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Dialkylamino Phosphorus Metal Carbonyls. 2. Bis(diisopropylamino)phosphido and (Diisopropylamino)phosphinidene Metal Carbonyl Complexes from Reactions of Manganese and Cobalt Carbonyls with Bis(diisopropylamino)phosphine[1–3]

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Photolysis of $(i\text{-Pr}_2\text{N})_2\text{PH}$ with $\text{Mn}_2(\text{CO})_{10}$ in tetrahydrofuran solution gives yellow air-stable sublimable $[\mu\text{-}(i\text{-Pr}_2\text{N})_2\text{P}](\mu\text{-H})\text{Mn}_2(\text{CO})_8$, shown by X-ray diffraction (monoclinic space group $P2_1/a$; $a = 14.662$ (4) Å, $b = 17.644$ (10) Å, $c = 10.071$ (4) Å, $\beta = 91.27$ (3)°, $Z = 4$) to have a structure in which an Mn–Mn bond (2.916 (2) Å) is bridged symmetrically by both a hydrogen and a bis(diisopropylamino)phosphido group. One of the two diisopropylamino groups is selectively cleaved from this complex with the hydrogen halides, HX (X = Cl, Br), to give the corresponding complex $(\mu\text{-}i\text{-Pr}_2\text{NPX})(\mu\text{-H})\text{Mn}_2(\text{CO})_8$ shown by its infrared ν(CO) and NMR spectra to have an analogous structure. Reaction of $(i\text{-Pr}_2\text{N})_2\text{PH}$ with $\text{Co}_2(\text{CO})_8$ in hexane at ambient temperature gives a complex mixture of relatively unstable products from which paramagnetic (2.0 μ_B) black, air-sensitive crystalline $(\mu_3\text{-}i\text{-Pr}_2\text{NP})\text{Co}_3(\text{CO})_9$ can be isolated after chromatography on silica gel. X-ray diffraction of this complex (monoclinic space group *Cc*; $a = 14.416$ (7) Å, $b = 10.000$ (5) Å, $c = 15.411$ (6) Å, $\beta = 103.84$ (3)°, $Z = 4$) indicates the expected structure having a PCo_3 tetrahedron with an average Co–Co distance of 2.712 (2) Å and an average Co–P distance of 2.135 (4) Å.

Introduction

The previous paper of this series[1] discussed reactions of bis(diisopropylamino)phosphine, $(i\text{-Pr}_2\text{N})_2\text{PH}$, with the mononuclear metal carbonyl derivatives $(\text{THF})\text{M}(\text{CO})_n$ ($n = 4$, M = Fe; $n = 5$, M = Cr, Mo, W), $(\text{THF})\text{Mn}(\text{CO})_2\text{Cp}$, and *fac*-$(\text{EtCN})_3\text{W}(\text{CO})_3$ to give the corresponding mononuclear $(i\text{-Pr}_2\text{N})_2\text{PH}$ metal carbonyl complexes. This paper describes reactions of $(i\text{-Pr}_2\text{N})_2\text{PH}$ with the metal–metal-bonded binuclear metal carbonyl derivatives $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$. Such reactions follow a different course, giving the binuclear bis(diisopropylamino)phosphido metal carbonyl hydride $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$ in the case of $\text{Mn}_2(\text{CO})_{10}$ and the trinuclear μ_3-diisopropylaminophosphinidene metal carbonyl complex $i\text{-Pr}_2\text{NPCo}_3(\text{CO})_9$ in the case of $\text{Co}_2(\text{CO})_8$. The structures of these two complexes have been determined by X-ray diffraction.

Experimental Section

The general techniques for microanalyses, infrared spectra (Table I), NMR spectra (Table I), melting points, solvent purification, and inert-atmosphere handling are similar to those given in the first paper of this series.[1] Commercial $\text{MeC}_5\text{H}_4\text{Mn}(\text{CO})_3$ (Ethyl Corp.) was converted to $\text{Mn}_2(\text{CO})_{10}$ by the published procedure,[4] and $\text{Co}_2(\text{CO})_8$ was purchased from Pressure Chemical Co., Pittsburgh, PA.

Preparation of $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$. A mixture of 2.0 g (5.1 mmol) of $\text{Mn}_2(\text{CO})_{10}$, 1.2 g (4.3 mmol) of $(i\text{-Pr}_2\text{N})_2\text{PH}$,[5] and 150 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 60 min in an immersion-type photochemical apparatus. Solvent and excess $\text{Mn}_2(\text{CO})_{10}$ were removed at 25 °C (25 mm) and 60 °C (0.1 mm), respectively. Sublimation of the red-brown residue at 100 °C (0.001 mm) gave 1.5 g (51% yield) of yellow air-stable $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$, mp 130 °C; infrared ν(CO) frequencies and proton and phosphorus-31 NMR spectra are listed in Table I. Proton-decoupled carbon-13 NMR in CDCl_3: CO not observed; CH at δ 54.3 ($J = 4$ Hz); CH_3 at δ 24.5. Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{Mn}_2\text{N}_2\text{O}_8\text{P}$: C, 42.4; H, 5.2; N, 4.7. Found: C, 42.6; H, 5.2; N, 4.9. The sample for X-ray crystallography was obtained by crystallization from pentane.

Preparation of $(i\text{-Pr}_2\text{NPCl})\text{Mn}_2(\text{CO})_8\text{H}$. A solution of 3.2 g (5.7 mmol) of $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$ in 300 mL of hexane was treated with hydrogen chloride gas for 10 min. Removal of solvent from the filtered orange solution at 25 °C (25 mm) gave 2.56 g (90% yield) of crude $(i\text{-Pr}_2\text{NPCl})\text{Mn}_2(\text{CO})_8\text{H}$. Recrystallization of the crude product from pentane gave 1.8 g (63% yield) of air-stable orange $(i\text{-Pr}_2\text{NPCl})\text{Mn}_2(\text{CO})_8\text{H}$, mp 100 °C dec. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{ClMn}_2\text{NO}_8\text{P}$: C, 33.5; H, 3.0; N, 2.8; Cl, 7.1. Found: C, 33.6; H, 3.0; N, 2.8; Cl, 7.1.

Preparation of $(i\text{-Pr}_2\text{NPBr})\text{Mn}_2(\text{CO})_8\text{H}$. A solution of 2.6 g (4.6 mmol) of $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$ in 300 mL of hexane was treated with hydrogen bromide gas for 10 min. Removal of solvent from the filtrate at 25 °C (25 mm) gave an orange residue. Crystallization of this residue from pentane gave 1.7 g (69% yield) of orange air-stable crystalline $(i\text{-Pr}_2\text{NPBr})\text{Mn}_2(\text{CO})_8\text{H}$, mp 110 °C dec. Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{BrMn}_2\text{NO}_8\text{P}$: C, 30.8; H, 2.8; N, 2.6; Br, 14.6. Found: C, 30.4; H, 2.8; N, 2.4; Br, 13.6.

Isolation of $i\text{-Pr}_2\text{NPCo}_3(\text{CO})_9$. A mixture of 3.4 g (10.0 mmol) of $\text{Co}_2(\text{CO})_8$, 1.6 g (6.7 mmol) of $(i\text{-Pr}_2\text{N})_2\text{PH}$,[5] and 100 mL of hexane was stirred for 5 days at room temperature. Solvent was removed at 25 °C (25 mm). The residue was dissolved in 30 mL of dichloromethane to give a deep black solution. About 10 g of 60–200 mesh silica gel was added to this solution followed by removal of the solvent at 25 °C (25 mm). The dry brown solid was placed at the top of a chromatography column packed with silica gel. Elution with pentane gave a deep green solution, which was collected under nitrogen. Removal of the solvent at 25 °C (25 mm) gave a deeply colored residue, which was dried at 25 °C (0.1 mm). This residue was dissolved in a minimum amount of pentane and kept at −10 °C for several days to give 0.3 g (7% yield based on $(i\text{-Pr}_2\text{N})_2\text{PH}$) of black, air-sensitive, crystalline $i\text{-Pr}_2\text{NPCo}_3(\text{CO})_9$. Infrared ν(CO) in pentane: 2085 (w), 2030 (s), 2000 (w) cm^{-1}. Magnetic moment: $\mu_{\text{eff}} = 2.0\ \mu_B$ (Faraday balance with $\text{HgCo}(\text{SCN})_4$ standard). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{Co}_3\text{NO}_9\text{P}$: C, 32.1; H, 2.5; N, 2.5. Found: C, 32.2; H, 3.2; N, 2.8. An attempt to sublime $i\text{-Pr}_2\text{NPCo}_3(\text{CO})_9$ at 40 °C (0.01 mm) led to extensive decomposition. The sample for X-ray crystallography was obtained by crystallization from pentane.

X-ray Structure Determinations (Table II). The solid materials used for X-ray diffraction were blocks of less than 0.25 mm in any dimension cleaved from larger crystals. These blocks were sealed in capillaries and mounted on a Syntex P3 automated diffractometer located at Oklahoma State University. Unit cell dimensions (Table II) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). The data were collected at room temperature with a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below Kα_1 and 1.2° above Kα_2 to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. Since the intensities of three standard reflections showed less than 8% variation, corrections for decomposition were considered unnecessary. Data were corrected for Lorentz, polarization, and background effects. Corrections for absorption were not made. The structures were solved by direct methods using MULTAN80. Refinements of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms were carried out to convergence. In the final stages of refinement a weight equal to $1/\sigma(F)$ was applied.

(a) $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$ (Figure 1). After removal of redundant and space group forbidden data from the 7211 collected data points, 1880

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(1) Part 1: King R. B.; Fu, W.-K. *Inorg. Chem.*, preceding paper in this issue.

(2) For a preliminary communication on this work see: King, R. B.; Fu, W.-K.; Holt, E. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1439.

(3) 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.

(4) King, R. B.; Stokes, J. C.; Korenowski, T. F. *J. Organomet. Chem.* **1968**, *11*, 641.

(5) King, R. B.; Sundaram, P. M. *J. Org. Chem.* **1984**, *49*, 1784.

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Table I. Spectroscopic Properties of (μ-*i*-$Pr_2NPX)Mn_2(CO)_8$ Derivatives

compd	IR ν(CO), cm^{-1}	^{1}H NMR^a			^{31}P NMR
		δ(C–H)	$\delta(CH_3)$	δ(Mn–H)	
X = *i*-Pr_2N	2084 w, 2052 m, 2000 s, 1993 m, 1962 s	4.40 m (7)	1.39 d (7)	–15.1 d (35)	292.8 br
X = Cl	2096 w, 2068 m, 2022 m, 2010 s, 1975 s	4.3 br	1.4 br	–16.5	305.1 br
X = Br	2097 w, 2069 m, 2020 m, 2010 s, 1978 s	4.25	1.5	–16.25 d (30)	306.9 br
$Ph_2PMn_2(CO)_8H$	2093 m, 2064 m, 2011 s, 2000 m, 1966 s^b			–16.18 d (36)^b	

^{a}d = doublet, m = multiplet, br = broad: coupling constants in Hz are given in parentheses. ^{b}Data of: Iggo, J. A.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1983**, 205.

Table II. Crystallographic and Data Collection Parameters

formula	$Mn_2PO_8N_2C_{20}H_{29}$	$Co_3PO_9NC_{15}H_{14}$
mol wt	566.3	546.05
cryst syst	monoclinic	monoclinic
space group	$P2_1/a$	Cc
a, Å	14.662 (4)	14.416 (7)
b, Å	17.644 (10)	10.000 (5)
c, Å	10.071 (4)	15.411 (6)
β	91.27 (3)	103.84 (3)
V, Å^3	2604.7 (19)	2157.0 (17)
F(000)	1168	1092
μ(Mo Kα), cm^{-1}	10.33	24.43
D_{calcd}, g cm^{-3}	1.444	1.684
Z	4	4
no. of obsd reflcns	1880	1851
octants collcd	$\pm h,+k,+l$	$\pm h,+k,+l$
R/R_w	0.057/0.075	0.042/0.052
cryst dimens, mm	0.15 × 0.2 × 0.25	0.2 × 0.2 × 0.2

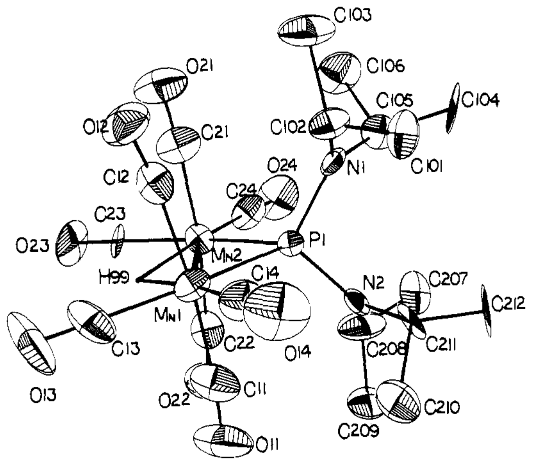

Figure 1. ORTEP diagram of the complex $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$.

reflections were considered observed $[I > 3.0\sigma(I)]$. After solution and refinement of the parameters of all non-hydrogen atoms to convergence, hydrogen positional parameters (supplementary material) were determined from a difference Fourier synthesis. These hydrogen positional parameters were included in the final cycles of refinement. The hydrogen atoms were assigned isotropic thermal parameters of $U = 0.03$. All parameters associated with hydrogen atoms were held invariant. The final cycle of refinement [function minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor of $R = 5.7\%$ $[R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100]$. Anomalous dispersion corrections were made for manganese. Scattering factors were taken from Cromer and Mann.[6] Positional parameters are given in Table III and bond distances and angles in Table IV.

(b) *i*-$Pr_2NPCo_3(CO)_9$ (Figure 2). Among the 2363 collected, independent, space group permitted points, 1851 reflections were considered observed $[I > 3.0\sigma(I)]$. The choice of the acentric space group *Cc* rather than the centric modification *C*2/*c* is justified by the geometry of the cluster. A *Z* of 4 in the centric cell would dictate a center of symmetry or a twofold axis internal to the cluster. Figure 2 indicates the lack of either possible symmetry element. After solution and refinement of the parameters of all non-hydrogen atoms to convergence, hydrogen positional parameters were not apparent from a difference Fourier synthesis. The final cycle of refinement led to a final agreement factor of $R = 4.2\%$. Anomalous dispersion corrections were made for cobalt. Scattering factors were taken from Cromer and Mann.[6] Unit weights were used throughout. Positional parameters are given in Table V and bond distances and angles in Table VI.

Table III. Positional Parameters for $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$

atom	*x* ($\sigma(x)$)	*y* ($\sigma(y)$)	*z* ($\sigma(z)$)
Mn1	0.6488 (1)	0.4856 (1)	0.7076 (2)
Mn2	0.8408 (1)	0.4677 (1)	0.7704 (2)
P1	0.7547 (2)	0.5788 (2)	0.7616 (2)
N1	0.7338 (6)	0.6296 (6)	0.9032 (7)
N2	0.7874 (6)	0.6451 (6)	0.6453 (8)
O11	0.6958 (7)	0.5004 (7)	0.4190 (8)
O12	0.5876 (6)	0.4420 (6)	0.9810 (9)
O13	0.5546 (9)	0.3408 (9)	0.6380 (12)
O14	0.4891 (6)	0.5864 (7)	0.6805 (10)
O21	0.7907 (6)	0.4444 (7)	1.0563 (8)
O22	0.8973 (7)	0.4571 (7)	0.4850 (8)
O23	0.9090 (10)	0.3072 (9)	0.7711 (11)
O24	1.0141 (7)	0.5417 (7)	0.8369 (10)
C11	0.6790 (8)	0.4977 (10)	0.5287 (12)
C12	0.6129 (8)	0.4624 (9)	0.8817 (12)
C13	0.5912 (10)	0.3939 (12)	0.6627 (13)
C14	0.5512 (8)	0.5476 (9)	0.6908 (11)
C21	0.8083 (8)	0.4559 (9)	0.9495 (11)
C22	0.8732 (8)	0.4651 (9)	0.5919 (12)
C23	0.8827 (10)	0.3666 (13)	0.7723 (12)
C24	0.9477 (9)	0.5124 (9)	0.8115 (11)
C101	0.5912 (10)	0.7057 (10)	0.9429 (13)
C102	0.6412 (8)	0.6345 (8)	0.9670 (10)
C103	0.6448 (9)	0.6170 (10)	1.1174 (11)
C104	0.7934 (11)	0.7542 (12)	0.9889 (15)
C105	0.8120 (8)	0.6743 (11)	0.9536 (11)
C106	0.8618 (10)	0.6358 (10)	1.0654 (13)
C207	0.9442 (10)	0.7060 (10)	0.6316 (14)
C208	0.8802 (8)	0.6450 (8)	0.5847 (10)
C209	0.8790 (10)	0.6487 (9)	0.4311 (12)
C210	0.6677 (11)	0.6913 (10)	0.4851 (14)
C211	0.7191 (10)	0.7034 (11)	0.6134 (11)
C212	0.7555 (14)	0.7856 (14)	0.6239 (17)

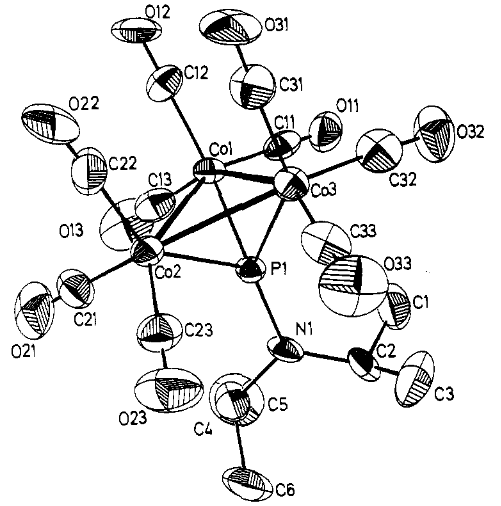

Figure 2. ORTEP diagram of the complex *i*-$Pr_2NPCo_3(CO)_9$.

Results and Discussion

(A) Manganese Carbonyl Derivatives. Ultraviolet irradiation of $(i\text{-}Pr_2N)_2PH$ with $Mn_2(CO)_{10}$ in tetrahydrofuran gives a yellow

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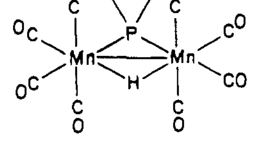
[6] Cromer, D. T.; Mann, I. B. *Acta Crystallogr. Sect. A: Cryst. Phys. Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

Table IV. Bond Distances (Å) and Angles (deg) for $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$

Mn1–Mn2	2.916 (2)	N2–C211	1.48 (2)
Mn1–P1	2.334 (4)	C101–C102	1.48 (2)
Mn2–P1	2.335 (4)	C102–C103	1.55 (2)
Mn1–C11	1.895 (12)	C104–C105	1.48 (3)
Mn1–C12	1.865 (12)	C105–C106	1.52 (2)
Mn1–C13	1.891 (20)	C207–C208	1.51 (2)
Mn1–C14	1.812 (14)	C208–C209	1.55 (2)
Mn1–H99	1.926 (2)	C210–C211	1.52 (2)
Mn2–C21	1.866 (11)	C211–C212	1.55 (3)
Mn2–C22	1.850 (12)	C11–O11	1.13 (1)
Mn2–C23	1.887 (22)	C12–O12	1.12 (2)
Mn2–C24	1.811 (14)	C13–O13	1.10 (2)
Mn2–H99	1.823 (2)	C14–O14	1.15 (2)
P1–N1	1.716 (10)	C21–O21	1.12 (1)
P1–N2	1.706 (9)	C22–O22	1.13 (2)
N1–C102	1.49 (1)	C23–O23	1.12 (3)
N1–C105	1.49 (2)	C24–O24	1.14 (2)
N2–C208	1.48 (1)		

Mn1–H99–Mn2	102.1 (1)	Mn2–C23–O23	178.3 (13)
Mn1–P1–Mn2	77.3 (1)	Mn2–C24–O24	178.7 (16)
Mn1–P1–N1	117.2 (3)	C11–Mn1–C12	173.3 (7)
Mn1–P1–N2	119.9 (3)	C11–Mn1–C13	88.1 (6)
Mn2–P1–N1	119.9 (3)	C11–Mn1–C14	90.7 (6)
Mn2–P1–N2	117.0 (4)	C11–Mn1–H99	85.9 (4)
P1–N1–C102	122.4 (7)	C12–Mn1–C14	90.7 (5)
P1–N1–C105	115.9 (7)	C12–Mn1–P1	96.4 (4)
P1–N2–C108	121.5 (8)	C12–Mn1–H99	92.0 (4)
P1–N2–C111	116.3 (8)	C13–Mn1–C14	97.5 (7)
C102–N1–C105	121.5 (9)	C13–Mn1–P1	165.1 (5)
C108–N2–C111	122.2 (10)	C13–Mn1–H99	76.4 (3)
N1–P1–C111	104.8 (5)	C14–Mn1–P1	97.3 (5)
N1–C102–C101	115.4 (11)	C14–Mn1–H99	173.9 (4)
N1–C102–C103	111.1 (9)	P1–Mn1–H99	88.8 (1)
C101–C102–C103	111.0 (11)	C21–Mn2–C22	172.2 (7)
N1–C105–C104	116.6 (11)	C21–Mn2–C23	87.8 (6)
N1–C105–C106	113.8 (13)	C21–Mn2–C24	91.8 (5)
C104–C105–C106	109.7 (12)	C21–Mn2–P1	90.2 (4)
N2–C208–C207	116.3 (11)	C21–Mn2–H99	94.8 (4)
N2–C208–C207	112.4 (9)	C22–Mn2–C23	84.8 (6)
C207–C208–C209	107.6 (11)	C22–Mn2–C24	91.6 (5)
N2–C211–C210	115.9 (13)	C22–Mn2–P1	96.4 (4)
N2–C211–C212	113.7 (12)	C22–Mn2–H99	81.0 (4)
C210–C211–C212	111.5 (14)	C23–Mn2–C24	97.2 (7)
Mn1–C11–O11	175.6 (15)	C23–Mn2–P1	166.1 (5)
Mn1–C12–O12	173.0 (13)	C23–Mn2–H99	75.2 (5)
Mn1–C13–O13	178.6 (14)	C24–Mn2–P1	96.6 (5)
Mn1–C14–O14	179.6 (17)	C24–Mn2–H99	169.8 (4)
Mn2–C21–O21	175.8 (14)	P1–Mn2–H99	91.3 (1)
Mn2–C22–O22	173.4 (13)		

air-stable sublimable solid that analyzed (C, H, N) approximately as expected for the substitution product $(i\text{-}Pr_2N)_2PHMn_2(CO)_9$, a binuclear version of the mononuclear derivatives $(i\text{-}Pr_2N)_2PHM(CO)_n$ ($n = 4$, M = Fe; $n = 5$, M = Cr, Mo, W) discussed in the first paper of this series.[1] However, the X-ray structure determination (Figure 1) of this manganese carbonyl complex indicates the formula $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$ and structure I (X = Y = i-Pr_2N) similar to a previously reported[7]



I

structure for $(C_6H_5)_2PMn_2(CO)_8H$ (I: X = Y = C_6H_5). Thus, in $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$ the two manganese tetracarbonyl groups are bridged by both a bis(diisopropylamino)phosphido group and a hydrogen (Mn–P = 2.334 (4) and 2.335 (4) Å; Mn–H = 1.926 (2) and 1.823 (2) Å); these bridges may be regarded as symmetrical after allowing for the expected uncertainties in the determination of hydrogen positions by X-ray diffraction. The Mn–Mn distance of 2.916 (2) Å indicates the metal–metal bond required to give each manganese atom the rare-gas configuration. These bond distances are close to the Mn–Mn bond distance of 2.937 (5) Å and the Mn–P bond distances of 2.284 (6) Å found in $(C_6H_5)_2PMn_2(CO)_8H$.[7] The Mn_2PH moiety in $(i\text{-}Pr_2N)_2PMn_2(CO)_8$ is nearly planar (σ = 0.06 Å) as it is in $(C_6H_5)_2PMn_2(CO)_8H$.[7] All carbonyl groups are terminal (Mn–C–O angles range from 173.0 (13) to 179.6 (17)°) with consistent Mn–C distances (average 1.860 (15) Å) and normal C–O distances (average 1.13 (2) Å).

Table V. Positional Parameters for $i\text{-}Pr_2NPCo_3(CO)_9$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Co1	0.1992 (0)	0.2661 (2)	0.7308 (0)
Co2	0.3135 (1)	0.4309 (2)	0.8483 (1)
Co3	0.3696 (1)	0.1743 (2)	0.8256 (1)
P1	0.2509 (2)	0.2457 (3)	0.8725 (2)
O11	0.1191 (7)	−0.0014 (11)	0.6820 (7)
O12	0.2631 (8)	0.3540 (12)	0.5717 (7)
O13	0.0200 (8)	0.4132 (14)	0.7147 (9)
O21	0.1653 (9)	0.6367 (12)	0.8415 (9)
O22	0.4212 (9)	0.5608 (12)	0.7297 (9)
O23	0.4341 (9)	0.4644 (14)	1.0288 (7)
O31	0.4708 (9)	0.2437 (13)	0.6857 (9)
O32	0.3328 (8)	−0.1117 (11)	0.7896 (9)
O33	0.5223 (8)	0.1669 (14)	0.9897 (7)
N1	0.2029 (7)	0.2051 (10)	0.9568 (6)
C11	0.6500 (9)	0.1024 (14)	0.6995 (8)
C12	0.2404 (9)	0.3206 (14)	0.6323 (8)
C13	0.0888 (10)	0.3598 (16)	0.7207 (9)
C21	0.2210 (10)	0.5583 (14)	0.8440 (10)
C22	0.3804 (11)	0.5100 (14)	0.7719 (11)
C23	0.3883 (9)	0.9519 (14)	0.4588 (8)
C31	0.4340 (11)	0.2189 (15)	0.7376 (11)
C32	0.3473 (9)	−0.0010 (5)	0.8012 (10)
C33	0.4639 (9)	0.1720 (15)	0.9259 (9)
C1	0.1519 (12)	−0.0332 (14)	0.9223 (12)
C2	0.2017 (10)	0.0687 (12)	0.9932 (9)
C3	0.3018 (12)	0.0243 (17)	1.0422 (12)
C4	0.0396 (12)	0.2794 (21)	0.9657 (14)
C5	0.1461 (11)	0.3103 (13)	0.9898 (10)
C6	0.1865 (16)	0.3259 (17)	1.0924 (11)

Table I compares some pertinent spectroscopic properties of $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$ (I: X = Y = i-Pr_2N) with those of $(C_6H_5)_2PMn_2(CO)_8H$. The patterns of ν(CO) frequencies in both complexes are very similar. The proton NMR spectrum of $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$ exhibits a high-field resonance from the bridging hydrogen atom similar to that found in the proton NMR spectrum of $(C_6H_5)_2PMn_2(CO)_8H$. In both cases this high-field resonance is split into a doublet owing to coupling with the phosphorus atom.

A characteristic feature of the $(i\text{-}Pr_2N)_2PH$ metal carbonyl complexes is the facile and selective cleavage of one of the two diisopropylamino groups with hydrogen halides HX (X = Cl, Br) to give the corresponding $i\text{-}Pr_2NP(H)X$ metal carbonyl complexes.[1] The binuclear complex $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$ undergoes an analogous cleavage with hydrogen halides according to the equation

$$(i\text{-}Pr_2N)_2PMn_2(CO)_8H + 2HX \rightarrow (i\text{-}Pr_2NPX)Mn_2(CO)_8H + [i\text{-}Pr_2NH_2]X \quad (1)$$

The preservation of the Mn–H–Mn bridge in the $(i\text{-}Pr_2NPX)Mn_2(CO)_8H$ products (I: X = Cl, Br; Y = i-Pr_2N) is indicated by a high-field proton NMR resonance similar to that found in $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$. The patterns of infrared ν(CO) frequencies in the $(i\text{-}Pr_2NPX)Mn_2(CO)_8H$ derivatives are similar to that in $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$ except for the expected 12–22 cm^{-1} higher frequencies upon replacement of a diisopropylamino group with a halogen atom thereby increasing the π-acceptor strength and/or lowering the basicity of the resulting bridging phosphido group.

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[7] Doedens, R. J.; Robinson, W. T.; Ibers, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4323.

Table VI. Bond Distances (Å) and Angles (deg) for *i*-$Pr_2NPCo_3(CO)_9$

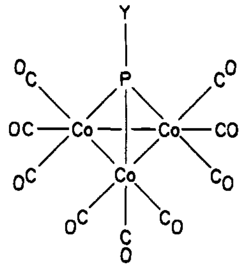
Co1–Co2	2.698 (2)	Co2–O21	1.83 (1)
Co2–Co3	2.737 (3)	Co2–O22	1.87 (2)
Co1–Co3	2.700 (2)	Co2–O23	1.80 (1)
Co1–P1	2.142 (3)	Co3–O31	1.87 (2)
Co2–P2	2.131 (4)	Co3–O32	1.80 (1)
Co3–P3	2.134 (4)	Co3–O33	1.80 (1)
P1–N1	1.66 (1)	C11–O11	1.14 (2)
N1–C2	1.48 (2)	C12–O12	1.11 (2)
N1–C5	1.50 (2)	C13–O13	1.11 (2)
C1–C2	1.54 (2)	C21–O21	1.12 (2)
C2–C3	1.52 (2)	C22–O22	1.10 (2)
C4–C5	1.52 (2)	C23–O23	1.13 (2)
C5–C6	1.56 (2)	C31–O31	1.09 (2)
Co1–O11	1.80 (1)	C32–O32	1.13 (2)
Co1–O12	1.84 (1)	C33–O33	1.13 (2)
Co1–O13	1.82 (2)		

Co1–Co2–Co3	59.57 (6)	P1–Co1–C12	140.1 (4)
Co2–Co3–Co1	59.50 (6)	P1–Co1–C11	101.8 (4)
Co3–Co1–Co2	60.93 (6)	P1–Co1–Co2	50.6 (9)
Co1–P1–Co2	78.3 (1)	P1–Co1–Co3	50.7 (9)
Co1–P1–Co3	78.3 (1)	C13–Co1–C12	103.0 (6)
Co2–P1–Co3	79.8 (1)	C13–Co1–C11	99.5 (6)
Co1–P1–N1	135.4 (4)	C12–Co1–C11	103.4 (6)
Co2–P1–N1	128.5 (4)	Co1–Co2–C21	94.4 (4)
Co3–P1–N1	134.5 (4)	Co1–Co2–C22	99.2 (4)
P1–N1–C2	124.6 (9)	Co1–Co2–C23	147.1 (5)
P1–N1–C5	117.3 (8)	Co3–Co2–C21	151.7 (4)
C2–N1–C5	117.6 (11)	Co3–Co2–C22	96.0 (5)
N1–C2–C1	112.8 (11)	Co3–Co2–C23	95.9 (5)
N1–C2–C3	111.2 (12)	P1–Co2–C21	106.0 (5)
C1–C2–C3	112.6 (12)	P1–Co2–C22	141.5 (5)
N1–C5–C4	112.1 (12)	P1–Co2–C23	96.9 (5)
N1–C5–C6	108.3 (12)	P1–Co2–Co1	51.0 (1)
C4–C5–C6	112.2 (16)	P1–Co2–Co3	50.1 (1)
Co1–C11–O11	178.2 (13)	C21–Co2–C22	99.4 (7)
Co1–C12–O12	178.4 (12)	C21–Co2–C23	102.7 (6)
Co1–C13–O13	177.8 (15)	C22–Co2–C23	105.3 (6)
Co2–C21–O21	179.4 (15)	Co1–Co3–C32	97.1 (4)
Co2–C22–O22	176.9 (14)	Co1–Co3–C31	94.1 (4)
Co2–C23–O23	178.8 (12)	Co1–Co3–C33	150.7 (5)
Co3–C31–O31	178.6 (14)	Co2–Co3–C32	153.3 (4)
Co3–C32–O32	177.0 (15)	Co2–Co3–C31	94.7 (5)
Co3–C33–O33	177.8 (14)	Co2–Co3–C33	95.0 (5)
Co2–Co1–C13	97.2 (4)	P1–Co3–C32	106.2 (5)
Co2–Co1–C12	96.2 (4)	P1–Co3–C31	138.0 (5)
Co2–Co1–C11	150.6 (4)	P1–Co3–C33	102.4 (5)
Co3–Co1–C13	152.2 (4)	P1–Co3–Co1	51.0 (8)
Co3–Co1–C12	96.6 (4)	P1–Co3–Co2	50.0 (10)
Co3–Co1–C11	94.8 (4)	C32–Co3–C31	100.1 (7)
P1–Co1–C13	102.7 (4)	C32–Co3–C33	103.1 (6)
		C31–Co3–C33	102.8 (6)

Previous work indicates varying reactivities of diisopropylamino phosphorus derivatives toward alcoholysis reactions. Thus, uncomplexed $(i\text{-}Pr_2N)_2PH$ reacts rapidly with methanol to give $(i\text{-}Pr_2N)(MeO)PH$ and $(MeO)_2PH$[5] and $(i\text{-}Pr_2N)_2PHMn(CO)_2Cp$ reacts with methanol to give $i\text{-}Pr_2NP(H)(OMe)Mn(CO)_2Cp$[1] whereas $(i\text{-}Pr_2N)_2PHW(CO)_5$ is unreactive toward boiling methanol. The complex $(i\text{-}Pr_2N)_2PMn_2(CO)_8H$ was also found to be unreactive toward methanol, being recovered unchanged after boiling in methanol for 24 h.

(B) Cobalt Carbonyl Derivative *i*-$Pr_2NPCo_3(CO)_9$. The reaction of $(i\text{-}Pr_2N)_2PH$ with $Co_2(CO)_8$ in saturated hydrocarbon solvents at ambient temperature appears to be complicated, yielding a number of deep colored products of limited stability. A limiting product can be isolated in low yield by stirring $(i\text{-}Pr_2N)_2PH$ with $Co_2(CO)_8$ for 5 days at room temperature in hexane solution by using a 2/3 $(i\text{-}Pr_2N)_2PH/Co_2(CO)_8$ molar ratio. Chromatography of this mixture on silica gel in pentane solution gave a green-black air-sensitive product of limited thermal stability after crystallization from pentane at −10 °C.

This complex was indicated by X-ray diffraction (Figure 2) to be the μ_3-(diisopropylamino)phosphinidene complex $i\text{-}Pr_2NPCo_3(CO)_9$ (II: Y = $i\text{-}Pr_2N$) with a $PCo_3(CO)_9$ framework very similar to that found[8] for $t\text{-}BuPCo_3(CO)_9$ (II: Y = *t*-Bu).



II

The three cobalt atoms in $i\text{-}Pr_2NPCo_3(CO)_9$ form the vertices of an equilateral triangle that is face-bridged by the $\mu_3\text{-}i\text{-}Pr_2NP$ group. The Co–P distances of 2.142 (3), 2.131 (4), and 2.134 (4) Å in $i\text{-}Pr_2NPCo_3(CO)_9$ are essentially the same as the average Co–P distance of 2.127 Å found in $t\text{-}BuPCo_3(CO)_9$. The average Co–Co distance of 2.712 (2) Å in $(\mu_3\text{-}i\text{-}Pr_2NP)Co_3(CO)_9$ falls in the 2.709–2.725-Å range found[8] for $t\text{-}BuPCo_3(CO)_9$ but is longer than that found in other tricobalt clusters including even the closely related isoelectronic compounds $Co_3(CO)_9S$ (2.64 Å)[8,9] and $Co_3(CO)_9Se$ (2.62 Å)[8,10] as well as less closely related clusters such as $MeCCo_3(CO)_9$ (2.467 Å),[11] $Cp_3Co_3(CO)(S)$ (2.452 (2) Å),[12] and $Cp_3Co_3S_2$ (2.687 (3) Å).[12] The average Co–P–Co bond angle in $i\text{-}Pr_2NPCo_3(CO)_9$ of 78.8° is close to that of 79.45° in $t\text{-}BuPCo_3(CO)_9$[8] but significantly larger than the 76.1° Co–S–Co bond angle in $Co_3(CO)_9S$[8,9] and particularly the 69.95° Co–Se–Co bond angle in $Co_3(CO)_9Se$.[8,10] The 359.5° sum of angles at nitrogen and the essential planarity (σ = 0.03) of C2, C5, N1, and P1 indicate sp^2 hybridization of the nitrogen, suggesting phosphorus–nitrogen double bonding although a lack of structural information on *closely related* model phosphorus–nitrogen compounds precludes a more definitive indication of phosphorus–nitrogen double bonding from the observed P–N distance of 1.66 (1) Å. The plane P1, N1, C2, C5 is essentially orthogonal (89.03°) with the plane formed by the three cobalt atoms. All nine carbonyl groups in $i\text{-}Pr_2NPCo_3(CO)_9$ are clearly indicated by the structural study to be terminal, in accord with the observed infrared ν(CO) spectrum.

The structure of $i\text{-}Pr_2NPCo_3(CO)_9$ (II: Y = $i\text{-}Pr_2N$), like those of the isoelectronic $t\text{-}BuPCo_3(CO)_9$ (II: Y = *t*-Bu)[8], $Co_3(CO)_9S$,[9] and $Co_3(CO)_9Se$,[10] has an odd number of electrons and therefore should be paramagnetic. Indeed, $t\text{-}BuPCo_3(CO)_9$ exhibits a solution EPR spectrum[8] showing hyperfine coupling with all three cobalt nuclei but not with the phosphorus atom. A similar EPR spectrum is also found for $Co_3(CO)_9S$. The paramagnetism of $i\text{-}Pr_2NPCo_3(CO)_9$ (II: Y = $i\text{-}Pr_2N$) was confirmed by a magnetic susceptibility measurement by the Faraday method that gives a magnetic moment of 2.0 μ_B, in approximate agreement with that expected for one unpaired electron. In view of the paramagnetism of $i\text{-}Pr_2NPCo_3(CO)_9$ as well as the limited quantities available, its NMR spectra were not investigated.

The formation of $i\text{-}Pr_2NPCo_3(CO)_9$ as a limiting product from the reaction of $(i\text{-}Pr_2N)_2PH$ with $Co_2(CO)_8$ may be viewed as proceeding according to the overall reaction

$$2(i\text{-}Pr_2N)_2PH + 3Co_2(CO)_8 \rightarrow 2i\text{-}Pr_2NPCo_3(CO)_9 + 6CO + 2i\text{-}Pr_2NH \quad (2)$$

The apparent variety of unstable products in the system suggest considerable mechanistic complexity of this reaction. However, this system may be considered to be the first formal example of the formation of a (dialkylamino)phosphinidene from a bis(dialkylamino)phosphine through elimination of dialkylamine by hydrogen migration from phosphorus to nitrogen according to the equation

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(8) Ryan, R. C. Ph.D. Dissertation, University of Wisconsin, Madison, Wisconsin, 1976; pp 134–149.

(9) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1967**, *6*, 1229.

(10) Strouse, C. E.; Dahl, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 6032.

(11) Sutton, P. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 261.

(12) Frisch, P. D.; Dahl, L. F. *J. Am. Chem. Soc.* **1972**, *94*, 5082.

$$(i\text{-Pr}_2\text{N})_2\text{PH} \rightarrow \text{“}i\text{-Pr}_2\text{NP”} + i\text{-Pr}_2\text{NH} \qquad (3)$$

Complexation of $(i\text{-Pr}_2\text{N})_2\text{PH}$ to a labile cobalt carbonyl system of an as yet unknown nature undoubtedly facilitates its conversion to the phosphinidene $i\text{-Pr}_2\text{NP}$, probably through stabilization of the latter through bonding to the Co_3 triangle in $(\mu_3\text{-}i\text{-Pr}_2\text{NP})\text{Co}_3(\text{CO})_9$. Also, related μ_3-phosphinidene derivatives $\text{XPCo}_3(\text{CO})_9$ (I: Y = Et_2N, Ph, *t*-Bu) have been obtained by Markó and Markó[13] from reactions of $\text{Co}_2(\text{CO})_8$ with XPCl_2. Such reactions could involve dehalogenation by $\text{Co}_2(\text{CO})_8$ or $\text{Co}(\text{CO})_4^-$ of XPCl_2 to the phosphinidene "XP" after the XPCl_2 unit is appropriately complexed with a cobalt carbonyl unit.

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Registry No. $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$, 94423-73-1; $(i\text{-Pr}_2\text{NPCl})\text{Mn}_2(\text{CO})_8\text{H}$, 94423-75-3; $(i\text{-Pr}_2\text{NPBr})\text{Mn}_2(\text{CO})_8\text{H}$, 94423-76-4; $i\text{-Pr}_2\text{NPCo}_3(\text{CO})_9$, 94423-74-2; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; $\text{Co}_2(\text{CO})_8$, 10210-68-1; $(i\text{-Pr}_2\text{N})_2\text{PH}$, 86660-77-7; HCl, 7647-01-0; HBr, 10035-10-6; Mn, 7439-96-5.

Supplementary Material Available: Listings of anisotropic thermal parameters for both compounds and hydrogen positional parameters for $(i\text{-Pr}_2\text{N})_2\text{PMn}_2(\text{CO})_8\text{H}$ (3 pages). Ordering information is given on any current masthead page.

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(13) Markó, L.; Markó, B. *Inorg. Chim. Acta* **1975**, *14*, L39.

Contribution from the Departments of Chemistry, University of Georgia, Athens, Georgia 30602,
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Dialkylamino Phosphorus Metal Carbonyls. 3. Heterobimetallic μ-Phosphido Derivatives from Reactions of (Diisopropylamino)halophosphine Metal Carbonyl Complexes with Sodium Cyclopentadienyldicarbonylferrate[1-3]

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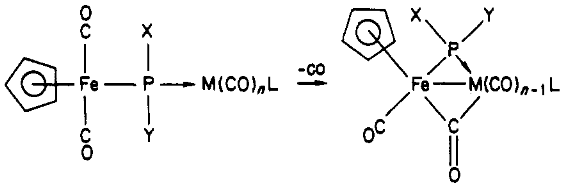
Reactions of $i\text{-Pr}_2\text{NP(H)XM(CO)}_5$ (X = Br, M = Cr; X = Cl, M = Mo, W) and $i\text{-Pr}_2\text{NP(H)ClMn(CO)}_2\text{Cp}$ with $\text{NaFe(CO)}_2\text{Cp}$ give relatively good yields of deep orange $\text{CpFe(CO)}_2\text{PH(N-}i\text{-Pr}_2\text{)M(CO)}_5$ and deep red $\text{CpFe(CO)}_2\text{PH(N-}i\text{-Pr}_2\text{)Mn(CO)}_2\text{Cp}$, respectively, which do not contain metal–metal bonds. Photolyses of $\text{CpFe(CO)}_2\text{PH(N-}i\text{-Pr}_2\text{)M(CO)}_5$ (M = Cr, W) and $\text{CpFe(CO)}_2\text{PH(N-}i\text{-Pr}_2\text{)Mn(CO)}_2\text{Cp}$ in pentane or cyclohexane solution result in rapid decarbonylation to give black $\text{CpFeM(CO)}_6\text{PH(N-}i\text{-Pr}_2\text{)}$ (M = Cr, W) and $\text{Cp}_2\text{FeMn(CO)}_3\text{PH(N-}i\text{-Pr}_2\text{)}$, respectively. X-ray diffraction of $\text{CpFeM(CO)}_6\text{PH(N-}i\text{-Pr}_2\text{)}$ (space group $P2_1/c$, $Z = 4$; M = Cr, $a = 14.362$ (5) Å, $b = 7.733$ (2) Å, $c = 19.244$ (8) Å, $\beta = 104.00$ (3)°; M = W, $a = 14.491$ (5) Å, $b = 7.808$ (2) Å, $c = 19.456$ (8) Å, $\beta = 103.17$ (3)°) indicates structures in which a heteronuclear Fe–M bond is bridged by both a carbonyl group and a $i\text{-Pr}_2\text{NPH}$ phosphido group. A similar structure is postulated for $\text{Cp}_2\text{FeMn(CO)}_3\text{PH(N-}i\text{-Pr}_2\text{)}$ on the basis of the observation of two terminal and one bridging ν(CO) frequencies. Reactions of $\text{CpFe(CO)}_2\text{PH(N-}i\text{-Pr}_2\text{)M(CO)}_5$ (M = Cr, Mo, W) with HX (X = Cl, Br) result in cleavage of the P–N bond to give the corresponding $\text{CpFe(CO)}_2\text{PHXM(CO)}_5$ derivatives (X = Cl, Br; M = Cr, Mo, W). Reactions of $\text{CpFe(CO)}_2\text{PHClM(CO)}_5$ (M = Cr, W) and $\text{CpFe(CO)}_2\text{PH(N-}i\text{-Pr}_2\text{)Mn(CO)}_2\text{Cp}$ with boiling methanol give the methoxyphosphorus derivatives $\text{CpFe(CO)}_2\text{PH(OMe)M(CO)}_5$ and $\text{CpFe(CO)}_2\text{PH(OMe)Mn(CO)}_2\text{Cp}$, respectively.

Introduction

The (diisopropylamino)halophosphine metal carbonyl complexes $i\text{-Pr}_2\text{NP(H)XM(CO)}_5$ (X = Cl, Br; M = Cr, Mo, W) and $i\text{-Pr}_2\text{NP(H)ClMn(CO)}_2\text{Cp}$ are readily available by selective cleavage of one of the phosphorus–nitrogen bonds in the corresponding $(i\text{-Pr}_2\text{N})_2\text{PH}$ metal carbonyl derivatives with the corresponding hydrogen halide, HX.[4] The phosphorus–halogen bonds in these (diisopropylamino)halophosphine metal carbonyl complexes are potentially reactive toward nucleophiles including transition-metal nucleophiles[5] that provide possible routes to bimetallic derivatives. This paper describes reactions of the above $i\text{-Pr}_2\text{NP(H)X}$ metal carbonyl complexes with the highly nucleophilic metal carbonyl anion $\text{C}_5\text{H}_5\text{Fe(CO)}_2^-$ to give novel heterobimetallic complexes that may be regarded as metal carbonyl derivatives of the trivalent phosphorus ligand $\text{CpFe(CO)}_2\text{P(H)(N-}i\text{-Pr}_2\text{)}$ in which the phosphorus atom is bonded to hydrogen, nitrogen, and iron. Such complexes do not have direct metal–metal bonds but undergo facile photochemical loss of one carbonyl group to give metal–metal-bonded μ-phosphido derivatives according to the general scheme (X = H, Y = $\text{N-}i\text{-Pr}_2$)



(1)

This paper also reports the X-ray determinations of the structures of two of these decarbonylation products of the type $\text{CpFeM(CO)}_6\text{PH(N-}i\text{-Pr}_2\text{)}$ (M = Cr, W). Early examples of pairs of μ-diphenylphosphido heterobimetallic complexes related by decarbonylation as in eq 1 (X = Y = C_6H_5) were prepared by Yasufuku and Yamazaki[6] using completely different methods.

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(1) Part 2: King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.*, preceding paper in this issue.

(2) For a preliminary communication of this work see: King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 3094.

(3) 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.

(4) King, R. B.; Fu, W.-K. *Inorg. Chem.*, preceding paper in this issue.

(5) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

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