to the formation of a divalent species that displays far less stability for chromium complexes than for those of molybdenum and tungsten.

There are two pathways which generate Mo(II) and W(II) dpe complexes—direct oxidation of *mer*-$[M(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$ or the disproportionation of this complex. The *fac*- and *mer*-$M(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$ (M = Mo, W) complexes display rather different behavior with no evidence seen for a M(I) intermediate. However, the first oxidation for dpe and dpm complexes occurs at similar potentials (and very different from the second oxidation for the dpe compounds), which strongly suggests that the initial product of oxidation is $[M(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})]^+$, which then very rapidly disproportionates to M(0) and M(II) by the process described in eq 5, which would result in an apparent two-electron-oxidation process on the coulometric time scale. It would be expected that formation of the seven-coordinate $[M(CO)_3(\eta^2\text{-P-P})_2]^{2+}$ from $[M(CO)_3(\eta^1\text{-P-P})(\eta^2\text{-P-P})]^+$ would be more efficient with dpm than with dpe because the pendant phosphorus would be close to the metal because of the geometry of the ligand. In the case of the much more flexible dpe ligand it is probable that significant molecular rearrangement would be necessary before the second dpe ligand chelates to the metal. Since the disproportionation of *mer*-$[M(CO)_3(\eta^1\text{-P-P})(\eta^2\text{-P-P})]^+$ simply involves electron transfer between similar molecules, which is known to be extremely fast for similar compounds,[11,12] it is likely that coordination of the free phosphorus is the rate-determining step in the overall disproportionation reaction and thus dpm complexes would be expected to disproportionate faster than the dpe complexes. Hence the apparent electrochemical differences between dpm and dpe complexes of molybdenum and tungsten are due to differences in the stability of M(I) complexes toward disproportionation.

The greater differences between chromium and the other two metals lies in the fact that seven-coordinate Cr(II) compounds are not readily formed, and this removes the driving force for the disproportionation reaction to proceed, thus giving rise to stable Cr(I) complexes. Although the seven-coordinate $[Cr(CO)_3(\eta^2\text{-dpm})_2]^{2+}$ cation is very unstable, being only observed at low temperature on the voltammetric time scale, it is presumably more stable than its 16-electron precursor $[Cr(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})]^{2+}$. No evidence could be found for the corresponding seven-coordinate dpe cation. Presumably, the slower rate of chelation of the second ligand for dpe, discussed above, allows complete decomposition of $[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^{2+}$, in a manner analogous to that shown in eq 2, before the second dpe ligand can chelate.

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Registry No. *fac*-$W(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$, 93401-93-5; *fac*-$Mo(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$, 56009-06-4; *fac*-$W(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$, 102132-79-6; *fac*-$Mo(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$, 97202-31-8; *fac*-$Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$, 102132-78-5; *mer*-$W(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$, 93453-38-4; *mer*-$Mo(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$, 56085-32-6; *mer*-$Cr(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})$, 93401-94-6; *mer*-$W(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$, 102209-57-4; *mer*-$Mo(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$, 102209-56-3; *mer*-$Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})$, 102209-55-2; *mer*-$[W(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$, 102132-85-4; *mer*-$[Mo(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$, 102132-83-2; *mer*-$[Cr(CO)_3(\eta^1\text{-dpe})(\eta^2\text{-dpe})]^+$, 102132-80-9; *mer*-$[Cr(CO)_3(\eta^1\text{-dpm})(\eta^2\text{-dpm})]^+$, 98152-90-0; $[W(CO)_3(\eta^2\text{-dpm})_2]^{2+}$, 102132-82-1; $[Mo(CO)_3(\eta^2\text{-dpm})_2]^{2+}$, 102132-81-0; $[Cr(CO)_3(\eta^2\text{-dpm})_2]^{2+}$, 102153-35-5; $[W(CO)_3(\eta^2\text{-dpe})_2]^{2+}$, 102132-86-5; $[Mo(CO)_3(\eta^2\text{-dpe})_2]^{2+}$, 102132-84-3; $(C_7H_8)W(CO)_3$, 12128-81-3; $(C_7H_8)Mo(CO)_3$, 12125-77-8; $(C_7H_8)Cr(CO)_3$, 12125-72-3.

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Dialkylamino Phosphorus Metal Carbonyls. 1. Mononuclear Derivatives from Reactions of Bis(diisopropylamino)phosphine with Metal Carbonyls[1]

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Reactions of $(i\text{-}Pr_2N)_2PH$ with the tetrahydrofuran complexes $(THF)M(CO)_n$ (n = 4, M = Fe; n = 5, M = Cr, Mo, W) and $(THF)Mn(CO)_2Cp$ give the corresponding $(i\text{-}Pr_2N)_2PHM(CO)_n$ and $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ complexes as air-stable sublimable hydrocarbon-soluble solids. A similar reaction of $(i\text{-}Pr_2N)_2PH$ with *fac*-$(EtCN)_3W(CO)_3$ results in ligand redistribution to give *cis*-$[(i\text{-}Pr_2N)_2PH]_2W(CO)_4$. In general these $(i\text{-}Pr_2N)_2PH$ complexes react rapidly with the hydrogen halides HX (X = Cl, Br) to cleave selectively in good yield one of the two diisopropylamino groups to give the corresponding $i\text{-}Pr_2NP(H)X$ complexes; the exception to this reactivity pattern is the reaction of $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ with HBr, which proceeds all the way to $Br_2P(H)Mn(CO)_2Cp$. Methanolyses of $Br_2P(H)Mn(CO)_2Cp$ and $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ give $(MeO)_2PHMn(CO)_2Cp$ and $i\text{-}Pr_2NP(H)(OMe)Mn(CO)_2Cp$, respectively; treatment of the latter complex with HCl gives $MeOP(H)ClMn(CO)_2Cp$. Dehydrochlorination of $i\text{-}Pr_2NP(H)ClFe(CO)_4$ with excess triethylamine gives a low yield of the phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, previously obtained from the reaction of $Na_2Fe(CO)_4$ with $i\text{-}Pr_2NPCl_2$. The infrared $\nu(CO)$ spectra and the proton, phosphorus-31, and carbon-13 NMR spectra of the new complexes are described.

Introduction

Bis(diisopropylamino)phosphine, $(i\text{-}Pr_2N)_2PH$, has recently become readily available[2] through the $LiAlH_4$ reduction of $(i\text{-}Pr_2N)_2PCl$. Metal carbonyl complexes of $(i\text{-}Pr_2N)_2PH$ are of interest because they contain potentially reactive phosphorus–hydrogen and phosphorus–nitrogen bonds. This paper describes a number of mononuclear $(i\text{-}Pr_2N)_2PH$ metal carbonyl complexes as well as the cleavage of one or, in one case, both phosphorus–nitrogen bonds in such complexes with hydrogen halides to give the corresponding metal carbonyl complexes of the ligands $i\text{-}Pr_2NP(H)X$ (X = Cl, Br) and Br_2PH. Subsequent papers of this series discuss the formation of $(i\text{-}Pr_2N)_2P$ and $i\text{-}Pr_2NP$ metal carbonyl derivatives from $(i\text{-}Pr_2N)_2PH$ and the binuclear metal carbonyls $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ as well as the nucleophilic substitution of the reactive halogen atoms in $i\text{-}Pr_2NP(H)X$ metal carbonyl complexes with the reactive transition-metal nucleophile $C_5H_5Fe(CO)_2^-$ to give novel heterobimetallic derivatives.

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(1) (a) Portions of this work were presented at the 12th International Conference on Organometallic Chemistry, Vienna, Austria, Sept 1985, and the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985. (b) For a preliminary communication on this work see: King, R. B.; Fu, W.-K. *J. Organomet. Chem.* **1984**, *272*, C33.

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Table I. Diisopropylamino Phosphorus Metal Carbonyl Complexes

complex	yield, %	color	mp, °C	bp, °C (P, mm)[a]	anal.				
						% C	% H	% N	% X
(A) (i-Pr$_2$N)$_2$PH Complexes									
(i-Pr$_2$N)$_2$PHFe(CO)$_4$	48	yellow	62–64	60 (0.15)	calcd	48.0	7.2	7.0	
					found	47.1	7.2	6.8	
(i-Pr$_2$N)$_2$PHCr(CO)$_5$	85	yellow	77–78	75 (0.01)	calcd	48.1	6.8	6.6	
					found	48.1	6.9	6.6	
(i-Pr$_2$N)$_2$PHMo(CO)$_5$	55	white	60–62	90 (0.01)	calcd	43.6	6.3	6.0	
					found	43.4	6.3	5.9	
(i-Pr$_2$N)$_2$PHW(CO)$_5$	76	yellow	102–103	100 (0.01)	calcd	36.7	5.2	5.0	
					found	36.7	5.2	5.0	
cis-[(i-Pr$_2$N)$_2$PH]$_2$W(CO)$_4$	52	yellow	120 dec		calcd	44.2	7.6	7.4	
					found	44.2	7.6	7.3	
(i-Pr$_2$N)$_2$PHMn(CO)$_2$Cp	86	yellow	108–110	90 (0.01)	calcd	55.9	8.3	6.9	
					found	55.8	8.4	6.8	
(B) i-Pr$_2$NP(H)X Complexes									
i-Pr$_2$NP(H)ClFe(CO)$_4$	77	orange	liquid	105 (0.02)	calcd	35.8	4.5	4.2	10.6 (Cl)
					found	35.8	4.1	4.1	10.6 (Cl)
i-Pr$_2$NP(H)BrFe(CO)$_4$	39	orange	37	50 (0.01)	calcd	31.6	3.9	3.7	21.1 (Br)
					found	30.4	4.2	3.6	20.5 (Br)
i-Pr$_2$NP(H)ClCr(CO)$_5$	94	yellow	52–53	55 (0.01)	calcd	36.7	4.2	3.9	9.9 (Cl)
					found	36.6	4.3	3.7	9.5 (Cl)
i-Pr$_2$NP(H)BrCr(CO)$_5$	77	yellow	56	70 (0.1)	calcd	32.7	3.7	3.5	19.8 (Br)
					found	32.5	3.8	3.4	19.5 (Br)
i-Pr$_2$NP(H)ClMo(CO)$_5$	64	white	66–68	55 (0.001)	calcd	32.7	3.7	3.5	8.8 (Cl)
					found	32.2	3.8	3.4	8.6 (Cl)
i-Pr$_2$NP(H)BrMo(CO)$_5$	27	orange	67 dec		calcd	29.5	3.3	3.1	7.9 (Br)
					found	29.0	3.3	2.8	7.0 (Br)
i-Pr$_2$NP(H)ClW(CO)$_5$	88	white	75–76	50 (0.001)	calcd	26.9	3.1	2.8	7.2 (Cl)
					found	26.8	3.0	2.8	7.2 (Cl)
i-Pr$_2$NP(H)BrW(CO)$_5$	85	yellow	80	70 (0.1)	calcd	24.6	2.8	2.6	14.9 (B)
					found	24.0	2.7	2.5	14.5 (Br)
cis-[i-Pr$_2$NP(H)Cl]$_2$W(CO)$_4$	79	yellow	85		calcd	30.4	4.7	4.4	11.3 (Cl)
					found	29.9	4.7	4.4	11.1 (Cl)
i-Pr$_2$NP(H)ClMn(CO)$_2$Cp	89	yellow	80 dec	70 (0.1)	calcd	45.4	5.8	4.1	10.3 (Cl)
					found	44.7	6.0	3.9	9.9 (Cl)
(C) Other CpMn(CO)$_2$ Derivatives									
Br$_2$P(H)Mn(CO)$_2$Cp	94	orange	90	50 (0.1)	calcd	22.8	1.6		43.5 (Br)
					found	23.3	1.6		43.2 (Br)
(MeO)$_2$PHMn(CO)$_2$Cp	58	yellow	liquid	80–90 (0.065)	calcd	40.0	4.4		
					found	40.0	4.4		
i-Pr$_2$NP(H)(OMe)Mn(CO)$_2$Cp	72	yellow	liquid	120–130 (0.05)	calcd	49.6	6.8	4.1	
					found	50.6	7.7	5.1	
MeOP(H)ClMn(CO)$_2$Cp	50	orange	liquid	100–110 (0.04)	calcd	35.0	3.3		12.9 (Cl)
					found	34.8	3.5		11.0 (Cl)

[a] Sublimation temperatures of solids are given.

Experimental Section

Microanalyses (Table I) were performed by the Atlantic Microanalytical Laboratory, Atlanta, GA. Infrared spectra (Table II) were run in the 2200–1600-cm^{-1} metal carbonyl region in pentane or hexane solution and recorded on a Perkin-Elmer 599B spectrometer calibrated against polystyrene film. Proton NMR spectra (Table III) were run on a Varian TS-60 or EM-390 CW spectrometer at 60 or 90 MHz, respectively, using internal tetramethylsilane as a reference. Phosphorus-31 (Table III) and carbon-13 (Table IV) NMR spectra were taken on a JEOL FX-90Q multinuclear pulsed Fourier transform spectrometer using external 85% phosphoric acid and internal tetramethylsilane, respectively. In general, CDCl$_3$ solutions were used for the NMR spectra, and chemical shifts are given in ppm *downfield* from the reference. Mass spectra were obtained on a Finnegan 4023 mass spectrometer at 70 eV with a modified direct-inlet system; relative intensities are given in parentheses after the ion formula containing ^{35}Cl, ^{79}Br, and ^{184}W for the indicated polyisotopic elements. Melting and decomposition points (Table I) were taken in capillaries and are uncorrected.

The metal carbonyls Fe(CO)$_5$ (GAF Corp.), M(CO)$_6$ (M = Cr, Mo, W) (Pressure Chemical Corp.), and C$_5$H$_5$Mn(CO)$_3$ (Ethyl Corp.) were obtained from the indicated commercial sources. The cited published procedures were used to prepare Fe$_2$(CO)$_9$,[3] (i-Pr$_2$N)$_2$PClFe(CO)$_4$,[4] and *fac*-(EtCN)$_3$W(CO)$_3$.[5] The ligand (i-Pr$_2$N)$_2$PH was prepared by the published procedure,[2] which could be scaled up to give 45 g (51% yield) of vacuum-distilled (i-Pr$_2$N)$_2$PH from 100.0 g (0.375 mol) of (i-Pr$_2$N)$_2$PCl[2] and 12.0 g (0.315 mol) of LiAlH$_4$ in 1000 mL of diethyl ether.

Before use all solvents were distilled under dry nitrogen over appropriate drying agents (sodium benzophenone ketyl or metal hydrides except for chlorinated solvents). A dry-nitrogen atmosphere was always provided for the following three operations: (a) filling evacuated vessels containing potentially air-sensitive materials; (b) carrying out reactions; (c) handling air-sensitive organophosphorus compounds. When necessary, Schlenkware[6] or a polyethylene glovebag was used to provide the dry-nitrogen atmosphere. The ligand (i-Pr$_2$N)$_2$PH was handled with a syringe using double-needle techniques[6] without any significant decomposition. A 550-W 4.5-A ultraviolet lamp from Ace Glass Co. was used for the ultraviolet irradiations.

Preparation of (i-Pr$_2$N)$_2$PHFe(CO)$_4$. (a) From Fe$_2$(CO)$_9$ and (i-Pr$_2$N)$_2$PH. A mixture of 7.3 g (20.1 mmol) of Fe$_2$(CO)$_9$, 4.6 g (20.0 mmol) of (i-Pr$_2$N)$_2$PH, and 250 mL of tetrahydrofuran was stirred overnight at room temperature. Solvent and Fe(CO)$_5$ were removed from the deep brown solution at 25 °C (25 mm). Sublimation of the dry residue at 60 °C (0.15 mm) gave 4.0 g (50% yield) of yellow, crystalline, air-stable (i-Pr$_2$N)$_2$PHFe(CO)$_4$, which was readily soluble in nonpolar organic solvents.

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Table II. Infrared ν(CO) Frequencies of Diisopropylamino Phosphorus Metal Carbonyl Complexes

complex	ν(CO), cm^{-1}
(*i*-Pr$_2$N)$_2$PHFe(CO)$_4$	2044 m (A$_1$), 1974 m (A$_1$), 1943 s (E), 1932 (E)
i-Pr$_2$NP(H)ClFe(CO)$_4$	2065 m (A$_1$), 1995 m (A$_1$), 1965 s (E), 1955 s (E)
i-Pr$_2$NP(H)BrFe(CO)$_4$	2060 m (A$_1$), 1995 m (A$_1$), 1967 s (E), 1956 s (E)
(*i*-Pr$_2$N)$_2$PHCr(CO)$_5$	2031 m (A$_1$), 1940 s (E), 1911 w (A$_1$)
i-Pr$_2$NP(H)ClCr(CO)$_5$	2080 m (A$_1$), 2000 m (B), 1960 s (E), 1925 vw (A$_1$)
i-Pr$_2$NP(H)BrCr(CO)$_5$	2072 w (A$_1$), 1994 w (B), 1956 s (E)
(*i*-Pr$_2$N)$_2$PHMo(CO)$_5$	2035 m (A$_1$), 1940 s (E), 1916 w (A$_1$)
i-Pr$_2$NP(H)ClMo(CO)$_5$	2080 m (A$_1$), 2000 m (B), 1962 vs (E), 1925 vw (A$_1$)
i-Pr$_2$NP(H)BrMo(CO)$_5$	2082 m (A$_1$), 2002 m (B), 1967 vs (E), 1928 w (A$_1$)
(*i*-Pr$_2$N)$_2$PHW(CO)$_5$	2033 m (A$_1$), 1935 s (E), 1909 w (A$_1$)
i-Pr$_2$NP(H)ClW(CO)$_5$	2090 m (A$_1$), 1995 m (B), 1955 s (E), 1920 w (A$_1$)
i-Pr$_2$NP(H)BrW(CO)$_5$	2082 m (A$_1$), 2000 m (B), 1958 s (E)
cis-[(*i*-Pr$_2$N)$_2$PH]$_2$W(CO)$_4$	2010 m (A$_1$), 1911 m (A$_1$), 1892 s (B$_1$), 1880 s (B$_2$)
cis-[*i*-Pr$_2$NP(H)Cl]$_2$W(CO)$_4$	2042 m (A$_1$), 1947 m (A$_1$), 1927 s (B$_1$, B$_2$)
(*i*-Pr$_2$N)$_2$PHMn(CO)$_2$Cp	1939 s (A′), 1875 s (A″)
i-Pr$_2$NP(H)ClMn(CO)$_2$Cp	1961 s (A′), 1901 s (A″)
i-Pr$_2$NP(H)(OMe)Mn(CO)$_2$Cp	1947 s (A′), 1882 s (A″)
(MeO)$_2$P(H)Mn(CO)$_2$Cp	1959 s (A′), 1894 s (A″)
MeOP(H)ClMn(CO)$_2$Cp	1976 s (A′), 1962 m (A′), 1918 (A″), 1905 m (A″)
Br$_2$P(H)Mn(CO)$_2$Cp	1989 s (A′), 1936 s (A″)

This procedure could be scaled up to give 32.5 g (54% yield) of (*i*-Pr$_2$N)$_2$PHFe(CO)$_4$ from 58 g (160 mmol) of Fe$_2$(CO)$_9$ and 35 g (150 mmol) of (*i*-Pr$_2$N)$_2$PH in 500 mL of tetrahydrofuran.

(b) From (*i*-Pr$_2$N)$_2$PClFe(CO)$_4$ and LiAlH$_4$. A mixture of 7.4 g (17.0 mmol) of (*i*-Pr$_2$N)$_2$PClFe(CO)$_4$,[4] 1.3 g (34 mmol) of LiAlH$_4$, and 150 mL of diethyl ether was stirred at room temperature for 2 days. Solvent and volatile materials were removed in a vacuum. Sublimation of the dry residue at 60 °C (0.15 mm) gave 1.3 g (20% yield) of yellow (*i*-Pr$_2$N)$_2$PHFe(CO)$_4$.

Preparation of (*i*-Pr$_2$N)$_2$PHCr(CO)$_5$. A mixture of 10.0 g (45.5 mmol) of Cr(CO)$_6$, 10.0 g (43.0 mmol) of (*i*-Pr$_2$N)$_2$PH, and 200 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 90 min in an immersion type photochemical apparatus. Solvent and excess Cr(CO)$_6$ were removed at 25 °C (25 mm) and 30 °C (0.1 mm), respectively, to give 15.5 g (85% yield) of yellow (*i*-Pr$_2$N)$_2$PHCr(CO)$_5$. The analytical sample was purified by sublimation at 75 °C (0.01 mm).

Preparation of (*i*-Pr$_2$N)$_2$PHMo(CO)$_5$. A mixture of 13.2 g (50.0 mmol) of Mo(CO)$_6$, 10.0 g (43.1 mmol) of (*i*-Pr$_2$N)$_2$PH, and 400 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 90 min. Solvent and excess Mo(CO)$_6$ were removed at 25 °C (25 mm) and 40 °C (0.1 mm), respectively, to give 11.0 g (55% yield) of crude (*i*-Pr$_2$N)$_2$PHMo(CO)$_5$. The analytical sample was purified by sublimation at 90 °C (0.01 mm).

Preparation of (*i*-Pr$_2$N)$_2$PHW(CO)$_5$. A solution of 20.0 g (37.3 mmol) of W(CO)$_6$ in 400 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 36 h. The resulting dark yellow solution of (THF)W(CO)$_5$ was treated with 5.0 g (21.6 mmol) of (*i*-Pr$_2$N)$_2$PH. After the mixture was stirred for 1 h, solvent and excess W(CO)$_6$ were removed at 25 °C (25 mm) and 50 °C (0.1 mm), respectively. Sublimation of the dark residue at 100 °C (0.01 mm) gave 9.1 g (76% yield) of yellow crystalline air-stable (*i*-Pr$_2$N)$_2$PHW(CO)$_5$.

Preparation of (*i*-Pr$_2$N)$_2$PHMn(CO)$_2$Cp. A mixture of 5.0 g (24.5 mmol) of CpMn(CO)$_3$, 4.6 g (20.0 mmol) of (*i*-Pr$_2$N)$_2$PH, and 400 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 8 h. Solvent and excess CpMn(CO)$_3$ were then removed at 25 °C (25 mm) and 40 °C (0.1 mm), respectively. The residue was then extracted with pentane. Removal of solvent from the pentane filtrate at 25 °C (25 mm) gave 7.1 g (86% yield) of yellow crystalline air-stable (*i*-Pr$_2$N)$_2$PHMn(CO)$_2$Cp. The analytical sample was purified by sublimation at 90 °C (0.01 mm).

Preparation of *cis*-[(*i*-Pr$_2$N)$_2$PH]$_2$W(CO)$_4$. A mixture of 2.2 g (5.1 mmol) of *fac*-(EtCN)$_3$W(CO)$_3$, 3.8 g (16.4 mmol) of (*i*-Pr$_2$N)$_2$PH, and 150 mL of heptane was boiled under reflux for 40 h. Solvent was removed from the deep colored mixture at 60 °C (25 mm). The black residue was extracted with pentane. Concentration of the filtered pentane extract followed by cooling overnight in a −10 °C freezer gave 1.5 g (52% yield based on CO groups) of air-stable yellow crystalline *cis*-[(*i*-Pr$_2$N)$_2$PH]$_2$W(CO)$_4$. The analytical sample was purified by recrystallization from pentane.

Reactions of (*i*-Pr$_2$N)$_2$PH Metal Carbonyl Complexes with Hydrogen Halides. A solution of 2–12 g of the (*i*-Pr$_2$N)$_2$PH metal carbonyl complex in 300 mL of hexane was treated with a stream of gaseous hydrogen chloride or hydrogen bromide for 10 min. Removal of solvent from the filtered reaction mixture at 25 °C (25 mm) followed by vacuum sublimation gave the corresponding *i*-Pr$_2$NP(H)X metal carbonyl derivatives. Yields and sublimation conditions are given in Table I. The liquid *i*-Pr$_2$NP(H)ClFe(CO)$_4$ was purified by vacuum distillation at 105 °C (0.02 mm).

Reactions of (*i*-Pr$_2$N)$_2$PHCr(CO)$_5$ with Acid Halides. (a) Acetyl Chloride. A solution of 2.0 g (4.7 mmol) of (*i*-Pr$_2$N)$_2$PHCr(CO)$_5$ was boiled under reflux with 1.0 g (12.7 mmol) of acetyl chloride in dichloromethane. Removal of volatile materials at 25 °C (25 mm) followed by pentane extraction gave 0.95 g (56% yield) of yellow *i*-Pr$_2$NP-

Table III. Proton and Phosphorus-31 NMR Spectra of Diisopropylamino Phosphorus Metal Carbonyl Complexes

	^{31}P NMR[a]		^{1}H NMR[b]			
complex	δ(P)	$\lvert {}^1J(\text{P–H})\rvert$	δ(P–H)	δ(C–H)	δ(CH$_3$)	other
(*i*-Pr$_2$N)$_2$PH	42.1	254	5.73 d	3.38 m	1.06 dd (6, 3)	
(*i*-Pr$_2$N)$_2$PHFe(CO)$_4$	93.9	410	7.44 d	3.93 sp (7)	1.27 d (7)	
(*i*-Pr$_2$N)$_2$PHCr(CO)$_5$	91.8	363	7.32 d	3.71 sp (7)	1.25 d (7)	
(*i*-Pr$_2$N)$_2$PHMo(CO)$_5$	67.0	356	7.43 d	3.74 sp (6)	1.25 d (6)	
(*i*-Pr$_2$N)$_2$PHW(CO)$_5$	41.7	359	7.73 d	3.74 sp (7)	1.26 d (7)	$\lvert J(W\text{–}P)\rvert$ = 286 Hz
cis-[(*i*-Pr$_2$N)$_2$PH]$_2$W(CO)$_4$	74.8	359	7.43 d	3.85 sp (7)	1.27 d (7)	$\lvert J(\text{W–P})\rvert$ = 286 Hz
(*i*-Pr$_2$N)$_2$PHMn(CO)$_2$Cp	123.1	381	7.66 d	3.80 sp (7)	1.22 d (7)	Cp 4.41 d (2)
i-Pr$_2$NP(H)ClFe(CO)$_4$	113.3	444	8.35 d	4.02 sp (7)	1.35 d (7), 1.23 d (7)	
i-Pr$_2$NP(H)BrFe(CO)$_4$	93.3	435	7.87 d	4.01 sp (7)	1.37 d (7), 1.24 d (7)	
i-Pr$_2$NP(H)ClCr(CO)$_5$	112.0	376	8.27 d	3.88 sp (7)	1.38 d (7), 1.27 d (7)	
i-Pr$_2$NP(H)BrCr(CO)$_5$	97.3	375	7.86 d	3.80 sp (7)	1.36 d (7), 1.22 d (7)	
i-Pr$_2$NP(H)ClMo(CO)$_5$	83.1	374	8.26 d	3.87 sp (7)	1.37 d (7), 1.22 d (7)	
i-Pr$_2$NP(H)BrMo(CO)$_5$	66.7	366	8.01 d	3.90 sp (7)	1.39 d (7), 1.22 d (7)	
i-Pr$_2$NP(H)ClW(CO)$_5$	50.1	393	8.60 d	3.86 sp (7)	1.35 d (7), 1.23 d (7)	$\lvert J(\text{W–P})\rvert$ = 318 Hz
i-Pr$_2$NP(H)BrW(CO)$_5$	31.0	386	8.35 d	3.89 sp (7)	1.38 d (7), 1.22 d (7)	$\lvert J(\text{W–P})\rvert$ = 317 Hz
cis-[*i*-Pr$_2$NP(H)Cl]$_2$W(CO)$_4$	62.5	393	8.74 d	3.96 sp (7)	1.37 d (7), 1.23 d (7)	$\lvert J(\text{W–P})\rvert$ = 315 Hz
i-Pr$_2$NP(H)ClMn(CO)$_2$Cp	144.2	396	8.58 d	3.88 sp (7)	1.36 d (7), 1.21 d (7)	Cp 4.58 s
Br$_2$P(H)Mn(CO)$_2$Cp	95.4	422	7.89 d			Cp 4.63 d (2)
(MeO)$_2$PHMn(CO)$_2$Cp	229.8	400	8.12 d		3.68 d (12)	Cp 4.58 d (2)
i-Pr$_2$NP(H)(OMe)Mn(CO)$_2$Cp	167.1	396	8.09 d	3.74 sp (7)	1.27 d (7), 1.17 d (7)	Cp 4.52 d (2), MeO 3.40 d (13)
MeOP(H)ClMn(CO)$_2$Cp	212.8	403	8.73 d		3.84 d (14)	Cp 4.66 d (2)

[a] Chemical shifts, δ(P), are given downfield from external 85% H$_3$PO$_4$; coupling constants, $\lvert {}^1J(\text{P–H})\rvert$, are given in Hz. [b] s = singlet, d = doublet, sp = septet, m = multiplet; coupling constants in Hz are given in parentheses.

Table IV. Proton-Decoupled Carbon-13 NMR Spectra of Diisopropylamino Phosphorus Metal Carbonyl Complexes

	$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR[a]			
complex	δ(C≡O)	δ(C—H)	$\delta(\mathrm{CH_3})$	$\delta(\mathrm{C_5H_5})$
$(i\text{-}\mathrm{Pr_2N)_2PH}$		50.6 d (9)	24.1 d (4), 23.9 d (7)	
$(i\text{-}\mathrm{Pr_2N)_2PHFe(CO)_4}$	214.4 d (16)	48.3 d (7)	23.4 d (28)	
$(i\text{-}\mathrm{Pr_2N)_2PHMo(CO)_5}$	207.5 d (15), 206.1 d (10)	49.4 d (9)	23.7 d (31)	
$(i\text{-}\mathrm{Pr_2N)_2PHW(CO)_5}$	199.5 d (25), 197.9 d (7)	49.4 d (9)	23.7 d (31)	
cis-$[(i\text{-}\mathrm{Pr_2N)_2PH]_2W(CO)_4}$	207.2 t (11), 203.2 t (8)	49.5 t (4)	24.2 d (23)	
$(i\text{-}\mathrm{Pr_2N)_2PHMn(CO)_2Cp}$	233.6 d (~30)	47.2 d (7)	23.5 d (29)	81.8 s
$i\text{-}\mathrm{Pr_2NP(H)ClFe(CO)_4}$	211.8 d (19)	49.7	23.0 d (43), 22.3 s	
$i\text{-}\mathrm{Pr_2NP(H)BrFe(CO)_4}$	211.9 d (20)	49.9	21.5 d (28)	
$i\text{-}\mathrm{Pr_2NP(H)BrCr(CO)_5}$	219.7 s, 214.6 d (16)	50.4	21.6 d (54), 20.4 s	
$i\text{-}\mathrm{Pr_2NP(H)ClMo(CO)_5}$	209.3 d (40), 204.0 d (11)	50.5	22.6 d (26), 22.5 d (16)	
$i\text{-}\mathrm{Pr_2NP(H)BrMo(CO)_5}$	207.4 d (~30), 204.1 d (10)	50.6	24.1 d (49), 20.8 s	
$i\text{-}\mathrm{Pr_2NP(H)ClW(CO)_5}$	198.4 d (~40), 195.4 d (7)	50.4	22.6 d (29), 22.5 d (17)	

[a] s = singlet, d = doublet, t = triplet; coupling constants in Hz are given in parentheses.

$\mathrm{(H)ClCr(CO)_5}$ after sublimation at 55 °C (0.01 mm).

Heating 1.0 g of $(i\text{-}\mathrm{Pr_2N)_2PHCr(CO)_5}$ in 15 mL of boiling acetyl chloride for 16 h gave only $i\text{-}\mathrm{Pr_2N(H)ClCr(CO)_5}$ with no evidence for the formation of any $\mathrm{Cl_2PHCr(CO)_5}$.

(b) Trimethylchlorosilane. A mixture of 4.2 g (10.0 mmol) of $(i\text{-}\mathrm{Pr_2N)_2PHCr(CO)_5}$, 2.7 g (25.0 mmol) of trimethylchlorosilane, and 30 mL of hexane was boiled under reflux for 20 h. Removal of volatile materials at 25 °C (25 mm) gave a yellow solid indicated by its NMR spectrum to be unchanged $(i\text{-}\mathrm{Pr_2N)_2PHCr(CO)_5}$.

(c) Phosgene. A solution of 4.2 g (10.0 mmol) of $(i\text{-}\mathrm{Pr_2N)_2PHCr(CO)_5}$ in 100 mL of hexane was treated with gaseous phosgene at room temperature for 2 h and then at the boiling point for 2 h. Removal of solvent at 25 °C (25 mm) gave a yellow solid residue shown by its NMR spectrum to be unchanged $(i\text{-}\mathrm{Pr_2N)_2PHCr(CO)_5}$.

Preparation of $\mathrm{Br_2P(H)Mn(CO)_2Cp}$. A solution of 4.0 g (9.8 mmol) of $(i\text{-}\mathrm{Pr_2N)_2PHMn(CO)_2Cp}$ in 300 mL of pentane was treated with gaseous hydrogen bromide for 10 min. Removal of the solvent from the filtered solution at 25 °C (25 mm) gave 3.4 g (94% yield) of orange air-sensitive solid $\mathrm{Br_2P(H)Mn(CO)_2Cp}$. The analytical sample was purified by sublimation at 50 °C (0.1 mm).

A similar reaction of 1.0 g (2.9 mmol) of $i\text{-}\mathrm{Pr_2NP(H)ClMn(CO)_2Cp}$ in 300 mL of pentane with gaseous hydrogen bromide gave 0.7 g (66% yield) of $\mathrm{Br_2P(H)Mn(CO)_2Cp}$.

Alcoholysis Reactions. (a) $(i\text{-}\mathrm{Pr_2N)_2PHMn(CO)_2Cp}$. A solution of 1.0 g (2.5 mmol) of $(i\text{-}\mathrm{Pr_2N)_2PHMn(CO)_2Cp}$ in 30 mL of methanol was boiled under reflux for 2 days. Removal of volatile materials at 25 °C (25 mm) followed by vacuum distillation gave 0.6 g (72% yield) of yellow liquid $i\text{-}\mathrm{Pr_2NP(H)(OMe)Mn(CO)_2Cp}$, bp 120–130 °C (0.05 mm).

(b) $\mathrm{Br_2P(H)Mn(CO)_2Cp}$. A solution of 1.2 g (3.3 mmol) of $\mathrm{Br_2P(H)Mn(CO)_2Cp}$ in 30 mL of methanol was boiled under reflux for 12 h. Removal of volatile materials from the pale yellow solution followed by vacuum distillation gave 0.5 g (58% yield) of yellow liquid $\mathrm{(MeO)_2PHMn(CO)_2Cp}$, mp 80–90 °C (0.65 mm), which solidified in a −10 °C freezer.

(c) $i\text{-}\mathrm{Pr_2NP(H)ClMn(CO)_2Cp}$. A solution of 0.9 g (2.6 mmol) of $i\text{-}\mathrm{Pr_2NP(H)ClMn(CO)_2Cp}$ in 50 mL of methanol and 10 mL of triethylamine was boiled under reflux for 24 h. Removal of volatile materials at 25 °C (25 mm) followed by vacuum distillation at 100 °C (0.025 mm) gave 0.5 g of a yellow liquid shown by its proton NMR spectrum to be a mixture of $\mathrm{(MeO)_2PHMn(CO)_2Cp}$ and $i\text{-}\mathrm{Pr_2NP(H)(OMe)Mn(CO)_2Cp}$ in a 6:1 mole ratio.

(d) $(i\text{-}\mathrm{Pr_2N)_2PHW(CO)_5}$. A solution of 1.6 g (2.9 mmol) of $(i\text{-}\mathrm{Pr_2N)_2PHW(CO)_5}$ in 50 mL of methanol and 100 mL of *n*-heptane was boiled under reflux for 48 h. Removal of solvent at 25 °C (25 mm) gave a yellow residue shown by its proton NMR spectrum to be unchanged $(i\text{-}\mathrm{Pr_2N)_2PHW(CO)_5}$. The complex $(i\text{-}\mathrm{Pr_2N)_2PHW(CO)_5}$ was also recovered unchanged after boiling in excess isopropanol for 24 h.

Preparation of $\mathrm{MeOP(H)ClMn(CO)_2Cp}$. A solution of 1.5 g (4.4 mmol) of $i\text{-}\mathrm{Pr_2NP(H)(OMe)Mn(CO)_2Cp}$ in 400 mL of pentane was treated with gaseous hydrogen chloride for 10 min. Removal of solvent from the filtered solution followed by vacuum distillation gave 0.6 g (50% yield) of orange liquid $\mathrm{MeOP(H)ClMn(CO)_2Cp}$, bp 100–110 °C (0.04 mm).

Conversion of $(i\text{-}\mathrm{Pr_2N)_2PHFe(CO)_4}$ to $(i\text{-}\mathrm{Pr_2NP)_2COFe_2(CO)_6}$. A mixture of 20 mL of triethylamine and 80 mL of pentane cooled to −78 °C was treated with a solution of 2.9 g (6.0 mmol) of $i\text{-}\mathrm{Pr_2NP(H)ClFe(CO)_4}$ in 20 mL of pentane. The resulting mixture was stirred at room temperature for 10 h. Removal of volatile materials at 25 °C (25 mm) gave an oily residue. Chromatography of a hexane solution of this residue on silica gel gave an orange band. Elution of this orange band with hexane followed by evaporation of the eluate gave 0.3 g (9% yield) of orange $(i\text{-}\mathrm{Pr_2NP)_2COFe_2(CO)_6}$, identified by comparison of its ν(CO) frequencies and phosphorus-31 NMR spectrum with those of authentic $(i\text{-}\mathrm{Pr_2NP)_2COFe_2(CO)_6}$ obtained from $i\text{-}\mathrm{Pr_2NPCl_2}$ and $\mathrm{Na_2Fe(CO)_4}$ according to the published procedure.[7]

Mass Spectra. (a) $(i\text{-}\mathrm{Pr_2N)_2PHFe(CO)_4}$: $\mathrm{[(C_3H_7)_2N]_2PHFe(CO)_4^+}$ (0.4), $\mathrm{[(C_3H_7)_2N]_2PHFe(CO)_3^+}$ (3.4), $\mathrm{[(C_3H_7)_2N]_2PHFe(CO)_2^+}$ (4.1), $\mathrm{[(C_3H_7)_2N]_2PHFeCO^+}$ (22), $\mathrm{(C_3H_7)_2NPHFe(CO)_4^+}$ (3), $\mathrm{[(C_3H_7)_2N]_2PHFe^+}$ (13), $\mathrm{C_3H_7NC_3H_6FeN(C_3H_7)_2^+}$ (100), $\mathrm{(C_3H_7NC_3H_6)_2Fe^+}$ (62), $\mathrm{C_6H_{12}NFeNC_6H_{13}^+}$ (30), $\mathrm{[(C_3H_7)_2N]_2PH^+}$ (27), $\mathrm{(C_3H_7)_2NFe^+}$ (79), $\mathrm{(C_3H_7)_2NPH^+}$ (210), $\mathrm{C_3H_7NPH_2^+}$ (81), $\mathrm{C_3H_7NH^+}$ (58), $\mathrm{C_3H_8^+}$ (385), $\mathrm{C_3H_6^+}$ (250).

(b) $(i\text{-}\mathrm{Pr_2N)_2PHCr(CO)_5}$: $\mathrm{[(C_3H_7)_2N]_2PHCr(CO)_5^+}$ (1.2), $\mathrm{[(C_3H_7)_2N]_2PHCr(CO)_4^+}$ (3.6), $\mathrm{[(C_3H_7)_2N]_2PHCr(CO)_2^+}$ (1.6), $\mathrm{(C_3H_7)_2NPHCr(CO)_5^+}$ (1.2), $\mathrm{[(C_3H_7)_2N]_2PHCrCO^+}$ (27), $\mathrm{C_6H_{12}NCrNC_6H_{13}^+}$ (100), $\mathrm{[(C_3H_7)_2N]_2PH^+}$ (160), $\mathrm{(C_3H_7)_2NPH^+}$ (1300), $\mathrm{C_3H_7NPH_2^+}$ (510), $\mathrm{C_3H_7NH^+}$ (310), $\mathrm{C_3H_8^+}$ (2100), $\mathrm{C_3H_6^+}$ (1300).

(c) $(i\text{-}\mathrm{Pr_2N)_2PHMn(CO)_2Cp}$: $\mathrm{[(C_3H_7)_2N]_2PHMn(CO)_2C_5H_5^+}$ (12), $\mathrm{[(C_3H_7)_2N]_2PHMnC_5H_5^+}$ (35), $\mathrm{(C_3H_7)_2NPHMn(CO)_2,C_5H_5^+}$ (24), $\mathrm{[(C_3H_7)_2N]_2P^+}$ (72), $\mathrm{C_3H_7NC_3H_6MnC_5H_5^+}$ (100), $\mathrm{C_3H_7NPH^+}$ (97), $\mathrm{C_5H_5Mn^+}$ (17), $\mathrm{(C_3H_7)_2N^+}$ (24), $\mathrm{C_6H_{12}N^+}$ (19), $\mathrm{C_3H_7NPH_2^+}$ (39), $\mathrm{Mn^+}$ (15).

(d) $i\text{-}\mathrm{Pr_2NP(H)ClCr(CO)_5}$: $\mathrm{(C_3H_7)_2NP(H)ClCr(CO)_5^+}$ (5), $\mathrm{(C_3H_7)_2NP(H)ClCr(CO)_4^+}$ (1.4), $\mathrm{(C_3H_7)_2NPHCr(CO)_5^+}$ (8.6), $\mathrm{(C_3H_7)_2NP(H)ClCr(CO)_3^+}$ (0.5), $\mathrm{(C_3H_7)_2NPHCr(CO)_4^+}$ (9.5), $\mathrm{(C_3H_7)_2NP(H)ClCr(CO)_2^+}$ (3.6), $\mathrm{(C_3H_7)_2NP(H)ClCrCO^+}$ (16), $\mathrm{(C_3H_7)_2NPHCr(CO)_2^+}$ (7.7), $\mathrm{(C_3H_7)_2NP(H)ClCr^+}$ (100), $\mathrm{[(C_3H_7)_2N]_2PH^+}$ (460), $\mathrm{C_3H_7NPH_2^+}$ (95), $\mathrm{C_3H_8^+}$ (780).

(e) $i\text{-}\mathrm{Pr_2NP(H)ClW(CO)_5^+}$: $\mathrm{(C_3H_7)_2NP(H)ClW(CO)_5^+}$ (4.4), $\mathrm{(C_3H_7)_2NPHW(CO)_5^+}$ (94), $\mathrm{(C_3H_7)_2NPHW(CO)_4^+}$ (13), $\mathrm{C_3H_7NC_3H_6PClW^+}$ (100), $\mathrm{(C_3H_7)_2NPH^+}$ (5000), $\mathrm{(C_3H_7)_2N^+}$ (1800), $\mathrm{C_3H_7NPH_2^+}$ (1000), $\mathrm{C_3H_8^+}$ (5100), $\mathrm{C_3H_6^+}$ (4000).

(f) $i\text{-}\mathrm{Pr_2NP(H)BrCr(CO)_5}$: $\mathrm{(C_3H_7)_2NP(H)BrCr(CO)_5^+}$ (0.4), $\mathrm{(C_3H_7)_2NPHCr(CO)_5^+}$ (13), $\mathrm{(C_3H_7)_2NPHCr(CO)_4^+}$ (6.5), $\mathrm{(C_3H_7)_2NP(H)BrCr^+}$ (12), $\mathrm{(C_3H_7)_2NPHCr(CO)_2^+}$ (2.7), $\mathrm{(C_3H_7)_2NPHCrCO^+}$ (8.8), $\mathrm{(C_3H_7)_2NPHCr^+}$ (18), $\mathrm{(C_3H_7)_2NPH^+}$ (280), $\mathrm{C_3H_7NPH_2^+}$ (67), $\mathrm{C_3H_7NH^+}$ (77), $\mathrm{Cr^+}$ (100), $\mathrm{C_3H_8^+}$ (665), $\mathrm{C_3H_6^+}$ (290).

(g) $i\text{-}\mathrm{Pr_2NP(H)ClMn(CO)_2Cp}$: $\mathrm{(C_3H_7)_2NP(H)ClMn(CO)_2C_5H_5^+}$ (1.5), $\mathrm{(C_3H_7)_2NPHMn(CO)_2C_5H_5^+}$ (6.5), $\mathrm{(C_3H_7)_2NP(H)ClMnC_5H_5^+}$ (1.2), $\mathrm{(C_3H_7)_2NPMnC_5H_5^+}$ (10.3), $\mathrm{C_3H_7NC_3H_6MnC_5H_5^+}$ (3.5), $\mathrm{C_3H_7NPHMnC_5H_5^+}$ (9.4), $\mathrm{C_3H_7NPMnC_5H_5^+}$ (19), $\mathrm{(C_3H_7)_2NPH^+}$ (185), $\mathrm{C_5H_5Mn^+}$ (71), $\mathrm{C_3H_7NPH_2^+}$ (94), $\mathrm{C_3H_7NH^+}$ (74), $\mathrm{Mn^+}$ (100), $\mathrm{C_3H_8^+}$ (500).

(h) $\mathrm{Br_2P(H)Mn(CO)_2Cp}$: $\mathrm{Br_2PHMn(CO)_2C_5H_5^+}$ (9.3), $\mathrm{BrPHMn(CO)_2C_5H_5^+}$ (43), $\mathrm{BrPHMnC_5H_5^+}$ (8.1), $\mathrm{C_5H_5MnBr^+}$ (5.8), $\mathrm{MnBr^+}$ (15), $\mathrm{C_5H_5Mn^+}$ (37), $\mathrm{C_3H_6Mn^+}$ (100), $\mathrm{Mn^+}$ (98), $\mathrm{C_3H_3^+}$ (39).

Results and Discussion

The bis(diisopropylamino)phosphine metal carbonyl complexes were prepared by standard methods involving displacement of relatively weakly bonded tetrahydrofuran or propionitrile from metal carbonyl complexes. The required $\mathrm{(THF)Fe(CO)_4}$ complex was generated from $\mathrm{Fe_2(CO)_9}$ and tetrahydrofuran under ambient conditions[8] whereas $\mathrm{(THF)M(CO)_5}$ (M = Cr, Mo, W) were generated by photochemical methods.[9] Reaction of *fac*-

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[7] King, R. B.; Wu, F.-J.; Sadanani, N. D.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 4449.

[8] Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 3438.

$(EtCN)_3W(CO)_3$ with $(i\text{-}Pr_2N)_2PH$ not only involved displacement of the coordinated propionitrile but redistribution of carbonyl groups to give *cis*-$[(i\text{-}Pr_2N)_2PH]_2W(CO)_4$. Similar redistribution reactions are found in the metal carbonyl chemistry of tris(dimethylamino)phosphine[10] and tris(dimethylamino)arsine[11] and apparently arise from excessive steric hindrance in the hypothetical *fac*-$L_3M(CO)_3$ derivatives from the relatively bulky dialkylamino substituents on the phosphorus ligand L. The iron complex $(i\text{-}Pr_2N)_2PHFe(CO)_4$ was also obtained in modest yield from the $LiAlH_4$ reduction of $(i\text{-}Pr_2N)_2PClFe(CO)_4$.

The bis(diisopropylamino)phosphine metal carbonyl complexes are readily soluble even in saturated hydrocarbon solvents and are air-stable in contrast to the air-sensitive free ligand. Their spectroscopic properties are in accord with the proposed structures. Thus, the patterns of their infrared $\nu(CO)$ frequencies (Table II) correspond to those of similarly substituted metal carbonyl derivatives.[10,12] Their proton-decoupled phosphorus-31 NMR spectra (Table III) exhibit singlet resonances that split into doublets when the proton decoupling is turned off, indicating the large $|^1J(P-H)|$ from the hydrogen directly bonded to the phosphorus. This coupling constant increases from 254 Hz in free $(i\text{-}Pr_2N)_2PH$ to 350–410 Hz in its metal carbonyl complexes; such increases in coupling constants are normal when a trivalent phosphorus atom is complexed to a transition metal.[13] The proton NMR spectra (Table III) exhibit the expected CH_3, CH, and PH resonances with the PH resonance being a widely spaced doublet owing to the large $|^1J(P-H)|$. The PH proton chemical shift of δ 5.73 in free $(i\text{-}Pr_2N)_2PH$ moves downfield by about 2 ppm upon completion with a metal carbonyl group. The proton-decoupled carbon-13 NMR spectra exhibit the expected CH_3, CH, and CO resonances. In the complexes $(i\text{-}Pr_2N)_2PHM(CO)_5$ the resonances of the single CO group trans to the $(i\text{-}Pr_2N)_2PH$ ligand can be distinguished from those of the four equivalent CO groups cis to the $(i\text{-}Pr_2N)_2PH$ ligand. Those corresponding to the trans CO groups (i.e., the resonance at δ 207.5 in $(i\text{-}Pr_2N)_2PHMo(CO)_5$) exhibit larger $|^2J(P-C)|$ coupling constants than those corresponding to the cis CO groups (i.e., the resonance at δ 206.1 in $(i\text{-}Pr_2N)_2PHMo(CO)_5$) in accord with the generally observed[14] larger coupling across trans positions in an octahedral metal complex relative to cis positions. The mass spectra of the $(i\text{-}Pr_2N)_2PH$ metal carbonyl complexes exhibit features similar to the mass spectra of metal carbonyl complexes of tris(dimethylamino)phosphine[15] and tris(dimethylamino)arsine[16] including competitive loss of carbonyl groups and diisopropylamino groups from the parent molecular ion and relatively intense ions clearly having metal–nitrogen bonds such as $C_3H_7NC_3H_6FeN(C_3H_7)_2^+$, $C_6H_{12}NCrNC_6H_{13}^+$, and $C_3H_7NC_3H_6MnC_5H_5^+$ in the mass spectra of $(i\text{-}Pr_2N)_2PHFe(CO)_4$, $(i\text{-}Pr_2N)_2PHCr(CO)_5$, and $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$, respectively.

The most important chemical property of the bis(diisopropylamino)phosphine metal carbonyl complexes is the rapid and selective cleavage of one diisopropylamino group with hydrogen halides according to the general equation (X = Cl, Br)

$$(i\text{-}Pr_2N)_2PHM(CO)_n + 2HX \rightarrow i\text{-}Pr_2NP(H)XM(CO)_n + [i\text{-}Pr_2NH_2]X \quad (1)$$

The resulting products are metal carbonyl complexes of the unknown $i\text{-}Pr_2NP(H)X$ ligands and contain potentially reactive P–X bonds for further chemical transformations. A similar conversion of $(i\text{-}Pr_2N)_2PHCr(CO)_5$ to $i\text{-}Pr_2NP(H)ClCr(CO)_5$ can be effected with acetyl chloride but not with trimethylchlorosilane or phosgene, at least under the conditions given in the Experimental Section. The only observed example of the cleavage of *both* diisopropylamino groups from a bis(diisopropylamino)phosphine metal carbonyl complex is the reaction of $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ with HBr to give $Br_2P(H)Mn(CO)_2Cp$ according to

$$(i\text{-}Pr_2N)_2PHMn(CO)_2Cp + 4HBr \rightarrow Br_2P(H)Mn(CO)_2Cp + 2[i\text{-}Pr_2NH_2]Br \quad (2)$$

Reaction of $i\text{-}Pr_2NP(H)ClMn(CO)_2Cp$ with hydrogen bromide also gives $Br_2P(H)Mn(CO)_2Cp$ rather than the mixed-halogen compound $BrClP(H)Mn(CO)_2Cp$. Phosphorus–nitrogen cleavage reactions with hydrogen halides such as the above reactions (eq 1 and 2) are frequently found in the chemistry of (dialkylamido)phosphorus derivatives.[17-23]

The three important features of the reactions of $(i\text{-}Pr_2N)_2PH$ metal carbonyl complexes with hydrogen halides to give the corresponding $i\text{-}Pr_2NP(H)X$ metal carbonyl complexes are retention of the phosphorus–hydrogen bond, an increase in the π-acceptor strength of the organophosphorus ligand, and a decrease of the effective symmetry around the phosphorus and transition-metal atoms. The retention of the phosphorus–hydrogen bond is indicated by the observation of PH resonances in the proton NMR spectra of the $i\text{-}Pr_2NP(H)X$ metal carbonyl derivatives and doublet phosphorus-31 NMR spectra run without proton decoupling (Table III); the $|^1J(P-H)|$ coupling constant increases upon conversion of a $(i\text{-}Pr_2N)_2PH$ metal carbonyl complex to the corresponding $i\text{-}Pr_2NP(H)X$ derivative. The increase in π-acceptor strength of $i\text{-}Pr_2NP(H)X$ ligands relative to $(i\text{-}Pr_2N)_2PH$ is reflected by an increase in the $\nu(CO)$ frequencies in otherwise analogous complexes, typically by about 20 cm^{-1} (Table II). In addition the $|^1J(W-P)|$ coupling constants of 286 Hz in the tungsten carbonyl complexes of $(i\text{-}Pr_2N)_2PH$ (i.e., $(i\text{-}Pr_2N)_2PHW(CO)_5$ and *cis*-$[(i\text{-}Pr_2N)_2PH]_2W(CO)_4$) increase to 315–318 Hz in the tungsten carbonyl complexes of $i\text{-}Pr_2NP(H)X$ (i.e., $i\text{-}Pr_2NP(H)XW(CO)_5$ (X = Cl, Br) and *cis*-$[i\text{-}Pr_2NP(H)Cl]_2W(CO)_4$) in accord with the previously observed[24-26] relationship between $|^1J(W-P)|$ and π-acceptor strength. The reduction of effective symmetry around the phosphorus atom in going from $(i\text{-}Pr_2N)_2PH$ to corresponding $i\text{-}Pr_2NP(H)X$ (X = Cl, Br) complexes is reflected in the following spectroscopic observations: (1) The methyl resonances of the isopropyl groups in the $(i\text{-}Pr_2N)_2PH$ metal carbonyl complexes exhibit a single doublet around δ 1.3 (J = 7 Hz) whereas the methyl resonances of the isopropyl groups in the $i\text{-}Pr_2NP(H)X$ (X = Cl, Br) metal carbonyl complexes exhibit two such doublets of equal relative intensities (Table III). (2) The B_1 mode, which is infrared inactive in ideal C_{4v} symmetry,[27] appears as a weak band around 2000 cm^{-1} in the $\nu(CO)$ infrared spectra of the $i\text{-}Pr_2NP(H)XM(CO)_5$ complexes (X = Cl, Br; M = Cr, Mo, W) but not in those of the corresponding $(i\text{-}Pr_2N)_2PHM(CO)_5$ complexes; a similar effect has been documented in $RM(CO)_5$ (M = Mn, Re) derivatives depending upon the symmetry of the R group.[27]

The mass spectra of several of the $i\text{-}Pr_2NP(H)X$ metal carbonyl complexes were determined. In general, halogen loss from the molecular ion was found to be competitive with carbonyl loss leading to ions of the type $i\text{-}Pr_2NP(H)M(CO)_n^+$ (e.g., M = Cr, n = 5, 4, 2, 1, 0; M = W, n = 5, 4), which are formally phosphenium ion metal carbonyl complexes similar to isolated species

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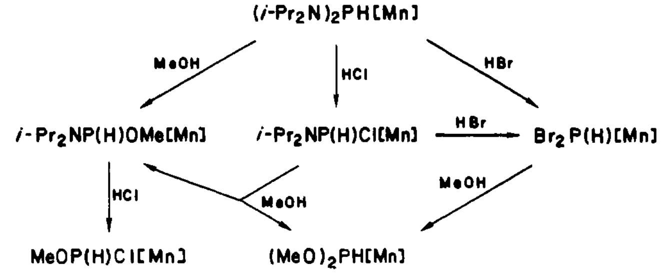
such as $[(i\text{-}Pr_2N)_2PFe(CO)_4]^+$.[4]

A characteristic reaction of the free ligand $(i\text{-}Pr_2N)_2PH$ is its facile alcoholysis, even under ambient conditions, to give $(i\text{-}Pr_2N)(RO)PH$ derivatives.[2] Such reactivity toward alcohols is greatly reduced upon complexation with metal carbonyl fragments. Thus, $(i\text{-}Pr_2N)_2PHW(CO)_5$ is unreactive toward a large excess of methanol in boiling heptane or toward a large excess of boiling isopropanol. However, $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ is more reactive toward alcohols just as it is toward hydrogen bromide, as noted above. Thus, reaction of $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ with boiling methanol for 2 days gives $i\text{-}Pr_2NP(H)(OMe)Mn(CO)_2Cp$ with no evidence for the formation of any $(MeO)_2PHMn(CO)_2Cp$. However, $(MeO)_2PHMn(CO)_2Cp$ can readily be obtained by reaction of $Br_2P(H)Mn(CO)_2Cp$ with methanol in accord with the expected greater reactivity of phosphorus–halogen bonds relative to phosphorus–nitrogen bonds.

Reactions with HX (X = Cl, Br) and methanol can be applied to $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ in various sequences according to the scheme ([Mn] = $Mn(CO)_2Cp$)

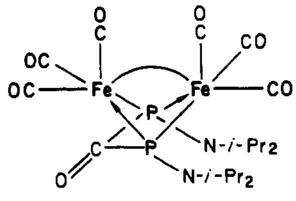


This provides a source of $Mn(CO)_2Cp$ derivatives of a variety of trivalent phosphorus ligands, most of which are not available in the uncomplexed state. The $\nu(CO)$ frequencies (Table II) suggest that the π-acceptor strengths of the trivalent phosphorus ligands in the above series of complexes increase in the sequence

$$(i\text{-}Pr_2N)_2PH < i\text{-}Pr_2NP(H)OMe < (MeO)_2PH < i\text{-}Pr_2NP(H)Cl < MeOP(H)Cl < Br_2PH$$

This sequence covers examples of all distinct combinations of a PH group bonding to R_2N, RO, and X substituents and is consistent with the expected sequence $R_2N < RO < X$ in affecting the π-acceptor strength of a trivalent phosphorus atom bearing these substituents. The infrared $\nu(CO)$ spectrum of $MeOP(H)ClMn(CO)_2Cp$ is also of interest in showing two pairs of $\nu(CO)$ frequencies, suggesting the presence of two conformers similar to that observed in 1967 for complexes of similar stereochemistry such as $MeSiCl_2Fe(CO)_2Cp$.[28] Note that an Mn–P unit is isoelectronic with an Fe–Si unit.

The reactivity of the phosphorus–halogen bonds in the $i\text{-}Pr_2NP(H)X$ complexes toward nucleophiles provides potential routes to new types of organophosphorus metal carbonyl derivatives. Dehydrohalogenation of $i\text{-}Pr_2NP(H)X$ complexes thus provides a potential route to phosphinidene complexes containing the $i\text{-}Pr_2NP$ ligand. In this connection the reaction of $i\text{-}Pr_2NP(H)ClFe(CO)_4$ with a large excess of triethylamine gives an orange crystalline solid of stoichiometry $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, which formally is $Fe_2(CO)_9$ with two of the three bridging carbonyl groups replaced by the $i\text{-}Pr_2NP$ phosphinidene ligand; such a product might be an expected decarbonylation product of a mononuclear $i\text{-}Pr_2NPFe(CO)_4$ complex formed by dehydrochlorination of $i\text{-}Pr_2NP(H)ClFe(CO)_4$. However, the spectroscopic properties (infrared and phosphorus-31 NMR) of this $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ complex indicate it to be the phosphorus-bridging carbonyl derivative I recently characterized structurally[7] as an unexpected product from the reaction of $Na_2Fe(CO)_4$ with $i\text{-}Pr_2NPCl_2$.



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Registry No. $(i\text{-}Pr_2N)_2PHFe(CO)_4$, 93582-14-0; $(i\text{-}Pr_2N)_2PHCr(CO)_5$, 93582-11-7; $(i\text{-}Pr_2N)_2PHMo(CO)_5$, 93582-12-8; $(i\text{-}PrN)_2PHW(CO)_5$, 93582-13-9; *cis*-$[(i\text{-}Pr_2N)_2PH]_2W(CO)_5$, 102211-18-7; $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$, 93612-14-7; $i\text{-}Pr_2NP(H)ClFe(CO)_4$, 93582-18-4; $i\text{-}Pr_2NP(H)BrFe(CO)_4$, 102211-19-8; $i\text{-}Pr_2NP(H)ClCr(CO)_5$, 93582-15-1; $i\text{-}Pr_2NP(H)BrCr(CO)_5$, 97825-66-6; $i\text{-}Pr_2NP(H)ClMo(CO)_5$, 93582-16-2; $i\text{-}Pr_2NP(H)BrMo(CO)_5$, 102211-20-1; $i\text{-}Pr_2NP(H)ClW(CO)_5$, 93582-17-3; $i\text{-}Pr_2NP(H)BrW(CO)_5$, 102211-21-2; *cis*-$[i\text{-}Pr_2NP(H)Cl]_2W(CO)_4$, 102211-22-3; $i\text{-}Pr_2NP(H)ClMn(CO)_2Cp$, 97825-74-6; $Br_2P(H)Mn(CO)_2Cp$, 102211-23-4; $(MeO)_2PHMn(CO)_2Cp$, 102211-24-5; $i\text{-}Pr_2NP(H)(OMe)Mn(CO)_2Cp$, 102211-25-6; $MeOP(H)ClMn(CO)_2Cp$, 102211-26-7; $Fe_2(CO)_9$, 15321-51-4; $(i\text{-}Pr_2N)_2PClFe(CO)_4$, 78939-95-4; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $CpMn(CO)_3$, 12079-65-1; *fac*-$(EtCN)_3W(CO)_3$, 83732-33-6; $(i\text{-}Pr_2N)_2PH$, 86660-77-7; HCl, 7647-01-0; HBr, 10035-10-6; CH_3OH, 67-56-1; $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, 99495-63-3; Br_2PH, 15176-93-9; $i\text{-}Pr_2NP(H)Cl$, 93696-28-7; acetyl chloride, 75-36-5; trimethylchlorosilane, 75-77-4; phosgene, 75-44-5.

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