larger than the corresponding rate for FeO_4^{2-}. Preliminary studies in this laboratory with other organic compounds indicate that Fe(V)/Fe(IV) indeed react orders of magnitude faster than Fe(VI). This suggests that Fe(VI) oxidation processes may be significantly accelerated if carried out in the presence of appropriate one-electron-reducing agents.

The reduction of FeO_4^{2-} by O_2^- is relatively slow ($k_4 = 5.7 \times 10^3\ M^{-1}\ s^{-1}$) and does not show evidence of hypervalent iron transients. In this case, if Fe(V) and Fe(IV) react orders of magnitude faster than Fe(VI) with the superoxide radical, one would not expect to observe these transients. Since the reaction between Fe(III) and O_2^- is fast ($k = 1.5 \times 10^8\ M^{-1}\ s^{-1}$),[34] one would expect similar or higher rates for the reaction(s) of superoxide radical with Fe(V) and/or Fe(IV).

Acknowledgment. This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. NADH, 58-68-4; DTPA, 67-43-6; FeO_4^{2-}, 16836-06-9; FeO_4^{3-}, 37114-36-6; CO_2^-, 14485-07-5; ethanol, 64-17-5; formate, 64-18-6.

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(34) Rush, J. D.; Bielski, B. H. J. *J. Phys. Chem.* **1985**, *89*, 5062.

Dialkylamino Phosphorus Metal Carbonyls. 4. Novel Phosphorus-Bridging Carbonyl Derivatives and Triphosphine Derivatives from Reactions of Tetracarbonylferrate(-II) with (Dialkylamino)dichlorophosphines[1-4]

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Received April 24, 1987

Abstract: Reactions of R_2NPCl_2 (R = isopropyl, cyclohexyl) with $Na_2Fe(CO)_4$ give orange $(R_2NP)_2COFe_2(CO)_6$ as the major product in diethyl ether solution and orange $(R_2NP)_3Fe_2(CO)_6$ as the major product in tetrahydrofuran solution. X-ray diffraction on $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (monoclinic, $P2_1/n$; $a = 10.197$ (3), $b = 31.403$ (13), $c = 9.170$ (3) Å; $\beta = 112.18$ (2)°; $Z = 4$) indicates a structure in which an iron–iron bond (2.603 (2) Å) in an $Fe_2(CO)_6$ unit is bridged by two phosphorus atoms and these two phosphorus atoms are bridged by one of the seven carbonyl groups, thereby suggesting a novel migration of a carbonyl group from iron to phosphorus. X-ray diffraction on $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (monoclinic, $P2_1/n$; $a = 11.554$ (2), $b = 14.294$ (6), $c = 20.405$ (4) Å; $\beta = 90.96$°; $Z = 4$) indicates an $Fe_2(CO)_6$ unit (Fe–Fe = 2.602 (2) Å) bridged by a triphosphine chain. Minor products from the reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in diethyl ether include an orange trinuclear derivative $(R_2NP)_2Fe_3(CO)_9$ and an unstable diphosphene complex $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$. The latter product adds water upon attempted chromatography to give $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ shown by X-ray diffraction (monoclinic, $P2_1/n$; $a = 15.682$ (3), $b = 14.458$ (3), $c = 13.044$ (8) Å, $\beta = 99.80$ (4)°; $Z = 4$) to have an oxo-bridged structure (P–O–P = 136.4 (3)°), axially substituted trigonal-bipyramidal $LFe(CO)_4$ units, and no iron–iron bond. Minor products from the reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in tetrahydrofuran include $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ as well as orange $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ shown by X-ray diffraction (monoclinic, $P2_1/a$; $a = 14.910$ (5), $b = 12.064$ (6), $c = 19.733$ (10) Å; $\beta = 105.31$ (4)°; $Z = 4$) to have a structure similar to that of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ but with a carbonyl group inserted into the triphosphine chain. Reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether gives totally different types of products arising from migrations of diethylamino groups. The initial major product, isolated when the temperature is kept below 0 °C, is a deep orange solid of stoichiometry $(Et_2NP)_3Fe_3(CO)_{12}$ shown by X-ray diffraction (monoclinic, $P2_1/n$; $a = 17.071$ (7), $b = 19.116$ (8), $c = 10.853$ (3) Å; $\beta = 96.82$°) to have a four-membered FeP_3 ring bonded to two isolated $Fe(CO)_4$ groups, a four-membered FePOC ring formed by a diethylcarbamoyl group bridging an Fe–P bond, an $(Et_2N)_2P$ unit formed by diethylamino migration, but no Fe–Fe bonds. This complex undergoes facile decarbonylation in solution at room temperature to give an orange solid of stoichiometry $(Et_2NP)_3Fe_3(CO)_{11}$. Structure determination of this decarbonylation product by X-ray diffraction (monoclinic, $P2_1/n$; $a = 9.054$ (4), $b = 38.752$ (34), $c = 19.737$ (8) Å, $\beta = 104.05$ (3)°; $Z = 8$) indicates that this decarbonylation reaction involves conversion of a bridging diethylcarbamoyl group to a terminal diethylcarbamoyl group, formation of an Fe–Fe bond, and formation of a new Fe–P bond. The products formed from reactions of R_2NPCl_2 with $Na_2Fe(CO)_4$ can be rationalized by schemes involving the terminal (dialkylamino)phosphinidene complex $R_2NP{=}Fe(CO)_4$ as a reactive intermediate, which can undergo a redox reaction with $Fe(CO)_4^{2-}$ in tetrahydrofuran but not in diethyl ether.

Recent interest in the chemistry of diphosphenes,[5] RP=PR, because of the presence of the phosphorus–phosphorus double bond, has led to numerous studies on their preparation by dehalogenation of $RPCl_2$ derivatives with diverse strong reducing agents. Such reactions with metal carbonyl anions as the reducing agents have yielded products that may be regarded as metal carbonyl complexes of the diphosphenes. In this connection reactions of the readily available[6,7] dianion $Fe(CO)_4^{2-}$ with diverse $RPCl_2$ derivatives, mainly those containing bulky R groups, have

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(1) Part 3: King, R. B.; Fu, W.-K.; Holt, E. M. *Inorg. Chem.* **1986**, *25*, 2394.

(2) This work was taken in part from the doctoral dissertation of F.-J.W., University of Georgia, 1987.

(3) Portions of this work were presented at the 191st National Meeting of the American Chemical Society, New York, NY, April 1986, and the 10th International Conference on Phosphorus Chemistry, Bonn, Germany, Sept 1986.

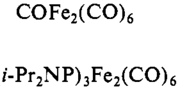
0002-7863/87/1509-7764$01.50/0

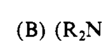
Table I. ^{31}P NMR Spectra and Infrared $\nu(CO)$ Frequencies of Dialkylamino Phosphorus Iron Carbonyl Derivatives

compound	^{31}P NMR,[a] δ	infrared $\nu(CO)$ frequencies, cm^{-1}: terminal	infrared $\nu(CO)$ frequencies, cm^{-1}: bridging
		(A) $(R_2NP)_2COFe_2(CO)_6$, Derivatives	
$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$	225.6 s	2060 m, 2016 s, 1996 s, 1925 s, 1964 m	1720 m
$(Cx_2NP)_2COFe_2(CO)_6$	229.7 s	2060 m, 2016 s, 1996 s, 1973 s, 1962 m	1721 m
$[(CH_2)_3(CMe_2)_2NP]_2\text{-}COFe_2(CO)_6$	204.6 s	2058, m, 2016 s, 1992 s, 1977 s, 1962 m,	1715 m
		(B) $(R_2NP)_3Fe_2(CO)_6$ Derivatives	
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	292.2 t (264), 170.3 d (264)	2048 s, 2008 s, 1986 s, 1958 s, 1947 m	
$(Cx_2NP)_3Fe_2(CO)_6$	294.9 t (269), 178.8 d (269)	2043 s, 2000 s, 1982 s, 1955 s, 1945 m	
		(C) $(R_2NP)_3COFe_2(CO)_6$ Derivatives	
$(i\text{-}Pr_2NP)_3COFe_2(CO)_6$	189.4 dd (83, 24), 223.8 dd (405, 83), 1.2 dd (405, 24)	2057 m, 2020 s, 1995 s, 1985 m, 1975 s, 1964 m	1645 w
$(Cx_2NP)_3COFe_2(CO)_6$	230.4 dd (85, 39), 191.3 dd (431, 85), 3.5 dd (431, 39)	2060 m, 2022 s, 1997 s, 1995 s, 1975 s, 1964 m	1645 w
		(D) $(R_2NP)_2Fe_3(CO)_9$ Derivatives	
$(i\text{-}Pr_2NP)_2Fe_3(CO)_9$	398.6 s	2062 w, 2030 s, 2010 s, 1998 s, 1990 m, 1982 m, 1976 s	
$(Cx_2NP)_2Fe_3(CO)_9$	403.6 s	2060 w, 2025 s, 2007 s, 1997 s, 1990 s, 1980 m, 1974 s	
		(E) Miscellaneous Derivatives	
$(Et_2NP)_3Fe_3(CO)_{12}$[b]	228.5 dd (367, 37), 156.1 dd (367, 301), 118.6 dd (301, 37)	2080 m, 2055 s, 2037 s, 2007 m, 1957 br s, 1941 br s	
$(Et_2NP)_3Fe_3(CO)_{11}$	123.0 dd (195, 54), 97.7 dd (264, 54), 85.5 dd (264, 195)	2070 m, 2048 s, 2025 s, 1998 s, 1990 m, 1983 m, 1973 m, 1960 m, 1955 m, 1948	1648 w
$[i\text{-}Pr_2NPHFe(CO)_4]_2O$[c]	120.7 s	2057 m [A_1], 1992 m [A_1], 1957 vs [E]	

[a] The ^{31}P NMR spectra reported here were run with proton decoupling: s = singlet, d = doublet, t = triplet, dd = double doublet; coupling constants in hertz are given in parentheses. [b] The infrared $\nu(CO)$ frequencies were determined in $CHCl_3$ solution because of insufficient solubility in hydrocarbon solvents. [c] $|^1J(P\text{-}H)| = 433$ Hz; assignments of the $\nu(CO)$ frequencies for an axial $LFe(CO)_4$ derivative are given in brackets.

yielded several types of $Fe(CO)_4$ complexes of the corresponding diphosphenes including I (R = 2,4,6-*t*-$Bu_3C_6H_2$),[8] II (R = $(Me_3Si)_2CH$ and $(Me_3Si)_2N$),[9,10] and III (R = 2,4,6-*t*-$Bu_3C_6H_2O$).[11] Under similar conditions the reaction of $Na_2Fe(CO)_4$ with 4-Me-2,6-*t*-$Bu_2C_6H_2OPCl_2$ was found to give the stable "diphosphadiferracyclobutadiene" derivative (4-Me-2,6-*t*-$Bu_2C_6H_2O)_2P_2Fe_2(CO)_6$ (IV: R = 4-Me-2,6-*t*-$Bu_2C_6H_2O$).[12] In addition, the phenyl derivative III (R = Ph)[13] has been obtained from the reaction of $HFe(CO)_4^-$ with $PhPCl_2$.


I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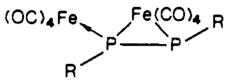
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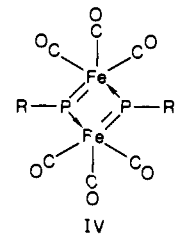
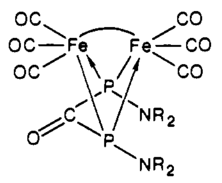
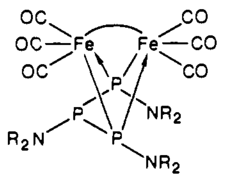

IV

The research discussed in this paper originally arose from an attempt to extend the above chemistry to reactions of $Na_2Fe(CO)_4$ with R_2NPCl_2 derivatives, which are readily available from reactions of PCl_3 with secondary amines.[14] Such R_2NPCl_2 derivatives are also attractive precursors for this type of chemistry because of the ability to vary the steric bulk of the R_2N group within wide limits from dimethylamino to 2,2,6,6-tetramethylpiperidino. Our preliminary studies[4] indicated that such reactions were particularly interesting since they yielded products of radically different types than the products I–IV obtained by the $RPCl_2$ systems discussed above.[8-13] Thus the reaction of *i*-Pr_2NPCl_2 (*i*-Pr = isopropyl) with $Na_2Fe(CO)_4$ in diethyl ether[4a] or tetrahydrofuran[4b] provided preparatively useful methods for the synthesis of the phosphorus-bridging carbonyl derivative (*i*-$Pr_2NP)_2COFe_2(CO)_6$ (V: R = *i*-Pr) or the triphosphine derivative (*i*-$Pr_2NP)_3Fe_2(CO)_6$ (VI: R = *i*-Pr), respectively, in quantities of ca. 30 g from a single preparation. This paper presents further details of such reactions, structural studies on the products of particular interest, and experiments designed to provide insight into the mechanisms of the obviously complicated reactions of $Na_2Fe(CO)_4$ with R_2NPCl_2 derivatives and their relationships to the reported[8-12] reactions of $Na_2Fe(CO)_4$ with other $RPCl_2$ derivatives.


V


VI

Experimental Section

Microanalyses were performed by the Atlantic Microanalytical Laboratory, Atlanta, GA. Infrared spectra (Table I) were run in the 2200–1600-cm^{-1} metal-carbonyl region in hexane or cyclohexane solution and

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(4) For preliminary communications of portions of this work, see the following references: (a) King, R. B.; Wu, F.-J.; Sadanani, N. D.; Holt, E. M. *Inorg. Chem.* **1985**, *24*, 4449. (b) King, R. B.; Wu, F.-J.; Holt, E. M. *Inorg. Chem.* **1986**, *25*, 1733. (c) King, R. B.; Wu, F.-J.; Holt, E. M. *J. Organomet. Chem.* **1986**, *314*, C27.

(5) Cowley, A. H.; Norman, N. C. *Prog. Inorg. Chem.* **1986**, *34*, 1.

(6) Collman, J. P. *Acc. Chem. Res.* **1975**, *8*, 342.

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

(8) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Organometallics* **1984**, *3*, 1044.

(9) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085.

(10) Flynn, K. M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7460.

(11) Flynn, K. M.; Hope, H.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 7751.

(12) Flynn, K. M.; Bartlett, R. A.; Olmstead, M. M.; Power, P. P. *Organometallics* **1986**, *5*, 813.

(13) Mathieu, R.; Caminade, A.-M.; Majoral, J.-P.; Attali, S.; Sanchez, M. *Organometallics* **1986**, *5*, 1914.

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

Table II. ^1H and ^{13}C NMR spectra of Dialkylamino Phosphorus Iron Carbonyl Derivatives

	^{13}C NMR,[a] δ			^1H NMR, δ	
compound	CH or CH_2	CH_2 or CH_3	CO	CH_2 or CH_2	CH_2 or CH_3
$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$	53.6	22.6	212.2, 209.2 t (83)[b]	3.9–3.2[c]	1.27 d (7)
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	53.5, 49.0	24.6, 23.3, 22.7	215.2, 214.6, 213.2	4.48 (2 H) 3.41 (4 H)	1.28 d (7), 1.23 d (7) 1.20 d (7)
$(i\text{-}Pr_2NP)_3COFe_2(CO)_6$	55.8, 54.4, 53.5	25.0, 24.7, 24.6, 23.7, 23.2, 22.5	212.0, 211.7, 244.3 dt (73, 42)[b]	3.83 (2 H) 3.53 (4 H)	1.46–1.09[c]
$(i\text{-}Pr_2NP)_2Fe_3(CO)_9$	55.5	23.1	214.4, 206.9	3.87	1.37 d (7)
$(Cx_2NP)_2COFe_2(CO)_6$	62.9	33.4, 26.3, 25.2	213.2, 209.5 t (84)[b]		
$(Cx_2NP)_3Fe_2(CO)_6$	63.1, 57.7	33.9, 33.3, 26.4, 26.3, 25.4	214.6, 213.4	4.79 (2 H) 2.90 (4 H)	1.66–1.16[c]
$(Cx_2NP)_3COFe_2(CO)_6$	66.1, 64.2	35.5, 34.2, 33.5, 22.8, 25.7, 25.5	212 m, 245.6 ddd (42, 73, 78)[b]	3.31 (2 H) 2.98 (4 H)	2.30–1.19[c]
$(Cx_2NP)_2Fe_3(CO)_9$	65.1	33.9, 26.7, 25.4	216.4, 206.8	3.33	1.84–1.26[c]
$(Et_2NP)_3Fe_3(CO)_{12}$	49.2, 44.3, 43.6, 41.7, 41.6	13.8, 13.6, 13.4, 13.3, 13.3	217.4 ddd (7, 6, 4), 214.5 ddd (15, 6, 2), 202–209[c]	3.9–2.7[c]	1.6–1.0[c]
$(Et_2NP)_3Fe_3(CO)_{11}$	44.3, 42.9, 41.6, 40.4	14.4, 13.8, 13.5, 12.7	215.3, 211.3, 210.3	3.9–2.7[c]	1.6–0.8[c]
$[i\text{-}Pr_2NPHFe(CO)_4]_2O$	49.6	23.8, 22.6	213.0 t (10)	3.95m[d]	1.34 d (7), 1.25 d (7)[d]

[a] The ^{13}C NMR spectra were run with proton decoupling. Resonances are singlets unless otherwise indicated: t = triplet; dt = doublet of triplets; ddd = double of doublets of doublets. Coupling constants in hertz are given in parentheses. [b] These ^{13}C resonances are assigned to the phosphorus-bridging carbonyl group. [c] These resonances were not clearly resolved. [d] The proton NMR spectrum of $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ also exhibits a doublet P–H resonance centered at δ 8.12 with a 433-Hz separation corresponding to the $|(^1J(P\text{–}H)|$ coupling constant.

recorded on a Perkin-Elmer 599B spectrometer calibrated against polystyrene film. Proton NMR spectra (Table II) were run on a continuous-wave EM-390 spectrometer or a multinuclear pulsed Fourier transform JEOL FX-90Q spectrometer at a nominal frequency of 90 MHz with internal tetramethylsilane as a reference. ^{31}P (Table I) and ^{13}C (Table II) NMR spectra were taken on the JEOL FX-90Q spectrometer at nominal frequencies of 36.19 and 22.49 MHz, respectively, with external 85% phosphoric acid and internal tetramethylsilane, respectively, as references. ^{31}P and ^{13}C NMR spectra were normally run with proton decoupling. All chemical shifts (δ) are given downfield from the reference. The relaxation reagent $Cr(acac)_3$[15] was added to NMR samples requiring a good signal-to-noise ratio in the carbonyl region. Melting and decomposition points were taken in capillaries and are uncorrected.

Commercial $Fe(CO)_5$ (GAF Corp., New York, NY) was converted to $Na_2Fe(CO)_4{\cdot}1.5C_4H_8O_2$ by the published procedure.[7] The R_2NPCl_2 derivatives were prepared by reactions of PCl_3 with the corresponding secondary amine.[14] All other starting materials were purchased from standard suppliers, mainly Aldrich Chemical Co. (Milwaukee, WI).

Before use, all solvents were distilled under dry nitrogen over appropriate drying agents (sodium benzophenone ketyl or metal hydrides except for chlorinated solvents). A dry nitrogen atmosphere was always provided for the following three operations: (a) filling evacuated vessels containing potentially air-sensitive materials; (b) carrying out reactions; (c) handling air-sensitive compounds. When necessary, Schlenkware[16] or a polyethylene glovebag was used to provide the dry nitrogen atmosphere. Such a dry nitrogen atmosphere was mandatory for handling the pyrophoric $Na_2Fe(CO)_4{\cdot}1.5$ dioxane.[7]

Reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in Diethyl Ether. (a) Synthesis of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$. The reaction was carried out in a 2-L three-necked round-bottom flask equipped with an air-driven stirrer and a nitrogen inlet and topped with a rubber septum. This flask containing a suspension of freshly prepared $Na_2Fe(CO)_4{\cdot}1.5$dioxane (147 g, 420 mmol) in 1200 mL of diethyl ether was cooled to −78 °C. To this cooled suspension with vigorous stirring was added a stoichiometric amount of $i\text{-}Pr_2NPCl_2$ (85.1 g, 420 mmol) with a syringe. No color change was observed at this time. The reaction mixture was allowed to warm slowly while stirring was continued. At about −35 °C the color of the solution started to change from colorless to orange. After the solution was stirred overnight at room temperature, the solvent was removed under reduced pressure [25 °C (25 mm)]. The residue was extracted with a total of 1000 mL of hexanes in several portions. Concentrating the filtered hexane extracts and cooling in a −10 °C freezer gave 39 g (35% yield) of orange, air-stable $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (mp 114–115 °C, sublimes at 70 °C (0.05 mm)] which was readily soluble in nonpolar organic solvents. Anal. Calcd for $C_{19}H_{28}Fe_2N_2O_7P_2$: C, 40.0; H, 4.9; N, 4.9. Found: C, 40.0; H, 5.0; N, 4.9.

(b) Isolation of $[i\text{-}Pr_2NPHFe(CO)_4]_2O$. The mother liquor from the isolation of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ by the above procedure contained a mixture of products that required chromatography for further purification. Chromatography of this mixture on silica gel with hexane as the eluent resulted in decomposition of the diphosphene complex $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ and separation of $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$, $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, and $[i\text{-}Pr_2NPHFe(CO)_4]_2O$, as indicated by the ^{31}P NMR spectrum. Complete separation of pure $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ required repeated chromatography and fractional crystallization from hexane, leading to extensive losses resulting in isolation of pure product in less than 1% yield (e.g., ~0.2 g a run with 38 mmol of $Na_2Fe(CO)_4{\cdot}1.5$dioxane). The progress of the separation was monitored by ^{31}P NMR spectroscopy. Anal. Calcd for $C_{20}H_{30}Fe_2N_2O_9P_2$: C, 39.0; H, 4.9; N, 4.5. Found: C, 38.9; H, 4.9; N, 4.5.

Synthesis of $(Cx_2NP)_2COFe_2(CO)_6$. A procedure similar to that given above but with Cx_2NPCl_2 (Cx = cyclohexyl) instead of $i\text{-}Pr_2NPCl_2$ gave a 16% yield of orange, air-stable $(Cx_2NP)_2COFe_2(CO)_6$, mp 164 °C. Anal. Calcd for $C_{31}H_{44}Fe_2N_2O_7P_2$: C, 51.0; H, 6.0; N, 3.8. Found: C, 50.9; H, 6.1; N, 3.7.

Synthesis of $[(CH_2)_3(CMe_2)_2NP]_2COFe_2(CO)_6$. A procedure similar to that given above but with $(CH_2)_3(CMe_2)_2NPCl_2$ [(2,2,6,6-tetramethylpiperidino)dichlorophosphine] instead of $i\text{-}Pr_2NPCl_2$ gave a 25% yield of orange, air-stable $[(CH_2)_3(CMe_2)_2NP]_2COFe_2(CO)_6$, mp 160 °C. Anal. Calcd for $C_{25}H_{36}Fe_2N_2O_7P_2$: C, 46.2; H, 5.5; N, 4.3. Found: C, 46.2; H, 5.6; N, 4.3.

Reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in Tetrahydrofuran. (a) Synthesis of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$. The reaction was carried out in a 5-L three-necked round-bottom flask equipped with an air-driven stirrer and a nitrogen inlet and topped with a rubber septum. This flask containing an orange suspension of 440 mmol of freshly prepared $Na_2Fe(CO)_4{\cdot}1.5$dioxane in 4 L of dry tetrahydrofuran was cooled to −78 °C and treated with $i\text{-}Pr_2NPCl_2$ (410 mmol) with use of a syringe. The reaction mixture became darker orange immediately when the $i\text{-}Pr_2NPCl_2$ was added. The reaction mixture was allowed to warm slowly to 0 °C over a period of at least 12 h by adding wet ice to the dry ice/acetone bath. After the reaction was allowed to proceed for 36 h, the air-driven stirrer was replaced by a rubber septum and solvent was removed under reduced pressure [25 °C (25 mm)]. The reaction mixture was dried at ~25 °C (0.005 mm) and then exposed to air for another 24 h to remove air-sensitive byproducts. The resulting mixture was extracted with 2000 mL of hexane in three portions. Concentration of the filtered hexane extracts to 800 mL and cooling in a −10 °C freezer gave 27 g (30% yield) of air-stable orange $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ mp 181–185 °C dec. Anal. Calcd for $C_{24}H_{42}Fe_2N_3O_6P_3$: C, 42.8; H, 6.2; N, 6.2. Found: C, 43.1; H, 6.3; N, 6.2.

(b) Isolation of $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ and $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$. The mother liquor from the isolation of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ by the above procedure contained a mixture of the four iron carbonyl complexes $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$, $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$, $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$, and $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$, which were separated by repeated chromatography on silica gel and fractional crystallization from hexane. The

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[15] Gansow, O. A.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1972**, *94*, 2550.

[16] Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

Table III. Product Distributions from Reactions of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ under Various Reaction Conditions[a]

	solvent			
temp, °C	THF/18-crown-6	THF[b] or Et_2O/18-crown-6	Et_2O	hexanes
−78 to −25	$(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ [6] $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ [6] $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [1]	$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [6] $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ [6] $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ [2] $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ [1]	$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [10] $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ [1] $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ [1]	$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [8] $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ [8]
−78 to 0		$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ [8] $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [2] $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ [2] $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ [1]	$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [10] $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ [1]	$(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ [8] $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [3]
−78 to −40		$[i\text{-}Pr_2NPHFe(CO)_4]_2O$	no reaction	no reaction

[a] The relative amounts of products were estimated from the ^{31}P NMR spectrum of the crude reaction mixture and are given in brackets after the corresponding formulas. [b] If the reaction is conducted in tetrahydrofuran at ambient temperature without cooling, the product distribution is $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ [8], $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ [6], $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ [1].

progress of the separation was monitored by ^{31}P NMR spectroscopy since the orange bands of the four compounds were not distinguishable on the chromatography column. Three sizes of chromatography columns (25 cm × 2.5 cm, 25 cm × 4.0 cm, and 25 cm × 6.0 cm) were used depending upon the amount of material. The complete separation of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ and $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ required mechanical separation of the crystals. The solubilities of the four products in hexane decreased in the sequence $(i\text{-}Pr_2NP)_2Fe_3(CO)_9 > (i\text{-}Pr_2NP)_3Fe_2(CO)_6 > (i\text{-}Pr_2NP)_2COFe_2(CO)_6 \sim (i\text{-}Pr_2NP)_3COFe_2(CO)_6$, and the yields were 5, 35, 5, and 3%, respectively, including the $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ separated from the original reaction mixture by crystallization (see above). All four complexes are orange with different color intensities $((i\text{-}Pr_2NP)_2Fe_3(CO)_9 \sim (i\text{-}Pr_2NP)_3COFe_2(CO)_6 > (i\text{-}Pr_2NP)_3Fe_2(CO)_6 > (i\text{-}Pr_2NP)_2COFe_2(CO)_6)$ and are air-stable and soluble in nonpolar organic solvents. $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$: mp 128–129 °C. Anal. Calcd for $C_{21}H_{28}Fe_3N_2O_9P_2$: C, 37.0; H, 4.1; N, 4.1. Found: C, 36.7; H, 4.1; N, 4.1. $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$: mp 178–179 °C. Anal. Calcd for $C_{25}H_{42}Fe_2N_3O_7P_3$: C, 42.8; H, 6.0; N, 6.0. Found: C, 42.4; H, 6.0; N, 5.8.

Reaction of Cx_2NPCl_2 with $Na_2Fe(CO)_4$ in Tetrahydrofuran. The procedure was the same as above except that a 2-L flask, 99 mmol of $Na_2Fe(CO)_4\cdot 1.5$dioxane, 800 mL of tetrahydrofuran, 87 mmol of Cx_2NPCl_2, and 800 mL of hexane were used. The solubilities of the four products in hexanes decrease in the sequence $(Cx_2NP)_2Fe_3(CO)_9 > (Cx_2NP)_2COFe_2(CO)_6 > (Cx_2NP)_3Fe_2(CO)_6 \sim (Cx_2NP)_3COFe_2(CO)_6$, and the yields were 5, 8, 30, and 5%, respectively. All four complexes are orange, air-stable, modestly soluble in nonpolar organic solvents, and very soluble in polar organic solvents. $(Cx_2NP)_3Fe_2(CO)_6$: mp 190–195 °C. Anal. Calcd for $C_{42}H_{66}Fe_2N_3O_6P_3$: C, 55.2; H, 7.2; N, 4.6. Found: C, 55.2; H, 7.4; N, 4.4. $(Cx_2NP)_2Fe_3(CO)_9$: mp 141–142 °C. Anal. Calcd for $C_{33}H_{44}Fe_3N_2O_9P_2$: C, 47.0; H, 5.2; N, 3.3. Found: C, 47.2; H, 5.3; N, 3.3. $(Cx_2NP)_3COFe_2(CO)_6$: mp 200–201 °C. Anal. Calcd for $C_{43}H_{66}Fe_2N_3O_7P_3$: C, 55.2; H, 7.2; N, 4.6. Found: C, 54.9; H, 7.0; N, 4.3.

Effects of Solvent and Temperature on the Product Distributions from the Reactions of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ (Table III). All of the reactions summarized in Table III were carried out in standard Schlenk flasks.[16] The $Na_2Fe(CO)_4\cdot 1.5$dioxane[7] was packed in an inert atmosphere (nitrogen, glovebag) into Pyrex tubes, which were then sealed with an oxygen flame for easy handling. The glass tube was chosen to be small enough (diameter 1.9 cm) to be insertable against a nitrogen stream into a Schlenk flask with a 24/40 joint but large enough to contain 4–8 g of the reagent. The amount of $Na_2Fe(CO)_4\cdot 1.5$dioxane introduced was determined by weighing the glass tube before and after (including the debris) the addition. The −40 °C reactions were performed with an acetonitrile/dry ice bath. General aspects of the procedure other than the reaction scale, solvent or solvent mixture, and temperature control were similar to those described above for the reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in tetrahydrofuran. The product distributions reported in Table III were roughly estimated from the ^{31}P NMR spectra of the original reaction mixtures before any attempts at product separation and isolation.

Reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in Diethyl Ether from −78 to 0 °C. The reaction was carried out in a 2-L three-necked round-bottom flask equipped with an air-driven stirrer, and a nitrogen inlet and topped with a rubber septum. The flask containing a suspension of 180 mmol of freshly prepared $Na_2Fe(CO)_4\cdot 1.5$dioxane in 1400 mL of diethyl ether was cooled to −78 °C and treated with 160 mmol of Et_2NPCl_2 with use of a syringe. The solutions remained unchanged at first but began to turn orange upon warming to about −55 °C. The mixture was allowed to warm slowly and finally kept at 0 °C for 20 h with vigorous stirring. The reaction mixture was filtered as rapidly as possible through a coarse frit without excluding air. Solvent was removed at 0 °C (15 mm). A concentrated solution of the residue was chromatographed on a 20 cm × 4 cm silica gel column. The chromatogram was first eluted with hexane. The initial deep orange band gave a mixture of two products, shown by its ^{31}P NMR spectrum to be a mixture of $(Et_2NP)_2Fe_3(CO)_9$ (δ 401.2; lit.[43] δ 401.6) and $[Et_2NPHFe(CO)_4]_2O$ (δ 124.7, $|^1J(P\text{-}H)| = 418$ Hz). Subsequent elution of the chromatogram with mixtures of dichloromethane and hexane followed by concentration at 0 °C (25 mm) and crystallization in a −10 °C freezer gave 16 g (37% yield) of deep orange $(Et_2NP)_3Fe_3(CO)_{12}$: mp 101–102 °C. Anal. Calcd for $C_{24}H_{30}Fe_3N_3O_{12}P_3$: C, 35.4; H, 3.7; N, 5.2. Found: C, 35.5; H, 3.9; N, 5.2. This product is air-stable in the solid state, thermally unstable in solution, insoluble in nonpolar organic solvents, and soluble in polar organic solvents.

Reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in Diethyl Ether from −78 °C to Room Temperature. The procedure was the same as above except that 92 mmol of $Na_2Fe(CO)_4\cdot 1.5$dioxane, 700 mL of diethyl ether, and 81 mmol of Et_2NPCl_2 were used and the reaction mixture was allowed to warm to room temperature for 24 h before product isolation. The filtration and chromatography steps were also performed as rapidly as possible to suppress thermal decomposition. The product, $(Et_2NP)_3Fe_3(CO)_{11}$, was isolated in 35% yield (7.9 g) as orange needles: mp 75–80 °C dec. Anal. Calcd for $C_{23}H_{30}Fe_3N_3O_{11}P_3$: C, 35.2; H, 3.8; N, 5.4. Found: C, 35.2; H, 3.9; N, 5.3. This product is air-stable in the solid state but thermally unstable in solution, decomposing into some intractable materials. It is sparingly soluble in nonpolar organic solvents but very soluble in polar organic solvents.

Reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in Tetrahydrofuran at −40 °C. A suspension of 31.3 mmol of $Na_2Fe(CO)_4$ in 350 mL of dry tetrahydrofuran at −40 °C (acetonitrile/dry ice bath) was treated with Et_2NPCl_2 (31 mmol) with use of a syringe. As soon as the Et_2NPCl_2 was added, the solution immediately turned deeper orange. The reaction solution was stirred and kept at −40 °C for 12 h. Removal of the solvent gave a deep orange residue shown by its ^{31}P NMR spectrum to be a mixture of at least three different products exhibiting AMX patterns as well as a number of additional diethylamino phosphorus derivatives. Because of the complexity of this reaction mixture, it was not investigated further.

Reaction of Me_2NPCl_2 with $Na_2Fe(CO)_4$ in Diethyl Ether. A suspension of $Na_2Fe(CO)_4$ (3.3 g, 9.5 mmol) in 280 mL of anhydrous diethyl ether at −78 °C was treated with Me_2NPCl_2 (9.2 mmol) with use of a syringe. The mixture was allowed to warm to room temperature and stirred for 24 h. Removal of solvent gave a residue shown by its ^{31}P NMR spectrum to be a complicated mixture containing at least three different P_3Fe_3 complexes.

X-ray Structure Determinations (Table IV). The structures of the six compounds $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (Table V; Figure 1), $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ (Table VI; Figure 2), $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (Table VII; Figure 3), $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (Table VIII; Figure 4), $(Et_2NP)_3Fe_3(CO)_{12}$ (Table IX; Figure 5), and $(Et_2NP)_3Fe_3(CO)_{11}$ (Table X; Figure 6) were determined by X-ray diffraction. The crystallographic and data collection parameters are summarized in Table IV. 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 IV) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta < 15°$) during normal alignment procedures by using molybdenum radiation ($\lambda = 0.71069$ 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 $K\alpha_1$ and 1.2°

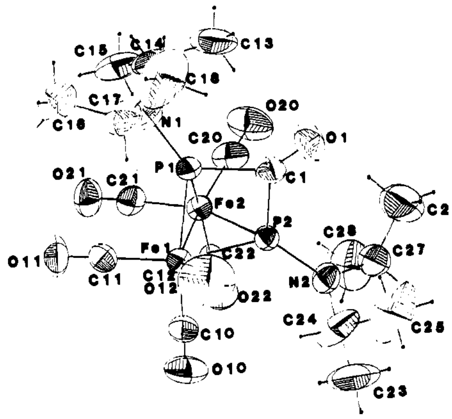

Figure 1. ORTEP diagram of the complex $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (V: R = *i*-Pr).

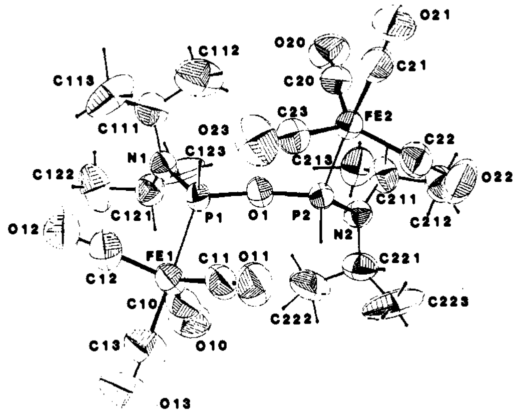

Figure 2. ORTEP diagram of the complex $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ (XII: R = *i*-Pr).

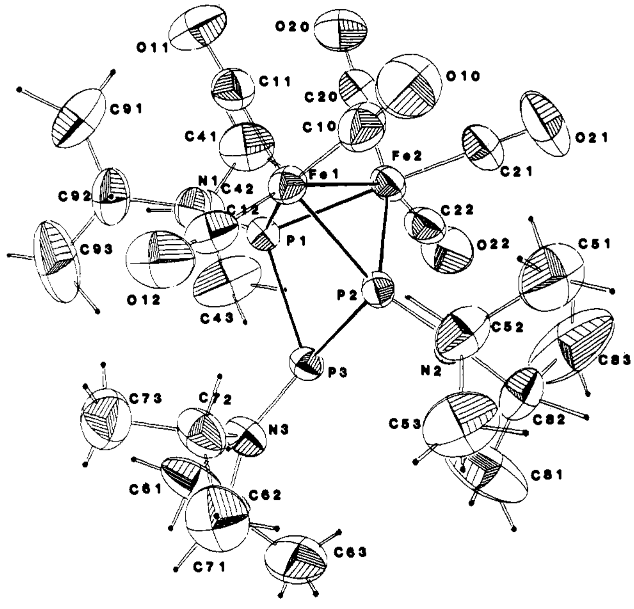

Figure 3. ORTEP diagram of the complex $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (VI: R = *i*-Pr).

above $K\alpha_2$ to the maximum 2θ values indicated in Table IV. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of 3 standard reflections were remeasured after every 97 reflections. Since the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space group forbidden data, the observed data with $I > 3.0\sigma$ were used for solution and refinement as indicated below. Anomalous dispersion corrections were made for Fe and P. Scattering factors were taken from Cromer and Mann.[17] Weights equal to $1/\sigma F$ were introduced into the final cycles of refinement.

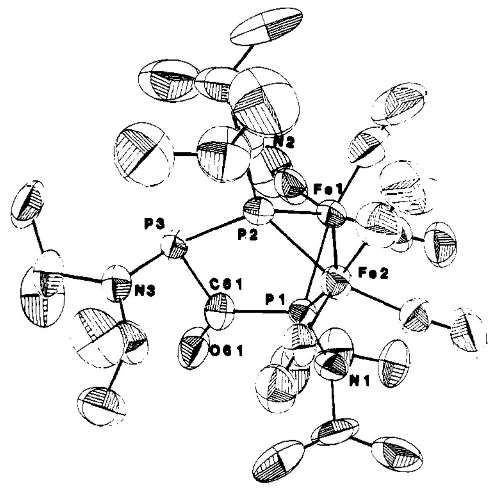

Figure 4. ORTEP diagram of the complex $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (XIII: R = *i*-Pr).

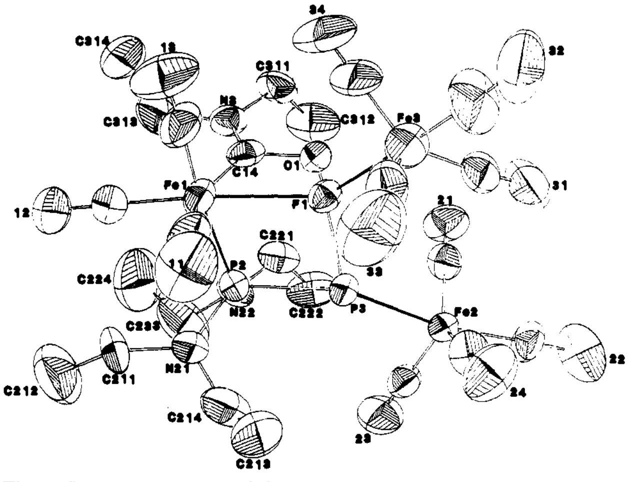

Figure 5. ORTEP diagram of the complex $(Et_2NP)_3Fe_3(CO)_{12}$ (XIV: R = Et).

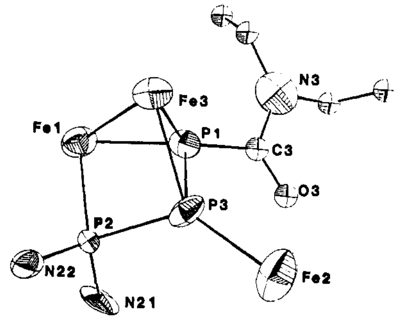

Figure 6. ORTEP diagram of the complex $(Et_2NP)_3Fe_3(CO)_{11}$ (XV: R = Et). For clarity the ten metal carbonyl groups and two of the diethylamino groups are not shown.

The structures were solved for heavy-atom positions with MULTAN-80.[18] Successive least-squares/difference Fourier cycles allowed the location of the remainder of the non-hydrogen atoms to be found. Refinement of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence.[19] For $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ (Table VI), $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (Table VII), and $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (Table VIII) hydrogen positions were apparent

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

(18) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M., University of York, England, 1980.

(19) Stewart, J. M., Ed. *The XRAY System-Version of 1980, Technical Report TR446 of the Computer Center*; University of Maryland: College Park, MD, 1980.

Table IV. Crystallographic and Data Collection Parameters for the Six Dialkylamino Phosphorus Iron Carbonyl Derivatives

	(i-$Pr_2NP)_2$-$COFe_2(CO)_6$	[i-Pr_2NPHFe-$(CO)_4]_2O$	(i-$Pr_2NP)_3$-$Fe_2(CO)_6$	(i-$Pr_2NP)_3$-$COFe_2(CO)_6$	$(Et_2NP)_3$-$Fe_3(CO)_{12}$	$(Et_2NP)_3$-$Fe_3(CO)_{11}$
formula	$C_{19}H_{28}N_2O_7P_2Fe_2$	$C_{20}H_{30}N_2O_9P_2Fe_2$	$C_{24}H_{42}N_3O_6P_3Fe_2$	$C_{25}H_{42}N_3O_7P_3Fe_2$	$C_{24}H_{30}N_3O_{12}P_3Fe_3$	$C_{23}H_{30}N_3O_{11}P_3Fe_3$
mol wt	570.1	616.1	673.2	701.2	813.0	785.0
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space gp	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	10.197 (3)	15.682 (3)	11.554 (2)	14.910 (5)	17.071 (7)	9.054 (4)
b, Å	31.403 (13)	14.458 (3)	14.294 (6)	12.064 (6)	19.116 (8)	38.75 (3)
c, Å	9.170 (3)	13.044 (8)	20.405 (4)	19.733 (10)	10.853 (3)	19.737 (8)
β, deg	112.18 (2)	99.80 (4)	90.96 (2)	105.31 (4)	96.82 (3)	104.05 (3)
V, Å^3	2719.1 (17)	2914.3 (21)	3369.4 (18)	3423.6 (28)	3516.6 (23)	6717.8 (70)
$F(000)$	1176	1272	1408	1464	1656	3200
μ(Mo Kα), cm^{-1}	12.18	11.46	10.37	10.25	14.11	14.72
D_{calcd}, g cm^{-1}	1.392	1.404	1.327	1.360	1.535	1.552
Z	4	4	4	4	4	8
no. of obsd reflcns	3109	2487	4164	3021	3238	2524
octants colld	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,+k,+l$	$\pm h,+k,+l$
max 2θ	116°	45°	60°	60°	60°	60°
R	0.075	0.051	0.059	0.074	0.071	0.109
R_w	0.094	0.066	0.074	0.096	0.090	0.138

Table V. Selected Bond Distances (Å) and Angles (deg) for (i-$Pr_2NP)_2COFe_2(CO)_6$

	Distances		
Fe1–Fe2	2.603 (2)	P1–C1	1.884 (9)
Fe1–P1	2.227 (3)	P2–C1	1.895 (10)
Fe1–P2	2.220 (3)	C1–O1	1.185 (12)
Fe1–C10	1.806 (10)	Fe1–C10	1.806 (10)
Fe1–C11	1.805 (10)	Fe1–C11	1.805 (10)
Fe1–C12	1.770 (12)	Fe1–C12	1.770 (12)
Fe2–P1	2.224 (3)	Fe2–C20	1.118 (13)
Fe2–P2	2.230 (3)	Fe2–C21	1.798 (8)
Fe2–C20	1.778 (13)	Fe2–C22	1.804 (11)
Fe2–C21	1.798 (8)	P1–N1	1.645 (8)
Fe2–C22	1.804 (11)	P2–N2	1.647 (7)
	Angles		
Fe1–P1–Fe2	71.60 (9)	P1–Fe1–C10	152.8 (4)
Fe1–P2–Fe2	71.60 (7)	P1–Fe1–C11	93.4 (4)
Fe1–P1–C1	91.1 (3)	P1–Fe1–C12	101.9 (4)
Fe1–P2–C1	91.0 (3)	P2–Fe1–C10	92.5 (3)
Fe2–P1–C1	94.2 (4)	P2–Fe1–C11	153.4 (4)
Fe2–P2–C1	93.6 (3)	P2–Fe1–C12	101.8 (3)
P1–C1–P2	84.4 (4)	C10–Fe1–C11	94.7 (4)
P1–C1–O1	138.3 (7)	C10–Fe1–C12	101.8 (5)
P2–C1–O1	137.2 (7)	C11–Fe1–C12	101.7 (5)
Fe1–C10–O10	178.3 (11)	P1–Fe2–P2	69.48 (9)
Fe1–C11–O11	179.5 (16)	P1–Fe2–C20	101.5 (4)
Fe1–C12–O12	176.4 (11)	P1–Fe2–C21	93.2 (4)
Fe2–C20–O20	177.0 (11)	P1–Fe2–C22	154.2 (4)
Fe2–C21–O21	177.8 (11)	P2–Fe2–C20	106.8 (3)
Fe2–C22–O22	179.7 (22)	P2–Fe2–C21	148.9 (4)
Fe1–P1–N1	131.0 (4)	P2–Fe2–C22	91.0 (3)
Fe1–P2–N2	128.7 (3)	C20–Fe2–C21	101.7 (5)
Fe2–P1–N1	134.9 (3)	C20–Fe2–C22	100.3 (5)
Fe2–P2–N2	134.6 (4)	C21–Fe2–C22	95.8 (4)
P1–Fe1–P2	69.60 (9)		

from a final difference Fourier synthesis. For (i-$Pr_2NP)_2COFe_2(CO)_6$ (Table V) and $(Et_2NP)_3Fe_3(CO)_{12}$ (Table IX), hydrogen positions were calculated. Hydrogen positional parameters and isotropic thermal parameters $U = 0.038$ were included in the final cycles of refinement but were held variant. Final difference Fourier syntheses revealed no electron density of interpretable level.

Special difficulties were encountered in determining the structure of $(Et_2NP)_3Fe_3(CO)_{11}$ (Table X). This structure showed two seemingly identical $(Et_2NP)_3Fe_3(CO)_{11}$ molecules per asymmetric unit. Problems with refinement of the ethyl groups attached to N3 of molecule A and carbonyl groups attached to Fe92 and Fe93 could not be resolved. In view of the small amount of observed data (2524 points), refinement was completed with anisotropic thermal parameters for Fe, P, N, O, and the carbonyl groups and isotropic thermal approximations for the carbons of the ethyl groups for a total of 646 varying parameters. Results indicate that the positions of Fe, P, N, and the $CONEt_2$ ligand may be viewed as reliable if not of optimum accuracy, and details of connectivity, general bond lengths, angles, and geometry derived from these positions should be valid.

Table VI. Selected Bond Distances (Å) and Angles (deg) for [i-$Pr_2NPHFe(CO)_4]_2O$

	Distances		
Fe1–P1	2.218 (2)	Fe1–C11	1.784 (9)
Fe2–P2	2.212 (2)	Fe1–C12	1.706 (10)
P1–O1	1.640 (5)	Fe1–C13	1.781 (10)
P2–O1	1.643 (5)	Fe2–C20	1.782 (9)
P1–N1	1.637 (6)	Fe2–C21	1.768 (8)
P2–N2	1.632 (6)	Fe2–C22	1.777 (8)
Fe1–C10	1.747 (8)	Fe2–C23	1.783 (8)
	Angles		
P1–O1–P2	136.4 (3)	P2–Fe2–C21	176.1 (4)
Fe1–P1–O1	116.1 (2)	P2–Fe2–C22	86.8 (2)
Fe2–P2–O1	114.6 (2)	P2–Fe2–C23	91.2 (2)
Fe1–P1–N1	118.9 (2)	C20–Fe2–C21	90.0 (4)
Fe2–P2–N2	118.5 (2)	C20–Fe2–C22	122.1 (4)
N1–P1–O1	107.0 (3)	C20–Fe2–C23	119.1 (3)
N2–P2–O1	107.8 (3)	C21–Fe2–C22	89.6 (3)
C10–Fe1–P1	93.6 (3)	C21–Fe2–C23	89.2 (4)
C11–Fe1–P1	89.5 (3)	C22–Fe2–C23	118.8 (4)
C12–Fe1–P1	87.3 (3)	Fe1–C10–O10	177.8 (9)
C13–Fe1–P1	177.3 (3)	Fe1–C11–O11	176.1 (8)
C10–Fe1–C11	123.1 (4)	Fe1–C12–O12	177.7 (8)
C10–Fe1–C12	120.5 (4)	Fe1–C13–O13	179.0 (10)
C10–Fe1–C13	89.1 (4)	Fe2–C20–O20	177.7 (8)
C11–Fe1–C12	116.4 (4)	Fe2–C21–O21	178.4 (8)
C11–Fe1–C13	89.5 (4)	Fe2–C22–O22	178.6 (8)
C12–Fe1–C13	91.0 (5)	Fe2–C23–O23	175.0 (7)
P2–Fe2–C20	93.1 (2)		

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

Results

(A) Reactions of Sterically Hindered R_2NPCl_2 Derivatives with $Na_2Fe(CO)_4$ in Diethyl Ether. Synthesis of $(R_2NP)_2COFe_2(CO)_6$ Derivatives. The major products from reactions of sterically hindered R_2NPCl_2 derivatives (R_2N = i-Pr_2N, Cx_2N, 2,2,6,6-tetramethylpiperidino) with $Na_2Fe(CO)_4 \cdot 1.5$dioxane in diethyl ether solutions are air-stable orange crystalline $(R_2NP)_2COFe_2(CO)_6$ compounds obtained in up to 35% isolated yield. The structure of the diisopropylamino derivative (i-$Pr_2NP)_2COFe_2(CO)_6$ has been determined by X-ray diffraction (Table V; Figure 1) to be V (R = isopropyl). This structure consists of a typical $Fe_2(CO)_6$ unit bridged by two phosphido phosphorus atoms similar to the many known $(R_2P)_2Fe_2(CO)_6$ derivatives.[20] Much more unusual in (i-$Pr_2NP)_2COFe_2(CO)_6$ is the carbonyl group (C1–O1 in Figure 1) bridging the two phosphorus atoms. When we first reported (i-$Pr_2NP)_2COFe_2$-

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[20] Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

Table VII. Selected Bond Distances (Å) and Angles (deg) for (i-$Pr_2NP)_3Fe_2(CO)_6$

	Distances		
Fe1–Fe2	2.602 (2)	Fe1–C11	1.773 (7)
Fe1–P1	2.257 (2)	Fe1–C12	1.779 (8)
Fe1–P2	2.258 (2)	Fe2–C20	1.776 (7)
Fe2–P1	2.237 (2)	Fe2–C21	1.801 (8)
Fe2–P2	2.240 (2)	Fe2–C22	1.766 (7)
P1–P2	2.534 (2)	P1–N1	1.668 (5)
P1–P3	2.278 (2)	P2–N2	1.664 (5)
P2–P3	2.243 (2)	P3–N3	1.682 (5)
Fe1–C10	1.797 (7)		
	Angles		
P1–Fe1–P2	68.29 (6)	C10–Fe1–C11	98.8 (3)
P1–Fe2–P2	68.96 (6)	C10–Fe1–C12	99.2 (3)
P1–Fe1–Fe2	54.25 (4)	C11–Fe1–C12	98.8 (3)
P2–Fe1–Fe2	54.32 (5)	Fe1–Fe2–C20	95.5 (2)
P1–Fe2–Fe1	54.99 (5)	Fe1–Fe2–C21	100.8 (2)
P2–Fe2–Fe1	54.97 (5)	Fe1–Fe2–C22	152.0 (2)
Fe1–P1–Fe2	70.76 (5)	P1–Fe2–C20	94.4 (2)
Fe1–P2–Fe2	70.70 (6)	P1–Fe2–C21	154.8 (2)
P3–P1–P2	55.25 (6)	P1–Fe2–C22	101.5 (2)
P3–P2–P1	56.56 (6)	P2–Fe2–C20	150.5 (2)
P1–P3–P2	68.19 (7)	P2–Fe2–C21	92.0 (2)
P3–P1–Fe1	104.32 (7)	P2–Fe2–C22	105.2 (2)
P3–P1–Fe2	93.54 (7)	C20–Fe2–C21	95.1 (3)
P3–P2–Fe1	105.46 (8)	C20–Fe2–C22	101.8 (3)
P3–P2–Fe2	94.42 (7)	C21–Fe2–C22	99.3 (3)
Fe2–Fe1–C110	94.9 (2)	Fe1–P1–N1	127.0 (2)
Fe2–Fe1–C11	99.4 (2)	Fe2–P1–N1	128.0 (2)
Fe2–Fe1–C12	156.8 (2)	P3–P1–N1	120.3 (2)
P1–Fe1–C10	149.1 (2)	Fe1–P2–N2	127.3 (2)
P1–Fe1–C11	93.0 (2)	Fe2–P2–N2	130.5 (2)
P1–Fe1–C12	110.6 (2)	P3–P2–N2	117.3 (2)
P2–Fe1–C10	96.6 (2)	P1–P3–N3	117.3 (2)
P2–Fe1–C11	153.3 (2)	P2–P3–N3	113.0 (2)
P2–Fe1–C12	105.5 (2)		

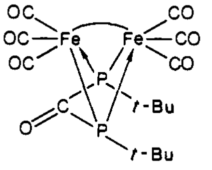
Table VIII. Selected Bond Distances (Å) and Bond Angles (deg) for (i-$Pr_2NP)_3COFe_2(CO)_6$

	Distances		
Fe1–Fe2	2.587 (2)	P3–C61	1.868 (12)
Fe1–P1	2.238 (3)	P1–C61	1.835 (11)
Fe1–P2	2.255 (4)	P1–N1	1.665 (11)
Fe1–C11	1.756 (13)	P2–N2	1.687 (12)
Fe1–C12	1.771 (14)	P3–N3	1.696 (9)
Fe1–C13	1.752 (17)	C11–O11	1.15 (2)
Fe2–P1	2.238 (4)	C12–O12	1.15 (2)
Fe2–P2	2.242 (3)	C13–O13	1.13 (2)
Fe2–C21	1.794 (11)	C21–O21	1.12 (1)
Fe2–C22	1.791 (17)	C22–O22	1.14 (2)
Fe2–C23	1.788 (14)	C23–O23	1.14 (2)
P2–P3	2.233 (5)	C61–O61	1.23 (2)
	Angles		
Fe1–P1–Fe2	70.6 (1)	C21–Fe2–C22	100.9 (6)
Fe1–P2–Fe2	70.2 (1)	C21–Fe2–C23	101.4 (5)
Fe1–P2–P3	103.3 (2)	C22–Fe2–C23	87.1 (7)
Fe2–P2–P3	119.1 (2)	P2–P3–C61	89.9 (4)
P1–Fe1–P2	77.2 (1)	P3–C61–P1	117.8 (7)
P1–Fe2–P2	77.5 (1)	Fe1–P1–C61	105.4 (4)
P1–Fe1–C11	91.4 (4)	Fe2–P2–C61	82.1 (2)
P1–Fe1–C12	105.3 (5)	Fe1–P1–N1	125.7 (4)
P1–Fe1–C13	151.2 (5)	Fe2–P1–N1	126.3 (4)
P2–Fe1–C11	156.3 (4)	N1–P1–C61	109.3 (6)
P2–Fe1–C12	101.7 (5)	Fe1–P2–N2	124.9 (4)
P2–Fe1–C13	91.4 (6)	Fe2–P2–N2	120.9 (4)
C11–Fe1–C12	101.3 (6)	N2–P2–P3	111.7 (4)
C11–Fe1–C13	88.8 (7)	P2–P3–N3	113.8 (4)
C12–Fe1–C13	101.8 (7)	C61–P3–N3	101.7 (5)
P1–Fe2–C21	103.4 (4)	P1–C61–O61	123.8 (9)
P1–Fe2–C22	155.3 (4)	P3–C61–O61	118.1 (8)
P1–Fe2–C23	92.0 (5)		

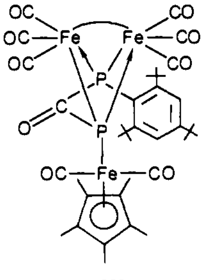
Table IX. Selected Bond Distances (Å) and Angles (deg) for $(Et_2NP)_3Fe_3(CO)_{12}$

	Distances		
Fe1–P1	2.302 (3)	Fe2–C22	1.73 (1)
Fe1–P2	2.312 (4)	Fe2–C23	1.77 (1)
Fe2–P3	2.270 (3)	Fe2–C24	1.75 (1)
Fe3–P1	2.223 (4)	Fe3–C31	1.77 (1)
Fe1–O1	2.725 (6)	Fe3–C32	1.75 (2)
P1–P2	2.923 (4)	Fe3–C33	1.58 (2)
P1–P3	2.122 (4)	Fe3–C34	1.74 (2)
P2–P3	2.183 (4)	O11–C11	1.15 (2)
P1–O1	1.746 (7)	O12–C12	1.14 (2)
P1–C14	2.41 (1)	O13–C13	1.13 (2)
P2–N21	1.66 (1)	O21–C21	1.14 (1)
P2–N22	1.67 (1)	O22–C22	1.15 (2)
O1–N3	2.21 (1)	O23–C23	1.15 (2)
O1–C14	1.35 (1)	O24–C24	1.15 (2)
Fe1–C11	1.78 (1)	O31–C31	1.11 (2)
Fe1–C12	1.79 (1)	O32–C32	1.14 (3)
Fe1–C13	1.81 (1)	O33–C33	1.30 (2)
Fe1–C14	2.00 (1)	O34–C34	1.15 (2)
Fe2–C21	1.78 (1)		
	Angles		
P1–Fe1–P2	78.6 (1)	Fe1–C13–O13	177. (1)
P1–Fe1–C11	91.2 (4)	Fe1–C14–O1	107.4 (7)
P1–Fe1–C12	165.6 (4)	Fe1–C14–N3	139.2 (8)
P1–Fe1–C13	95.4 (4)	O1–C14–N3	112.8 (9)
P1–Fe1–C14	67.7 (3)	P3–Fe2–C21	88.6 (3)
P2–Fe1–C11	87.7 (5)	P3–Fe2–C22	164.0 (4)
P2–Fe1–C12	90.6 (4)	P3–Fe2–C23	98.0 (4)
P2–Fe1–C13	173.7 (5)	P3–Fe2–C24	82.6 (4)
P2–Fe1–C14	91.4 (3)	C21–Fe2–C22	88.1 (5)
C11–Fe1–C12	98.0 (6)	C21–Fe2–C23	112.8 (5)
C11–Fe1–C13	90.4 (6)	C21–Fe2–C24	136.0 (6)
C11–Fe1–C14	158.6 (5)	C22–Fe2–C23	97.8 (6)
C12–Fe1–C13	95.6 (6)	C22–Fe2–C24	88.9 (6)
C12–Fe1–C14	103.4 (5)	C23–Fe2–C24	111.1 (6)
C13–Fe1–C14	88.1 (5)	Fe2–C21–O21	176. (1)
Fe1–P1–Fe3	133.4 (1)	Fe2–C22–O22	177. (1)
Fe1–P1–P3	96.4 (1)	Fe2–C23–O23	178. (1)
Fe1–P1–O1	83.4 (2)	Fe2–C24–O24	180. (3)
Fe3–P1–P3	118.9 (2)	P1–Fe3–C31	92.0 (5)
Fe3–P1–O1	107.0 (3)	P1–Fe3–C32	178.5 (7)
P3–P1–O1	112.5 (3)	P1–Fe3–C33	88.4 (7)
Fe1–P2–P3	94.4 (1)	P1–Fe3–C34	87.1 (6)
Fe1–P2–N21	113.6 (4)	C31–Fe3–C32	89.1 (7)
Fe1–P2–N22	122.4 (4)	C31–Fe3–C33	117.1 (8)
P3–P2–N21	108.2 (4)	C31–Fe3–C34	119.5 (7)
P3–P2–N22	112.2 (3)	C32–Fe3–C33	92.1 (9)
N21–P2–N22	105.3 (5)	C32–Fe3–C34	91.5 (8)
P1–P3–P2	85.5 (2)	C33–Fe3–C34	123.4 (8)
P1–P3–Fe2	124.2 (2)	Fe3–C31–O31	173. (1)
Fe2–P3–P2	129.9 (2)	Fe3–C32–O32	173. (2)
P1–O1–C11	101.4 (6)	Fe3–C33–O33	178. (2)
Fe1–C11–O11	175. (1)	Fe3–C34–O34	178. (1)
Fe1–C12–O12	179. (1)		

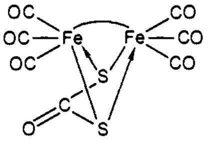
$(CO)_6$ in the preliminary communication in 1985,[4a] such a phosphorus-bridging carbonyl group was unprecedented in a metal carbonyl complex. However, in 1986 two examples of complexes closely related to (i-$Pr_2NP)_2COFe_2(CO)_6$ (V: R = i-Pr) appeared in the literature, namely (t-$BuP)_2COFe_2(CO)_6$ (VII)[21] and



VII



VIII



IX

$[Me_5C_5Fe(CO)_2PCOPC_6H_2$-$t$-$Bu_3$-2,4,6$]Fe_2(CO)_6$ (VIII).[22] In

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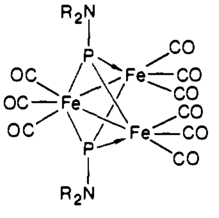
(21) De, R. L.; Walters, D.; Vahrenkamp, H. *Z. Naturforsch. B Anorg. Chem., Org. Chem.* **1986**, *41b*, 283.

Table X. Selected Bond Distances (Å) and Angles (deg) for $(Et_2NP)_3Fe_3(CO)_{11}$

	molecule A	molecule B
	Distances	
Fe1–Fe3	2.726 (9)	2.739 (19)
Fe1–P1	2.235 (12)	2.202 (14)
Fe1–P2	2.253 (11)	2.255 (13)
Fe2–P3	2.239 (13)	2.226 (16)
Fe3–P1	2.178 (13)	2.179 (13)
Fe3–P3	2.325 (12)	2.304 (14)
P1–P3	2.15 (1)	2.16 (2)
P2–P3	2.20 (2)	2.21 (2)
P2–P1	2.82 (1)	2.84 (2)
P2–N21	1.64 (4)	1.65 (4)
P2–N22	1.62 (3)	1.63 (3)
P1–C73	1.95 (5)	1.85 (4)
Fe1–C11	1.71 (4)	1.83 (6)
Fe1–C12	1.77 (4)	1.66 (5)
Fe1–C13	1.78 (4)	1.74 (4)
Fe2–C21	1.84 (4)	1.68 (4)
Fe2–C22	1.73 (4)	1.86 (5)
Fe2–C23	1.77 (5)	1.56 (7)
Fe2–C24	1.71 (6)	1.56 (5)
Fe3–C31	1.70 (5)	1.78 (4)
Fe3–C32	1.78 (5)	1.79 (4)
Fe3–C33	1.78 (5)	1.68 (6)
C11–O11	1.19 (5)	1.11 (7)
C12–O12	1.19 (5)	1.24 (6)
C13–O13	1.13 (6)	1.15 (6)
C21–O21	1.07 (5)	1.25 (5)
C22–O22	1.17 (5)	1.08 (6)
C23–O23	1.10 (6)	1.24 (9)
C24–O24	1.15 (7)	1.24 (6)
C31–O31	1.22 (6)	1.16 (5)
C32–O32	1.14 (7)	1.16 (6)
C33–O33	1.16 (6)	1.20 (7)
C73–O73	1.16 (6)	1.17 (5)
	Angles	
P1–Fe1–P2	78.0 (4)	79.2 (5)
P1–P3–P2	81.0 (5)	81.0 (6)
Fe1–P1–P3	94.7 (5)	95.3 (5)
Fe1–P2–P3	92.8 (5)	92.3 (5)
P1–Fe3–P3	56.9 (4)	57.6 (4)
Fe3–P1–P3	65.0 (4)	64.1 (5)
Fe3–P3–P1	58.1 (4)	58.3 (4)
Fe1–P1–Fe3	77.3 (4)	77.4 (4)
P2–P3–Fe3	94.0 (5)	93.5 (6)
P2–P3–Fe2	133.4 (6)	133.1 (6)
P1–P3–Fe2	133.7 (6)	136.3 (6)
Fe3–P3–Fe2	129.0 (6)	127.8 (6)
Fe1–P1–C73	141.9 (18)	141.7 (15)
P3–P1–C73	113.2 (15)	113.6 (15)
Fe3–P1–C73	138.3 (18)	137.1 (15)
Fe1–P2–N21	116.1 (11)	115.6 (14)
Fe1–P2–N22	123.1 (12)	115.3 (12)
P3–P2–N21	112.7 (14)	113.3 (14)
P3–P2–N22	109.3 (14)	109.7 (15)
N21–P2–N22	102.6 (16)	109.2 (17)

addition, the closely related complex $S_2COFe_2(CO)_6$ (IX) is known[23] in which the unique carbonyl group bridges a pair of sulfur atoms. The structural and spectroscopic parameters associated with the phosphorus-bridging carbonyl group in the three complexes V (R = isopropyl), VII, and VIII, despite the radically different external substituents on phosphorus, are remarkably similar including acute P–C–P angles, bonding Fe–Fe distances around 2.60 Å, and acyl ν(C=O) frequencies around 1700 cm^{-1} (Table XI). However, the complex $S_2COFe_2(CO)_6$ (IX)[23] with a sulfur-bridging carbonyl group has an obtuse S–C–S angle (99.6 (4)°), a significantly shorter bonding Fe–Fe distance of 2.488 (1) Å, and a significantly higher acyl ν(C=O) frequency at 1775 cm^{-1} (Table XI).

Two minor products were detected in the ^{31}P NMR spectrum of the mixture obtained from the reaction of i-Pr_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether. A singlet resonance at δ 398.6 is assigned to the trinuclear derivative $(i\text{-}Pr_2NP)_2Fe_3(CO)_9$ (X: R = i-Pr), which has been isolated in the pure state from the reaction of i-Pr_2NPCl_2 with $Na_2Fe(CO)_4$ in tetrahydrofuran (see below). The second minor product exhibits an AX pattern with resonances at δ 97.3 and 61.7 and $|^1J(P\text{–}P)|$ = 477 Hz. This product is formulated as the diphosphene derivative $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ (XI: R = i-Pr) by comparison of its ^{31}P NMR parameters with those of known[9,13] $R_2P_2[Fe(CO)_4]_2$ derivatives with structures III (R = 2,4,6-t-$Bu_3C_6H_2O$, Ph; see Table XII). Attempts to isolate $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ by chromatography on silica gel lead to decomposition to give a more stable product characterized by a single ^{31}P resonance at δ 120.7 with a $|^1J(P\text{–}H)|$ of 433 Hz determined by turning off the proton decoupling. With considerable difficulty, this product was isolated in minute quantities by repeated chromatography and fractional crystallization. An X-ray diffraction study of this product (Table VI; Figure 2) indicates formulation as $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ (XII: R = i-Pr) obtained from addition of H_2O to $(i\text{-}Pr_2N)_2P_2[Fe(CO)_4]_2$ (XI: R = i-Pr) through insertion of oxygen into the phosphorus–phosphorus bond with concurrent formation of two P–H bonds.



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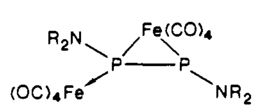
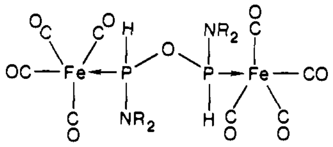
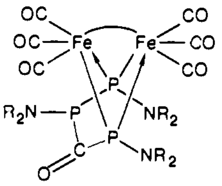


XI



XII



XIII

The product $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ (XII) is a dimer of two i-$Pr_2NPHFe(CO)_4$ units oxo bridged at the phosphorus atoms (P1–O1–P2 = 136.4 (3)°). Each phosphorus atom is tetrahedrally coordinated to an i-Pr_2N group, the bridging oxo groups, an $Fe(CO)_4$ group, and a hydrogen atom (average angle at phosphorus not involving hydrogen is 113.8 (2)°). The positions of the hydrogen atoms were clearly evident from a difference Fourier synthesis. Coordination about the plane of the P1–O1–P2 linkage places the $Fe(CO)_4$ groups on opposite sides of the plane (Figure 2) so that the two iron atoms are widely separated from each other. Each iron atom displays distorted trigonal-bipyramidal geometry with the coordinated phosphorus atom trans to a carbonyl group (P1–Fe1–C13 = 177.3 (3)°; P2–Fe2–C21 = 176.1 (4)°) and the axially coordinated atoms roughly perpendicular to the other three carbonyl groups, which display angles of approximately 120° to each other. The infrared spectrum of $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ (XII) in the ν(CO) region (Table I) exhibits the characteristic pattern of two A_1 frequencies and one E frequency for an axially substituted $LFe(CO)_4$ derivative.[24] The proton NMR spectrum of $[i\text{-}Pr_2NPHFe(CO)_4]_2O$, besides exhibiting the characteristic CH_3 and CH resonances for an isopropyl group, also exhibits a widely separated P–H doublet, with the 433-Hz separation corresponding to the $|^1J(P\text{–}H)|$ found in the ^{31}P NMR spectrum.

(B) Reactions of Sterically Hindered R_2NPCl_2 Derivatives with $Na_2Fe(CO)_4$ in Tetrahydrofuran. Synthesis of $(R_2NP)_3Fe_2(CO)_6$

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[22] Weber, L.; Reizig, K.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 755.

[23] Nametkin, N. S.; Kolobkov, B. I.; Tyurin, V. D.; Muratov, A. N.; Nekhaev, A. I.; Mavlonov, M.; Sideridu, A. Ya.; Aleksandrov, G. G.; Lebedev, A. V.; Tashev, M. T.; Dustov, H. B. *J. Organomet. Chem.* **1984**, *276*, 393.

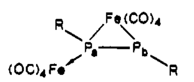
[24] Darensbourg, D. J.; Nelson, H. H., III; Hyde, C. L. *Inorg. Chem.* **1974**, *13*, 2135.

Table XI. Comparison of Some Structural and Spectroscopic Parameters Associated with the Bridging Carbonyl Groups in $E_2COFe_2(CO)_6$ Derivatives (E = S or RP)[a]

	structural parameters					acyl	^{13}C NMR of
	Fe–Fe	av Fe–E	av E–C	C–O	E–C–E	ν(C=O)	acyl CO[b]
$(i\text{-}Pr_2NP)_2COFe_2(CO)_6$[c]	2.603 (2)	2.224	1.890	1.185 (12)	84.4 (4)	1720	209.2 t (83)
$(t\text{-}BuP)_2COFe_2(CO)_6$[d]	2.623 (2)	2.230	1.877	1.172 (9)	84.6 (6)	1702	*g*
$[Me_5C_5Fe(CO)_2PCOPC_6H_2t\text{-}Bu_3]Fe_2(CO)_6$[e]	2.568 (1)	2.275	1.870	1.187 (7)	88.3 (2)	1692	209.8 dd (81, 60)
$S_2COFe_2(CO)_6$[f]	2.488 (1)	2.269	1.812	1.17 (1)	99.6 (4)	1775	*g*

[a] Distances are in angstroms, angles are in degrees, ν(C=O) frequencies are in reciprocal centimeters, and ^{13}C chemical shifts are in δ. [b] t = triplet, dd = double doublet; coupling constants in hertz are given in parentheses. [c] This work. [d] Data from ref 21. [e] Data from ref 22. [f] Data from ref 23. [g] Not reported.

Table XII. ^{31}P NMR Spectra of Unsymmetrical Diphosphene Bis(iron tetracarbonyl) Derivatives



	δ ^{31}P (AX pattern)		
R	P_a	P_b	$\lvert ^1J(P_a–P_b)\rvert$, Hz
$2,4,6\text{-}t\text{-}Bu_3C_6H_2O$[a]	233.7	193.4	532
Ph[b]	52.1	−34.5	415
$i\text{-}Pr_2N$	97.3	61.7	477
Cx_2N	99.8	63.2	488

[a] Data from ref 11. [b] Data from ref 13.

Derivatives. The course of the reaction of sterically hindered R_2NPCl_2 derivatives (R_2N = $i\text{-}Pr_2N$, Cx_2N) with $Na_2Fe(CO)_4\cdot 1.5$dioxane changes drastically if the solvent is changed from diethyl ether to tetrahydrofuran. The greater solubility of $Na_2Fe(CO)_4$ in tetrahydrofuran leads to an immediate reaction upon adding $i\text{-}Pr_2NPCl_2$ at −78 °C whereas no apparent reaction occurs in diethyl ether until the reaction mixture is warmed to about −40 °C. The major products from the reactions of such sterically hindered R_2NPCl_2 derivatives with $Na_2Fe(CO)_4$ in tetrahydrofuran are not the corresponding $(R_2NP)_2COFe_2(CO)_6$ derivatives (V) but instead are the corresponding triphosphine complexes $(R_2NP)_3Fe_2(CO)_6$ obtained in ~35% isolated yields by simple crystallization from the crude reaction mixture. The structure of the diisopropylamino derivative $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ has been determined by X-ray diffraction (Table VII; Figure 3) to be VI (R = *i*-Pr). This structure, like that of $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (V: R = *i*-Pr), consists of a typical $Fe_2(CO)_6$ unit bridged by two phosphido phosphorus atoms similar to the many known $(R_2P)_2Fe_2(CO)_6$ derivatives.[20] The two phosphido groups bridging the Fe–Fe bond (2.602 (2) Å) in $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (VI: R = *i*-Pr) are themselves bridged by a third phosphorus atom (P3 in Figure 3) in the form of an $i\text{-}Pr_2NP$ group leading to the triphosphine chain: P1–P3 = 2.278(2), P3–P2 = 2.243 (2) Å; P1–P3–P2 = 68.29 (7)°. The four bonding P–P–Fe angles are 104.32 (7), 105.46 (8), 93.54 (7), and 94.42 (7)°, indicating that the center phosphorus atom P3 deviates about 5.5° from the position for $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ to have ideal C_{2v} symmetry. In other words the P1–P2–P3 plane does not bisect the Fe1–Fe2 bond.

The most interesting structural feature of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (VI: R = *i*-Pr) is the acute P1–P3–P2 angle (68.19 (7)°), whith deviates drastically from the 109.47° tetrahedral angle of an sp^3-hybridized phosphorus atom. This compressed angle suggests an attractive interaction between P1 and P2, leading to a nonbonded P1⋯P2 distance of 2.534 Å, which is only about 0.26 Å longer than the average P–P bonding distances (P1–P3 and P2–P3) in $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$. This suggests the formal derivation of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (VI: R = *i*-Pr) from the cyclotriphosphine $(i\text{-}Pr_2N)_3P_3$ by coordination of an $Fe_2(CO)_6$ fragment to one of the phosphorus–phosphorus bonds, leading to an elongation of this phosphorus–phosphorus bond similar to elongations of carbon–carbon bonds observed upon olefin and acetylene coordination to metal atoms.

The most interesting spectroscopic property of the $(R_2NP)_3Fe_2(CO)_6$ complexes (VI) is the large downfield chemical shift of the central phosphorus atom below δ 290. To our knowledge, this represents the most downfield ^{31}P chemical shift ever observed except for multiply bonded phosphorus atoms in species such as phosphinidenes, diphosphenes, or phosphenium cations[25–27] and undoubtedly is related to the unusual bond angles at this central phosphorus atom as noted above. A similar, although smaller, downfield chemical shift (δ 226.1) is reported[28] for the central phosphorus atom in the related triphosphine complex $(PhP)_3Fe_2(CO)_6$. Other important spectroscopic properties of the $(R_2NP)_3Fe_2(CO)_6$ derivatives (VI) include the observation of five terminal ν(CO) frequencies (Table I) similar to those found in $(R_2NP)_2COFe_2(CO)_6$ (V) and the indication in the ^{1}H and ^{13}C NMR spectra of two different types of alkyl groups in a 2:1 ratio in the $(R_2NP)_3Fe_2(CO)_6$ derivatives in contrast to the single type of alkyl group in the $(R_2NP)_2COFe_2(CO)_6$ derivatives (Table II).

Three minor products are also formed in the reaction of R_2NPCl_2 (R = *i*-Pr and Cx) with $Na_2Fe(CO)_4$ in tetrahydrofuran solution. These include the $(R_2NP)_2COFe_2(CO)_6$ (V) derivatives formed as the major products from the corresponding reactions in diethyl ether solution as well as the trinuclear products $(R_2NP)_2Fe_3(CO)_9$ (X) and a second type of derivative, namely $(R_2NP)_3COFe_2CO)_6$ (XIII), shown by X-ray crystallography to have a phosphorus-bridging carbonyl group. These four products can be separated by repeated chromatography and fractional crystallization after first removing the major amounts of $(R_2NP)_3Fe_2(CO)_6$ (VI) by an initial crystallization. However, complete separation of $(R_2NP)_2COFe_2(CO)_6$ (V) and $(R_2NP)_3COFe_2(CO)_6$ (XIII) requires mechanical sorting of the crystals since these two types of compounds have almost identical hexane solubilities and mobilities on the chromatography column.

The trinuclear products $(R_2NP)_2Fe_3(CO)_9$ (X: R = *i*-Pr and Cx) appear to be analogous to known $(\mu_3\text{-}RP)_2Fe_3(CO)_9$ derivatives having structures with two iron–iron bonds.[28,30–33,43] Their ^{31}P NMR spectra exhibit the characteristically deshielded resonances around δ 400 for complexes of this type.

The diisopropylamino derivative of the type $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ was shown by X-ray diffraction (Table VIII; Figure 4) to have structure XIII (R = *i*-Pr) in which a carbonyl group has inserted into a triphosphine chain: P2–P3 = 2.233 (5), P3–C61 = 1.868 (12), C61–P1 = 1.835 (11) Å; P2–P3–C61 = 89.9 (4), P3–C61–P1 = 117.8 (7)°. The P1⋯P2 distance is 2.804 Å, indicating very little interaction between P1 and P2. The P–C–P angle of 117.8° at the phosphorus-bridging carbonyl group in $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ contrasts with the P–C–P angle of 84.4° at the phosphorus-bridging carbonyl group in (*i*-

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(25) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979.

(26) Crutchfield, M. M.; Dungan, C. H.; Letcher, J. H.; Mark, V.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5*.

(27) Thomas, M. G.; Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1977**, *16*, 994.

(28) Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *J. Organomet. Chem.* **1981**, *222*, 263.

(29) Halford, J. O. *J. Chem. Phys.* **1956**, *24*, 830.

(30) Treichel, P. M.; Dean, W. K.; Douglas, W. M. *Inorg. Chem.* **1972**, *11*, 1609.

(31) Cook, S. L.; Evans, J.; Gray, L. R.; Webster, M. *J. Organomet. Chem.* **1982**, *236*, 367.

(32) Kouba, J. K.; Muetterties, E. L.; Thompson, M. R.; Day, V. W. *Organometallics* **1983**, *2*, 1065.

(33) Vahrenkamp, H.; Wucherer, E. J.; Wolters, D. *Chem. Ber.* **1983**, *116*, 1219.

$Pr_2NP)_2COFe_2(CO)_6$, thereby accounting for the significantly different phosphorus-bridging ν(CO) frequencies in (i-$Pr_2NP)_3COFe_2(CO)_6$ (1645 cm^{-1}) and (i-$Pr_2NP)_2COFe_2(CO)_6$ (1720 cm^{-1}). A similar effect of bond angle at the carbonyl carbon on the ν(CO) frequency has long been known for cycloalkanones.[29] Also, the 1645-cm^{-1} phosphorus-bridging ν(CO) frequency in (i-$Pr_2NP)_3COFe_2(CO)_6$ is much weaker than the 1720-cm^{-1} phosphorus-bridging ν(CO) frequency in (i-$Pr_2NP)_2COFe_2(CO)_6$. The effective symmetry of the $(R_2NP)_3COFe_2(CO)_6$ derivatives is only C_s rather than C_{2v}, leading to six distinct terminal ν(CO) frequencies in the 2060–1960-cm^{-1} region (Table I) rather than the five terminal ν(CO) frequencies observed for the $(R_2NP)_2COFe_2(CO)_6$ and $(R_2NP)_3Fe_2(CO)_6$ derivatives. The lower symmetry of (i-$Pr_2NP)_3COFe_2(CO)_6$ (XIII: R = i-Pr) is also indicated by the observation of three different types of phosphorus atoms in the ^{31}P NMR spectrum (Table I) and three different types of isopropyl groups in the ^{13}C NMR spectrum (Table II). The center phosphorus atoms (i.e., those not bonded to an iron atom) in the $(R_2NP)_3COFe_2(CO)_6$ derivatives (XIII) appear at relatively high field positions (δ 4–1) in the ^{31}P NMR spectra (Table I) in contrast to the center phosphorus atoms in the $(R_2NP)_3Fe_2(CO)_6$ derivatives (VI), which appear at unusually low field positions as noted above. The proton-decoupled ^{13}C NMR spectrum (Table II) of the phosphorus-bridging carbonyl group in $(Cx_2NP)_3COFe_2(CO)_6$ (XIII: R = Cx) exhibits a doublet of doublets of doublets centered at δ 245.6 corresponding to three different P–C coupling constants of 78, 73, and 42 Hz. The corresponding resonance in (i-$Pr_2NP)_3COFe_2(CO)_6$ (XIII: R = i-Pr) appears at δ 244.3 as a doublet of triplets in a 1:1:2:2:1:1 ratio since two of the three P–C coupling constants are too close to be resolved (73 Hz for two, 42 Hz for the third).

(C) Solvent and Temperature Effects on the Distribution of Products in the Reaction of i-Pr_2NPCl_2 with $Na_2Fe(CO)_4$ (Table III). The drastic change in the product distribution from the reaction of i-Pr_2NPCl_2 with $Na_2Fe(CO)_4$ when tetrahydrofuran rather than diethyl ether is used as the solvent suggested a more detailed study of solvent and temperature effects on this reaction. The results of our experiments in this area are summarized in Table III.

The following solvent effects were observed:

(1) Diethyl Ether. The greatly favored product is (i-$Pr_2NP)_2COFe_2(CO)_6$ (V: R = i-Pr) corresponding to about 90% of the isolable recognized products. The complexes (i-$Pr_2NP)_2Fe_3(CO)_9$ (X: R = i-Pr) and (i-$Pr_2N)_2P_2[Fe(CO)_4]_2$ (XI: R = i-Pr) are observed as minor products. Since no reaction was observed below −40 °C, temperature effects were not found to be significant. The complex (i-$Pr_2N)_2P_2[Fe(CO)_4]_2$ (XI: R = i-Pr) appears to be slightly favored in reactions in lower temperatures. No evidence was found for the formation of the triphosphine complex (i-$Pr_2NP)_3Fe_2(CO)_6$ (VI: R = i-Pr) in diethyl ether solution.

(2) Tetrahydrofuran. Tetrahydrofuran provides a wider range for studies of temperature effects since reactions occur even at −78 °C. The compounds (i-$Pr_2NP)_2COFe_2(CO)_6$ (V: R = i-Pr), [i-$Pr_2NPHFe(CO)_4]_2O$ (XII: R = i-Pr), and (i-$Pr_2NP)_3Fe_2(CO)_6$ (VI: R = i-Pr) can be obtained as major products depending upon the reaction temperature as depicted in Table III. No evidence for the formation of (i-$Pr_2NP)_2COFe_2(CO)_6$ (V: R = i-Pr), (i-$Pr_2NP)_2Fe_3(CO)_9$ (X: R = i-Pr), (i-$Pr_2NP)_3Fe_2(CO)_6$ (VI: R = i-Pr), or (i-$Pr_2NP)_3COFe_2(CO)_6$ (XIII: R = i-Pr) was found when the reaction temperature was kept below −40 °C.

(3) Hexane. One of the products is now (i-$Pr_2N)_2P_2[Fe(CO)_4]_2$ (XI: R = i-Pr).

(4) Diethyl Ether/18-Crown-6. Addition of 30% of a stoichiometric amount of 18-crown-6 to a diethyl ether solution gives essentially the same product distribution as in tetrahydrofuran (Table III). This suggests that the solubility of $Na_2Fe(CO)_4$ in the ether solvent is the critical factor in determining the observed product differences from reaction between i-Pr_2NPCl_2 and $Na_2Fe(CO)_4$ carried out in diethyl ether and in tetrahydrofuran since the addition of the 18-crown-6 to diethyl ether greatly increases the solubility of $Na_2Fe(CO)_4$.

(5) Tetrahydrofuran/18-Crown-6. Complexes (i-$Pr_2NP)_2Fe_3(CO)_9$ (X: R = i-Pr) and (i-$Pr_2NP)_3Fe_2(CO)_6$ (VI: R = i-Pr) are both major products produced in approximately equal quantities. This suggests that the formation of (i-$Pr_2NP)_2Fe_3(CO)_9$ (X: R = i-Pr) is directly related to the solubility of $Na_2Fe(CO)_4$. The formation of (i-$Pr_2NP)_2COFe_2(CO)_6$ (V: R = i-Pr) is significantly suppressed, and (i-$Pr_2NP)_3COFe_2(CO)_6$ (XIII: R = i-Pr) is not produced at all. With use of this solvent mixture, the overall yield of various products is reduced significantly, owing to the vigorous reaction conditions. Also the separation of 18-crown-6 from the products can present difficulties.

The formation of the various iron carbonyl derivatives in different solvents at different temperatures can be summarized as follows:

(1) (i-$Pr_2NP)_2COFe_2(CO)_6$ (V: R = i-Pr). This complex is produced under all conditions except when the reaction temperature is kept lower than −40 °C. However, its formation is highly favored in diethyl ether and heavily suppressed in tetrahydrofuran/18-crown-6.

(2) (i-$Pr_2NP)_2Fe_3(CO)_9$ (X: R = i-Pr). This complex is favored in tetrahydrofuran/18-crown-6 and is not formed in hexane solution.

(3) (i-$Pr_2N)_2P_2[Fe(CO)_4]_2$ (XI: R = i-Pr). This complex appears to be the initially formed detectable product. It is thus favored under milder reaction conditions such as in hexane and at lower temperatures. Attempted purification of (i-$Pr_2N)_2P_2[Fe(CO)_4]_2$ by chromatography on silica gel leads to addition of water to form [i-$Pr_2NPHFe(CO)_4]_2O$ (XII: R = i-Pr).

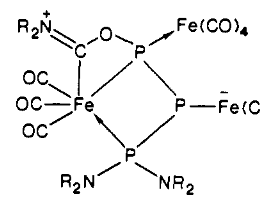
(4) (i-$Pr_2NP)_3Fe_2(CO)_6$ (VI: R = i-Pr). Use of tetrahydrofuran or addition of 18-crown-6 to diethyl ether appears to be essential for the introduction of the third i-Pr_2NP fragment to form this complex.

(5) (i-$Pr_2NP)_3COFe_2(CO)_6$ (XIII: R = i-Pr). This complex is produced only when tetrahydrofuran is used as the solvent. We were unable to find any reaction conditions, even when using a carbon monoxide rather than a nitrogen atmosphere, where this complex was a favored product or even obtained in sufficient quantities for a detailed study of its chemistry.

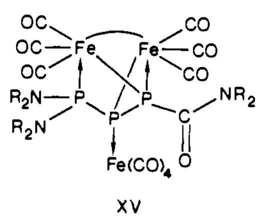
(6) [i-$Pr_2NPHFe(CO)_4]_2O$ (XII: R = i-Pr). This complex is produced either from the hydrolysis of (i-$Pr_2N)_2P_2[Fe(CO)_4]_2$ (XI: R = i-Pr) upon chromatography or from the reaction of i-Pr_2NPCl_2 with $Na_2Fe(CO)_4$ in tetrahydrofuran when the reaction temperature is kept lower than −40 °C. The latter source of [i-$Pr_2NPHFe(CO)_4]_2O$ obviously involves reaction with small quantities of adventitious water.

(D) Reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$. Diethylamino Migration Reactions. The reactions of R_2NPCl_2 derivatives with $Na_2Fe(CO)_4$ discussed in the previous sections require relatively large R_2N groups such as diisopropylamino, dicyclohexylamino, or 2,2,6,6-tetramethylpiperidino in order to obtain products such as the complexes $(R_2NP)_2COFe_2(CO)_6$ (V) and $(R_2NP)_3Fe_2(CO)_6$ (VI). Reactions of the less sterically hindered Et_2NPCl_2 with $Na_2Fe(CO)_4$ give totally different types of products shown by X-ray crystallography to have structures containing $(Et_2N)_2P$ and Et_2NCO units arising from migration of a diethylamino group from phosphorus to another phosphorus and to a carbonyl carbon, respectively.

The initial isolable product obtained from the reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether solution forms deep orange crystals of the stoichiometry $(Et_2NP)_3Fe_3(CO)_{12}$ and is isolated as a major product in 37% yield by keeping the temperature of the reaction mixture at 0 °C. An X-ray diffraction study on this complex (Table IX; Figure 5) indicates structure XIV (R = Et). This structure contains a bent triphosphine unit (P1–P3 = 2.122 (4), P2–P3 = 2.183 (4) Å; P1–P3–P2 = 85.5 (2)°) with two diethylamino groups bonded to one of the terminal phosphorus atoms and $Fe(CO)_4$ units coordinated both to the center (Fe2–Pe = 2.270 (3) Å) and other terminal (Fe3–P1 = 2.223 (4) Å) phosphorus atoms. In addition, an $Fe(CO)_3$ unit bridges the terminal phosphorus atoms to form a four-membered FeP_3 ring (Fe1–P1 = 2.302 (3), Fe1–P2 = 2.312 (4) Å; P2–Fe1–P1 = 78.6 (1), Fe1–P1–P3 = 96.4 (1), Fe1–P2–P3 = 94.7



XIV



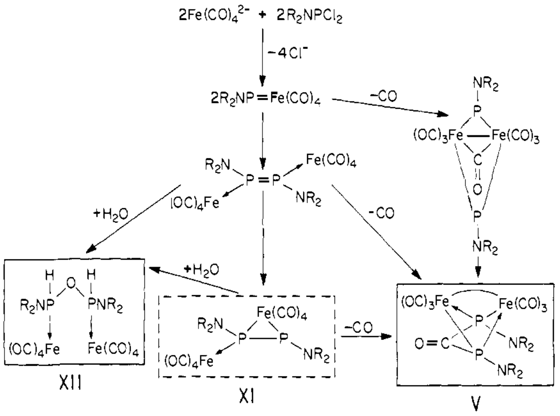
XV

(1)°). Most unusual, however, is the bridging of a diethylcarbamoyl group across the Fe1–P1 bond to form a four-membered FePOC ring (Fe1–C14 = 2.000 (1), C14–O1 = 1.35 (1), P1–O1 = 1.748 (7) Å; P1–Fe1–C14 = 67.7 (3), Fe1–C14–O1 = 107.4 (7), P1–O1–C14 = 101.4 (6), Fe1–P1–O1 = 83.4 (2)°). The short C14–N3 bond length of 1.30 (1) Å suggests C=N double-bond character and the bond orders indicated in structure XIV. All iron and phosphorus atoms in XIV have the rare gas electronic configurations. The three-coordinate phosphorus atom P3 has a pyramidal configuration (P1–P3–Fe2 = 124.2 (2), Fe2–P3–P2 = 129.2 (2)°) and an uncoordinated lone pair. There are no iron–iron bonds in this structure.

The complex $(Et_2NP)_3Fe_3(CO)_{12}$ (XIV: R = Et) is stable in the solid state. However, solutions of this complex in organic solvents such as $CDCl_3$, C_6D_6, CH_2Cl_2, or Et_2O undergo a major change over a period of hours at room temperature to form a second complex XV (R = Et) as indicated by following the ^{31}P NMR spectra of such solutions. The complex XV (R = Et) is an orange solid of stoichiometry $(Et_2NP)_3Fe_3(CO)_{11}$, which can be isolated in 35% yield from the original reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether if the reaction mixture is stirred at 25 °C rather than 0 °C for 24 h before product isolation by a procedure similar to that for $(Et_2NP)_3Fe_3(CO)_{12}$ (XIV: R = Et). An X-ray diffraction study on this complex (Table X; Figure 6) indicates structure XV (R = Et), thereby revealing that the facile conversion of XIV to XV involves conversion of the bridging diethylcarbamoyl group to a terminal diethylcarbamoyl group, formation of an iron–iron bond (Fe1–Fe3 = 2.733 (19) Å), and formation of a new iron–phosphorus bond (Fe3–P3 = 2.315 (14) Å) by displacement of a carbonyl group on Fe3 by the lone pair on P3 in XIV. The terminal diethylcarbamoyl group in $(Et_2NP)_3Fe_3(CO)_{11}$ (XV: R = Et) exhibits a weak infrared ν(CO) frequency at 1648 cm^{-1} and a ^{13}C NMR resonance at δ 165.3. The complex $(Et_2NP)_3Fe_3(CO)_{11}$ (XV: R = Et) is stable in the solid state but unstable in solution, decomposing into intractable materials.

The ^{31}P NMR spectrum of the original mixture from the reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether indicates the presence of two minor products. One of these minor products exhibits a resonance at δ 401.2 and thus is formulated as $(Et_2NP)_2Fe_3(CO)_9$ (X: R = Et). The second minor product exhibits a resonance at δ 124.7 with $|^1J(P\text{-}H)| = 418$ Hz corresponding to $[Et_2NPHFe(CO)_4]_2O$ (XII: R = Et). The observation of these minor products suggests that the initial course of the reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ is very similar to that of i-Pr_2NPCl_2 with $Na_2Fe(CO)_4$ discussed above. However, the subsequent course of the reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether to give $(Et_2NP)_3Fe_3(CO)_{12}$ (XIV: R = Et) and then $(Et_2NP)_3Fe_3(CO)_{11}$ (XV: R = Et) is very different from the corresponding reaction of i-Pr_2NPCl_2 with $Na_2Fe(CO)_4$, owing to the facile migration of diethylamino groups in contrast to the much more bulky diisopropylamino groups, which are unable to migrate. Reactions of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in tetrahydrofuran or of Me_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether appears to lead to even more extensive dialkylamino migration as suggested by the presence of at least three different AMX patterns in the ^{31}P NMR spectra of the reaction mixtures, indicating different types of P_3Fe_3 complexes.

Scheme I



Discussion

The products obtained from reactions of $Na_2Fe(CO)_4$ with R_2NPCl_2 derivatives can be rationalized by invoking the terminal phosphinidene complexes $R_2NP{=}Fe(CO)_4$ as a reactive intermediate initially formed by the nucleophilic substitution reaction in eq 1. The terminal (dialkylamino)phosphinidene ligand in this

$$R_2NPCl_2 + Fe(CO)_4{}^{2-} \rightarrow R_2NP{=}Fe(CO)_4 + 2Cl^- \quad (1)$$

intermediate may be regarded as a two-electron donor ligand analogous to a carbonyl group but with even stronger π-acceptor properties and bridging tendencies. Evidence supporting the possible intermediacy of $R_2NP{=}Fe(CO)_4$ in the reactions of $Na_2Fe(CO)_4$ with R_2NPCl_2 derivatives includes the following:

(1) The compound $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (V: R = i-Pr) forms by the reaction of i-$Pr_2NP(H)ClFe(CO)_4$ with triethylamine.[34] A likely intermediate in this reaction is also i-$Pr_2NP{=}Fe(CO)_4$ formed by dehydrochlorination of i-$Pr_2NP(H)ClFe(CO)_4$ in the reaction shown in eq 2.

$$i\text{-}Pr_2NP(H)ClFe(CO)_4 + Et_3N \rightarrow i\text{-}Pr_2NP{=}Fe(CO)_4 + (Et_3NH)Cl \quad (2)$$

(2) Extensive evidence exists for the formation of the related terminal phosphinidene complexes $RP{=}M(CO)_5$ (M = Cr, R = Ph; M = W, R = Ph, Me)[35-37] through trapping experiments and $[i\text{-}Pr_2NP{=}Fe(CO)_2C_5Me_5]^+$[38] through observation of a very low field ^{31}P resonance at δ 954. In the absence of excess $Fe(CO)_4{}^{2-}$ and under conditions where dialkylamino migration does not take place, further reaction of $R_2NP{=}Fe(CO)_4$ occurs through dimerization, either through phosphorus–phosphorus double-bond formation to form the diphosphene $[R_2NP{=}PNR_2][Fe(CO)_4]_2$ (XI) or through decarbonylation and iron–iron bond formation to form $(R_2NP)_2COFe_2(CO)_6$ (V) (see Scheme I). The work of Weber, Reizig, and Boese[22] also suggests the direct decarbonylation of $[R_2NP{=}PNR_2][Fe(CO)_4]_2$ (XI) to $(R_2NP)_2COFe_2(CO)_6$ (V) with the necessary bond reorganization. The diphosphene complex $(R_2N)_2P_2[Fe(CO)_4]_2$ can then add water with rupture of the phosphorus–phosphorus bond to form the oxo-bridged derivative $[R_2NPHFe(CO)_4]_2O$ (XII). All of the species in Scheme I have P/Fe ratios of 1 and account for all of the major products observed in reactions of R_2NPCl_2 (R = i-Pr or Cx or R_2N = 2,2,6,6-tetramethylpiperidino) with $Na_2Fe(CO)_4$ in diethyl ether in which $Na_2Fe(CO)_4$ is very sparingly soluble and thus does not provide a source of excess $Fe(CO)_4{}^{2-}$. The reactions of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in diethyl ether also give major products with P/Fe ratios of 1, namely $(Et_2NP)_3Fe_3(CO)_{12}$ (XIV: R = Et) and $(Et_2NP)_3Fe_3(CO)_{11}$ (XV: R = Et). In this case, however, the possibility for dialkylamino migration triggers a different and more complicated reaction pathway for the $R_2NP{=}Fe(CO)_4$ intermediate, leading ultimately to trimerization to give the observed $(Et_2NP)_3Fe_3(CO)_{12}$ (XIV: R = Et). A possible route for the formation of $(Et_2NP)_3Fe_3(CO)_{12}$ (XIV: R = Et) by the trimerization of $Et_2NP{=}Fe(CO)_4$ is depicted in Scheme II (R = Et). In this

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(34) King, R. B.; Fu, W.-K. *Inorg. Chem.* **1986**, *25*, 2384.

(35) Marinetti, A.; Mathey, F. *J. Am. Chem. Soc.* **1982**, *104*, 4484.

(36) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(37) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 1492.

(38) Nakazawa, H.; Buhro, W. E.; Bertrans, G.; Gladysz, J. A. *Inorg. Chem.* **1984**, *23*, 3431.

scheme two $R_2NP{=}Fe(CO)_4$ units combine initially through phosphorus–phosphorus double-bond formation to give the diphosphene A. Migration of a dialkylamino group from one phosphorus atom in A to the other phosphorus atom gives the new [bis(dialkylamino)phosphino]phosphinidene complex B. Addition of a third molecule of $R_2NP{=}Fe(CO)_4$ to the phosphinidene phosphorus in B through formation of a new phosphorus–phosphorus double bond leads to the [bis(dialkylamino)phosphino]-diphosphene complex C. Migration of the dialkylamino group on the diphosphene phosphorus in C to a carbonyl group of the $Fe(CO)_4$ moiety bonded to the bis(dialkylamino)phosphino end of the triphosphorus chain to give a bridging dialkylcarbamoyl group with concurrent formation of an FeP_3 four-membered ring through iron–phosphorus bond formation leads to D, which is equivalent to the observed product XIV. The reaction pathways depicted in Scheme II depend on the relative lability of dialkylamino groups directly bonded to phosphorus atoms, which are doubly bonded to other phosphorus atoms. Such dialkylamino migrations may be related to the recently reported rearrangement[39] shown in eq 3 or to dialkylamino migrations in reactions of

$$2(R_2N)_4P_4^{2+} \rightarrow 4(R_2N)_2P^+ + P_4 \qquad (3)$$

R_2NPCl_2 and $(R_2N)_2PCl$ derivatives with magnesium or $(Me_3Si)_2Hg$.[40,41]

The drastically different pathways of the reactions of R_2NPCl_2 derivatives with $Na_2Fe(CO)_4$ in tetrahydrofuran rather than diethyl ether can be related to the much greater solubility of $Na_2Fe(CO)_4$ in tetrahydrofuran. Under such conditions, the $R_2NP{=}Fe(CO)_4$ intermediate can react preferentially with $Fe(CO)_4^{2-}$ rather than itself, leading to the formation of $(R_2NP)_3Fe_2(CO)_6$ (VI) and $(R_2NP)_3COFe_2(CO)_6$ (XIII) through the following sequence of reactions shown in eq 4 and 5. Equation

$$R_2NPFe(CO)_4 + Fe(CO)_4^{2-} \rightarrow [R_2NPFe(CO)_3]^{2-} + Fe(CO)_5 \qquad (4a)$$

$$[R_2NPFe(CO)_3]^{2-} + R_2NPFe(CO)_4 \rightarrow [(R_2NP)_2Fe_2(CO)_6]^{2-} + CO \qquad (4b)$$

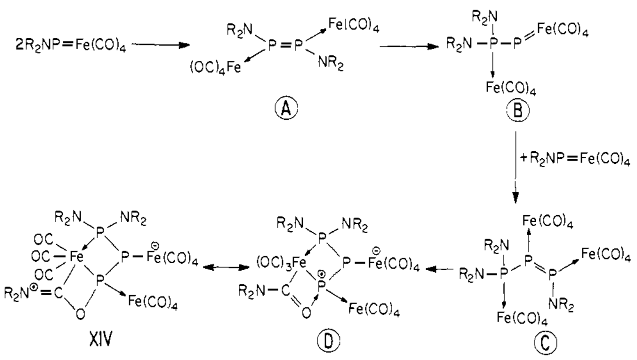
$$[(R_2NP)_2Fe_2(CO)_6]^{2+} + R_2NPCl_2 \rightarrow \underset{\text{VI}}{(R_2NP)_3Fe_2(CO)_6} + 2Cl^- \qquad (4c)$$

$$[R_2NPFe(CO)_3]^{2-} + R_2NPCl_2 \rightarrow (R_2NP)_2Fe(CO)_3 + 2Cl^- \qquad (5a)$$

$$(R_2NP)_2Fe(CO)_3 + R_2NPFe(CO)_4 \rightarrow \underset{\text{XIII}}{(R_2NP)_3COFe_2(CO)_6} \qquad (5b)$$

4a corresponds to the reduction of $R_2NP{=}Fe(CO)_4$ to the corresponding dianion by $Fe(CO)_4^{2-}$ and is driven by the stronger back-bonding properties of the (dialkylamino)phosphinidene ligand relative to the carbonyl ligand, thereby stabilizing $[R_2NPFe(CO)_3]^{2-}$ relative to $Fe(CO)_4^{2-}$ (i.e., $[R_2NPFe(CO)_3]^{2-}$ is a weaker nucleophile than $Fe(CO)_4^{2-}$). The reaction of $[R_2NPFe(CO)_3]^{2-}$ with $R_2NP{=}Fe(CO)_4$ to form $[(R_2NP)_2Fe_2(CO)_6]^{2-}$ (eq 4b) may be regarded as analogous to the known[42] reaction of $Fe(CO)_4^{2-}$ with $Fe(CO)_5$ to form $Fe_2(CO)_8^{-2}$, with an R_2NP ligand replacing a CO group in each reactant. Nucleophilic substitution of R_2NPCl_2 with the $[(R_2NP)_2Fe_2(CO)_6]^{2-}$ dianion (eq 4c) can form $(R_2NP)_3Fe_2(CO)_6$ (VI), the observed major product under these conditions. The $[R_2NPFe(CO)_3]^{2-}$ anion formed in eq 2a can react with R_2NPCl_2 to form the bis(dialkylamino)phosphinidene intermediate $(R_2NP)_2Fe(CO)_3$ (eq 5a), which can then combine with more $R_2NP{=}Fe(CO)_4$ to form the observed minor product $(R_2NP)_3COFe_2(CO)_6$ (XIII) by a pathway similar to the formation of $(R_2NP)_2COFe_2(CO)_6$ (V) from two molecules of $R_2NP{=}Fe(CO)_4$ in Scheme I. The products $(R_2NP)_3Fe_2(CO)_6$ (VI) and $(R_2NP)_3COFe_2(CO)_6$ (XIII) arising from the schemes represented by eq 4 and 5, respectively, have P/Fe ratios greater than 1, namely 1.5.

Scheme II



The only products found in the reactions of R_2NPCl_2 derivatives with $Na_2Fe(CO)_4$ that are not accounted for in Schemes I and II and eq 4 and 5 are the triiron derivatives $(R_2NP)_2Fe_3(CO)_9$ (X), which are the only observed products having P/Fe ratios less than unity, namely 2/3. The diethylamino derivative $(Et_2NP)_2Fe_3(CO)_9$ (X: R = Et) was reported in 1976 by Lampin and Mathey[43] to be the main iron carbonyl product from the reaction of Et_2NPCl_2 with $Na_2Fe(CO)_4$ in tetrahydrofuran, but the method of preparation of $Na_2Fe(CO)_4$ used by these authors (reaction of sodium metal with *excess* $Fe(CO)_5$) suggested that their "$Na_2Fe(CO)_4$" contained considerable amounts of $Na_2Fe_2(CO)_8$[42] so that comparison of their results with those reported in this paper is of questionable validity. Despite the relatively high content of iron in the $(R_2NP)_2Fe_3(CO)_9$ derivatives (X), they appear to form even under conditions where $Fe(CO)_4^{2-}$ is sparingly soluble in the reaction medium, i.e., in diethyl ether. Compounds of the type $(R_2NP)_2Fe_3(CO)_9$ (X) could arise by addition of an $Fe(CO)_4$ group to the phosphorus–iron double bond in $R_2NP{=}Fe(CO)_4$ followed by addition of another $R_2NP{=}Fe(CO)_4$ molecule to the resulting product and decarbonylation.

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

Supplementary Material Available: Listings of positional parameters, anisotropic thermal parameters, and bond angles (deg) and distances (Å) for $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (Tables 1–3), $[i\text{-}Pr_2NPHFe(CO)_4]_2O$ (Tables 4–6), $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (Tables 7–9), $(i\text{-}Pr_2NP)_3COFe_2(CO)_6$ (Tables 10–12), $(Et_2NP)_3Fe_3(CO)_{12}$ (Tables 13–15), and $(Et_2NP)_3Fe_3(CO)_{11}$ (Tables 16–18) (30 pages). Ordering information is given on any current masthead page.

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[39] Schäfer, H. G.; Schoeller, W. W.; Niemann, J.; Haug, W.; Dabisch, T.; Niecke, E. *J. Am. Chem. Soc.* **1986**, *108*, 7481.

[40] King, R. B.; Sundaram, P. M. *J. Organomet. Chem.* **1984**, *49*, 1784.

[41] King, R. B.; Sadanani, N. D. *J. Org. Chem.* **1984**, *50*, 1719.

[42] Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119.

[43] Lampin, J.-P.; Mathey, F. *C. R. Seances Acad. Sci. Ser. C* **1976**, *282C*, 979.