

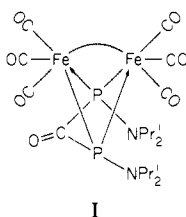
(Dialkylamino)phosphorus Metal Carbonyls. 5. Chemical Reactivity of the Phosphorus-Bridging Carbonyl Group in Carbonylbis[(diisopropylamino)phosphido]hexacarbonyldiiron¹⁻⁴

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Abstract: Treatment of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with NaBH_4 in methanol results in reduction of the phosphorus-bridging carbonyl group to give the corresponding secondary alcohol $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$. Similar treatment of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with LiAlH_4 in diethyl ether results in more extensive reduction to give a dark orange product of stoichiometry $((i\text{-Pr})_2\text{NP})_2\text{CH}_2\text{Fe}_2(\text{CO})_6$ shown, however, by X-ray diffraction (triclinic, $P\bar{1}$; $a = 14.412$ (6), $b = 10.409$ (5), $c = 10.014$ (4) Å; $\alpha = 111.80$ (3), $\beta = 82.19$ (3), $\gamma = 106.86$ (4)°; $Z = 2$) to be $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$ in which an iron-phosphorus bond has been broken and a new iron-carbon bond formed. Treatment of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with the alkylolithiums RLi ($\text{R} = \text{Me}, n\text{-Bu}$) results in addition to the phosphorus-bridging carbonyl group to give the corresponding tertiary alcohols $((i\text{-Pr})_2\text{NP})_2\text{C}(\text{R})(\text{OH})\text{Fe}_2(\text{CO})_6$. Reduction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with sodium amalgam in tetrahydrofuran results in cleavage of a diisopropylamino group to give the anion $[(i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6]^-$, which can be isolated as its orange bis(triphenylphosphine)iminium salt or as the light orange trimethyltin derivative $((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$. Reaction of $[(i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6]^-$ with $(i\text{-Pr})_2\text{NPCl}_2$ results in rearrangement with expulsion of the phosphorus-bridging carbonyl group to give orange $[(i\text{-Pr})_2\text{NP}((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6$. X-ray diffraction (monoclinic, $P2_1/a$; $a = 15.384$ (6), $b = 18.355$ (4), $c = 10.125$ (1) Å; $\beta = 108.19$ (2)°; $Z = 4$) indicates a structure with a triphosphorus chain bridging an $\text{Fe}_2(\text{CO})_6$ unit through the end phosphorus atoms. One of the end phosphorus atoms of this triphosphorus chain is an ordinary (diisopropylamino)phosphido group whereas the other end phosphorus atom is trigonal pyramidal with a lone pair. The center phosphorus atom of this triphosphorus chain is four-coordinate, being bonded to the other two phosphorus atoms, a diisopropylamino group, and a chlorine atom. Reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with alcohols ROH ($\text{R} = \text{Me}, \text{Et}$) under relatively vigorous conditions results in expulsion of the phosphorus-bridging carbonyl group to give yellow $((i\text{-Pr})_2\text{NPOR})(i\text{-Pr})_2\text{NPHFe}_2(\text{CO})_6$. Reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with hydrogen bromide results in expulsion of the phosphorus-bridging carbonyl group and selective cleavage of one of the diisopropylamino groups to give orange $((i\text{-Pr})_2\text{NPBr})(\text{HPBr})\text{Fe}_2(\text{CO})_6$; both stereoisomers have been detected by ^{31}P NMR, and one has been isolated in the pure state. Reaction of $((i\text{-Pr})_2\text{NPOEt})(i\text{-Pr})_2\text{NPHFe}_2(\text{CO})_6$ with hydrogen bromide results in selective cleavage of one of the two diisopropylamino groups to give orange $((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$. The formulation of this complex as a novel bis(phosphido)hexacarbonyldiiron derivative with four different terminal groups $((i\text{-Pr})_2\text{N}, \text{EtO}, \text{H}, \text{and Br})$ has been confirmed by structure determination using X-ray diffraction (triclinic, $P\bar{1}$; $a = 13.700$ (6), $b = 9.818$ (5), $c = 9.258$ (5) Å; $\alpha = 64.54$ (4), $\beta = 96.07$ (4), $\gamma = 84.80$ (4)°; $Z = 2$).

Recent results from our laboratory^{1,4} have shown that the reaction of $(i\text{-Pr})_2\text{NPCl}_2$ with $\text{Na}_2\text{Fe}(\text{CO})_4$ in diethyl ether solution provides a source of the phosphorus-bridging carbonyl complex $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) in ~35% yield, thereby making this



air-stable complex readily available in ~40-g quantities. This complex can be regarded as a novel analogue of a ketone in which the carbonyl group is bonded to two phosphorus atoms rather than two carbon atoms. Furthermore, the ready availability and stability of this complex provide an unprecedented opportunity for investigating the chemical reactivity of this unusual functionality. This paper presents some details on our studies of the chemical reactivity of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with particular emphasis on reactions of the following types: (1) reduction of the phosphorus-bridging carbonyl group using reagents such as NaBH_4 , LiAlH_4 , alkylolithiums, and sodium amalgam; (2) expulsion of the phosphorus-bridging carbonyl group upon treatment with protic reagents to give novel bis(phosphido)hexacarbonyldiiron derivatives containing phosphorus-hydrogen bonds.

Experimental Section

The general techniques for microanalyses, infrared spectra (Table I), ^{31}P (Table II), ^{13}C (Table III), and ^1H (Table IV) NMR spectra, melting points, solvent purification, and inert-atmosphere handling are similar to those given in the previous paper of this series.¹ Commercial $\text{Fe}(\text{CO})_5$, diisopropylamine, and PCl_3 were converted to $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) through $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5\text{C}_4\text{H}_6\text{O}_2^3$ and $(i\text{-Pr})_2\text{NPCl}_2^6$ by the published procedure.^{1,4} Other reagents were obtained from standard commercial sources, mainly Alfa and Aldrich.

Reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with NaBH_4 . A suspension of 0.15 g (4.0 mmol) of NaBH_4 in 100 mL of methanol was treated with 2.24 g (3.9 mmol) of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) at room temperature. The progress of the reaction over a period of 5 days at ambient temperature was monitored by disappearance of the infrared $\nu(\text{CO})$ frequencies of I. The reaction mixture was filtered at the end of the reaction period. Removal of solvent from the filtrate gave 1.5 g (67% yield) of yellow air-sensitive $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$, 125 °C dec. Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{Fe}_2\text{N}_2\text{O}_7\text{P}_2$: C, 39.9; H, 5.2; N, 4.9. Found: C, 40.1; H, 5.3; N, 4.8.

Reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with LiAlH_4 . An orange solution of 2.0 g (3.5 mmol) of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ in 100 mL of

(1) Part 4. King, R. B.; Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.* **1987**, *109*, 7764.

(2) This work was taken in part from: Wu, F. J. Doctoral Dissertation, University of Georgia, 1987.

(3) Portions of this work were presented at the 12th International Conference on Organometallic Chemistry, Vienna, Austria, Sept 1985, and the 191st National Meeting of the American Chemical Society, New York, April 1986.

(4) For a preliminary communication of some of this work, see: King, R. B.; Wu, F.-J.; Sadanani, N. D.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 4449.

(5) Finke, R. G.; Sorrell, T. N. *Org. Synth.* **1980**, *59*, 102.

(6) King, R. B.; Sadanani, N. D. *Synth. React. Inorg. Met-Org. Chem.* **1985**, *15*, 149.

(7) Akitt, J. W. *NMR and Chemistry*; Chapman and Hall: London, 1973.

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Table I. Infrared $\nu(\text{CO})$ Frequencies of Compounds Derived from $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6^a$

compound	IR $\nu(\text{CO})$, cm^{-1}
$((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$	2060 m, 2016 s, 1996 s, 1975 s, 1964 m, 1720 m ^b
$((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$	2050 m, 2010 s, 1993 s, 1979 s, 1965 m, 1715 m ^b
$(((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6$	2048 m, 2008 s, 1992 s, 1978 s, 1971 m, 1958 m
$[(\text{Ph}_3\text{P})_2\text{N}][((i\text{-Pr})_2\text{NPCOP})\text{Fe}_2(\text{CO})_6]^c$	2016 m, 1980 s, 1947 s, 1930 m
$((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$	2050 m, 2007 s, 1995 s, 1959 m, 1945 m
$((i\text{-Pr})_2\text{NP})_2\text{CMe}(\text{OH})\text{Fe}_2(\text{CO})_6$	2057 m, 2012 s, 1995 s, 1960 m, 1942 m
$((i\text{-Pr})_2\text{NP})_2\text{C}(n\text{-Bu})(\text{OH})\text{Fe}_2(\text{CO})_6$	2053 m, 2007 s, 1992 s, 1960 m, 1940 m
$((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$	2050 m, 2007 s, 1980 s, 1968 m, 1955 m
$((i\text{-Pr})_2\text{NPOMe})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$	2050 m, 2012 s, 1987 s, 1977 s, 1962 s, 1952 m
$((i\text{-Pr})_2\text{NPOEt})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$	2055 m, 2015 s, 1987 s, 1977 s, 1961 s, 1954 m
$((i\text{-Pr})_2\text{NPBr})(\text{HPBr})\text{Fe}_2(\text{CO})_6$	2080 m, 2045 s, 2026 s, 2002 s, 1993 s
$((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$	2068 m, 2030 s, 2010 s, 1990 s, 1980 m

^a Hexane solutions (unless otherwise indicated). ^b Bridging P-(CO)-P frequency. ^c This spectrum was run in CH_2Cl_2 solution because of solubility limitations and therefore was not nearly as well resolved as the other spectra.

Table II. ^{31}P NMR Spectra of Compounds Derived from $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$

compound	proton-decoupled ^{31}P NMR ^{a,b}			proton couplings, ^{b,c} Hz
	P_a , δ	P_b , δ	$^2J(\text{P-P})$, Hz	
$((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$	225.6 s			$^3J(\text{P-H}) = 7$
$((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$	169.4 s			$^2J(\text{P-H}) = 10$, $^3J(\text{P-H}) = 8$ (with $(i\text{-Pr})_2\text{N}$)
$((i\text{-Pr})_2\text{NP})_2\text{CMe}(\text{OH})\text{Fe}_2(\text{CO})_6$	187.4 s			$^3J(\text{P-H}) = 8$ (with $(i\text{-Pr})_2\text{N}$), $^3J(\text{P-H}) = 19$ (with Me)
$((i\text{-Pr})_2\text{NP})_2\text{C}(n\text{-Bu})(\text{OH})\text{Fe}_2(\text{CO})_6$	189.4 s			not resolved
$((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$	7.7 d	173.7 d	98	$^1J(\text{P}_a\text{-H}) = 421$, $^2J(\text{P}_a\text{-H}) = 8$, $^3J(\text{P}_a\text{-H}) = 13$, $^3J(\text{P}_b\text{-H}) = 16$ (with $(i\text{-Pr})_2\text{N}$), $^3J(\text{P}_b\text{-H}) = 32$ (Ph_3P) $_2\text{N}^+$ resonance, δ 21.0
$[(\text{Ph}_3\text{P})_2\text{N}][((i\text{-Pr})_2\text{NPCOP})\text{Fe}_2(\text{CO})_6]$	172.8 d	211.5 d	56	
$((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$	114.1 d	197.6 d	66	
$((i\text{-Pr})_2\text{NPOMe})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$	145.7 d	270.5 d	128	$^1J(\text{P}_a\text{-H}) = 398$, $^3J(\text{P}_a\text{-H}) = 15$, $^3J(\text{P}_b\text{-H}) = 23$, 11, 11
$((i\text{-Pr})_2\text{NPOEt})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$	146.1 d	264.4 d	127	$^1J(\text{P}_a\text{-H}) = 398$, $^3J(\text{P}_a\text{-H}) = 15$
$((i\text{-Pr})_2\text{NPBr})(\text{HPBr})\text{Fe}_2(\text{CO})_6$ (K) ^d	167.3	273.0 d	91	$^1J(\text{P}_a\text{-H}) = 440$
$((i\text{-Pr})_2\text{NPBr})(\text{HPBr})\text{Fe}_2(\text{CO})_6$ (T) ^d	151.1 d	242.1 d	136	$^1J(\text{P}_a\text{-H}) = 418$
$((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$	159.5 d	246.8 d	137	$^1J(\text{P}_a\text{-H}) = 405$

^a CDCl_3 solutions; chemical shifts are given (ppm) *downfield* from external 85% H_3PO_4 . ^b Key: s = singlet; d = doublet; coupling constants given in hertz. ^c These coupling constants were obtained from spectra run without proton decoupling. ^d K = initially formed (kinetically favored) isomer; T = finally isolated (thermodynamically favored) isomer.

Table III. Proton-Decoupled ^{13}C NMR Spectra of Compounds Derived from $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$

compound	proton-decoupled ^{13}C NMR spectral data ^{a,b}			
	isopropyl groups		terminal CO	other
CH	CH_3			
$((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$	53.6	22.6	212.2	PC(O)P, 209.2 t (83)
$((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$	53.4	22.8	213.6	PCP, 130.2 t (8); $^1J(\text{C-H}) = 163^c$
$((i\text{-Pr})_2\text{NP})_2\text{CMe}(\text{OH})\text{Fe}_2(\text{CO})_6$	53.0	23.6, 22.9	213.7	PCP, 144.6 t (8); PC(Me)P, 27.5 t (5)
$((i\text{-Pr})_2\text{NP})_2\text{C}(n\text{-Bu})(\text{OH})\text{Fe}_2(\text{CO})_6$	53.2	23.6, 22.6	213.2	PCP, 149.9 t (6); <i>n</i> -Bu, 41.7, 26.9, 13.5
$((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$	51.2, 45.8	23.4, 22.7	214.8, 214.2, 212.4	PCP, 25.2 dd (26, 13); $^1J(\text{C-H}) = 169^c$
$[(\text{Ph}_3\text{P})_2\text{N}][((i\text{-Pr})_2\text{NPCOP})\text{Fe}_2(\text{CO})_6]^d$	51.2	23.4	<i>d</i>	Ph, 134.5, 133.1 t (6), 130.3 t (7), 126.0
$((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$	51.5	21.1	211.5	PC(O)P, 212.5 dd (20, 8); Me_3Sn , -6.5
$(((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6$	53.7, 50.4	23.6, 21.9	212.4	
$((i\text{-Pr})_2\text{NPOMe})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$	53.3, 48.5	23.6, 21.8	213.8, 213.6, 213.4	MeO, 56.8 d (13)
$((i\text{-Pr})_2\text{NPOEt})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$	53.2, 48.6	21.9, 21.8	214.0, 213.8, 213.5	EtO, 65.4 d (13), 15.7 d (9)
$((i\text{-Pr})_2\text{NPBr})(\text{HPBr})\text{Fe}_2(\text{CO})_6$	55.8	21.7	210.0, 209.9, 209.7	
$((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$	53.4	23.6	211.4, 211.2, 211.0	EtO, 66.3 d (14), 15.7 d (10)

^a CDCl_3 solutions. ^b For proton-decoupled spectra: d = doublet, t = triplet, dd = double doublet; coupling constants in hertz given in parentheses. ^c Determined from the proton-coupled spectrum. ^d (CD_3) $_2\text{CO}$ solution to maximize solubility; the solvent obscured the carbonyl resonances. ^e This spectrum corresponds to the isomer isolated in the pure state (T in Table II).

diethyl ether was treated at -78°C with 3.6 mL of 1.0 M LiAlH_4 in diethyl ether. The orange solution slowly turned yellow. If the reaction was quenched at -78°C with several drops of saturated aqueous ammonium chloride after 10 min, the complex $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$ could be isolated in 90% yield by a procedure similar to that outlined above. If, however, the original yellow reaction mixture was allowed to warm slowly from -78°C , it started to change color from yellow to eventually deep orange above -45°C . One hour after the solution reached room temperature, the deep orange solution was treated with several drops of saturated aqueous ammonium chloride to quench the reaction. Solvent was removed from the reaction mixture in vacuo, and the residue was extracted with 150 mL of hexane. Concentrating and cooling (-10°C) the filtered extract gave 0.9 g (45% yield) of deep orange air-sensitive crystalline $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$, mp 97°C . Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{Fe}_2\text{N}_2\text{O}_6\text{P}_2$: C, 41.0; H, 5.4; N, 5.0. Found: C, 40.9; H, 5.5; N, 5.0.

Reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with Methylolithium. An orange solution of 1.05 g (1.84 mmol) of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ in 60 mL of diethyl ether was treated at room temperature with 3.2 mL of 1.0 M methylolithium in diethyl ether. The reaction was quenched 90 min later by several drops of trifluoroacetic acid. Solvent and volatile materials were removed under reduced pressure. The residue was extracted with 80 mL of hexane. Concentrating and cooling (-10°C) the filtered hexane extract gave 0.5 g (45% yield) of orange air-stable $((i\text{-Pr})_2\text{NP})_2\text{CMe}(\text{OH})\text{Fe}_2(\text{CO})_6$, mp 144°C . Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{Fe}_2\text{N}_2\text{O}_7\text{P}_2$: C, 40.9; H, 5.5; N, 4.8. Found: C, 40.5; H, 5.5; N, 4.7.

Reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with *n*-Butyllithium. A procedure similar to that outlined above using 1.0 g (1.75 mmol) of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$, 80 mL of diethyl ether, and 1.3 mL of 2.5 M *n*-butyllithium in diethyl ether gave 0.4 g (38% yield) of orange air-stable $((i\text{-Pr})_2\text{NP})_2\text{C}(n\text{-Bu})(\text{OH})\text{Fe}_2(\text{CO})_6$, mp 157°C . Anal. Calcd for

Table IV. ¹H NMR Spectra of Compounds Derived from ((i-Pr)₂NP)₂COFe₂(CO)₆

compound	¹ H NMR spectral data ^{a,b}			
	isopropyl groups		PH	other
	CH ^c	CH ₃		
((i-Pr) ₂ NP) ₂ COFe ₂ (CO) ₆	3.9–3.2	1.27 d (7)		
((i-Pr) ₂ NP) ₂ CH(OH)Fe ₂ (CO) ₆	3.46 sp (7)	1.21 d (7), 1.19d (7)		CH, 6.40 dt (11, 10); OH, 3.95 d (10)
((i-Pr) ₂ NP) ₂ CMe(OH)Fe ₂ (CO) ₆	3.50 sp (7)	1.14 d		Me, 1.77 dt (20, 3); OH, 4.20 d (3)
((i-Pr) ₂ NP) ₂ C(<i>n</i> -Bu)(OH)Fe ₂ (CO) ₆	3.8–3.1	1.2 d		<i>n</i> -Bu, 1.9–0.8; OH, 4.29 s
((i-Pr) ₂ NPHCHPN(i-Pr) ₂ Fe ₂ (CO) ₆	4.1–3.4	1.33 d (7), 1.24 d (7), 1.16 d (7)	6.16 dd (420, 32)	CH, 1.44 dd (8, 5)
[(Ph ₃ P) ₂ N]((i-Pr) ₂ NPCOPFe ₂ (CO) ₆) ^d	3.8–3.4	1.25 d (7)		Ph, 7.73 s, 7.60 s
((i-Pr) ₂ NP)(Me ₃ SnP)COFe ₂ (CO) ₆	3.63 sp (7)	1.27 d (7)		Me ₃ Sn, 0.71 s
((i-Pr) ₂ NPOMe)((i-Pr) ₂ NPH)Fe ₂ (CO) ₆	4.0–3.3	1.28 d (7), 1.20 d (7)	2.80 dd (400, 23)	MeO, 3.59 d (13)
((i-Pr) ₂ NPOEt)((i-Pr) ₂ NPH)Fe ₂ (CO) ₆	3.80 m (7)	1.25 d (7), 1.18 d (7)	5.70 dd (398, 23)	EtO, 3.8, 1.4
((i-Pr) ₂ NPBr)(HPBr)Fe ₂ (CO) ₆	4.4–3.6	1.35 d (7)	4.50 dd (416, 5)	
((i-Pr) ₂ NPOEt)(HPBr)Fe ₂ (CO) ₆	3.85 sp (7)	1.25 d (7)	4.66 dd (404, 7)	EtO, 3.9, 1.25 t (7)

^aCDCl₃ solutions. ^bKeys: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, sp = septet, m = multiplet, coupling constants in hertz given in parentheses. ^cNot all of the isopropyl CH resonances could be resolved. ^d(CD₃)₂CO solution.

C₂₃H₃₈Fe₂N₂O₇P₂: C, 44.0; H, 6.1; N, 4.5. Found: C, 43.6; H, 6.0; N, 4.4.

Preparation of [(Ph₃P)₂N]((i-Pr)₂NPCOPFe₂(CO)₆]. A solution of 2.0 g (3.5 mmol) of ((i-Pr)₂NP)₂COFe₂(CO)₆ in 100 mL of tetrahydrofuran was stirred at ambient temperature with the 0.2% sodium amalgam prepared from 0.4 g (17 mmol) of sodium and 200 g of mercury. The course of the reaction was monitored by ³¹P NMR and infrared spectroscopy. After 10 min of reaction, the ³¹P NMR spectrum indicated the complete disappearance of the δ 225 resonance of the ((i-Pr)₂NP)₂COFe₂(CO)₆ starting material but the formation of approximately equal quantities of the two species, namely a species exhibiting a singlet at δ 212 and a species exhibiting coupled doublets at δ 207 and 167 with a coupling constant of 61 Hz. The infrared spectrum of the reaction mixture at this same point exhibited terminal ν(CO) frequencies in the 1900–2000-cm⁻¹ range, approximately 40 cm⁻¹ lower than the corresponding frequencies in ((i-Pr)₂NP)₂COFe₂(CO)₆, and a new band at 1630 cm⁻¹. In the presence of the sodium amalgam, the reaction mixture was treated dropwise with 0.35 mL (2.0 mmol) of trifluoroacetic acid over a period of 30 min. This destroyed the species exhibiting the ³¹P NMR singlet at δ 212 while retaining the species exhibiting the two doublet ³¹P resonances and the 1630-cm⁻¹ infrared frequency, thereby effecting an important purification step. After removal of excess sodium amalgam, a solution of 1.5 g (2.6 mmol) of [(Ph₃P)₂N]Cl in 30 mL of dichloromethane was added. Removal of solvent followed by crystallization of the residue from a mixture of dichloromethane and diethyl ether gave 1.5 g (42% yield) of orange [(Ph₃P)₂N]((i-Pr)₂NPCOPFe₂(CO)₆], mp 153–154 °C. Anal. Calcd for C₄₉H₄₄Fe₂N₂O₇P₄: C, 58.3; H, 4.4; N, 2.8. Found: C, 57.9; H, 4.6; N, 2.7.

Preparation of ((i-Pr)₂NP)(Me₃SnP)COFe₂(CO)₆. A solution of [(i-Pr)₂NPCOPFe₂(CO)₆]⁻ was prepared by stirring 3.0 g (5.3 mmol) of ((i-Pr)₂NP)₂COFe₂(CO)₆ at ambient temperature in 200 mL of tetrahydrofuran for 90 min with the sodium amalgam obtained from 1.4 g (61 mmol) of sodium and 160 g of mercury. After removal of excess sodium amalgam, the resulting solution was treated at -78 °C with 2.2 g (11 mmol) of trimethyltin chloride. After stirring the reaction mixture for 8 h at room temperature, the solvent was removed in vacuo. The residue was extracted with 200 mL of hexane. The ³¹P NMR spectrum of the hexane solution indicated a mixture of ((i-Pr)₂NP)₂COFe₂(CO)₆ and ((i-Pr)₂NP)(Me₃SnP)COFe₂(CO)₆. Fractional crystallization from hexane using ³¹P NMR to monitor the progress of the separation gave 1.8 g (38% yield) of light orange ((i-Pr)₂NP)(Me₃SnP)COFe₂(CO)₆, 80 °C dec. Anal. Calcd for C₁₆H₂₃Fe₂N₂O₇Sn: C, 30.3; H, 3.6; N, 2.2. Found: C, 30.9; H, 3.7; N, 2.3.

Preparation of ((i-Pr)₂NP)((i-Pr)₂N)(Cl)PP]Fe₂(CO)₆. A solution of [(i-Pr)₂NPCOPFe₂(CO)₆]⁻ was prepared by stirring 5.0 g (8.8 mmol) of ((i-Pr)₂NP)₂COFe₂(CO)₆ in 280 mL of tetrahydrofuran at ambient temperature for 150 min with the sodium amalgam obtained from 1.8 g (78 mmol) of sodium and 180 g of mercury. After removal of excess amalgam, the solution was treated with 1.75 g (8.7 mmol) of (i-Pr)₂NPCl₂. After the solution was stirred overnight at ambient temperature, solvent was removed in vacuo. The sticky residue, indicated by its ³¹P NMR spectrum to be a mixture of ((i-Pr)₂NP)₂COFe₂(CO)₆, [(i-Pr)₂NP)((i-Pr)₂N)(Cl)PP]Fe₂(CO)₆, and other unstable unidentified species, was dried overnight at 25 °C/0.1 mm. The residue was extracted with 250 mL of hexane. Concentrating and cooling (-10 °C) the filtered hexane extract gave orange needles, which were purified further by fractional crystallization from hexane to give 1.1 g (20% yield) of orange acicular [(i-Pr)₂NP)((i-Pr)₂N)(Cl)PP]Fe₂(CO)₆, mp 131–132 °C. Anal. Calcd for C₁₈H₂₈ClFe₂N₂O₆P₃: C, 35.5; H, 4.6; N, 4.6; Cl, 5.8.

Found: C, 36.2; H, 4.7; N, 4.6; Cl, 5.8.

The ³¹P NMR spectrum of [(i-Pr)₂NP)((i-Pr)₂N)(Cl)PP]Fe₂(CO)₆ exhibited a second-order spectrum with a quintet centered at δ 203.0 and a quartet centered at δ 111.0. Interpretation of this spectrum as an ABX spectrum with the δ 203.0 quintet being an incompletely resolved AB spectrum and the δ 111.0 quartet being the X spectrum led to the parameters δ_A 209.0, δ_B 197.4, δ_X 110.8, |J(A-B)| = 292 Hz, and |J(A-X) + J(B-X)| = 348 Hz.

Reaction of ((i-Pr)₂NP)₂COFe₂(CO)₆ with Methanol. A mixture of 2.8 g (4.9 mmol) of ((i-Pr)₂NP)₂COFe₂(CO)₆ in 40 mL of methanol and 160 mL of toluene was boiled under reflux for 4 days. The progress of the reaction was monitored by the infrared ν(CO) frequencies. After the reaction was complete as indicated by the disappearance of the 1720-cm⁻¹ band, the solvent and volatile materials were removed in vacuo. The residue was extracted with 100 mL of hexane. Concentrating and cooling (-10 °C) the extract gave in several crops 2.2 g (79% yield) of bright yellow crystalline air-stable ((i-Pr)₂NPOMe)((i-Pr)₂NPH)Fe₂(CO)₆, mp 121 °C. Anal. Calcd for C₁₉H₃₂Fe₂N₂O₇P₂: C, 39.7; H, 5.6; N, 4.9. Found: C, 39.7; H, 5.6; N, 4.8.

Reaction of ((i-Pr)₂NP)₂COFe₂(CO)₆ with Ethanol. A procedure similar to that given above but using ethanol instead of methanol and a reaction time of 2 days gave 2.75 g (89% yield) of air-stable bright yellow crystalline ((i-Pr)₂NPOEt)((i-Pr)₂NPH)Fe₂(CO)₆, mp 114 °C. Anal. Calcd for C₂₀H₃₄Fe₂N₂O₇P₂: C, 40.8; H, 5.8; N, 4.8. Found: C, 40.9; H, 5.8; N, 4.8.

Reaction of ((i-Pr)₂NP)₂COFe₂(CO)₆ with Hydrogen Bromide. A solution of 3.8 g (6.6 mmol) of ((i-Pr)₂NP)₂COFe₂(CO)₆ in 250 mL of hexane was treated with anhydrous hydrogen bromide gas for 2 h at room temperature. A precipitate started to form after approximately 10 min of HBr treatment. Concentrating and cooling (-10 °C) the filtered solution gave 1.6 g (45% yield) of orange, slightly air-sensitive crystalline ((i-Pr)₂NPBr)(HPBr)Fe₂(CO)₆, mp 119 °C. Anal. Calcd for C₁₂H₁₅BrFe₂N₂O₆P₂: C, 23.9; H, 2.5; N, 2.3; Br, 26.5. Found: C, 24.3; H, 2.6; N, 2.3; Br, 26.0.

Reaction of ((i-Pr)₂NPOEt)((i-Pr)₂NPH)Fe₂(CO)₆ with Hydrogen Bromide. A solution of 0.5 g (0.88 mmol) of ((i-Pr)₂NPOEt)((i-Pr)₂NPH)Fe₂(CO)₆ in 50 mL of hexane was treated with anhydrous hydrogen bromide gas for 5 min at room temperature. A precipitate formed immediately. Concentrating and cooling (-10 °C) the filtered solution gave 0.36 g (72% yield) of air-sensitive orange crystalline ((i-Pr)₂NPOEt)(HPBr)Fe₂(CO)₆, 95 °C dec. Anal. Calcd for C₁₄H₁₉BrFe₂N₂O₇P₂: C, 29.6; H, 3.3; N, 2.5; Br, 14.1. Found: C, 29.8; H, 3.7; N, 2.5; Br, 14.2.

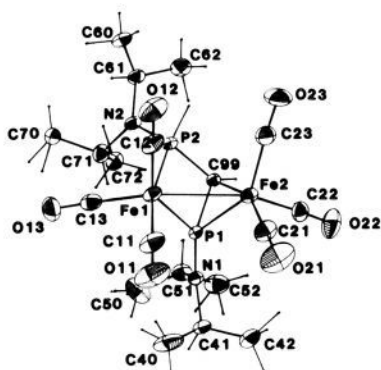
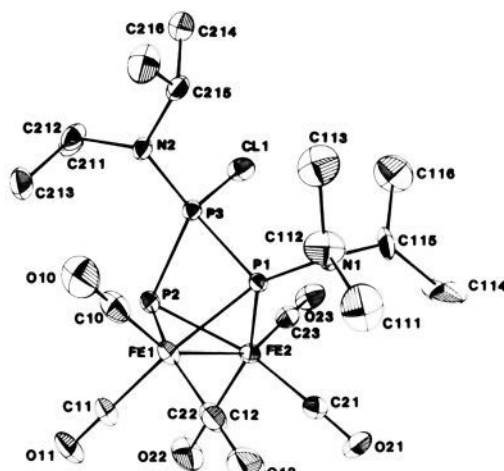
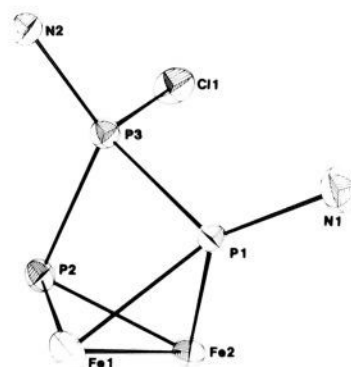
X-ray Structure Determinations (Table V). The structures of the three compounds ((i-Pr)₂NPHCHPN(i-Pr)₂Fe₂(CO)₆ (Figure 1 and Table VI), [(i-Pr)₂NP)((i-Pr)₂N)(Cl)PP]Fe₂(CO)₆ (Figures 2 and 3 and Table VII), and ((i-Pr)₂NPOEt)(HPBr)Fe₂(CO)₆ (Figure 4 and Table VIII) were determined by X-ray diffraction. The crystallographic and data collection parameters are summarized in Table V. In all cases suitable single crystals obtained from hexane solutions were sealed in capillaries and mounted on the Syntex P3 automated diffractometer located at Oklahoma State University. Unit cell dimensions (Table V) were determined by least-squares refinement of the best angular positions for 15 independent reflections (2θ > 15°) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). The data points were collected at room temperature with a variable scan rate, a θ-2θ scan mode, and a scan width of 1.2° below Kα₁ and 1.2° above Kα₂ to the maximum 2θ values indicated in Table V. Backgrounds were measured at each side of the scan for a combined time equal to the total

Table V. Crystal Data for $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2\text{Fe}_2(\text{CO})_6)$, $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6]$, and $((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$

	$((i\text{-Pr})_2\text{-NPHCHPN}(i\text{-Pr})_2\text{Fe}_2(\text{CO})_6)$	$[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6]$	$((i\text{-Pr})_2\text{-NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$
formula	$\text{C}_{19}\text{H}_{30}\text{N}_2\text{O}_6\text{P}_2\text{Fe}_2$	$\text{C}_{18}\text{H}_{28}\text{N}_2\text{O}_6\text{P}_3\text{ClFe}_2$	$\text{C}_{14}\text{H}_{19}\text{NO}_7\text{Fe}_2\text{Br}$
mol wt	556.10	608.5	566.85
cryst syst	triclinic	monoclinic	triclinic
space gp	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
a , Å	14.412 (6)	15.384 (6)	13.700 (6)
b , Å	10.409 (5)	18.355 (4)	9.818 (5)
c , Å	10.014 (4)	10.125 (1)	9.258 (5)
α , deg	111.80 (3)	90.0	64.54 (4)
β , deg	82.19 (3)	108.19 (2)	96.07 (4)
γ , deg	106.86 (4)	90.0	84.80 (4)
V , Å ³	1334.1 (9)	2716.2 (13)	1105.1 (9)
$F(000)$	576	1248	566
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	12.37	13.73	32.77
D_{calcd} , g cm ⁻³	1.384	1.488	1.703
Z	2	4	2
no. of obsd reflcns	3585	2790	2325
octants collcd	$\pm h, +k, \pm l$	$\pm h, +k, +l$	$\pm h, +k, \pm l$
max 2θ , deg	45	45	45
R	0.057	0.067	0.053
R_w	0.059	0.085	0.070

Table VI. Selected Bond Distances (Å) and Angles (deg) for $(i\text{-Pr})_2\text{NPCHPN}(i\text{-Pr})_2\text{Fe}_2(\text{CO})_6$

Fe1-Fe2	2.726 (2)	Fe2-C23	1.785 (12)
Fe1-P1	2.229 (2)	P1-N1	1.645 (6)
Fe1-P2	2.238 (2)	P2-N2	1.661 (6)
Fe2-P1	2.127 (3)	P2-H2	1.20
Fe2-C99	2.156 (6)	C99-H99	1.09
P1-C99	1.768 (6)	C11-O11	1.149 (10)
P2-C99	1.773 (6)	C12-O12	1.139 (13)
Fe1-C11	1.776 (8)	C13-O13	1.156 (13)
Fe1-C12	1.783 (10)	C21-O21	1.144 (10)
Fe1-C13	1.756 (10)	C22-O22	1.143 (11)
Fe2-C21	1.750 (8)	C23-O23	1.139 (15)
Fe2-C22	1.751 (9)		
Fe1-P1-Fe2	77.43 (8)	P1-Fe2-C23	142.1 (3)
P1-Fe1-P2	72.49 (7)	C99-Fe2-C21	156.0 (4)
Fe1-P1-C99	93.3 (2)	C99-Fe2-C22	91.4 (3)
Fe2-P1-C99	66.4 (2)	C99-Fe2-C23	102.3 (3)
Fe1-P2-C99	92.9 (2)	C21-Fe2-C22	93.9 (4)
Fe2-C99-P1	64.8 (2)	C21-Fe2-C23	99.6 (5)
Fe2-C99-P2	95.6 (3)	C22-Fe2-C23	101.6 (5)
P1-C99-P2	96.5 (3)	Fe1-C11-O11	178.6 (12)
P1-Fe1-C11	97.1 (3)	Fe1-C12-O12	179.0 (6)
P1-Fe1-C12	143.8 (3)	Fe1-C13-O13	177.6 (6)
P1-Fe1-C13	109.7 (3)	Fe2-C21-O21	176.9 (9)
P2-Fe1-C11	166.2 (3)	Fe2-C22-O22	177.7 (12)
P2-Fe1-C12	89.6 (2)	Fe2-C23-O23	177.1 (9)
P2-Fe1-C13	98.9 (3)	Fe1-P1-N1	142.6 (2)
C11-Fe1-C12	94.2 (4)	Fe2-P1-N1	134.4 (2)
C11-Fe1-C13	93.0 (4)	C99-P1-N1	115.8 (3)
C12-Fe1-C13	103.9 (4)	Fe1-P2-N2	124.6 (2)
P1-Fe2-C99	48.8 (2)	C99-P2-N2	117.0 (3)
P1-Fe2-C21	107.2 (4)	P1-N1-C41	122.5 (5)
P1-Fe2-C22	102.8 (4)	P1-N1-C51	120.1 (4)

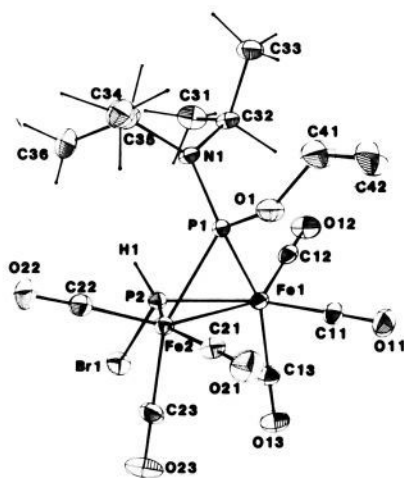
**Figure 1.** ORTEP diagram of $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2\text{Fe}_2(\text{CO})_6)$.**Figure 2.** ORTEP diagram of $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6]$.**Figure 3.** ORTEP diagram of $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6]$, with the isopropyl groups omitted in order to show more clearly the pyramidal three-coordinate phosphorus atom P2.

scan time. The intensities of three standard reflections were remeasured after every 97 reflections. Since the intensities of these standard reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were collected for Lorentz, polarization, and background effects. After removal of redundant and space group forbidden data, the observed data with $I > 3.0\sigma(I)$ were used for solution and refinement. Heavy-atom positions were located by direct methods.⁸

(8) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M. *Multan-80 System*; University of York: York, England, 1980.

Table VII. Selected Bond Distances (Å) and Angles (deg) for $[(i\text{-Pr})_2\text{NP}]\text{C}(\text{i-Pr})_2\text{N}(\text{Cl})\text{PP}]\text{Fe}_2(\text{CO})_6$

Fe1-Fe2	2.593 (2)	Fe2-C22	1.797 (12)
Fe1-P1	2.193 (3)	Fe2-C23	1.782 (12)
Fe1-P2	2.332 (3)	C10-O10	1.126 (19)
Fe2-P1	2.198 (3)	C11-O11	1.130 (13)
Fe2-P2	2.303 (3)	C12-O12	1.173 (14)
P1-P3	2.184 (3)	C21-O21	1.130 (14)
P2-P3	2.133 (4)	C22-O22	1.121 (15)
Fe1-C10	1.770 (15)	C23-O23	1.469 (15)
Fe1-C11	1.779 (11)	P1-N1	1.647 (8)
Fe1-C12	1.725 (11)	P3-N2	1.626 (8)
Fe2-C21	1.773 (11)	P3-C11	2.084 (4)
Fe1-P1-Fe2	72.4 (9)	Fe1-P1-P3	91.1 (1)
Fe1-P2-Fe2	68.0 (1)	P3-P1-N1	123.2 (3)
P1-Fe1-P2	76.1 (1)	P3-P1-Fe2	91.9 (1)
P1-Fe2-P2	76.6 (1)	Fe2-P1-N1	131.6 (3)
P1-Fe1-C10	103.2 (4)	Fe1-P2-P3	88.7 (1)
P1-Fe1-C11	152.7 (4)	Fe2-P2-P3	90.4 (1)
P1-Fe1-C12	96.1 (4)	P2-P3-P1	80.5 (1)
P2-Fe1-C10	108.8 (4)	P2-P3-C11	111.0 (2)
P2-Fe1-C11	82.3 (4)	P2-P3-N2	119.1 (3)
P2-Fe1-C12	151.5 (5)	P1-P3-C11	111.9 (2)
C11-Fe1-C12	94.8 (5)	P1-P3-N2	126.2 (3)
C11-Fe1-C10	99.5 (6)	N2-P3-C11	106.2 (3)
C12-Fe1-C10	99.6 (5)	P1-N1-C112	120.7 (8)
P1-Fe2-C21	93.3 (4)	P1-N1-C115	122.0 (8)
P1-Fe2-C22	150.6 (5)	P3-N2-C212	124.8 (7)
P1-Fe2-C23	108.1 (4)	P3-N2-C215	116.5 (6)
P2-Fe2-C21	156.1 (5)	Fe1-C10-C10	175.9 (11)
P2-Fe2-C22	85.9 (4)	Fe1-C11-O11	177.1 (13)
P2-Fe2-C23	103.1 (3)	Fe1-C12-O12	177.9 (12)
C21-Fe2-C22	93.4 (5)	Fe2-C21-O21	178.1 (12)
C21-Fe2-C23	100.6 (6)	Fe2-C22-O22	179.1 (12)
C22-Fe2-C23	98.7 (6)	Fe2-C23-O23	178.3 (19)
Fe1-P1-N1	131.0 (3)		

**Figure 4.** ORTEP diagram of $((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$.

Successive cycles of difference Fourier synthesis followed by least-squares refinement allowed location of the remainder of the non-hydrogen atoms. Least-squares refinement⁹ converged with anisotropic thermal parameters. In $((i\text{-Pr})_2\text{NPHCHN})(i\text{-Pr})_2\text{Fe}_2(\text{CO})_6$, the hydrogen positions were determined from a difference Fourier synthesis. In $[(i\text{-Pr})_2\text{NP}]\text{C}(\text{i-Pr})_2\text{N}(\text{Cl})\text{PP}]\text{Fe}_2(\text{CO})_6$ the hydrogen positions could not be located by a difference Fourier synthesis. The hydrogen positional parameters were calculated assuming normal geometry and a C-H bond length of 0.97 Å. In $((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$ all of the hydrogen positions except for those of the ethyl group could be located by a difference Fourier synthesis. Hydrogen positions were included in the final refinement with fixed isotropic thermal parameters but were held invariant. Difference Fourier revealed no electron density of interpretable level. Scattering factors were taken from Cromer and Mann.¹⁰ Anomalous

Table VIII. Bond Distances (Å) and Angles (deg) for $((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$

Fe1-Fe2	2.640 (2)	C34-C35	1.52 (2)
Fe1-P1	2.226 (2)	C35-C36	1.50 (1)
Fe1-P2	2.184 (3)	Fe1-C11	1.783 (12)
Fe2-P1	2.215 (2)	Fe1-C12	1.777 (10)
Fe2-P2	2.191 (3)	Fe1-C13	1.792 (8)
P1-O1	1.614 (8)	Fe2-C21	1.783 (12)
P1-N1	1.673 (8)	Fe2-C22	1.778 (10)
O1-C41	1.35 (1)	Fe2-C23	1.791 (8)
C41-C42	1.48 (2)	C11-O11	1.15 (2)
P2-Br1	2.203 (2)	C12-O12	1.14 (1)
N1-C32	1.49 (1)	C13-O13	1.14 (1)
N1-C35	1.48 (1)	C21-O21	1.15 (2)
C31-C32	1.52 (2)	C22-O22	1.13 (1)
C32-C33	1.51 (1)	C23-O23	1.14 (1)
Fe1-P1-Fe2	72.92 (8)	Fe1-Fe2-C23	99.3 (3)
Fe1-P2-Fe2	74.21 (10)	P1-Fe2-P2	76.52 (9)
Fe1-P2-Br1	122.1 (11)	P1-Fe2-C21	89.6 (2)
Fe2-P2-Br1	121.9 (11)	P1-Fe2-C22	107.2 (2)
Fe1-P1-N1	119.8 (3)	P1-Fe2-C23	152.6 (3)
Fe1-P1-O1	116.7 (3)	P2-Fe2-C21	153.4 (3)
Fe2-P1-N1	126.0 (2)	P2-Fe2-C22	106.0 (4)
Fe2-P1-O1	110.4 (2)	P2-Fe2-C23	91.0 (4)
N1-P1-O1	107.9 (3)	C21-Fe2-C22	99.6 (5)
P1-Fe1-C11	89.0 (3)	C21-Fe2-C23	91.5 (4)
P1-Fe1-C12	106.3 (3)	C22-Fe2-C23	99.5 (4)
P1-Fe1-C13	155.4 (3)	P1-O1-C41	128.9 (8)
P1-Fe1-Fe2	53.34 (6)	O1-C41-C42	114 (1)
Fe2-Fe1-C11	100.6 (3)	P1-N1-C32	118 (5)
Fe2-Fe1-C12	149.4 (3)	P1-N1-C35	124 (6)
Fe2-Fe1-C13	102.4 (3)	C32-N1-C35	116 (6)
C11-Fe1-C12	101.6 (4)	N1-C32-C31	112 (1)
C11-Fe1-C13	92.4 (5)	N1-C32-C33	114 (1)
C12-Fe1-C13	97.5 (4)	C31-C32-C33	109 (1)
P2-Fe1-Fe2	53.03 (8)	N1-C35-C34	114 (1)
P2-Fe1-P1	76.45 (10)	N1-C35-C36	113 (1)
P2-Fe1-C11	153.6 (3)	C34-C35-C36	112 (1)
P2-Fe1-C12	103.6 (4)	Fe1-C11-O11	179.1 (9)
P2-Fe1-C13	92.2 (3)	Fe1-C12-O12	177.9 (8)
Fe1-Fe2-P1	53.73 (6)	Fe1-C13-O13	179.1 (14)
Fe1-Fe2-P2	52.76 (7)	Fe2-C21-O21	178.4 (6)
Fe1-Fe2-C21	100.8 (3)	Fe2-C22-O22	177.4 (10)
Fe1-Fe2-C22	151.7 (4)	Fe2-C23-O23	180.0 (25)

dispersion corrections were made for Fe, Br, and P. The final cycles of refinement leading to the agreement factors (R) in Table V minimized the function $\sum(|F_o| - |F_c|)^2$. Weights equal to $1/\sigma F$ were introduced in the final cycles of refinement.

Complete listings of positional parameters, bond distances and angles, and anisotropic thermal parameters for the three compounds are provided as supplementary material.

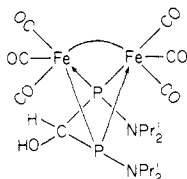
Results and Discussion

(A) Reduction of the Phosphorus-Bridging Carbonyl Group. An important property of the ketone carbonyl group is its facile reduction by hydric reducing agents to give the corresponding secondary alcohol. Analogous behavior was noted for the phosphorus-bridging carbonyl group in $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I), which underwent reduction by NaBH_4 in methanol at ambient temperature or LiAlH_4 in diethyl ether at -78°C to give the corresponding secondary alcohol $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$ (II) as a yellow solid. Important spectroscopic properties of this secondary alcohol supporting structure II include the following: (1) The infrared spectrum taken in Nujol mulls exhibit a weak broad $\nu(\text{OH})$ band at 3450 cm^{-1} in addition to the strong $\nu(\text{CO})$ frequencies around 2000 cm^{-1} . (2) The ^1H NMR spectrum (Table IV) exhibits a broad quartet at δ 6.40 and a broad doublet at δ 3.95 in addition to the characteristic isopropyl CH and CH_3 resonances. Treatment of the NMR sample with a trace of trifluoroacetic acid to accelerate hydroxyl proton exchange thereby chemically decoupling the hydroxyl proton causes the quartet to coalesce into a triplet ($|^2J(\text{P-H})| = 11\text{ Hz}$) and the broad doublet

(9) Stewart, J. M., Ed. "The XRAY System-Version of 1980"; Technical Report No. TR446; Computer Center of the University of Maryland: College Park, MD, 1980.

(10) Cromer, D. T.; Mann, I. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* 1968, A24, 321.

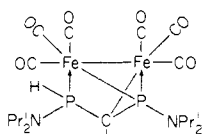
to become a broad singlet and to shift downfield to δ 4.25, thereby supporting assignment of the original δ 6.40 quartet to the PCHP proton and the original δ 3.95 doublet to the OH proton. (3) The ^{13}C NMR spectrum (Table III) exhibits a triplet at δ 130.2 ($|^1J(\text{P}-\text{C})| = 8$ Hz) assigned to the phosphorus-bridging carbon (α -carbon of the alcohol) in addition to the characteristic resonances of the isopropyl and metal carbonyl groups. The phosphorus-bridging carbon resonance splits further into a doublet of triplets ($|^1J(\text{C}-\text{H})| = 163$ Hz) when the proton decoupling is turned off. The drastic reduction of the phosphorus-bridging carbon $|^1J(\text{P}-\text{C})|$ from $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I: 83 Hz) to $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$ (II: 8 Hz) is undoubtedly a consequence of the change in its hybridization from sp^2 in I to sp^3 in II.



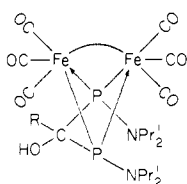
II

The reduction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with LiAlH_4 in diethyl ether also gives the secondary alcohol $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$ (II) if the reaction mixture is kept at -78°C and is quenched with saturated aqueous ammonium chloride at this temperature. However, if the reaction mixture is allowed to warm slowly from -78°C to room temperature without quenching, a color change from yellow to an eventual deep orange starting from -45°C can be observed. Quenching this reaction at room temperature with saturated aqueous ammonium chloride gives a product of stoichiometry $((i\text{-Pr})_2\text{NP})_2\text{CH}_2\text{Fe}_2(\text{CO})_6$. Quenching the $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6/\text{LiAlH}_4$ reaction at -8°C leads to a 3:2 mixture of $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$ and $((i\text{-Pr})_2\text{NP})_2\text{CH}_2\text{Fe}_2(\text{CO})_6$.

The idea that $((i\text{-Pr})_2\text{NP})_2\text{CH}_2\text{Fe}_2(\text{CO})_6$ might contain a phosphorus-bridging methylene group was disproved by structure determination using X-ray diffraction, which showed that this complex was actually the isomeric $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$ (III) (Figure 1 and Table VI). In the conversion of



III



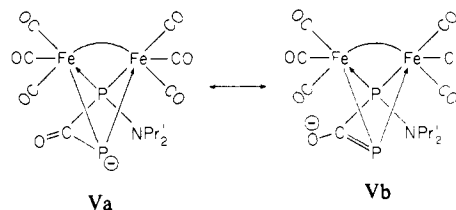
IV

$((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) to $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$ (III), the iron-iron bond lengthens slightly from 2.603 (2) Å in I to 2.726 (2) Å in III. In addition, an iron-phosphorus bond in I is broken, and a new iron-carbon bond (2.156 (6) Å) is formed in III. Closely related arrangements have been observed in reactions of $\text{CH}_2\text{S}_2\text{Fe}_2(\text{CO})_6$ with $(i\text{-Pr})_2\text{NLi}^{11-13}$ and of $\text{C}_6\text{H}_4(\text{CH}_2\text{PPh})_2\text{Fe}_2(\text{CO})_6$ with $n\text{-BuLi}$.¹⁴ The ^{31}P NMR spectrum of $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$ is consistent with structure III since one of the doublet resonances (that at δ 173.7) is in a typical position for a phosphido group bridging a metal-metal bond but the other resonance (that at δ 7.7) is shifted far upfield from the normal position for such phosphido groups consistent with the observed rupture of one of the iron-phosphorus bonds in going from I to III. The phosphorus-bridging carbon

in $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$ exhibits an unusual doublet of doublets of doublets of doublets in the proton-uncoupled ^{13}C NMR spectrum interspersed between the much stronger isopropyl methyl resonances. From this unusual pattern the following four coupling constants involving the phosphorus-bridging carbon atom can be obtained: $|^1J(\text{C}-\text{H})| = 169$ Hz; $|^1J(\text{C}-\text{P}_a)| = 26$ Hz; $|^1J(\text{C}-\text{P}_b)| = 13$ Hz; $|^2J(\text{C}-\text{H})| = 6$ Hz.

Another important reaction of the ketone carbonyl group is the facile addition of organolithium compounds to give the corresponding tertiary alcohols. Analogous behavior was noted for the phosphorus-bridging carbonyl group in $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I), which underwent reactions with methyllithium and with n -butyllithium to give the corresponding tertiary alcohols $((i\text{-Pr})_2\text{NP})_2\text{CR}(\text{OH})\text{Fe}_2(\text{CO})_6$ (IV: R = Me, n -Bu) after quenching with an acid. A similarly selective reaction was not observed upon treatment of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with the more reactive *tert*-butyllithium, which gave a complicated mixture as indicated by several pairs of doublets of doublets in the ^{31}P NMR spectrum. Several attempts to isolate one or more of the components of this mixture led instead to decomposition and reversion to the $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ starting material. The spectroscopic properties of the tertiary alcohols $((i\text{-Pr})_2\text{NP})_2\text{CR}(\text{OH})\text{Fe}_2(\text{CO})_6$ (IV: R = Me, Bu) support the proposed structure and in general are similar to those of the secondary alcohol $((i\text{-Pr})_2\text{NP})_2\text{CH}(\text{OH})\text{Fe}_2(\text{CO})_6$ (II) discussed above.

The phosphorus-bridging carbonyl derivative $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) was also reactive toward reduction with sodium amalgam in tetrahydrofuran at room temperature. Relatively little color change occurred during this reaction but the ^{31}P NMR spectrum of the reaction mixture after 10 min indicated replacement of the singlet δ 225.6 resonance of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with a mixture of approximately equal quantities of two products, a symmetric product exhibiting a singlet resonance at δ 212 and an asymmetric product exhibiting two coupled doublet ^{31}P resonances at δ 207 and 167 with $|J(\text{P}-\text{P})| = 61$ Hz (see the Experimental Section). After the symmetric product was destroyed with the minimum amount of trifluoroacetic acid, the asymmetric product with a relatively low nucleophilicity was isolated as a solid bis(triphenylphosphine)iminium salt of the stoichiometry $[(\text{Ph}_3\text{P})_2\text{N}][i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6]$ upon treatment with bis(triphenylphosphine)iminium chloride. This product stoichiometry coupled with integration of the methyl relative to the phenyl resonance in the ^1H NMR spectrum and the nonequivalence of the phosphorus atoms in the ^{31}P NMR spectrum suggests that the major result of the reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with sodium amalgam is reductive cleavage of one of the diisopropylamino groups and that the resulting anion is resonance-stabilized by interaction with the phosphorus-bridging carbonyl oxygen, i.e.,



Va

Vb

This resonance stabilization lowers the carbon-oxygen bond order of the phosphorus-bridging carbonyl thereby lowering the corresponding infrared $\nu(\text{CO})$ frequency into a region where it is obscured by bands from the bis(triphenylphosphine)iminium cation. However, the sodium salt of the $[(i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6]^-$ anion in the original reaction mixture after the trifluoroacetic acid quenching of the symmetric product exhibits a frequency of 1630 cm^{-1} assignable to the phosphorus-bridging $\nu(\text{CO})$ band in the anion. The structure of $\text{Na}[(i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6]$ is thereby best described as a "tight ion pair" or "cation-perturbed complex"¹⁵ derived from the anion Va. Attempts to obtain single crystals of $[(\text{Ph}_3\text{P})_2\text{N}][i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6]$

(11) Seyferth, D.; Womack, G. B.; Song, L.-C.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 928.

(12) Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1983**, *2*, 1696.

(13) Seyferth, D.; Womack, G. B.; Gallagher, M. K.; Cowie, M.; Hames, B. W.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1987**, *6*, 283.

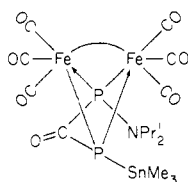
(14) Seyferth, D.; Wood, T. G.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1984**, *3*, 1121.

(15) Darenbourg, M. Y. *Prog. Inorg. Chem.* **1985**, *33*, 221.

$(i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6$] for structure determination by X-ray diffraction have so far been unsuccessful.

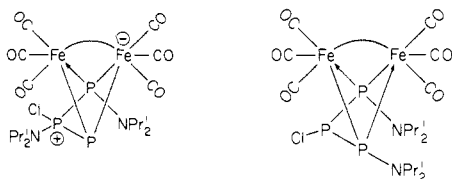
Our observations suggest the scheme in Figure 5 for the overall reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with sodium amalgam. Besides the approximate 1:1 ratio of the two anions, this scheme is also supported by the reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with lithium diisopropylamide to give a product exhibiting the same singlet δ 212 ^{31}P resonance as the symmetric product obtained from the sodium amalgam reduction of I. In the absence of sodium amalgam, this putative symmetric anion is very unstable, easily decomposing back to I. Thus, treatment of the symmetric anion with water or with bis(triphenylphosphine)iminium chloride did not give the corresponding alcohol or metathesis product, respectively, but instead gave the original $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I).

The retention of the phosphorus-bridging group in $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) upon reduction with sodium amalgam in tetrahydrofuran is further supported by the isolation of $((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$ (VI) upon treatment of the anion with trimethyltin chloride. The presence of the phosphorus-bridging carbonyl group in VI is supported by a strong infrared $\nu(\text{CO})$ frequency at 1715 cm^{-1} and a *doublet doublet* carbonyl resonance in the ^{13}C NMR spectrum centered at δ 212.5 (Table III). Thus, in $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) where the carbonyl group bridges equivalent phosphorus atoms, its ^{13}C resonance is a triplet, whereas in $((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$ (VI) where the carbonyl group bridges strongly nonequivalent phosphorus atoms, its ^{13}C resonance is a doublet doublet. Unfortunately, the available crystals of $((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$ (VI) were of unsuitable quality for a structure determination by X-ray diffraction.

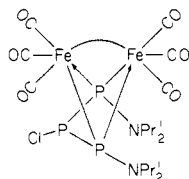


VI

The reaction of the anion $[((i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6)]^-$ with $(i\text{-Pr})_2\text{NP}(\text{Cl})_2$ gave an orange crystalline product shown by X-ray diffraction to be a novel triphosphorus derivative of structure VII



VII



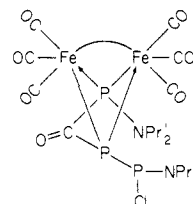
VIII

with a stoichiometry $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{Fe}_2(\text{CO})_6$ isomeric with the triphosphine complex $((i\text{-Pr})_2\text{NP})_2\text{P}(\text{Cl})\text{Fe}_2(\text{CO})_6$ (VIII) obtained¹⁶ by treatment of $((i\text{-Pr})_2\text{NP})_3\text{Fe}_2(\text{CO})_6$ with hydrogen chloride. The structure of VII (Figures 2 and 3 and Table VII) consists of a triphosphorus chain (P1-P3 = 2.184 (3) Å, P3-P2 = 2.133 (4) Å, P2-P3-P1 = 80.5 (1)°) bridging a metal-metal-bonded (Fe-Fe = 2.593 (2) Å) $\text{Fe}_2(\text{CO})_6$ unit through bonding of both end phosphorus atoms of the chain (P1 and P2) to both iron atoms (Fe1-P1 = 2.193 (3), Fe1-P2 = 2.332 (3), Fe2-P1 = 2.198 (3), Fe2-P2 = 2.303 (3) Å). One of these end phosphorus atoms, namely P2 (Figure 3), is a three-coordinate phosphorus atom with strongly pyramidal geometry (Fe1-P2-Fe2 = 68.0 (1), Fe2-P2-P3 = 90.4 (1), P3-P2-Fe1 = 88.7 (1)°, suggesting the possibility of using $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{Fe}_2(\text{CO})_6$ (VII) as a ligand to prepare novel transition-metal complexes through coordination of P2 to a transition-metal fragment such as $\text{Fe}(\text{CO})_4$ or $\text{Cr}(\text{CO})_5$. The other end phosphorus atom, namely P1, is a typical phosphido phosphorus atom similar

to the two phosphorus atoms in $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I). The center phosphorus atom in the triphosphorus chain of $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{Fe}_2(\text{CO})_6$ (VII), namely P3, is not bonded to either iron atom but is four-coordinate, being bonded to a diisopropylamino group (through N2), the chlorine atom, and the other two phosphorus atoms. The P2-P3-P1 angle of 80.5 (1)° in $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{Fe}_2(\text{CO})_6$ (VII) is not nearly as acute as the P-P-P angle of 68.19 (7)° in the triphosphine complex¹⁶ $((i\text{-Pr})_2\text{NP})_3\text{Fe}_2(\text{CO})_6$ in which the center phosphorus atom of the triphosphine chain is three-coordinate rather than four-coordinate.

The ^{31}P NMR spectrum of $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{Fe}_2(\text{CO})_6$ (VII) exhibits a complicated second-order spectrum, which can be interpreted as an ABX pattern with chemical shifts of δ 209.0, 197.4, and 110.8 (see the Experimental Section). The high-field X resonance can be assigned to the trivalent phosphorus atom P2. The second-order pattern is thus a consequence of the relatively small chemical shift difference between the four-coordinate center phosphorus atom P3 and the normal phosphido phosphorus atom P1.

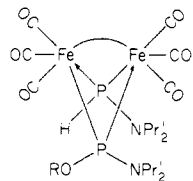
The formation of $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{Fe}_2(\text{CO})_6$ (VII) from the reaction of the anion $[((i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6)]^-$ (V) with $(i\text{-Pr})_2\text{NP}(\text{Cl})_2$ is not difficult to understand. The initial product from the reaction of $[((i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6)]^-$ with $(i\text{-Pr})_2\text{NP}(\text{Cl})_2$ is expected to be $((i\text{-Pr})_2\text{NP})[((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{COFe}_2(\text{CO})_6$ (IX) by analogy to the observed formation of



IX

$[((i\text{-Pr})_2\text{NP})(\text{Me}_3\text{SnP})\text{COFe}_2(\text{CO})_6$ (VI) from the reaction of $[((i\text{-Pr})_2\text{NPCOPFe}_2(\text{CO})_6)]^-$ with Me_3SnCl . Attack of the uncomplexed phosphorus atom in IX on the phosphorus atom to which it is not directly bonded with concurrent displacement of the phosphorus-bridging carbonyl group then leads to the formation of $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP}]_2\text{Fe}_2(\text{CO})_6$ (VII).

(B) Expulsion of the Phosphorus-Bridging Carbonyl Group. Treatment of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with methanol or ethanol under vigorous reaction conditions (boiling toluene for 2-4 days) results in loss of the phosphorus-bridging carbonyl group to give high yields of yellow air-stable $((i\text{-Pr})_2\text{NPOR})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$ (X; R = Me, Et) with no evidence for al-



X

coholysis of the diisopropylamino groups. This reaction indicates that expulsion of the phosphorus-bridging carbonyl groups occurs preferentially to solvolysis of the diisopropylamino groups. Such carbonyl expulsion reactions have no obvious parallel in ketone chemistry and reflect release of strain in the $\text{Fe}_2\text{P}_2\text{C}$ cage of I as well as differences in reactivity of phosphorus-carbon bonds relative to carbon-carbon bonds.

The spectroscopic properties of the complexes $((i\text{-Pr})_2\text{NPOR})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$ (X; R = Me, Et) are in accord with those of the proposed structure except that the spectroscopic information provides no basis for deciding between syn and anti configurations of the diisopropylamino groups. The infrared $\nu(\text{CO})$ spectra of these complexes exhibit six terminal $\nu(\text{CO})$ frequencies consistent with reduction of the C_{2v} local symmetry in $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) to C_s local symmetry

(16) King, R. B.; Wu, F.-J.; Holt, E. M. *Inorg. Chem.* 1986, 25, 1733.

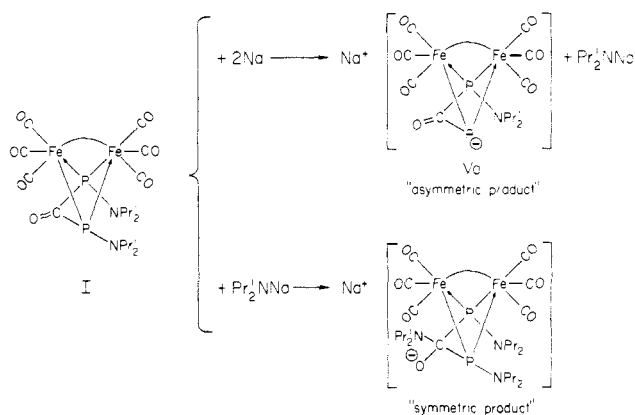
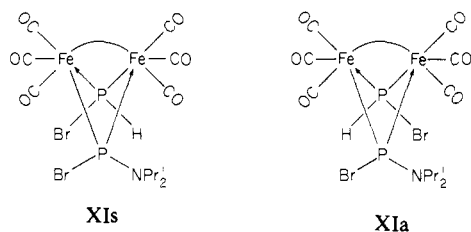


Figure 5. Possible mechanism for the reduction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with sodium amalgam.

in $((i\text{-Pr})_2\text{NPOR})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$ (X). The absence of a phosphorus-bridging $\nu(\text{CO})$ frequency around 1700 cm^{-1} in $((i\text{-Pr})_2\text{NPOR})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$ (X) confirms the loss of the phosphorus-bridging carbonyl group in the reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with alcohols. The proton-decoupled ^{31}P NMR spectra of the $((i\text{-Pr})_2\text{NPOR})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$ (X) complexes exhibit a pair of doublets, indicating coupled nonequivalent phosphorus atoms. Turning off the proton decoupling further splits the higher field doublet into a doublet of doublets of triplets arising from $^1J(\text{P-H})$, $^2J(\text{P-P})$, and $^3J(\text{P-H})$ couplings, indicating that one of the phosphorus atoms is directly bonded to hydrogen and the diisopropylamino group remains intact on this phosphorus. Turning off the proton decoupling also further splits the lower field doublet in $((i\text{-Pr})_2\text{NPOMe})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$ (X: R = Me) into a doublet of sextets in which the coupling constants $^3J(\text{P-H})$ (with P-H), $^3J(\text{P-H})$ (with MeO), and $^3J(\text{P-H})$ (with $(i\text{-Pr})_2\text{N}$) can be observed. The ^{13}C NMR spectra of the $((i\text{-Pr})_2\text{NPOR})((i\text{-Pr})_2\text{NPH})\text{Fe}_2(\text{CO})_6$ complexes exhibit two sets of isopropyl resonances in accord with the nonequivalence of the diisopropylamino groups in structure X.

Treatment of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with hydrogen bromide in hexane at room temperature follows a similar course to the alcoholysis reactions except that the much more strongly acidic hydrogen bromide reacts under much milder conditions and also cleaves one of the diisopropylamino groups to give $((i\text{-Pr})_2\text{NPBr})(\text{BrPH})\text{Fe}_2(\text{CO})_6$. Following the course of this reaction by ^{31}P NMR provides evidence for both of the possible stereoisomers XI and XIa as well as an interesting isomerization



process. Thus, the ^{31}P NMR spectrum of the $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6/\text{HBr}$ reaction mixture after only 15 min at room temperature (5 min after the precipitate started to form and approximately 30% of the reaction had occurred) indicated that the initially formed product was predominantly the isomer giving the lower field ^{31}P resonances (isomer K in Table II). Allowing this solution to stand for 4 days at 20°C resulted in gradual conversion of this isomer in an apparent first-order process to the isomer giving the higher field ^{31}P resonances (isomer T in Table II), and this latter isomer was isolated in the pure state (indicated by ^{31}P NMR) by crystallization as noted in the Experimental Section. The spectroscopic properties of $((i\text{-Pr})_2\text{NPBr})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ (XI) are in accord with the proposed structure. The lack of coupling corresponding to $^3J(\text{P}_a\text{-H})$ in the proton-coupled ^{31}P NMR spectrum of the higher field

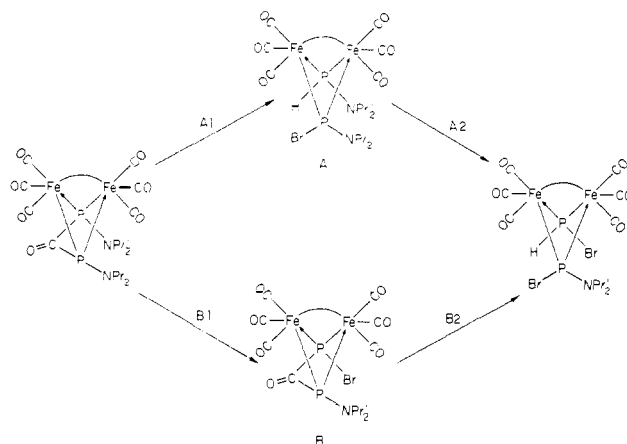
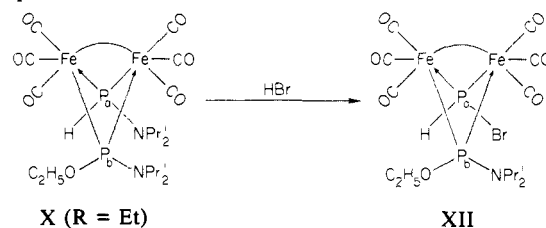


Figure 6. Two possible mechanisms for the reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with HBr.

phosphorus atom confirms that this phosphorus atom does not bear a diisopropylamino group.

There are two possible mechanisms (Figure 6) for the formation of $((i\text{-Pr})_2\text{NPBr})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ (XI) by reaction of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) with hydrogen bromide. The long times required for precipitation of the diisopropylammonium bromide to begin (10 min) and the reaction to proceed to completion (>2 h) suggest that the initial step involves decarbonylation (step A1) similar to the alcoholysis of $((i\text{-Pr})_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (I) discussed above rather than phosphorus-nitrogen bond cleavage (step B1), thereby suggesting path A rather than path B. Normally, phosphorus-nitrogen bond cleavage by hydrogen halides is rapid and complete at or below room temperature.¹⁷ Also selective cleavage of one of the diisopropylamino groups in step A2 (Figure 5) is reasonable in terms of electronic factors and is also supported by the following reaction, which is rapid and complete at room temperature:



The stereochemistry of the product $((i\text{-Pr})_2\text{NPOEt})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ (XII) was confirmed by X-ray crystallography (Figure 4 and Table VIII). This compound is of interest in representing the first example of a bis(phosphido)hexacarbonyliron derivative in which the four phosphorus terminal positions are occupied not only by different groups but by groups bonded to the phosphorus through different atoms, namely Br, H, O, and N. Otherwise, the structure and spectroscopic properties of $((i\text{-Pr})_2\text{NPOEt})(\text{BrPH})\text{Fe}_2(\text{CO})_6$ (XII) present no new features.

Acknowledgment. We are indebted to the Air Force Office of Scientific Research for partial support of this work at the University of Georgia under Grant AFOSR-84-0050.

Registry No. I, 99495-63-3; II, 99495-67-7; III, 99495-68-8; IV (R = Me), 113490-57-6; IV (R = *n*-Bu), 113490-58-7; V-[(Ph₃P)₂N], 113490-60-1; V-Na, 113490-61-2; VI, 113507-37-2; VII, 113507-38-3; X (R = Me), 99495-64-4; X (R = Et), 99495-65-5; XIa, 99495-66-6; XI, 113564-25-3; XII, 113490-62-3; $(i\text{-Pr})_2\text{NPCl}_2$, 921-26-6.

Supplementary Material Available: Positional parameters, anisotropic thermal parameters, and bond angles (deg) and distances (Å) for $((i\text{-Pr})_2\text{NPHCHPN}(i\text{-Pr})_2)\text{Fe}_2(\text{CO})_6$ (Tables 1-3), $[((i\text{-Pr})_2\text{NP})((i\text{-Pr})_2\text{N})(\text{Cl})\text{PP})\text{Fe}_2(\text{CO})_6$ (Tables 4-6), and $((i\text{-Pr})_2\text{NPOEt})(\text{HPBr})\text{Fe}_2(\text{CO})_6$ (Tables 7-9) (15 pages). Ordering information is given on any current masthead page.

(17) Febvay, J.; Casabianca, F.; Riess, J. G. *J. Am. Chem. Soc.* **1984**, *106*, 7985.