P(CH_3)_2$ ligand, and the uncomplexed $(CH_3)_2P$ group, respectively, on the basis of relative intensities and chemical shift comparisons with the CH_3 protons in the free ligand (δ 1.08) and (dmpm)Cr(CO)$_4$ (δ 1.57). Analogously, the proton CH_2 resonances of *mer*-(dmpm)$_2$Cr(CO)$_3$ centered at δ 3.20 and 1.78 are assigned to the chelating and monodentate $(CH_3)_2PCH_2P(CH_3)_2$ ligands, respectively. The fine structure of the δ 1.78 CH_2 proton resonance seems to be a combined result of virtual coupling involving P_a and P_b leading to a triplet with a further (real) coupling to the uncomplexed phosphorus atom P_d leading to additional doublet splitting.

Reactions of the acetonitrile metal carbonyl complexes *fac*-(CH$_3$CN)$_3$M(CO)$_3$ (VIII; M = Mo, W) with $(CH_3)_2PCH_2P(CH_3)_2$ in boiling acetonitrile lead to complete displacement of the acetonitrile ligands to give products of the stoichiometry *fac*-(dmpm)$_3$M(CO)$_3$ according to



VIII

IX

The indicated structure IX for the *fac*-(dmpm)$_3$M(CO)$_3$ products is based on the following spectroscopic evidence:

(1) The infrared spectra in the ν(CO) region (Table II) exhibits the two bands expected for *fac*-L$_3$M(CO)$_3$ rather than *mer*-L$_3$M(CO)$_3$ stereochemistry.

(2) The phosphorus-31 NMR spectrum of the molybdenum complex *fac*-(dmpm)$_3$Mo(CO)$_3$ (Table III) exhibits only two resonances, both of which are multiplets owing to overlap between the different possible phosphorus–phosphorus coupling constants. The resonance centered at δ −61.5 may be assigned to the three equivalent uncomplexed phosphorus atoms in structure IX by virtue of the similarity of its chemical shift to that of uncomplexed $(CH_3)_2PCH_2P(CH_3)_2$ (δ −56.5). The remaining resonance, which is centered at δ −8.7, may then be assigned to the three equivalent complexed phosphorus atoms in structure IX. The interpretation of the phosphorus-31 NMR spectrum of *fac*-(dmpm)$_3$W(CO)$_3$ (IX; M = W) is exactly analogous with the resonances at δ −29.6 and −61.3 corresponding to the complexed and uncomplexed phosphorus atoms, respectively.

The complexes *fac*-(dmpm)$_3$M(CO)$_3$ (IX; M = Mo, W) are yellow solids that are air sensitive in accord with the presence of three uncomplexed highly compact basic $(CH_3)_2P$ groups. They lose a $(CH_3)_2PCH_2P(CH_3)_2$ ligand upon attempted sublimation, which may be related to the observation of (dmpm)$_2$M(CO)$_3^+$ as the highest m/e ions in their mass spectra.

Photochemical reactions of the metal hexacarbonyls M(CO)$_6$ (M = Cr, Mo, W) with $(CH_3)_2PCH_2P(CH_3)_2$ were also investigated. The photochemical reaction of W(CO)$_6$ with $(CH_3)_2PCH_2P(CH_3)_2$ was most interesting, since a volatile

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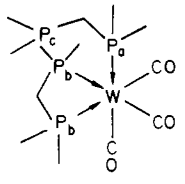
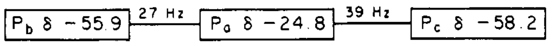
(21) Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702.

(22) King, R. B.; Lee, T. W. *Inorg. Chem.* **1982**, *21*, 319.

yellow product of stoichiometry $(dmpm)_3W_2(CO)_7$ was isolated. The spectroscopic properties of this compound indicated that it was a 1:1 mixture of *fac*-$(dmpm)_2W(CO)_3$ (X) and $(dmpm)W(CO)_4$ (IV; M = W), which could not be separated by either vacuum sublimation or column chromatography. Since pure $(dmpm)W(CO)_4$ (IV; M = W) can be obtained from the reaction of (norbornadiene)tetracarbonyltungsten (III; M = W) with $(CH_3)_2PCH_2P(CH_3)_2$ as described above, the spectra of pure $(dmpm)W(CO)_4$ are available for subtraction from the spectra of the 1:1 mixture $(dmpm)W(CO)_4$/*fac*-$(dmpm)_2W(CO)_3$ in order to determine the spectra of pure *fac*-$(dmpm)_2W(CO)_3$. In this way the following spectroscopic evidence is obtained for the support of the proposed *fac*-$(dmpm)_2W(CO)_3$ structure X:



X



X-NMR

(1) The infrared $\nu(CO)$ spectrum of *fac*-$(dmpm)_2W(CO)_3$ (Table II) exhibits the two bands expected for a *fac*-$L_3M(CO)_3$ derivative in contrast to the three $\nu(CO)$ frequencies observed for *mer*-$(dmpm)_2Cr(CO)_3$ (VII).

(2) The mass spectrum assigned to *fac*-$(dmpm)_2W(CO)_3$ exhibits the full complement of ions $(dmpm)_2W(CO)_n^+$ (n = 0–3).

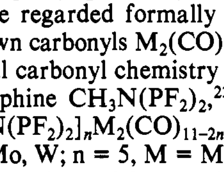
(3) The phosphorus-31 NMR spectrum of *fac*-$(dmpm)_2W(CO)_3$ (X) exhibits three distinct resonances at δ −24.8, −55.9, and −58.2 (Table III), which may be assigned to the coordinated phosphorus atom in the monodentate $(CH_3)_2PCH_2P(CH_3)_2$ ligand, the two equivalent phosphorus atoms of the chelating $(CH_3)_2PCH_2P(CH_3)_2$ ligand, and the single uncomplexed phosphorus atom, respectively. The multiplicities of these phosphorus-31 NMR resonances are consistent with the coupling constants indicated in X-NMR. Note that the symmetries of *mer*-$(dmpm)_2Cr(CO)_3$ (VII) and *fac*-$(dmpm)_2W(CO)_3$ (X) are different so that the two phosphorus atoms of the four-membered ring are nonequivalent in the Cr complex VII but equivalent in the W complex X.

(4) The interpretation of the proton NMR spectrum of *fac*-$(dmpm)_2W(CO)_3$ (X) is essentially analogous to that of *mer*-$(dmpm)_2Cr(CO)_3$ (VII). However, all of the CH_3 resonances are triplets in *mer*-$(dmpm)_2Cr(CO)_3$ (VII) but only doublets in *fac*-$(dmpm)_2W(CO)_3$ (X), indicating the absence of detectable virtual coupling in the W complex as compared with the Cr complex in accord with expectation and similar to the pair of complexes $(dmpm)M(CO)_4$ (M = Cr, W) discussed above. The triplet CH_2 resonance at δ 3.60 in *fac*-$(dmpm)_2W(CO)_3$ arises from real coupling of the CH_2 protons to both equivalently situated phosphorus atoms of the chelate ring. However, the triple doublet CH_2 resonance at δ 1.78 in *mer*-$(dmpm)_2Cr(CO)_3$ corresponds to a double resonance at δ 2.04 in *fac*-$(dmpm)_2W(CO)_3$, indicating that the triplet splitting in the former resonance arises from virtual rather than real coupling. Thus, a comparison of the proton NMR spectra of *mer*-$(dmpm)_2Cr(CO)_3$ and *fac*-$(dmpm)_2W(CO)_3$ provides a basis to distinguish between splittings arising from real coupling and those arising from virtual coupling.[18,19]

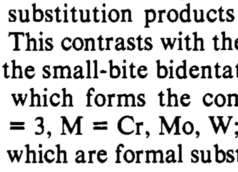
Ultraviolet irradiation of $Mo(CO)_6$ with $(CH_3)_2PCH_2P(CH_3)_2$ in tetrahydrofuran solution led to the formation of $(dmpm)Mo(CO)_4$ (IV; M = Mo) as the only isolable metal carbonyl derivative. An analogous ultraviolet irradiation of $Cr(CO)_6$ with $(CH_3)_2PCH_2P(CH_3)_2$ after vacuum sublimation of the crude product gave a yellow solid indicated by its infrared $\nu(CO)$ spectrum to contain a mixture of $(dmpm)Cr(CO)_4$ (IV; M = Cr) and an $LCr(CO)_5$ derivative, which was not identified. However, since the mass spectrum of this solid shows only the series of metal carbonyl ions $(dmpm)Cr(CO)_n^+$ (n = 0–4), this $LCr(CO)_5$ derivative is most likely $(dmpm)Cr(CO)_5$ containing a monodentate $(CH_3)_2PCH_2P(CH_3)_2$ ligand. Attempts to separate a pure product from this reaction by chromatography led only to the isolation of $(dmpm)Cr(CO)_4$ (IV; M = Cr). This is scarcely surprising in view of the expected high reactivity of the uncomplexed $(CH_3)_2P$ group in $(dmpm)Cr(CO)_5$, which would likely lead to decomposition during the chromatography process.

A characteristic feature of this group 6 metal carbonyl chemistry of $(CH_3)_2PCH_2P(CH_3)_2$ is the failure to observe any $(dmpm)_nM_2(CO)_{11-2n}$ (M = Cr, Mo, W) complexes, which may be regarded formally as substitution products of the unknown carbonyls $M_2(CO)_{11}$. This contrasts with the group 6 metal carbonyl chemistry of the small-bite bidentate fluorophosphine $CH_3N(PF_2)_2$,[22,23] which forms the complexes $[CH_3N(PF_2)_2]_nM_2(CO)_{11-2n}$ (n = 3, M = Cr, Mo, W; n = 4, M = Mo, W; n = 5, M = Mo), which are formal substitution products of $M_2(CO)_{11}$. This difference may relate to the relatively high π-acceptor strength and low basicity of $CH_3N(PF_2)_2$ as contrasted with the relatively low π-acceptor strength and high basicity of $(CH_3)_2PCH_2P(CH_3)_2$.

C. Manganese and Rhenium Complexes. Thermal reactions of the dimetal decacarbonyls $M_2(CO)_{10}$ (M = Mn, Re) with $(CH_3)_2PCH_2P(CH_3)_2$ lead to pairwise replacement of carbonyl groups to give the complexes $(dmpm)_nM_2(CO)_{10-2n}$ (n = 1, M = Mn; n = 2, M = Mn, Re). In each of these complexes the phosphorus-31 NMR spectrum (Table III) exhibits a single resonance, indicating equivalence of all of the phosphorus atoms. The infrared $\nu(CO)$ spectra of these complexes (Table II) are very similar to the reported[24] infrared spectra of $(dppm)_nMn_2(CO)_{10-2n}$ except for a low-frequency shift (typically ~15 cm^{-1}) consistent with the higher net basicity of $(CH_3)_2PCH_2P(CH_3)_2$ relative to $(C_6H_5)_2PCH_2P(C_6H_5)_2$. On the basis of their spectroscopic properties structures XI (M = Mn) and XII (M = Mn, Re) are postulated for the complexes $(dmpm)Mn_2(CO)_8$ and $(dmpm)_2M_2(CO)_6$, respectively, thereby providing examples of bimetallic five-membered chelate rings I. We were unable to prepare $(dmpm)Re_2(CO)_8$ by the reaction of $Re_2(CO)_{10}$ with $(CH_3)_2PCH_2P(CH_3)_2$ in a 1:1 mole ratio similar to the successful preparation of $(dmpm)Mn_2(CO)_8$. More significantly, we were unable to obtain any $(dmpm)_2Mn_2(CO)_5$ analogous to the reported[14,24,25] $(dmpm)_2Mn_2(CO)_5$ containing an unusual four-electron bridging CO group by using analogous reaction conditions. We suspect that the size of the phenyl groups in $(dppm)_2Mn_2(CO)_6$ might be a factor in facilitating decarbonylation to $(dppm)_2Mn_2(CO)_5$. Also the manganese atoms in dmpm complexes are more electron rich than the manganese



XI



XII

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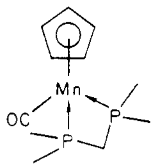
(23) Newton, M. G.; King, R. B.; Lee, T. W.; Norskov-Lauritzen, L.; Kumar, V. *Chem. Commun.* **1982**, 201.

(24) Colton, R.; Commons, C. J. *Aust. J. Chem.* **1975**, *28*, 1673.

(25) Caulton, K. G.; Adair, P. *J. Organomet. Chem.* **1976**, *114*, C11.

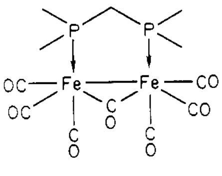
atoms in analogous dppm complexes, thereby making them less acidic and less able to receive electron density from a four-electron bridging CO group. In this connection, a four-electron-donor bridging CO group is probably less effective at removing electron density from metal atoms through back-bonding than two normal terminal CO groups, which donate the same number of electrons.

The photochemical reaction of $C_5H_5Mn(CO)_3$ with $(CH_3)_2PCH_2P(CH_3)_2$ proceeds in the usual manner with the loss of two CO groups to form the complex (dmpm)Mn(CO)(C_5H_5) (XIII). The metal atom in this complex is very electron rich as indicated by its extreme air sensitivity and its very low single terminal ν(CO) frequency at 1808 cm^{-1}, fully 46 cm^{-1} below the reported[15] ν(CO) frequency of 1854 cm^{-1} for the analogous (dppm)Mn(CO)(C_5H_5).

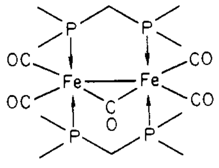


XIII

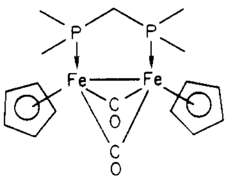
D. Iron Complexes. The conditions used to prepare the $Fe_2(CO)_9$ substitution products $(dmpm)_nFe_2(CO)_{9-2n}$ (n = 1, 2) parallel those used to prepare analogous complexes of other small-bite bidentate trivalent phosphorus ligands. Thus, the reaction of $Fe_2(CO)_9$ with $(CH_3)_2PCH_2P(CH_3)_2$ to give (dmpm)$Fe_2(CO)_7$ is analogous to reactions of $Fe_2(CO)_9$ with the small-bite bidentate ligands $CH_3N(PF_2)_2$,[26] $CH_3N[P(OCH_3)_2]_2$,[1] and $(C_6H_5)_2PCH_2P(C_6H_5)_2$[27] to give the corresponding (diphos)$Fe_2(CO)_7$ complexes. Similarly, the photolysis of $Fe(CO)_5$ with $(CH_3)_2PCH_2P(CH_3)_2$ to give $(dmpm)_2Fe_2(CO)_5$ parallels reported photolyses of $Fe(CO)_5$ with $CH_3N(PF_2)_2$[26] and $CH_3N[P(OCH_3)_2]_2$[1] to give the corresponding $(diphos)_2Fe_2(CO)_5$ complexes. The obvious structures XIV and XV for (dmpm)$Fe_2(CO)_7$ and $(dmpm)_2Fe_2(CO)_5$, respectively, are supported by the observation of single phosphorus-31 NMR resonances, single bridging infrared ν(CO) frequencies, and a pattern of terminal ν(CO) frequencies similar to those reported for other $(diphos)_nFe_2(CO)_{9-2n}$ derivatives[1,25,26] except for the expected shift to lower frequencies arising from the higher basicity and lower π-acceptor strength of $(CH_3)_2PCH_2P(CH_3)_2$ relative to the other small-bite bidentate trivalent phosphorus ligands.



XIV



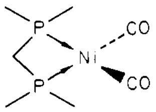
XV



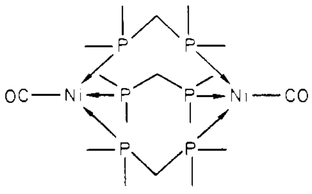
XVI

The reaction of $[C_5H_5Fe(CO)_2]_2$ with $(CH_3)_2PCH_2P(CH_3)_2$ results in the replacement of two carbonyl groups to give green (dmpm)$Fe_2(CO)_2(C_5H_5)_2$. Structure XVI is indicated by the observation of a single phosphorus-31 NMR resonance, a single bridging ν(CO) frequency, and no terminal ν(CO) frequencies. Products analogous to XVI are formed by the reactions of $[C_5H_5Fe(CO)_2]_2$ with other bis(tertiary phosphines).[28]

E. Nickel Complexes. The reaction of $Ni(CO)_4$ with $(CH_3)_2PCH_2P(CH_3)_2$ at room temperature results in displacement of two carbonyl groups to form (dmpm)$Ni(CO)_2$ (XVII).



XVII



XVIII

This structure is supported by the following observations:

(1) A single phosphorus-31 resonance is observed, which is the furthest upfield (δ −15.1) of any of the first-row transition-metal carbonyl complexes of dmpm (Table III), thereby suggesting the presence of a four-membered chelate ring with its characteristic upfield chelate chemical shift (see above).

(2) Two terminal ν(CO) frequencies are observed in similar locations to those of the closely related 1,2-bis(dimethylphosphino)ethane complex (dmpe)$Ni(CO)_2$.[29]

(3) A monomeric molecular weight was determined osmometrically in benzene. The compound sublimes only with extensive decomposition as indicated by the infrared and NMR spectra of the sublimate; therefore, the mass spectrum of this complex is not considered reliable.

The reaction of $[C_5H_5NiCO]_2$ with $(CH_3)_2PCH_2P(CH_3)_2$ in boiling tetrahydrofuran results in displacement of the cyclopentadienyl rather than carbonyl groups to give yellow $(dmpm)_3Ni_2(CO)_2$ formulated as XVIII on the basis of the following evidence:

(1) A single phosphorus-31 resonance indicates equivalence of all of the phosphorus atoms. The phosphorus resonance in $(dmpm)_3Ni_2(CO)_2$ is shifted about 27 ppm downfield from that in (dmpm)$Ni(CO)_2$ (XVII), thereby indicating that the phosphorus atoms are not in a four-membered chelate ring in the binuclear complex.

(2) The 11-cm^{-1} separation of the two ν(CO) frequencies in $(dmpm)_3Ni_2(CO)_2$ (XVIII) is similar to the 15-cm^{-1} reported[30] separation of the two ν(CO) frequencies in the complex $[CH_3N(PF_2)_2]_3Ni_2(CO)_2$ with an apparently closely related structure.

The osmometric molecular weight in benzene solution corresponds to that expected for a binuclear complex.

Displacement of cyclopentadienyl rings rather than carbonyl groups in reactions of $[C_5H_5NiCO]_2$ with trivalent phosphorus ligands is not unusual. An early example of a reaction of this type is the reported[20] reaction of $[C_5H_5NiCO]_2$ with tris(dimethylamino)phosphine to give $[(Me_2N)_3P]_2Ni(CO)_2$.

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Registry No. III (M = Cr), 12146-36-0; III (M = Mo), 12146-37-1; III (M = W), 12129-25-8; IV (M = Cr), 85752-24-5; IV (M = Mo), 90624-09-2; IV (M = W), 90624-10-5; V (M = Cr), 12125-72-3; V

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(M = Mo), 12125-77-8; V (M = W), 12128-81-3; VI (M = Cr), 90624-11-6; VI (M = Mo), 90624-12-7; VI (M = W), 90624-13-8; VII, 90624-14-9; VIII (M = Mo), 17731-95-2; VIII (M = W), 30958-95-3; IX (M = Mo), 90624-15-0; IX (M = W), 90624-16-1; X, 90624-17-2; XI (M = Mn), 90624-18-3; XII (M = Mn), 90624-19-4; XII (M = Re), 90624-20-7; XIII, 90624-21-8; XIV, 90624-22-9; XV, 90624-23-0; XVI, 90624-24-1; XVII, 90624-25-2; XVIII, 90624-26-3; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Mn_2(CO)_{10}$, 10170-69-1; $Re_2(CO)_{10}$, 14285-68-8; $C_5H_5Mn(CO)_3$, 12079-65-1; $Fe_2(CO)_9$, 15321-51-4; $Fe(CO)_5$, 13463-40-6; $[C_5H_5Fe(CO)_2]_2$, 12154-95-9; $Ni(CO)_4$, 13463-39-3; $[C_5H_5NiCO]_2$, 12170-92-2.

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Synthesis, Structure, and Chemistry of Sterically Crowded Metal Carbonyl Cluster Compounds: $[Fe_3M(CO)_{14}]^{2-}$ (M = Cr, Mo, W)

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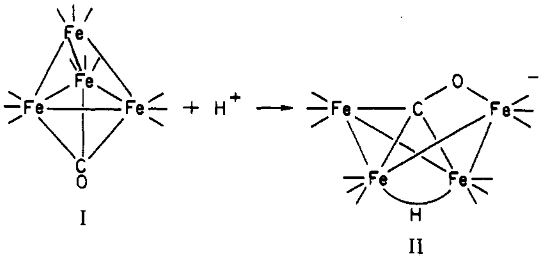
Despite previous indications in the literature that tetrahedral $M_4(CO)_{14}$ might be too crowded to be stable, the series $[Fe_3M(CO)_{14}]^{2-}$ (M = Cr, Mo, W) was synthesized by the interaction of $[Fe_3(CO)_{11}]^{2-}$ with $M(CO)_3(CH_3CN)_3$. The objective in synthesizing these sterically crowded compounds was to induce metal–metal bond breaking and a concomitant η^2-CO interaction. The structure of the compound in which M = Cr was determined by single-crystal X-ray diffraction. In contrast with the desired M–M scission, the metal framework is pseudotetrahedral with Fe–Cr distances averaging 2.633 (25) Å and Fe–Fe distances averaging 2.656 (3) Å. The latter distances are about 0.1 Å longer than expected from Fe–Fe distances in other clusters. The polygon formed by the carbonyl carbon atoms may be described as a hexacapped rectangular antiprism. Model calculations of strain energies in this compound indicate that the C–C repulsive potential, which successfully describes nonbonding forces for graphite and organic compounds, overestimates the nonbonded C–C repulsions in metal carbonyls. Strain energy calculations lead us to propose a modified potential function for C···C interactions in metal carbonyls. The reactions of the $[Fe_3M(CO)_{14}]^{2-}$ series with electrophiles, H^+ and CH_3^+, were explored, with the thought that these might induce M–M bond breaking, but this appears not to be the case. Crystallographic data for $[PPN]_2[Fe_3Cr(CO)_{14}]$: $P\bar{1}$ triclinic space group, $a = 13.428$ (5) Å, $b = 17.734$ (5) Å, $c = 18.254$ (9) Å, $\alpha = 95.46$ (3)°, $\beta = 105.74$ (3)°, $\gamma = 69.82$ (2)°, $Z = 2$.

Introduction

Steric effects are frequently invoked in inorganic chemistry; however, there is comparatively little quantitative understanding of the subject. The greatest progress has been made in the area of ring conformation for metal chelate complexes, where it has been possible to build on the methods of molecular mechanics developed for organic molecules.[2] For metal phosphine and related complexes, steric interactions may be approximated by effective cone angles for the ligands,[3] which can be used to systematize phosphine substitution reactions, oxidative-addition reactions, and the like. Recent investigations have shown that the disposition of CO ligands in metal cluster carbonyl compounds can be described with reasonable accuracy by a model based on ligand–ligand repulsions.[4] At the present stage of development, this model requires a relatively symmetrical metal framework in which M–M and M–C energies are reasonably constant.

The effects of CO ligand–ligand repulsions were discussed by Doedens and Dahl,[5] who suggested that the CO ligands in $[Fe_4(CO)_{13}]^{2-}$ (I) are in such close proximity that there is no room to accommodate the 14th CO required for the formation of the isoelectronic neutral carbonyl, $Fe_4(CO)_{14}$.[5] Mingos has reached a similar conclusion for this sytem, based on the effective cone angle of CO, and his treatment predicts that $M_4(CO)_{14}$ clusters with tetrahedral metal frameworks should be strained for the second and third transition series as well.[6] Even the introduction of a "hydride" ligand to produce $[HFe_4(CO)_{13}]^-$ (II) results in a drastic rearrangement, which has been attributed to steric effects.[7] As illustrated in eq 1, the protonation of $[Fe_4(CO)_{13}]^{2-}$ (I) leads to the scission of an Fe–Fe bond with the formation of the butterfly compound II.



Compound II is of great interest because it contains an η^2-CO ligand, which bridges the wing tips and contributes the two additional cluster valence electrons needed when the Fe–Fe bond is broken. The η^2-CO bonding mode is very interesting because it may occur as a precursor to the scission of CO on the surface of catalysts for Fischer–Tropsch and methanation.[8] Furthermore, an η^2-CO is strongly implicated in the proton-induced reduction of CO in metal cluster chemistry.[9,10] In the present research we sought to prepare $[M_4(CO)_{14}]^{2-}$

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