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

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

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-84-0050. We are also indebted to Prof. L. F. Dahl of the University of Wisconsin in Madison for calling our attention to Dr. R. C. Ryan's unpublished work in his laboratory and providing us with a copy of the relevant pages of Dr. Ryan's dissertation.[8]

Registry No. (i-Pr$_2$N)$_2$PMn$_2$(CO)$_8$H, 94423-73-1; (i-Pr$_2$NPCl)Mn$_2$(CO)$_8$H, 94423-75-3; (i-Pr$_2$NPBr)Mn$_2$(CO)$_8$H, 94423-76-4; i-Pr$_2$NPCo$_3$(CO)$_9$, 94423-74-2; Mn$_2$(CO)$_{10}$, 10170-69-1; Co$_2$(CO)$_8$, 10210-68-1; (i-Pr$_2$N)$_2$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-Pr$_2$N)$_2$PMn$_2$(CO)$_8$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, and Oklahoma State University, Stillwater, Oklahoma 74078

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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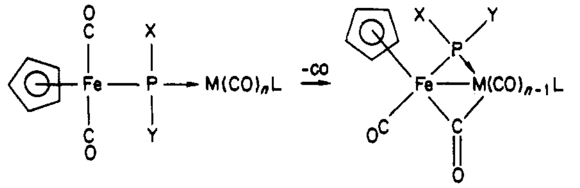
Reactions of i-Pr$_2$NP(H)XM(CO)$_5$ (X = Br, M = Cr; X = Cl, M = Mo, W) and i-Pr$_2$NP(H)ClMn(CO)$_2$Cp with NaFe(CO)$_2$Cp give relatively good yields of deep orange CpFe(CO)$_2$PH(N-i-Pr$_2$)M(CO)$_5$ and deep red CpFe(CO)$_2$PH(N-i-Pr$_2$)Mn(CO)$_2$Cp, respectively, which do not contain metal–metal bonds. Photolyses of CpFe(CO)$_2$PH(N-i-Pr$_2$)M(CO)$_5$ (M = Cr, W) and CpFe(CO)$_2$PH(N-i-Pr$_2$)Mn(CO)$_2$Cp in pentane or cyclohexane solution result in rapid decarbonylation to give black CpFeM(CO)$_6$PH(N-i-Pr$_2$) (M = Cr, W) and Cp$_2$FeMn(CO)$_3$PH(N-i-Pr$_2$), respectively. X-ray diffraction of CpFeM(CO)$_6$PH(N-i-Pr$_2$) (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-Pr$_2$NPH phosphido group. A similar structure is postulated for Cp$_2$FeMn(CO)$_3$PH(N-i-Pr$_2$) on the basis of the observation of two terminal and one bridging ν(CO) frequencies. Reactions of CpFe(CO)$_2$PH(N-i-Pr$_2$)M(CO)$_5$ (M = Cr, Mo, W) with HX (X = Cl, Br) result in cleavage of the P–N bond to give the corresponding CpFe(CO)$_2$PHXM(CO)$_5$ derivatives (X = Cl, Br; M = Cr, Mo, W). Reactions of CpFe(CO)$_2$PHClM(CO)$_5$ (M = Cr, W) and CpFe(CO)$_2$PH(N-i-Pr$_2$)Mn(CO)$_2$Cp with boiling methanol give the methoxyphosphorus derivatives CpFe(CO)$_2$PH(OMe)M(CO)$_5$ and CpFe(CO)$_2$PH(OMe)Mn(CO)$_2$Cp, respectively.

Introduction

The (diisopropylamino)halophosphine metal carbonyl complexes i-Pr$_2$NP(H)XM(CO)$_5$ (X = Cl, Br; M = Cr, Mo, W) and i-Pr$_2$NP(H)ClMn(CO)$_2$Cp are readily available by selective cleavage of one of the phosphorus–nitrogen bonds in the corresponding (i-Pr$_2$N)$_2$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-Pr$_2$NP(H)X metal carbonyl complexes with the highly nucleophilic metal carbonyl anion C$_5$H$_5$Fe(CO)$_2^-$ to give novel heterobimetallic complexes that may be regarded as metal carbonyl derivatives of the trivalent phosphorus ligand CpFe(CO)$_2$P(H)(N-i-Pr$_2$) 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 = N-i-Pr$_2$)



(1)

This paper also reports the X-ray determinations of the structures of two of these decarbonylation products of the type CpFeM(CO)$_6$PH(N-i-Pr$_2$) (M = Cr, W). Early examples of pairs of μ-diphenylphosphido heterobimetallic complexes related by decarbonylation as in eq 1 (X = Y = C$_6$H$_5$) 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.

0020-1669/86/1325-2394$01.50/0

Table I. New Heterobimetallic Complexes

complex	yield, %	color	mp, °C	anal.			
					% C	% H	% N or X
		(A) Iron–Chromium Derivatives					
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Cr(CO)_5$	73	orange	145 dec	calcd	43.1	4.0	2.8 (N)
				found	43.0	4.0	2.6 (N)
$CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$	53	black	110 dec	calcd	43.2	4.2	3.0 (N)
				found	42.7	4.2	2.8 (N)
$CpFe(CO)_2PHClCr(CO)_5$	67	brown	74 dec	calcd	33.0	1.4	8.1 (Cl)
				found	32.7	1.4	7.8 (Cl)
$CpFe(CO)_2PHBrCr(CO)_5$	67	orange	85	calcd	30.0	1.2	16.6 (Br)
				found	30.3	1.2	16.6 (Br)
$CpFe(CO)_2PH(OMe)Cr(CO)_5$	84	yellow	100	calcd	36.1	2.1	
				found	34.6	2.1	
		(B) Iron–Molybdenum Derivatives					
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mo(CO)_5$	66	yellow-brown	100–105 dec	calcd	39.7	3.7	2.6 (N)
				found	39.5	3.8	2.6 (N)
$CpFe(CO)_2PHClMo(CO)_5$	39	brown	75 dec	calcd	30.0	1.3	7.4 (Cl)
				found	30.8	1.6	6.5 (Cl)
$CpFe(CO)_2PHBrMo(CO)_5$	41	orange	85	calcd	27.4	1.1	15.2 (Br)
				found	27.5	1.4	15.2 (Br)
		(C) Iron–Tungsten Derivatives					
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)W(CO)_5$	69	brown	120 dec	calcd	34.1	3.2	2.2 (N)
				found	34.7	3.2	2.0 (N)
$CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$	52	black	105–110 dec	calcd	33.7	3.3	2.3 (N)
				found	33.7	3.4	2.1 (N)
$CpFe(CO)_2PHClW(CO)_5$	58	brown	80 dec	calcd	25.3	1.1	6.2 (Cl)
				found	24.2	1.3	6.5 (Cl)
$CpFe(CO)_2PHBrW(CO)_5$	43	brown	97 dec	calcd	23.5	1.0	13.0 (Br)
				found	23.9	1.1	13.6 (Br)
$CpFe(CO)_2PH(OMe)W(CO)_5$	61	yellow	88–90	calcd	27.7	1.6	
				found	27.5	1.7	
		(D) Iron–Manganese Derivatives					
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$	63	deep red	140 dec	calcd	49.5	5.2	2.9 (N)
				found	49.4	5.2	2.8 (N)
$CpFeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$	21	black	100 dec	calcd	49.9	5.5	3.1 (N)
				found	49.9	5.5	2.8 (N)
$CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$	57	red	125 dec	calcd	43.3	3.4	
				found	43.5	3.5	

The new complexes reported in this paper are of interest since unlike previously reported heterobimetallic μ-phosphido complexes they contain reactive phosphorus–nitrogen and phosphorus–hydrogen bonds. Examples of cleavage of the phosphorus–nitrogen bonds in these new heterobimetallic derivatives with hydrogen halides are given in this paper; such cleavage reactions lead to the first species having M–PHX–M′ structural units.

Experimental Section

The general techniques for microanalyses (Table I), melting points (Table I), infrared ν(CO) spectra (Table II), NMR spectra (Table III), solvent purification, and inert-atmosphere manipulations are the same as those given in the first paper of this series.[4] The preparations of the $i\text{-}Pr_2NP(H)X$ metal carbonyl derivatives are also given in the first paper of this series.[4] The sodium salt $NaFe(CO)_2Cp$ was prepared from $[CpFe(CO)_2]_2$ and 1% sodium amalgam in tetrahydrofuran by the standard method.[7]

Preparation of $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5$ (M = Cr, Mo, W). A yellow-orange solution of $NaFe(CO)_2Cp$ prepared in 300 mL of tetrahydrofuran from 1.3 g (3.8 mmol) of $[CpFe(CO)_2]_2$ and excess 1% sodium amalgam and freed from excess mercury was treated at −78 °C with a solution of 3.0 g (7.4 mmol) of $i\text{-}Pr_2NP(H)BrCr(CO)_5$. After the mixture was stirred for 10 h at ambient temperature, solvent was removed at 25 °C (25 mm). The resulting orange-brown residue was extracted with 500 mL of pentane. The pentane extract was concentrated under a vacuum and cooled overnight in a −10 °C freezer to give 2.7 g (73% yield) of orange air-stable $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Cr(CO)_5$, mp 145 °C dec.

Analogous procedures were used to prepare $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5$ (M = Mo, W) from $NaFe(CO)_2Cp$ and $i\text{-}Pr_2NP(H)ClM(CO)_5$ (M = Mo, W) on a 10–15-mmol scale.

Table II. Infrared ν(CO) Frequencies of the New Heterobimetallic Complexes

complex	ν(CO),[a] cm^{-1}
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Cr(CO)_5$	2040 w, 2005 m, 1970 s, 1955 w, 1935 s, 1920 s
$CpFe(CO)_2PHClCr(CO)_5$	2068 w, 2033 m, 2002 m, 1958 s, 1938 s
$CpFe(CO)_2PHBrCr(CO)_5$	2058 w, 2033 m, 2002 m, 1957 s, 1946 s, 1935 s
$CpFe(CO)_2PH(OMe)Cr(CO)_5$	2056 w, 2026 m, 1987 m, 1951 s, 1941 s, 1933 s
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mo(CO)_5$	2056 w, 2006 m, 1973 m, 1939 s, 1931 s
$CpFe(CO)_2PHClMo(CO)_5$	2068 w, 2033 m, 2001 m, 1951 s, 1939 s
$CpFe(CO)_2PHBrMo(CO)_5$	2068 w, 2036 m, 2002 m, 1958 s, 1938 s
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)W(CO)_5$	2060 w, 2010 m, 1970 m, 1945 s, 1935 s, 1920 s
$CpFe(CO)_2PHClW(CO)_5$	2069 w, 2038 m, 2003 m, 1954 s, 1948 s, 1933 s
$CpFe(CO)_2PHBrW(CO)_5$	2069 w, 2037 m, 2002 m, 1947 s, 1941 s, 1932 s
$CpFe(CO)_2PH(OMe)W(CO)_5$	2064 w, 2024 m, 1989 m, 1939 sh, 1929 s
$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$	2004 s, 1956 s, 1929 s, 1864 s
$CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$	2023 s, 1976 s, 1926 s, 1860 s
$Cp_2FeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$	1947 s, 1889 m, 1758[b] m
$CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$	2031 m, 1961 s, 1959 s, 1926 s, 1811[b] m
$CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$	2047 m, 1968 s, 1952 s, 1931 s, 1810[b] vw

[a] These frequencies were measured in pentane or hexane solution. [b] Bridging ν(CO) frequency.

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Table III. Proton and Phosphorus-31 NMR Spectra of the Heterobimetallic Complexes

	^{31}P NMR		^1H NMR[a]			
complex	$\delta(P)$	$\lvert ^1J(P-H)\rvert$	$\delta(P-H)$	$\delta(C-H)$	$\delta(CH_3)$	$\delta(C_5H_5)$
$CpFe(CO)_2PH(N-i-Pr_2)Cr(CO)_5$	62.6	292	7.31 d	3.32 sp (7)	1.23 d (7)	5.04 d (2)
$CpFe(CO)_2PHClCr(CO)_5$	169.8	282	7.50 d			5.20 d (2)
$CpFe(CO)_2PHBrCr(CO)_5$	149.5	273	6.71 d			5.21 d (2)
$CpFe(CO)_2PH(OMe)Cr(CO)_5$	208.4	273	7.77 d		3.59 d (13)[b]	5.12 d (2)
$CpFe(CO)_2PH(N-i-Pr_2)Mo(CO)_5$	36.7	291	7.36 d	3.32 sp (7)	1.20 d (7)	4.94 d (2)
$CpFe(CO)_2PHClMo(CO)_5$	133.3	273	7.57 d			5.16 d (2)
$CpFe(CO)_2PHBrMo(CO)_5$	109.8	269	6.64 d			5.18 d (2)
$CpFe(CO)_2PH(N-i-Pr_2)W(CO)_5$[c]	6.7	300	7.57 d	3.35 sp (7)	1.22 d (7)	4.98 d (2)
$CpFe(CO)_2PHClW(CO)_5$	89.9	283	7.72 d			5.17 d (2)
$CpFe(CO)_2PHBrW(CO)_5$	63.7	284	6.82 d			5.19 d (2)
$CpFe(CO)_2PH(OMe)W(CO)_5$	145.5	278	8.05 d		3.56 d (13)[b]	5.13 d (2)
$CpFe(CO)_2PH(N-i-Pr_2)Mn(CO)_2Cp$	98.5	306	7.68 d	3.46 br	1.20 br	4.92 s, 4.50 s
$CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$	230.8	283	8.29 d		3.50 d (12)[b]	5.03 s, 4.56 s
$CpFeCr(CO)_6PH(N-i-Pr_2)$	206.3	360	9.2 d	3.45 m (7)	1.40 d (7), 1.37 d (7)	4.75 d (2)
$CpFeW(CO)_6PH(N-i-Pr_2)$	159.8	363	9.9 d	3.4	1.3	4.6
$Cp_2FeMn(CO)_3PH(N-i-Pr_2)$	225.0	347	*d*	3.45 br	1.29 d (7)	4.57 s, 4.47 d (2)

[a] s = singlet, d = doublet, br = broad, sp = septet; coupling constants in Hz are given in parentheses. [b] Methoxy resonance. [c] $J(W-P) = 224$ Hz. Carbon-13 NMR in $CDCl_3$: δ 200.2 (d, $J = 6$ Hz, CO), δ 86.9 (s, C_5H_5), δ 48.5 (d, $J = 6$ Hz, CH), δ 21.7 (d, $J = 17$ Hz, CH_3). [d] Paramagnetic impurities in solution prevented observation of this P–H resonance.

Table IV. Crystal Data for $CpFeM(CO)_6PH(N-i-Pr_2)$ (M = Cr, W)

	M = Cr	M = W
formula	$FeCrC_{17}H_{20}O_6NP$	$FeWC_{17}H_{20}O_6NP$
mw	473.2	605.0
a, Å	14.362 (5)	14.491 (5)
b, Å	7.733 (2)	7.808 (2)
c, Å	19.244 (8)	19.456 (8)
β, deg	104.00 (3)	103.17 (3)
V, Å^3	2073.8 (12)	2143.6 (12)
$F(000)$	968	1168
μ(Mo Kα), cm^{-1}	13.16	62.56
λ(Mo Kα), Å	0.71069	0.71069
D_{calcd}, g cm^{-3}	1.515	1.874
Z	4	4
no. of obsd reflcns	2414	2271
octants collcd	$\pm h,+k,+l$	$\pm h,+k,+l$
R/R_w	0.053/0.058	0.068/0.078
space group	$P2_1/c$	$P2_1/c$
cryst dimens, mm	0.2 × 0.2 × 0.25	0.2 × 0.15 × 0.2

Preparation of $CpFe(CO)_2PH(N-i-Pr_2)Mn(CO)_2Cp$. A solution of $NaFe(CO)_2Cp$ from 2.4 g (6.8 mmol) of $[CpFe(CO)_2]_2$ was allowed to react with 4.6 g (13.4 mmol) of $i-Pr_2NP(H)ClMn(CO)_2Cp$ by the procedure outlined above for $CpFe(CO)_2PH(N-i-Pr_2)Cr(CO)_5$. A deep red solution was obtained when the dry residue from the evaporated reaction mixture was extracted with 500 mL of hexane. Concentration of the hexane extract under vacuum followed by cooling overnight in a −10 °C freezer gave 4.1 g (63% yield) of deep red air-stable $CpFe(CO)_2PH(N-i-Pr_2)Mn(CO)_2Cp$, mp 140 °C dec.

Preparation of $CpFeM(CO)_6PH(N-i-Pr_2)$ (M = Cr, W). A solution of 1.0 g of $CpFe(CO)_2PH(N-i-Pr_2)M(CO)_5$ (M = Cr, W) in 200 mL of pentane was exposed to ultraviolet irradiation for 10 min. Removal of solvent from the deep brown filtered reaction mixture gave a black residue. Crystallization of this residue from pentane gave black air-stable $CpFeM(CO)_6PH(N-i-Pr_2)$ in ~50% yield (Table I).

Preparation of $Cp_2FeMn(CO)_3PH(N-i-Pr_2)$. A solution of 1.0 g (2.1 mmol) of $CpFe(CO)_2PH(N-i-Pr_2)Mn(CO)_2Cp$ in 150 mL of cyclohexane was exposed to ultraviolet irradiation for 20 min. Solvent was removed from the resulting deep brown solution at 25 °C (25 mm). The residue was extracted with a 1:1 mixture of diethyl ether and pentane. The extract was concentrated under vacuum and cooled for several days in a −10 °C freezer to give 0.2 g (21% yield) of black air-stable crystalline $Cp_2FeMn(CO)_3PH(N-i-Pr_2)$, mp 100 °C dec.

Reactions of $CpFe(CO)_2PH(N-i-Pr_2)M(CO)_5$ (M = Cr, Mo, W) with Hydrogen Halides. A solution of 0.5–2.5 g of the $CpFe(CO)_2PH(N-i-Pr_2)M(CO)_5$ derivative in 400 mL of pentane or hexane was treated with a stream of gaseous hydrogen chloride or hydrogen bromide for 10 min. Solvent was removed from the filtered reaction mixture at 25 °C (25 mm). Crystallization of the residue from pentane gave the $CpFe(CO)_2PHXM(CO)_5$ derivative (Table I).

Methanolysis Reactions. (a) $CpFe(CO)_2PHClCr(CO)_5$. A solution of 0.6 g (1.38 mmol) of $CpFe(CO)_2PHClCr(CO)_5$ in 50 mL of methanol was boiled under reflux for 24 h. Removal of solvent at 25 °C (25 mm) followed by crystallization from pentane gave 0.5 g (84% yield) of yellow $CpFe(CO)_2PH(OMe)Cr(CO)_5$, mp 100 °C.

(b) $CpFe(CO)_2PHClW(CO)_5$. A solution of 0.5 g (0.88 mmol) of $CpFe(CO)_2PHClW(CO)_5$ in 30 mL of methanol was boiled under reflux for 24 h. Removal of solvent at 25 °C (25 mm) followed by crystallization from pentane gave 0.3 g (61% yield) of yellow $CpFe(CO)_2PH(OMe)W(CO)_5$, mp 88–90 °C.

(c) $CpFe(CO)_2PH(N-i-Pr_2)Mn(CO)_2Cp$. A solution of 1.0 g (2.1 mmol) of $CpFe(CO)_2PH(N-i-Pr_2)Mn(CO)_2Cp$ in 30 mL of methanol was boiled under reflux for 24 h. Removal of solvent at 25 °C (25 mm) followed by crystallization from a 1:1 mixture of dichloromethane and hexane gave 0.5 g (57% yield) of red $CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$.

X-ray Structure Determinations of $CpFeM(CO)_6PH(N-i-Pr_2)$ (M = Cr and W). Small chunks cut from crystals of $FeMC_{17}H_{20}O_6NP$ (M = Cr and W), crystallized from pentane, were sealed in capillaries and mounted on a Syntex P3 automated diffractometer located at Oklahoma State University. Unit cell dimensions (Table IV) 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). Data (5734 points for M = Cr and 5929 points for M = W) were collected at room temperature by using a variable scan rate, a $\theta-2\theta$ 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. The intensities of three standard reflections were remeasured after every 97 reflectons, and since the intensities of these reflections showed less than 8% variation, corrections for decomposition were considered unnecessary. Data were corrected for Lorentz, polarization, and background effects. No correction was made for absorption. After removal of redundant and space group forbidden data 2414 and 2271 reflections were considered observed [$I > 3.0\sigma(I)$] for M = Cr and W, respectively. The structures were solved for heavy-atom positions by direct methods using MULTAN 80. Successive least-squares/difference Fourier cycles allowed location of the non-hydrogen atoms. Refinement of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. Hydrogen positional parameters were determined from a difference Fourier synthesis of $CpFeCr(CO)_6PH(N-i-Pr_2)$. For $CpFeW(CO)_6PH(N-i-Pr_2)$, the hydrogen atom HP1 was located from a difference Fourier synthesis and all other hydrogen positions were calculated. 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 $R = 5.3\%$ for M = Cr and 6.8% for M = W where $R = (\sum||F_o| - |F_c||/\sum|F_o|) \times 100$. Anomalous scattering corrections were made for Fe, Cr, and P for $CpFeCr(CO)_6PH(N-i-Pr_2)$ and for Fe, W, and P for $CpFeW(CO)_6PH(N-i-Pr_2)$. Scattering factors were taken from Cromer and Mann.[8] In the final stages of refinement, a weight equal to $1/\sigma(F)$ was introduced.

Tables V and VI give the positional parameters and the bond distances and angles for $CpFeCr(CO)_6PH(N-i-Pr_2)$. Tables VII and VIII give the positional parameters and the bond distances and angles for CpFeW-

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Table V. Positional Parameters for $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
Cr1	0.3399 (1)	0.2399 (2)	0.1095 (1)
Fe1	0.1546 (1)	0.1239 (1)	0.1450 (1)
P1	0.2606 (1)	0.0761 (2)	0.0428 (1)
C1	0.1402 (7)	−0.0294 (12)	0.2392 (5)
C2	0.1611 (6)	−0.1359 (11)	0.1785 (5)
C3	0.0897 (7)	−0.1193 (12)	0.1424 (4)
C4	0.0231 (7)	0.0023 (15)	0.1800 (6)
C5	0.0568 (5)	0.0545 (13)	0.2393 (5)
C10	0.2269 (5)	0.2939 (11)	0.1924 (4)
O10	0.2002 (4)	0.3798 (8)	0.2436 (3)
C11	0.3732 (6)	0.0322 (12)	0.1515 (4)
O11	0.3949 (5)	−0.0860 (10)	0.1780 (4)
C12	0.4097 (7)	0.3574 (14)	0.1652 (5)
O12	0.4500 (6)	0.4284 (13)	0.2006 (4)
C13	0.3122 (6)	0.4552 (11)	0.0737 (4)
O13	0.2969 (5)	0.5897 (8)	0.0546 (4)
C14	0.4471 (6)	0.2232 (12)	0.0314 (5)
O14	0.5095 (5)	0.2155 (11)	−0.0175 (4)
C20	0.0997 (6)	0.3001 (11)	0.1150 (4)
O20	0.0607 (5)	0.4180 (9)	0.0981 (3)
N2	0.2450 (4)	0.1144 (8)	−0.0389 (3)
C40	0.2491 (6)	−0.0222 (10)	−0.0929 (4)
C41	0.3480 (7)	−0.1055 (14)	−0.1169 (5)
C42	0.1724 (7)	−0.1547 (11)	−0.0699 (5)
C50	0.2247 (6)	0.2908 (9)	−0.0592 (4)
C51	0.1285 (6)	0.3063 (12)	−0.0782 (5)
C52	0.3036 (7)	0.3622 (12)	−0.1177 (5)
HP1	0.2756	−0.0691	0.0376
H1	0.1975	−0.0811	0.2597
H2	0.2348	−0.1990	0.1671
H3	0.0963	−0.1721	0.0915
H4	−0.0335	−0.0312	0.1465
H5	0.0191	0.0928	0.2801
H40	0.2431	0.0317	−0.1424
H411	0.3977	−0.0056	−0.1486
H412	0.3660	−0.1413	−0.0810
H413	0.3058	−0.1411	−0.1507
H421	0.1980	−0.2519	−0.0313
H422	0.1160	−0.1088	−0.0383
H423	0.1463	−0.2214	−0.0831
H50	0.2327	0.3723	−0.0197
H511	0.0785	0.2709	−0.0447
H512	0.1353	0.2300	−0.1343
H513	0.1005	0.4098	−0.0813
H521	0.3688	0.3679	−0.1821
H522	0.3037	0.4950	−0.1314
H523	0.3215	0.3020	−0.1580

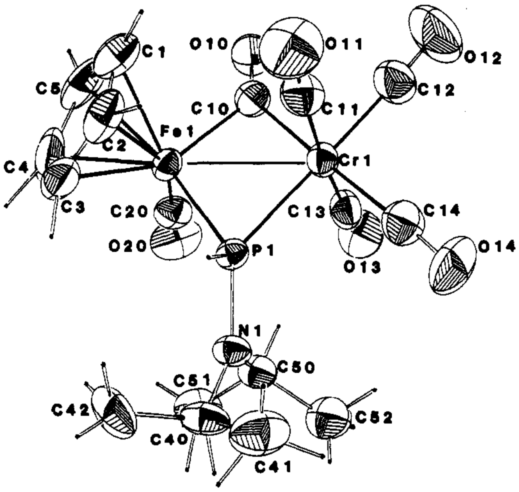


Figure 1. ORTEP diagram of $CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$.

$(CO)_6PH(N\text{-}i\text{-}Pr_2)$. The structures of $CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$ and $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$ are depicted in Figures 1 and 2, respectively.

Table VI. Bond Distances (Å) and Angles (deg) for $CpFeCr(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$

Fe1–Cr1	2.733 (2)	C12–O12	1.157 (11)
Fe1–C1	2.133 (9)	C13–O13	1.142 (11)
Fe1–C2	2.118 (9)	C14–O14	1.133 (10)
Fe1–C3	2.105 (10)	C20–O20	1.136 (14)
Fe1–C4	2.070 (10)	C1–C2	1.40 (1)
Fe1–C5	2.076 (9)	C2–C3	1.38 (1)
Fe1–C10	2.023 (9)	C3–C4	1.41 (1)
Fe1–P1	2.207 (2)	C4–C5	1.40 (2)
Fe1–C20	1.741 (9)	C5–C1	1.36 (2)
Cr1–C10	2.023 (7)	P1–N1	1.668 (6)
Cr1–C11	1.910 (9)	N1–C40	1.473 (10)
Cr1–C12	1.870 (11)	N1–C50	1.468 (10)
Cr1–C13	1.880 (9)	C40–C41	1.526 (13)
Cr1–C14	1.879 (8)	C40–C42	1.491 (12)
Cr1–P1	2.292 (2)	C50–C51	1.517 (13)
C10–O10	1.173 (10)	C50–C52	1.495 (11)
C11–O11	1.127 (12)		

Cr1–Fe1–P1	54.01 (6)	P1–Cr1–C14	86.3 (3)
Cr1–Fe1–C10	47.5 (2)	Fe1–C10–Cr1	85.0 (3)
Cr1–Fe1–C20	98.7 (3)	Fe1–P1–Cr1	74.80 (7)
P1–Fe1–C10	101.0 (2)	Fe1–C10–O10	130.3 (6)
P1–Fe1–C20	96.0 (2)	Cr1–C10–O10	144.6 (6)
C10–Fe1–C20	87.9 (4)	Fe1–P1–N1	126.1 (2)
Fe1–Cr1–C10	47.5 (2)	Cr1–P1–N1	128.9 (2)
Fe1–Cr1–C11	87.0 (2)	Fe1–C20–O20	177.0 (7)
Fe1–Cr1–C12	129.8 (3)	Cr1–C11–O11	176.9 (9)
Fe1–Cr1–C13	95.9 (2)	Cr1–C12–O12	178.1 (8)
Fe1–Cr1–C14	137.5 (3)	Cr1–C13–O13	176.7 (8)
Fe1–Cr1–P1	51.59 (6)	Cr1–C14–O14	177.2 (9)
C10–Cr1–C11	94.4 (3)	P1–N1–C40	123.1 (5)
C10–Cr1–C12	83.6 (4)	P1–N1–C50	119.8 (5)
C10–Cr1–C13	84.6 (3)	N1–C40–C41	113.0 (8)
C10–Cr1–C14	172.0 (4)	N1–C40–C42	112.5 (6)
C11–Cr1–C12	86.7 (4)	C41–C40–C42	111.5 (7)
C11–Cr1–C13	175.0 (4)	N1–C50–C51	112.9 (6)
C11–Cr1–C14	92.2 (4)	N1–C50–C52	112.4 (6)
C12–Cr1–C13	88.3 (4)	C51–C50–C52	111.0 (7)
C12–Cr1–C14	92.4 (4)	C1–C2–C3	109.3 (8)
C13–Cr1–C14	88.4 (4)	C2–C3–C4	107.4 (8)
P1–Cr1–C10	98.2 (2)	C3–C4–C5	106.5 (9)
P1–Cr1–C11	88.9 (3)	C4–C5–C1	109.8 (9)
P1–Cr1–C12	175.4 (4)	C5–C1–C2	106.9 (9)
P1–Cr1–C13	96.1 (3)		

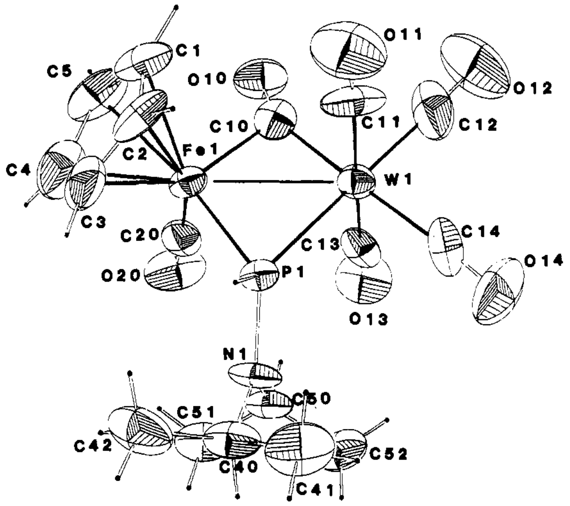


Figure 2. ORTEP diagram of $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$.

Results and Discussion

The reactions of $i\text{-}Pr_2NP(H)XM(CO)_5$ (X = Br, M = Cr; X = Cl, M = Mo, W) and $i\text{-}Pr_2NP(H)ClMn(CO)_2Cp$ with the very nucleophilic[5] metal carbonyl anion $CpFe(CO)_2^-$ proceed smoothly in tetrahydrofuran with replacement of the halogen atom by a $CpFe(CO)_2$ group according to the equations

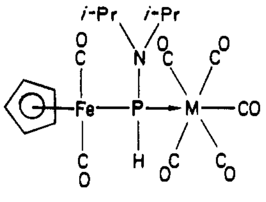
$$i\text{-}Pr_2NP(H)XM(CO)_5 + NaFe(CO)_2Cp \rightarrow CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5 + NaX \quad (2a)$$

$$i\text{-}Pr_2NP(H)ClMn(CO)_2Cp + NaFe(CO)_2Cp \rightarrow CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp + NaCl \quad (2b)$$

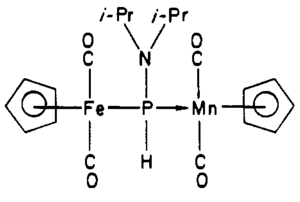
Table VII. Positional Parameters for $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$

atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)
W	0.1570 (1)	0.2592 (1)	0.1130 (0)
Fe1	0.3458 (2)	0.3805 (4)	0.1464 (2)
P1	0.2456 (4)	0.4281 (7)	0.0449 (3)
C1	0.3614 (25)	0.5278 (25)	0.2399 (13)
C2	0.3387 (22)	0.6344 (32)	0.1819 (15)
C3	0.4117 (27)	0.6168 (45)	0.1456 (17)
C4	0.4759 (21)	0.5028 (48)	0.1782 (21)
C5	0.4452 (26)	0.4420 (37)	0.2391 (15)
C10	0.2698 (18)	0.2075 (28)	0.1967 (14)
O10	0.3055 (14)	0.1255 (25)	0.2485 (9)
C11	0.1197 (22)	0.4811 (43)	0.1556 (13)
O11	0.1013 (18)	0.6058 (31)	0.1799 (13)
C12	0.0778 (23)	0.1422 (42)	0.1663 (21)
O12	0.0322 (23)	0.0670 (37)	0.2012 (16)
C13	0.1922 (18)	0.0286 (35)	0.0738 (13)
O13	0.2114 (17)	−0.1003 (23)	0.0544 (12)
C14	0.0450 (17)	0.2764 (37)	0.0329 (16)
O14	−0.0172 (15)	0.2813 (36)	−0.0170 (12)
C20	0.3996 (17)	0.2034 (33)	0.1180 (12)
O20	0.4392 (15)	0.0851 (27)	0.1022 (10)
N1	0.2630 (15)	0.3858 (22)	−0.0346 (9)
C40	0.2621 (20)	0.5214 (28)	−0.0886 (12)
C41	0.1646 (21)	0.6048 (37)	−0.1127 (14)
C42	0.3398 (23)	0.6525 (35)	−0.0662 (15)
C50	0.2843 (18)	0.2089 (29)	−0.0547 (11)
C51	0.3773 (21)	0.1931 (33)	−0.0718 (14)
C52	0.2027 (20)	0.1417 (33)	−0.1111 (13)
H1	0.3230	0.5139	0.2764
H2	0.2803	0.7092	0.1680
H3	0.4156	0.6817	0.1019
H4	0.5347	0.4685	0.1629
H5	0.4787	0.3585	0.2745
HP1	0.2322	0.6191	0.0299
H40	0.2700	0.4664	−0.1336
H411	0.1461	0.6589	−0.0723
H412	0.1154	0.5178	−0.1316
H413	0.1605	0.6919	−0.1493
H421	0.4042	0.5955	−0.0561
H422	0.3355	0.7092	−0.0224
H423	0.3424	0.7407	−0.1014
H50	0.2843	0.1316	−0.0150
H511	0.4279	0.2293	−0.0318
H512	0.3802	0.2699	−0.1118
H513	0.3931	0.0786	−0.0854
H521	0.1910	0.2155	−0.1536
H522	0.1429	0.1414	−0.0945
H523	0.2138	0.0260	−0.1256

These reactions appear to proceed cleanly with a minimum of side reactions so that pure products can be isolated from the reaction mixtures by crystallization from pentane or hexane without the need for chromatography. The high nucleophilicity of $CpFe(CO)_2^-$ seems to be an important requirement for the success of this preparation since reactions of $i\text{-}Pr_2NP(H)ClM(CO)_5$ (M = Cr, W) with the much less nucleophilic[5] $CpW(CO)_3^-$ failed to give analogous products under similar conditions. Similar observations were made many years ago in connection with reactions of metal carbonyl anions with polyfluoroarenes[9] and with chlorosilanes[10] in tetrahydrofuran where only highly nucleophilic metal carbonyl anions such as $CpFe(CO)_2^-$ give significant yields of the expected substitution products. Also, the reaction of $i\text{-}Pr_2NP(H)ClFe(CO)_4$ with $NaFe(CO)_2Cp$ under conditions similar to those used for the other reactions of $NaFe(CO)_2Cp$ failed to give any evidence for the formation of significant quantities of a crystalline bimetallic product.



I



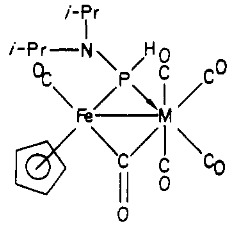
II

These heterobimetallic products are deep orange (Fe/Cr, Fe/Mo, Fe/W) to deep red (Fe/Mn) solids that are soluble in nonpolar and polar organic solvents and apparently very stable toward atmospheric oxygen and moisture. Their spectroscopic properties are in accord with structures I and II, in which the phosphorus atom is bonded to four different elements: hydrogen, nitrogen, and two different transition metals. Thus, their infrared $\nu(CO)$ spectra (Table II) exhibit frequencies assignable to both the $CpFe(CO)_2$ and $M(CO)_5$ or $CpMn(CO)_2$ units in structures I and II, respectively. For example, in $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Cr(CO)_5$ (I: M = Cr) the strong $\nu(CO)$ frequencies at 1970 and 1920 cm^{-1} can be assigned to the $CpFe(CO)_2$ unit and the remaining $\nu(CO)$ frequencies at 2040, 2005, 1955, and 1935 cm^{-1} can be assigned to the A_1, B_1, A_1, and E frequencies of the $Cr(CO)_5$ unit on the basis of their positions and relative intensities. Note that the very low symmetry of the $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)$ ligand leads to an infrared-active B_1 frequency in contrast to the infrared *inactivity* of this frequency expected[11,12] for ideal C_{4v} symmetry in an $LM(CO)_5$ derivative. The infrared spectrum of $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$ (II) exhibits four terminal $\nu(CO)$ frequencies, two for the $CpFe(CO)_2$ unit and two for the $CpMn(CO)_2$ unit. The proton NMR spectra of I and II (Table III) exhibit the expected resonances for the PH, C_5H_5, CH, and CH_3 groups. The $|^1J(P\text{–}H)|$ coupling constants *decrease* by 80–90 Hz when an $i\text{-}Pr_2NP(H)X$ metal carbonyl complex is converted to the corresponding $i\text{-}Pr_2NP(H)Fe(CO)_2Cp$ metal carbonyl complex (I and II) by reaction with $NaFe(CO)_2Cp$. The proton NMR P–H chemical shifts (Table III) change relatively little in going from an $(i\text{-}Pr_2N)_2PH$ metal carbonyl complex to the corresponding $i\text{-}Pr_2NP(H)Fe(CO)_2Cp$ metal carbonyl complex. The phosphorus-31 NMR chemical shifts (measured as δ values *downfield* from 85% H_3PO_4) of $i\text{-}Pr_2NP(H)X$ complexes of the same metal carbonyl system (Table III) decrease in the sequence

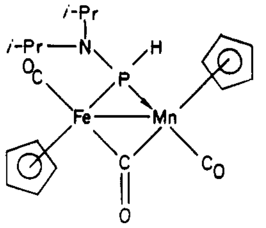
$$i\text{-}Pr_2NP(H)Cl > i\text{-}Pr_2NP(H)Br > (i\text{-}Pr_2N)_2PH > i\text{-}Pr_2NP(H)Fe(CO)_2Cp$$

The upfield phosphorus-31 NMR chemical shift in going from an $(i\text{-}Pr_2N)_2PH$ metal carbonyl complex to the corresponding $i\text{-}Pr_2NP(H)Fe(CO)_2Cp$ metal carbonyl complex is 25–40 ppm (Table III).

The most important chemical property of the complexes $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5$ (I: M = Cr, W) and $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$ (II) is their facile photochemical decarbonylation in hydrocarbon solvents to give $CpFeM(CO)_6PH(N\text{-}i\text{-}Pr_2)$ (M = Cr, W) and $Cp_2FeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$, respectively. Structural studies by X-ray diffraction indicate $CpFeM(CO)_6PH(N\text{-}i\text{-}Pr_2)$ to have structure III (M = Cr, W).



III



IV

A related structure, IV, is suggested for $Cp_2FeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$ on the basis of its infrared spectrum in the $\nu(CO)$ region (Table II), which exhibits two fairly strong terminal $\nu(CO)$ frequencies at 1947 and 1889 cm^{-1} and a single bridging $\nu(CO)$ frequency at 1758 cm^{-1}.

The complexes $CpFeM(CO)_6PH(N\text{-}i\text{-}Pr_2)$ (M = Cr, W) were found to be isomorphous, forming monoclinic crystals of the space group $P2_1/c$ with $Z = 4$. Least-squares refinement (Table IV) as indicated in the Experimental Section yields the structures (III:

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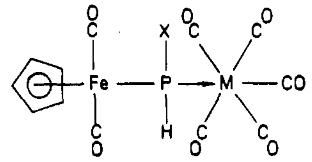
Table VIII. Bond Distances (Å) and Angles (deg) for $CpFeW(CO)_6P(H)(N\text{-}i\text{-}Pr_2)$

Fe1–W	2.827 (4)	C12–O12	1.20 (5)
Fe1–C1	2.12 (3)	C13–O13	1.13 (3)
Fe1–C2	2.11 (3)	C14–O14	1.16 (3)
Fe1–C3	2.08 (4)	C20–O20	1.16 (3)
Fe1–C4	2.08 (3)	C1–C2	1.38 (4)
Fe1–C5	2.09 (3)	C2–C3	1.41 (5)
Fe1–C10	2.12 (3)	C3–C4	1.34 (5)
Fe1–P1	2.201 (5)	C4–C5	1.44 (5)
Fe1–C20	1.74 (3)	C5–C1	1.39 (5)
W–C10	2.07 (2)	P1–N1	1.65 (2)
W–C11	2.04 (3)	N1–C40	1.49 (3)
W–C12	1.94 (4)	N1–C50	1.49 (3)
W–C13	2.06 (3)	C40–C41	1.53 (4)
W–C14	1.98 (2)	C40–C42	1.51 (4)
W–P1	2.433 (6)	C50–C51	1.46 (4)
C10–O10	1.21 (3)	C50–C52	1.51 (3)
C11–O11	1.14 (4)		
W–Fe1–P1	56.2 (2)	P1–W–C14	88 (1)
W–Fe1–C10	46.7 (6)	Fe1–C10–W	85.0 (9)
W–Fe1–C20	98.1 (8)	Fe1–P1–W	75.0 (2)
P1–Fe1–C10	102.5 (6)	Fe1–C10–O10	124 (2)
P1–Fe1–C20	95.8 (7)	W–C10–O10	151 (2)
C10–Fe1–C20	88 (1)	Fe1–C20–O20	176 (2)
Fe1–W–C10	48.2 (7)	W–C11–O11	178 (3)
Fe1–W–C11	87.4 (9)	W–C12–O12	177 (3)
Fe1–W–C12	134.0 (10)	W–C13–O13	178 (2)
Fe1–W–C13	94.0 (7)	W–C14–O14	175 (3)
Fe1–W–C14	137.2 (4)	Fe1–P1–N1	126.5 (8)
Fe1–W–P1	48.8 (1)	W–P1–N1	127.7 (7)
C10–W–C11	95 (1)	P1–N1–C40	122 (1)
C10–W–C12	87 (1)	P1–N1–C50	121 (1)
C10–W–C13	84 (1)	N1–C40–C41	112 (2)
C10–W–C14	172 (1)	N1–C40–C42	113 (2)
C11–W–C12	86 (1)	C41–C40–C42	112 (2)
C11–W–C13	177 (1)	N1–C50–C51	113 (2)
C11–W–C14	91 (1)	N1–C50–C52	110 (2)
C12–W–C13	91 (1)	C51–C50–C52	114 (2)
C12–W–C14	88 (1)	C1–C2–C3	107 (3)
C13–W–C14	90 (1)	C2–C3–C4	110 (3)
P1–W–C10	96 (1)	C3–C4–C5	107 (3)
P1–W–C11	89 (1)	C4–C5–C1	107 (2)
P1–W–C12	174 (1)	C5–C1–C2	109 (3)
P1–W–C13	94 (1)		

M = Cr, W) depicted in Figures 1 and 2 for the chromium and tungsten complexes, respectively. In these structures, the iron atom is bonded to a terminal carbonyl group and a η^5-cyclopentadienyl ring and the group 6 metal M is bonded to four terminal carbonyl groups. The iron and group 6 metals are within bonding distance (Fe–Cr = 2.733 (2) Å in $CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$ and Fe–W = 2.827 (4) Å in $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$). These metal–metal bonds are bridged by a carbonyl group (Fe–C = 2.023 (9) Å, Cr–C = 2.023 (7) Å in $CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$ and Fe–C = 2.12 (3) Å, W–C = 2.07 (2) Å in $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$) and an $i\text{-}Pr_2NPH$ phosphido group (Fe–P = 2.207 (2) Å, Cr–P = 2.292 (2) Å in $CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$ and Fe–P = 2.201 (5) Å, W–P = 2.433 (6) Å in $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$). The bridging phosphido group is unsymmetrical, but the bridging carbonyl group is symmetrical within experimental error despite the dissimilarity of the metal atoms being bridged.

The spectroscopic properties of the three heterobimetallic complexes $CpFeM(CO)_6PH(N\text{-}i\text{-}Pr_2)$ (III: M = Cr, W) and $Cp_2FeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$ (IV) are in accord with the observed (III) and proposed (IV) structures, respectively. The infrared spectra of all three of these complexes (Table II) exhibit a single bridging $\nu(CO)$ frequency in addition to the expected number of terminal $\nu(CO)$ frequencies, but the bridging $\nu(CO)$ frequency in $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$ in contrast to that in its chromium analogue is so weak that it was only identified after the structure determination was completed. Replacement of three carbonyl groups in $CpFeM(CO)_6PH(N\text{-}i\text{-}Pr_2)$ (III: M = Cr, W) with a cyclopentadienyl ring to give $Cp_2FeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$ (IV) with the necessary adjustment in the non-iron transition metal lowers the bridging $\nu(CO)$ frequency by about 60 cm^{-1} (1810 → 1758 cm^{-1}), in accord with the weaker π-acceptor strength of a cyclopentadienyl ring relative to three carbonyl groups. Substantial changes occur in various NMR parameters (Table III) upon decarbonylation of I to III and II to IV with heteronuclear metal–metal bond formation leading to a FePM three-membered ring. Most dramatic is the 125–155 ppm downfield phosphorus-31 NMR chemical shift, which clearly appears to be a consequence of ring formation. Also significant are a 40–75 Hz increase in the $|^1J(P\text{–}H)|$ coupling constant and a ~2-ppm downfield proton NMR chemical shift of the P–H hydrogen.

One of the interesting features of the heterobimetallic μ-phosphido compounds described in this paper is the presence of potentially reactive phosphorus–nitrogen bonds, in contrast to previously reported dialkylphosphido and diarylphosphido heterobimetallic derivatives such as $MnFe(\mu\text{-}PPh_2)(CO)_8$,[6] $CpNiFe(CO)_3(\mu\text{-}CO)(\mu\text{-}PPh_2)$,[6] $WRe(\mu\text{-}PMe_2)(CO)_{10}$,[13] $WRe(\mu\text{-}PPh_2)(CO)_9$,[14] $WIrH(\mu\text{-}PPh_2)_2(CO)_5(PPh_3)$,[15] $(OC)_4Mn(\mu\text{-}PR_2)(\mu\text{-}H)Mo(CO)_2Cp$ (R = *p*-tolyl),[16] and $Cp_2ZrW(\mu\text{-}PPh_2)_2(CO)_4$,[17] which contain only relatively unreactive phosphorus–carbon bonds in addition to the phosphorus–transition-metal bonds. One feature of phosphorus–nitrogen bonds that has been exploited in the previous papers of this series[1,4] is their facile cleavage with hydrogen halides to give the corresponding phosphorus–halogen compounds. In this connection the complexes $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5$ (I: M = Cr, Mo, W) react readily with the hydrogen halides HX (X = Cl, Br) in hydrocarbon solvents to give the corresponding $CpFe(CO)_2PHXM(CO)_5$ derivatives (V)



V

according to the equation

$$CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5 + 2HX \rightarrow CpFe(CO)_2PHXM(CO)_5 + [i\text{-}Pr_2NH_2]X \quad (3)$$

The $CpFe(CO)_2PHXM(CO)_5$ derivatives (V) are orange to brown, air- and moisture-sensitive crystalline solids that are soluble in both nonplanar and polar organic solvents. Their infrared $\nu(CO)$ spectra (Table II) resemble those of their $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5$ precursors (I), but corresponding bands are shifted to higher frequencies by up to 30 cm^{-1}, in accord with the expected effect upon replacement of a dialkylamino group on phosphorus with a halogen atom. The phosphorus-31 NMR chemical shifts move downfield by 60–82 ppm and by 80–107 ppm as the diisopropylamino group is replaced by bromine and by chlorine, respectively, with the shifts being larger in the sequence W < Mo < Cr. The proton P–H NMR chemical shifts move downfield by about 0.6–0.75 ppm as the diisopropylamino group is replaced by bromine but move upfield by 0.15–0.2 ppm as the diisopropylamino group is replaced by chlorine.

The conversion of $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5$ (I) to $CpFe(CO)_2PHXM(CO)_5$ (V) with the hydrogen halides, HX, represents the final step of the synthetic sequence

$$(i\text{-}Pr_2N)_2PHM(CO)_5 \rightarrow i\text{-}Pr_2NP(H)XM(CO)_5 \rightarrow CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)M(CO)_5 \text{ (I)} \rightarrow CpFe(CO)_2PHXM(CO)_5 \text{ (V)} \quad (4)$$

This synthetic sequence shows how the two diisopropylamino groups in $(i\text{-}Pr_2N)_2PH$ metal carbonyl complexes[4] can be replaced

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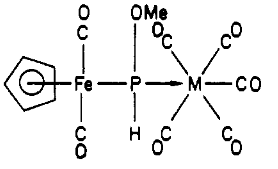
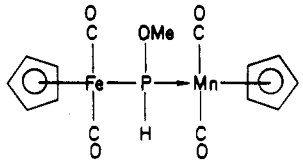
stepwise by the other groups of interest and suggests potential synthetic applications of these systems in organophosphorus coordination chemistry.

Some methanolysis reactions were also investigated. Thus, treatment of $CpFe(CO)_2PHClM(CO)_5$ (M = Cr, W) with boiling methanol gives the corresponding $CpFe(CO)_2PH(OMe)M(CO)_5$ derivatives, VI. A manganese analogue, $CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$ (VII), was prepared directly from $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$ by heating in boiling methanol. The patterns of the ν(CO) frequencies of these methoxy derivatives (Table II) resemble those of the analogous diisopropylamino and halo derivatives. The proton NMR spectra of these methoxy derivatives exhibit the expected doublet OCH_3 resonances around δ 3.5–3.6 (J = 12–13 Hz) in addition to the PH and C_5H_5 resonances.


VI


VII

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Registry No. $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Cr(CO)_5$, 97825-67-7; $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mo(CO)_5$, 97825-68-8; $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)W(CO)_5$, 97825-69-9; $NaFe(CO)_2Cp$, 12152-20-4; $[CpFe(CO)_2]_2$, 12154-95-9; $i\text{-}Pr_2NP(H)BrCr(CO)_5$, 102283-12-5; $i\text{-}Pr_2NP(H)ClMo(CO)_5$, 102260-82-2; $i\text{-}Pr_2NP(H)ClW(CO)_5$, 102260-83-3; $CpFe(CO)_2PH(N\text{-}i\text{-}Pr_2)Mn(CO)_2Cp$, 97825-75-7; $i\text{-}Pr_2NP(H)ClMn(CO)_2Cp$, 102260-84-4; $CpFeCr(CO)_6PH(N\text{-}i\text{-}Pr_2)$, 102260-85-5; $CpFeW(CO)_6PH(N\text{-}i\text{-}Pr_2)$, 102260-86-6; $Cp_2FeMn(CO)_3PH(N\text{-}i\text{-}Pr_2)$, 97825-76-8; $CpFe(CO)_2PHClCr(CO)_5$, 102260-87-7; $CpFe(CO)_2PHBrCr(CO)_5$, 102260-88-8; $CpFe(CO)_2PHClMo(CO)_5$, 102260-89-9; $CpFe(CO)_2PHBrMo(CO)_5$, 102260-90-2; $CpFe(CO)_2PHClW(CO)_5$, 102260-91-3; $CpFe(CO)_2PHBrW(CO)_5$, 97825-71-3; $CpFe(CO)_2PH(OMe)Cr(CO)_5$, 102260-92-4; $CpFe(CO)_2PH(OMe)W(CO)_5$, 102260-93-5; $CpFe(CO)_2PH(OMe)Mn(CO)_2Cp$, 102260-94-6; Fe, 7439-89-6; W, 7440-33-7; Cr, 7440-47-3; Mn, 7439-96-5; Mo, 7439-98-7.

Supplementary Material Available: Listings of anisotropic thermal parameters (2 pages). Ordering information is given on any current masthead page.

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Electron-Transfer Barriers in Cobalt(III) and Cobalt(II) Bis Complexes of 1,4,7-Triazacyclononane (tacn) and 1,4,7-Trithiacyclononane (ttcn). Crystal Structures of $[Co^{II}(tacn)_2]I_2\cdot 2H_2O$ and of $[Co^{III}(ttcn)_2](ClO_4)_3$

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The structures of $[Co(tacn)_2]I_2\cdot 2H_2O$ and of $[Co(ttcn)_2](ClO_4)_3$ have been determined, where tacn is 1,4,7-triazacyclononane ($C_6H_{15}N_3$) and ttcn is 1,4,7-trithiacyclononane ($C_6H_{12}S_3$). The cobalt(II) complex crystallizes in the orthorhombic crystal system, space group *Ibca* (D_{2h}^{27}), with a = 13.60 (2) Å, b = 15.43 (1) Å, c = 20.81 (2) Å, and Z = 8. The structure was refined to a conventional R value of 0.067. The coordination sphere consists of six nitrogen atoms of two tacn ligands in a distorted octahedral arrangement about the cobalt(II). The average Co–N distance is 2.155 Å. The cobalt(III) complex crystallizes in the monoclinic crystal system, space group $C2/c$ (C_{2h}^6), with a = 12.194 (3) Å, b = 15.146 (4) Å, c = 13.418 (3) Å, β = 94.42 (2)°, and Z = 4. The structure was refined to R = 0.0395. The coordination sphere consists of six sulfur atoms of two ttcn ligands in a nearly regular octahedral arrangement about the cobalt(III). The average Co–S distance is 2.253 Å. The electron-exchange rate constant for the reaction of $[((R)\text{-Metacn})Co(tacn)]^{2+}$ and $[((S)\text{-Metacn})Co(tacn)]^{3+}$ has been determined ($k_{ex} = 0.19\ M^{-1}\ s^{-1}$ at 25 °C; I = 0.1 M ($LiClO_4$)). The corresponding rate constant for the couple $[Co(ttcn)_2]^{3+/2+}$ has been evaluated to be $1.3 \times 10^4\ M^{-1}\ s^{-1}$ at 25 °C (I = 0.2 M) from the cross-reaction between $[Co(ttcn)_2]^{3+}$ and $[Co(phen)_3]^{2+}$. The redox reactivities of $[Co(tacn)_2]^{3+/2+}$ and $[Co(ttcn)_2]^{3+/2+}$ have been analyzed in the frame of the Marcus–Sutin model for outer-sphere electron-transfer reactions.

Introduction

In the past 5 years a variety of complexes of first transition series metals containing two tridentate macrocyclic ligands such as 1,4,7-triazacyclononane (tacn) have been synthesized and have in many instances been characterized spectroscopically and crystallographically. The most remarkable property of these complexes is their pronounced stability in aqueous solution toward ligand dissociation. Thus, $[Ni(tacn)_2]^{2+}$[2] and $[Ni(tacn)_2]^{3+}$,[3,4] $[Fe(tacn)_2]^{2+}$[3,5] and $[Fe(tacn)_2]^{3+}$,[3,5] and $[Co(tacn)_2]^{2+}$[3] and $[Co(tacn)_2]^{3+}$[6] have been synthesized. The Ni[2,7] and Fe[5] pairs have been studied by X-ray crystallography, and metrical information concerning the metal–ligand distances is available. It is the change of these distances in changing the oxidation state of the central metal ion that governs the redox reactivity of these complexes. Electron-transfer rates are currently successfully analyzed by using a semiclassical model developed by Marcus and Sutin.[8-10]

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