The best fit is shown as the solid line in Figure 3. In fact, for $Cu(pyz)(CF_3SO_3)_2$, the fit of the magnetic susceptibility data to the one-dimensional model is slightly improved over that for the two-dimensional model, as measured by the relative values of *F* and judged visually. The similarity between the magnetic properties of $Cu(pyz)(CF_3SO_3)_2$ and $Cu(pyz)_2(CH_3SO_3)_2$ suggests that the feature common to both complexes is strongly bridging pyrazine groups along one dimension. These groups provide a more facile route for magnetic exchange interactions than the other bridging entities (the axial pyrazine groups in $Cu(pyz)_2(CH_3SO_3)_2$ and the triflate anions in $Cu(pyz)(CF_3SO_3)_2$).

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Registry No. $Cu(py)_4(CF_3SO_3)_2$, 113110-58-0; $Cu(pyz)_4(CF_3SO_3)_2{\cdot}H_2O$, 113110-59-1; $Cu(pyz)(CF_3SO_3)_2$, 113110-61-5.

Supplementary Material Available: Listings of calculated hydrogen parameters, anisotropic thermal parameters, and torsion angles (4 pages); a table of calculated and observed structure factors (14 pages). Ordering information is given on any current masthead page.

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Dialkylamino Phosphorus Metal Carbonyls. 6. Chemistry of (Tris(diisopropylamino)triphosphine)diiron Hexacarbonyl Derivatives Including the Synthesis and Structure of Heterometallic Derivatives[1-4]

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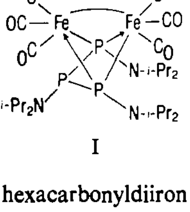
Reactions of the triphosphine complex $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ with hydrogen halides (HX) result in selective cleavage of the diisopropylamino group attached to the center phosphorus atom to give orange $(i\text{-}Pr_2NP)_2P(X)Fe_2(CO)_6$ (X = Cl, Br). The complex $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ reacts similarly with the boiling alcohols ROH (R = Me, Et) in the presence of catalytic acetic acid to give orange $(i\text{-}Pr_2NP)_2P(OR)Fe_2(CO)_6$. Reduction of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with $NaBH_4$ in tetrahydrofuran solution gives yellow $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$. However, reduction of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ with $LiAlH_4$ results in phosphorus–phosphorus bond cleavage to give yellow $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$. Reactions of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with $(THF)Cr(CO)_5$ and with $NaMn(CO)_5$ give orange $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ and red $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$, respectively. An X-ray diffraction study of $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (monoclinic, $P2_1/c$; $a = 10.222$ (6) Å, $b = 33.576$ (29) Å, $c = 10.577$ (6) Å, $\beta = 112.25$ (4)°, $Z = 4$) indicates coordination of the distorted tetrahedral center phosphorus of the triphosphine chain to a $Cr(CO)_5$ fragment (Cr–P = 2.341 (12) Å). A similar X-ray diffraction structure of $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (monoclinic, $P2_1/n$; $a = 13.200$ (3) Å, $b = 13.972$ (2) Å, $c = 17.855$ (9) Å, $\beta = 93.82(3)$°, $Z = 4$) indicates σ-bonding of the pyramidal center of the triphosphine chain to an $Mn(CO)_5$ group (Mn–P = 2.492 (3) Å). Reactions of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ with $(THF)Cr(CO)_5$ and with $Fe_2(CO)_9$/THF gives orange $(i\text{-}Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$ and orange $(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$, respectively, in which the center phosphorus atom of the triphosphine chain is bonded to the $M(CO)_n$ fragment (M = Cr, n = 5; M = Fe, n = 4).

Introduction

Recent results from our laboratory[4,5] have shown that the reaction of $i\text{-}Pr_2NPCl_2$ with $Na_2Fe(CO)_4$ in tetrahydrofuran solution provides a source of the (tris(diisopropylamino)triphosphine)hexacarbonyldiiron complex $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (I) in ~30% yield, thereby making this complex readily available in ~30-g quantities. This complex is of interest because the rigid $P_2Fe_2(CO)_6$ framework holds the center phosphorus atom in an unusual environment as indicated by the unusual low-field chemical shift (δ 292.2) relative to those of phosphorus atoms in other systems not involved in multiple bonding. Furthermore, the selective acid cleavage of the diisopropylamino group bonded to the center phosphorus atom without disturbing the diisopropylamino groups bonded to the two terminal phosphorus atoms of the triphosphine chain makes $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (I) a versatile precursor to other (triphosphine)hexacarbonyldiiron derivatives, mainly species of the general formula $(i\text{-}Pr_2NP)_2P(X)Fe_2(CO)_6$ (II). This paper presents details of our studies on (triphosphine)hexacarbonyldiiron complexes of this and related types.



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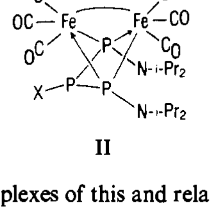
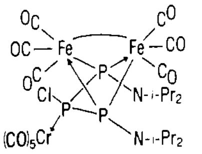
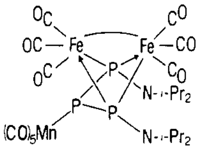


II

Our work in this area includes a study of the following two different approaches to bonding a second metal carbonyl moiety, not necessarily an iron carbonyl moiety, to the center phosphorus atom in such triphosphine complexes: (1) coordination of a suitably unhindered central phosphorus atom to a suitable transition metal fragment such as $Cr(CO)_5$ or $Fe(CO)_4$; (2) nucleophilic substitution of the halogen atom in $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (II, X = Cl) with a metal carbonyl anion, namely $Mn(CO)_5^-$. This paper includes details of structure determinations by X-ray diffraction on prototypical heterometallic compounds of each type, namely $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (III) and $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (IV).



III



IV

Experimental Section

The general techniques for microanalyses; infrared spectra (Table I); phosphorus-31 (Table II), carbon-13 (Table III), and proton (Table IV) NMR spectra; melting points; solvent purification; and inert-atmosphere

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(1) Part 5: King, R. B.; Wu, F.-J.; Holt, E. M. *J. Am. Chem. Soc.*, in press.

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

(3) Portions of this work were presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987.

(4) For a preliminary communication of a portion of this work, see King, R. B.; Wu, F.-J.; Holt, E. M. *Inorg. Chem.* **1986**, *25*, 1733.

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

Table I. Infrared[a] ν(CO) Data for Compounds Derived from $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$

compd	IR (ν(CO)), cm^{-1}
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	2048 s, 2008 s, 1986 s, 1958 s, 1947 m
$(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$	2062 m, 2023 s, 1996 s, 1982 s, 1967 s
$(i\text{-}Pr_2NP)_2P(Br)Fe_2(CO)_6$	2059 m, 2020 s, 1993 s, 1984 m, 1967 s
$(i\text{-}Pr_2NP)_2P(OMe)Fe_2(CO)_6$	2058 m, 2019 s, 1993 s, 1975 m, 1961 m
$(i\text{-}Pr_2NP)_2P(OEt)Fe_2(CO)_6$	2056 m, 2016 s, 1991 s, 1973 m, 1960 m
$(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$	2050 m, 2008 s, 1991 s, 1967 s, 1957 m
$(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$	2040 m, 2008 s, 1985 m, 1975 s, 1964 s
$(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$	2056 s, 2025 s, 2000 s, 1978 m, 1966 s[d] 2075 w (A_1), 1990 m (B_1), 1957 s (E), 1952 s (E), 1924 vw (A_1)
$(i\text{-}Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$	2042 s, 2012 s, 1995 m, 1966 s, 1959 s[d] 2060 w (A_1), 1984 m (B_1), 1952 s (E), 1947 s (E), 1918 vw (A_1)
$(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$	2050 s, 2027 s, 2005 s, 1987 s, 1954 m[d] 2070 w (A_1), 1977 s (E), 1973 (E)[b]
$(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$	2032 s, 2016 s, 2003 s, 1961 s, 1951 m[d] 2098 m (A_1), 1984 (E)[c]

[a] Hexane or cyclohexane (bimetallic compounds) solutions. [b] Another A_1 mode is obscured by the 2005 s peak of the $Fe_2(CO)_6$ unit. [c] Another A_1 mode is obscured by the 1961 s or 1951 m peak of the $Fe_2(CO)_6$ unit. [d] These five bands arise from the $Fe_2(CO)_6$ unit.

Table II. Proton-Decoupled ^{31}P NMR Data[a] for Compounds Derived from $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$

	δ		J, Hz	
compd	P_c	P_t	$^1J_{PP}$	$^1J_{HP}$
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	292.2 t	170.3 d	264	
$(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$	318.7 t	147.8 d	254	
$(i\text{-}Pr_2NP)_2P(Br)Fe_2(CO)_6$	302.9 t	142.2 d	257	
$(i\text{-}Pr_2NP)_2P(OMe)Fe_2(CO)_6$	382.8 t	155.1 d	242	
$(i\text{-}Pr_2NP)_2P(OEt)Fe_2(CO)_6$	378.8 t	157.0 d	238	
$(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$	277.3 t	102.3 d	154	132
$(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$		156.0 s[b]		
$(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$	384.7 t	197.5 d	269	
$(i\text{-}Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$	296.3 t	138.1 d	174	253
$(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$	272.5 t	148.8 d	194	278
$(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$	389.9 t	141.4 d	235	

[a] $CDCl_3$ solution; s = singlet, d = doublet, and t = triplet. [b] Proton coupling gave a complicated second-order spectrum, which is not inconsistent with an $A_2M_2X_4$ system (A = P, M = PH, X = CH).

Table III. Proton-Decoupled ^{13}C NMR Data[a] for Compounds Derived from $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$

	δ		
	isopropyl		
compd	CH	CH_3	CO
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	53.5 49.0	24.6 23.3 22.7	215.2 214.6 213.2
$(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$	53.9	22.7	212.8 212.2 209.5
$(i\text{-}Pr_2NP)_2P(Br)Fe_2(CO)_6$	54.0	22.7	212.5 br
$(i\text{-}Pr_2NP)_2P(OEt)Fe_2(CO)_6$[b]	53.6	22.9	213.4 br
$(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$	54.2	22.6 22.5 22.1	212.3
$(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$	48.7	21.8	212.2
$(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$	54.9	24.5	214.9 214.5 211.3
$(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$	54.8	22.8	215.2 214.7 210.8 br
$(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$	53.6	23.0	213.2 211.2

[a] $CDCl_3$ solutions. [b] –OEt, CH_2: δ 68.0 d, $^2J_{CP}$ = 12.9 Hz. CH_3: δ 17.2 d, $^3J_{CP}$ = 5.3 Hz.

handling are similar to those given in the fourth paper of this series.[5] Commercial $Fe(CO)_5$, diisopropylamine, and PCl_3 were converted to $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (I) through $Na_2Fe(CO)_4\cdot1.5$diox (diox = dioxane) and $i\text{-}Pr_2NPCl_2$ by the published procedure.[4–6] The metal carbonyl reagents $NaMn(CO)_5$[7] and $(THF)Cr(CO)_5$ (THF = tetrahydrofuran)[8] were prepared by standard procedures and used in situ, and $Fe_2(CO)_9$ was prepared by the usual procedure.[9]

Preparation of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$. A vigorously stirred solution of 1.0 g (1.5 mmol) of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ in 100 mL of hexanes were treated with anhydrous hydrogen chloride for 5 min. A precipitate formed immediately. Removal of solvent from the filtered solution gave 0.9 g (100% yield) of spectroscopically pure $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ as a yellow-orange modestly air-sensitive solid, mp 91–92 °C. Anal. Calcd for $C_{18}H_{28}ClFe_2N_2O_6P_3$: C, 35.5; H, 4.6; N 4.6; Cl, 5.8. Found: C, 35.1; H, 4.7 N, 4.5; Cl, 5.7.

Preparation of $(i\text{-}Pr_2NP)_2P(Br)Fe_2(CO)_6$. A vigorously stirred solution of 1.0 g (1.5 mmol) of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ in 100 mL of hexanes was treated with anhydrous hydrogen bromide for 5 min. A precipitate formed immediately. Removal of solvent from the filtered solution gave 0.95 g (97% yield) of orange, modestly air-sensitive $(i\text{-}Pr_2NP)_2P(Br)Fe_2(CO)_6$, mp 99–100 °C. Anal. Calcd for $C_{18}H_{28}BrFe_2N_2O_6P_3$: C, 33.1; H, 4.3; N, 4.3; Br, 12.2. Found: C, 32.8; H, 4.5; N, 4.1; Br, 11.8.

Preparation of $(i\text{-}Pr_2NP)_2P(OMe)Fe_2(CO)_6$. A solution of 1.0 g. (1.5 mmol) of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ in 200 mL of methanol containing several drops of acetic acid was boiled under reflux for 3 days. The solid dissolved only when the temperature was elevated. The progress of the reaction was monitored by the infrared ν(CO) frequencies. After completion of the reaction, the solvent and volatile materials were removed in vacuum. The residue was extracted with 50 mL of hexanes. Concentration and cooling the filtered extracts to −10 °C in a freezer gave in several crops orange crystalline, slightly air-sensitive $(i\text{-}Pr_2NP)_2P(OMe)Fe_2(CO)_6$, mp 91–92 °C. Anal. Calcd for $C_{19}H_{31}Fe_2N_2O_7P_3$: C, 37.7; H, 5.1; N, 4.6. Found: C, 37.9; H, 5.2; N, 4.6.

Preparation of $(i\text{-}Pr_2NP)_2P(OEt)Fe_2(CO)_6$. The procedure was the same as the preparation of $(i\text{-}Pr_2NP)_2P(OMe)Fe_2(CO)_6$ described above except that 250 mL of ethanol was used and the reaction time was 7 days. The product $(i\text{-}Pr_2NP)_2P(OEt)Fe_2(CO)_6$ was isolated in 70% yield (0.65 g) as orange, slightly air-sensitive crystals, mp 137–138 °C. Anal. Calcd for $C_{20}H_{33}Fe_2N_2O_7P_3$: C, 38.8; H, 5.3; N, 4.5. Found: C, 39.1; H, 5.7; N, 4.5.

Reaction of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with Methanol. An orange solution of 0.3 g (0.48 mmol) of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ in 70 mL of methanol was boiled under reflux for 2 h. After removal of solvent in a vacuum, the phosphorus-31 NMR spectrum indicated the product to be a mixture of $(i\text{-}Pr_2NP)_2P(OMe)Fe_2(CO)_6$ and an unknown compound with an AMX phosphorus-31 NMR spectrum of δ 194.1 dd (302, 104 Hz), 97.3 dd (258, 104 Hz), and δ −2.3 dd (302, 258 Hz).

Preparation of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$. A mixture of 0.18 g (1.62 mmol) of $NaBH_4$, 1.1 g (1.63 mmol) of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$, and 80 mL of tetrahydrofuran was stirred at room temperature for 2 days. The progress of the reaction was followed by phosphorus-31 NMR spectroscopy. After 24 h, approximately 50% of the reaction had proceeded. After 48 h, approximately 90% of the reaction had proceeded and about 5% of a minor product, $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$, was also detected. The solvent was removed in a vacuum and the residue was extracted with 100 mL of hexanes. Concentrating and cooling (−10 °C) the filtered solution gave 0.72 g (78% yield) of air-stable yellow crystalline $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ in several crops, mp 120–121 °C. Anal. Calcd for $C_{18}H_{29}Fe_2N_2O_6P_3$: C, 37.6; H, 5.0; N, 4.9. Found: C, 39.2; H, 5.5; N, 4.7. The individual crops were analyzed by phosphorus-31 NMR, since the later crops of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ contained impurities of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ and $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$, which

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Table IV. Proton NMR[a] Data for Compounds Derived from $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$

	δ		
	isopropyl		
compd	CH[a]	CH_3[b] ($^3J_{HH}$, Hz)	other (J, Hz)
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	4.48 (2 H)	1.28 (7.1)	
	3.41 (4 H)	1.23 (6.6)	
		1.20 (6.8)	
$(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$	3.51	1.23 (6.8)	
$(i\text{-}Pr_2NP)_2P(Br)Fe_2(CO)_6$	3.51	1.26 (6.7)	
		1.24 (6.7)	
$(i\text{-}Pr_2NP)_2P(OEt)Fe_2(CO)_6$	3.43	1.18 (6.6)	–OEt: 3 H, 1.34 t (7.1);[e] 2 H, 4.04 quintet (7.3)[d]
$(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$	3.50	1.15 (6.7)	–PH: 9.05 dt (129.2,[f] 7.9[g])
		1.14 (6.7)	
$(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$	3.55	1.20 (6.2)	–PH: 4.4 d (448)[f]
$(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$	3.65	1.34 (5.9)	
		1.27 (6.1)	
$(i\text{-}Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$	3.45	1.19 (6.7)	–PH: 9.22 d (253.4)[f]
		1.16 (6.7)	
$(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$	3.52	1.25 (6.7)	–PH: 8.84 d (278)[f]
		1.23 (6.7)	
$(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$	3.47	1.30 (6.5)	
		1.18 (6.5)	

[a] $CDCl_3$ solutions; d = doublet, and t = triplet. [b] Unresolved multiplet. [c] All resonances are doublets. [d] $^3J_{PH} + {}^3J_{HH}$. [e] $^3J_{PH}$. [f] $^1J_{PH}$. [g] $^3J_{PH}$.

were very difficult to remove by chromatography or fractional crystallization.

Treatment of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with $NaBH_4$ in diethyl ether rather than tetrahydrofuran at room temperature for 2 days led to no reaction. After removal of the solvent, the phosphorus-31 NMR spectrum of the resulting material showed only resonances from unchanged $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$.

Reactions of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with $LiAlH_4$. (a) In Diethyl Ether. An orange solution of 1.13 g (1.86 mmol) of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ in 130 mL of diethyl ether was slowly treated at –78 °C with 1.6 mmol of $LiAlH_4$ as a 1.0 M solution in diethyl ether by means of a syringe. The solution was allowed to warm slowly to room temperature, becoming darker with a rise in temperature. After the mixture was stirred overnight, the solvent was removed under vacuum. The residue was shown by its phosphorus-31 NMR spectrum to contain $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ and $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ as major components in approximately equal amounts.

(b) In Tetrahydrofuran. An orange solution of 1.17 g (1.92 mmol) of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ in 110 mL of tetrahydrofuran was slowly treated at –78 °C with 1.0 mmol of $LiAlH_4$ as a 1.0 M solution in tetrahydrofuran by using a syringe. The solution, which turned darker immediately upon addition of $LiAlH_4$, was allowed to warm slowly to room temperature. After the mixture was stirred overnight at room temperature, the solvent and volatile materials were removed in vacuum. The residue was extracted with 100 mL of hexanes. The phosphorus-31 NMR spectrum of the concentrated filtered solution indicated a mixture containing a large portion (about 80%) of $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$. Concentrating and cooling (–10 °C) this solution gave 0.44 g (45% yield) of yellow $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$, mp 126–127 °C. Anal. Calcd for $C_{18}H_{30}Fe_2N_2O_6P_2$: C, 39.7; H, 5.5; N, 5.2. Found: C, 39.8; H, 5.6; N, 5.0.

Preparation of $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$. A solution of 1.30 g (5.91 mmol) of $Cr(CO)_6$ in 500 mL of tetrahydrofuran was exposed to ultraviolet irradiation for 5 h in an immersion type photochemical apparatus. The resulting orange solution of $(THF)Cr(CO)_5$ was treated at room temperature with a solution of 3.1 g (5.1 mmol) of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ in 50 mL of tetrahydrofuran. After the mixture was stirred for 12 h at ambient temperature, solvent and excess $Cr(CO)_6$ were removed at 25 °C (25 mm) and 45 °C (0.02 mm), respectively. The residue was extracted with 250 mL of 5:1 hexane/dichloromethane. Concentrating and cooling (–10 °C) the filtered extract gave in several crops 1.83 g (45% yield) of air-stable orange acicular $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$, mp 146–147 °C. Anal. Calcd for $C_{23}H_{28}ClCrFe_2N_2O_{11}P_3$: C, 34.5; H, 3.5; N, 3.5; Cl, 4.4. Found: C, 35.4; H, 3.7; N, 3.6; Cl, 4.4.

Preparation of $(i\text{-}Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$. A procedure similar to the preparation of $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ using 1.06 g (4.8 mmol) of $Cr(CO)_6$ and 2.0 g (3.0 mmol) of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ gave 1.26 g (55% yield) of air-stable orange acicular $(i\text{-}Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$, mp 170–171 °C. Anal. Calcd for $C_{23}H_{29}CrFe_2N_2O_{11}P_3$: C, 36.0; H, 3.8; N, 3.7. Found: C, 36.2; H, 4.0; N, 3.6.

Preparation of $(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$. A mixture of 3.5 g (6.1 mmol) of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$, 2.2 g (6.0 mmol) of $Fe_2(CO)_9$, and 200 mL of tetrahydrofuran was stirred for 18 h at room temperature. The $Fe_2(CO)_9$ dissolved slowly, and the color of the solution became deeper. After removal of solvent and volatile materials in a vacuum, the residue was extracted with 150 mL of hexanes. Concentrating and cooling the filtered extracts gave in several crops 3.5 g (77% yield) of air-stable deep orange $(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$, mp >140 °C dec. Anal. Calcd for $C_{22}H_{29}Fe_3N_2O_{10}P_3$: C, 35.6; H, 3.9; N, 3.8. Found: C, 36.1; H, 4.0; N, 3.7.

Preparation of $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$. A solution of $NaMn(CO)_5$ was prepared[7] in 160 mL of tetrahydrofuran from 0.93 g (2.4 mmol) of $Mn_2(CO)_{10}$ and excess 1% sodium amalgam. After excess mercury was removed, this solution was treated at –78 °C with a solution of 2.9 g (4.8 mmol) of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ in 50 mL of tetrahydrofuran. After being stirred for 12 h at room temperature, the resulting solution was filtered through a medium frit padded with 1.5 cm of silica gel. Concentrating and cooling the filtered solution to –78 °C gave 3.3 g (82% yield) of spectroscopically pure air-sensitive red microcrystalline $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6{\cdot}C_4H_8O$, dec pt >90 °C. Anal. Calcd for $C_{27}H_{36}Fe_2MnN_2O_{12}P_3$: C, 38.6; H, 4.3; N, 3.3. Found: C, 38.6; H, 4.4; N, 3.3. The tetrahydrofuran of crystallization was indicated by multiplet resonances at δ 3.75 and 1.84 in the proton NMR spectrum. The crystallographic sample was obtained by slow recrystallization from a mixture of dichloromethane and hexane; this process removed the tetrahydrofuran of crystallization.

X-ray Structure Determinations (Table V). Crystals of $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (from hexane) and $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (from a mixture of dichloromethane and hexane) were mounted on a 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 ($2\theta > 15°$) during normal alignment procedures by using molybdenum radiation ($\lambda = 0.71069$ Å). The data (8889 points for the $CrFe_2$ derivative III and 8221 points for the $MnFe_2$ derivative IV) were collected at room temperature by using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum of 2θ value of 60.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 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, observed data (4590 points for III and 3156 points for IV) with $I > 3.0\,\sigma(I)$ were used for solution and refinement. Heavy-atom positions were located by using direct methods.[10] Successive cycles of difference Fourier synthesis followed by least-squares refinement allowed location of the remainder of the non-hydrogen atoms. Least-squares refinement[11] converged with anisotropic thermal parameters. A difference Fourier synthesis did not

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

(11) Stewart, J. M., Ed. "The X-RAY System-Version of 1980"; Technical Report TR446; Computer Center, University of Maryland: College Park, MD.

Table V. Crystal Data for $(i\text{-Pr}_2\text{NP})_2\text{P(Cl)}[\text{Cr(CO)}_5]\text{Fe}_2(\text{CO})_6$ and $(i\text{-Pr}_2\text{NP})_2\text{P}[\text{Mn(CO)}_5]\text{Fe}_2(\text{CO})_6$

	$(i\text{-Pr}_2\text{NP})_2\text{P(Cl)}$-$[\text{Cr(CO)}_5]\text{Fe}_2(\text{CO})_6$	$(i\text{-Pr}_2\text{NP})_2\text{P}[\text{Mn(CO)}_5]$-$[\text{Fe}_2(\text{CO})_6]$
formula	$C_{23}H_{28}N_2O_{11}P_3ClCrFe_2$	$C_{23}H_{28}N_2O_{11}P_3MnFe_2$
mol wt	800.5	768.0
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	10.222 (6)	13.200 (3)
b, Å	33.576 (29)	13.972 (2)
c, Å	10.577 (6)	17.855 (9)
β, deg	112.25 (4)	93.82 (3)
V, Å^3	3359.9 (32)	3285.6 (18)
$F(000)$	1624	1560
μ(Mo Kα), cm^{-1}	14.35	14.31
D_{calcd}, g cm^{-3}	1.582	1.552
Z	4	4
no. of obsd reflcns	4590	3156
octants collcd	$\pm h,+k,+l$	$\pm h,+k,+l$
max 2θ, deg	60	60
R^a	0.058	0.063
$R_w{}^b$	0.077	0.081

[a] $R = (\sum ||F_o| - |F_c|| / \sum |F_o|)$. [b] The values for R_w were obtained by introducing a weight equal to $1/\sigma(F)$ into the final cycles of refinement.

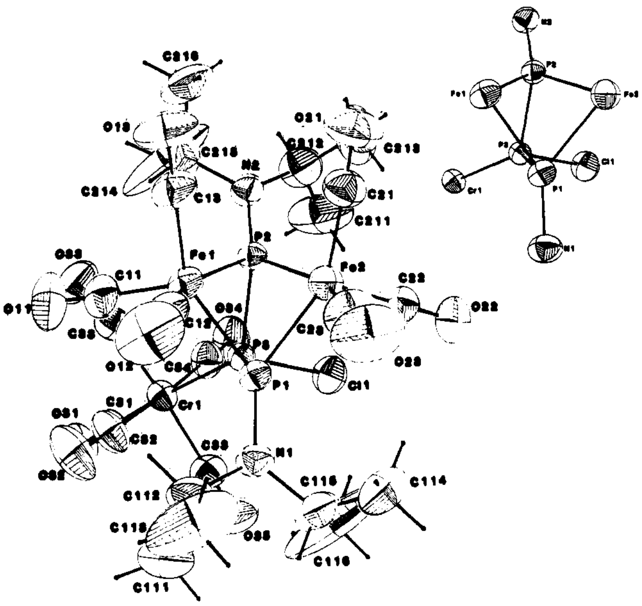


Figure 1. ORTEP diagram of $(i\text{-Pr}_2\text{NP})_2\text{P(Cl)}[\text{Cr(CO)}_5]\text{Fe}_2(\text{CO})_6$ (III), showing the $N_2P_3ClCrFe_2$ central portion of the molecule as an insert.

allow location of the hydrogen positions. Hydrogen positional parameters were therefore calculated by assuming normal geometry and a C–H bond length of 0.97 Å. These hydrogen positions were included in the final refinement with isotropic parameters, but hydrogen atom positional and thermal parameters were held fixed. A difference Fourier revealed no electron density of an interpretable level. Scattering factors were taken from Cromer and Mann.[12] Anomalous dispersion corrections were made for Fe, Mn, Cr, and P.

The final cycle of refinement minimizing the function $\sum(|F_o| - |F_c|)^2$ led to final agreement factors shown in Table V. The structure of $(i\text{-Pr}_2\text{NP})_2\text{P(Cl)}[\text{Cr(CO)}_5]\text{Fe}_2(\text{CO})_6$ is depicted in Figure 1 and that of $(i\text{-Pr}_2\text{NP})_2\text{P}[\text{Mn(CO)}_5]\text{Fe}_2(\text{CO})_6$, in Figure 2.

Results and Discussion

(A) Triphosphine Derivatives $(i\text{-Pr}_2\text{NP})_2\text{P(X)Fe}_2(\text{CO})_6$. An important chemical property of $(i\text{-Pr}_2\text{NP})_3\text{Fe}_2(\text{CO})_6$ (I) is the ability upon treatment with acidic reagents to replace the diisopropylamino group on the central phosphorus atom with other groups without disturbing the diisopropylamino groups on the terminal phosphorus atoms. This related to the greater ease of acidic cleavage of phosphorus–nitrogen bonds involving uncomplexed phosphorus atoms relative to complexed phosphorus atoms, which was observed several years ago in the extensive chemistry of metal carbonyl complexes of $\text{CH}_3\text{N(PF}_2)_2$.[13-15] The most useful example of such selective phosphorus–nitrogen cleavage reactions of $(i\text{-Pr}_2\text{NP})_3\text{Fe}_2(\text{CO})_6$ is the quantitative conversion of $(i\text{-Pr}_2\text{NP})_2\text{P(X)Fe}_2(\text{CO})_6$ (II, X = Cl, Br) by treatment with the corresponding anhydrous hydrogen halide in hexane solution since further nucleophilic replacement of the halogen atom on the central phosphorus can lead to other (triphosphine)$\text{Fe}_2(\text{CO})_6$ derivatives with interesting groups (e.g., H, Mn(CO)_5) attached to the central phosphorus atom (see below). A further example of the selective acidic cleavage of the diisopropylamino group on the central phosphorus atom in $(i\text{-Pr}_2\text{NP})_3\text{Fe}_2(\text{CO})_6$ (I) is its reaction with boiling alcohols in the presence of a catalytic amount of acetic acid to give the alkoxy derivatives $(i\text{-Pr}_2\text{NP})_2\text{P(OR)Fe}_2(\text{CO})_6$ (V, R = Me, Et). The phosphorus-31 NMR spectra (Table II) of all of these $(i\text{-Pr}_2\text{NP})_2\text{P(X)Fe}_2(\text{CO})_6$ derivatives (II, X = Cl, Br; V, R = Me, Et) exhibit AX_2 patterns confirming the selective cleavage of the diisopropylamino group bonded to the center phosphorus atom. In all cases the triplet resonance from the center phosphorus atom (Table II) appears at a very low field (δ 277.3–389.9) compared with the doublet resonances from the terminal phosphorus atoms (δ 102.3–170.3). Furthermore, the chemical shifts for the center phosphorus atom in the $(i\text{-Pr}_2\text{NP})_2\text{P(X)Fe}_2(\text{CO})_6$ derivatives move downfield in the general

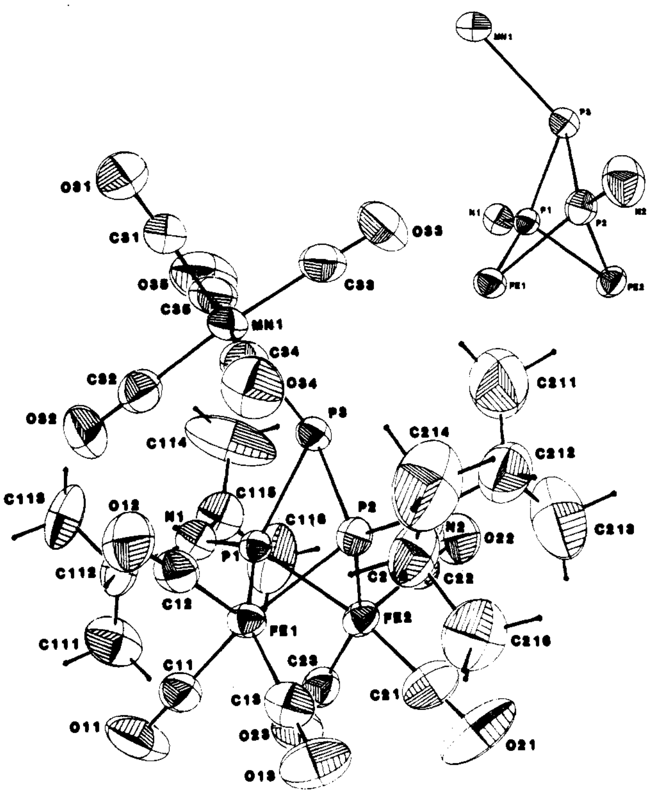
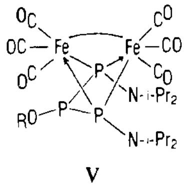


Figure 2. ORTEP diagram of $(i\text{-Pr}_2\text{NP})_2\text{P}[\text{Mn(CO)}_5]\text{Fe}_2(\text{CO})_6$ (IV), showing the $N_2P_3MnFe_2$ central portion of the molecule as an insert.



V

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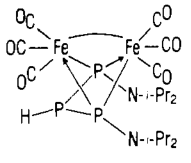
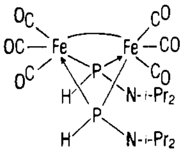
sequence X = H < i-Pr_2N < Br < Cl < OEt ~ OMe < $Mn(CO)_5$. The infrared ν(CO) spectra of the $Fe_2(CO)_6$ group in the $(i\text{-}Pr_2NP)_2P(X)Fe_2(CO)_6$ derivatives all exhibit five ν(CO) frequencies, which increase in the sequence X = H ~ i-Pr_2N < OEt ~ OMe < Cl ~ Br. These sequences relate to various combinations of electronegativity and π-bonding effects for the different X groups.

(B) Phosphorus-Hydrogen Derivatives $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ and $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$. The complex $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (II; X = Cl) can be reduced to either $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) or $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII) depending upon the reducing agent ($NaBH_4$ or $LiAlH_4$) and the solvent (diethyl ether or tetrahydrofuran). The reducing power of these hydride systems decreases in the sequence: $LiAlH_4$/THF > $LiAlH_4/Et_2O$ > $NaBH_4$/THF > $NaBH_4/Et_2O$. The most powerful $LiAlH_4$/THF reductant results in phosphorus-phosphorus bond cleavage to give $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII) as the major product. The $NaBH_4$/THF reductant is an ideal method to prepare $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) despite the slow reaction rate (3–4 days at ambient temperature) because $LiAlH_4$ is too powerful a reducing agent for the reduction of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (II, X = Cl) to stop at the $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) stage even at −78 °C. The reduction of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (II, X = Cl) with $NaBH_4/Et_2O$ at ambient temperature gave no sign of reaction after several days. The complex $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) is a precursor of $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII), as suggested by the treatment of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ with $LiAlH_4$/THF at room temperature to give $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$. Several iron carbonyl complexes related to $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ have been reported.[16,17] Conversion of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ to $(i\text{-}Pr_2NP)_2P(X)Fe_2(CO)_6$ (II, X = Cl or probably Br) is necessary for the preparation of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) and $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII) since treatment of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ with $LiAlH_4$/THF at room temperature for 2 days results in a complicated reaction mixture (^{31}P NMR with mainly unreacted starting material.



VI

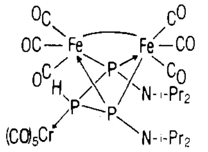


VII

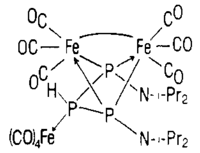
Several features of the NMR spectra of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) and $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII) are of interest. The $|^1J(P\text{-}P)|$ coupling constant of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) is 154 Hz (Table II), which is much smaller than the $|^1J(P\text{-}P)|$ coupling constants of 238–264 Hz for the other $(i\text{-}Pr_2NP)_2P(X)Fe_2(CO)_6$ derivatives (X = Cl, Br, OMe, OEt, i-Pr_2N). The resonance of the P–H hydrogen in the proton NMR spectrum of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) appears as a doublet of triplets at δ 9.05 with $|^1J(P\text{-}H)|$ and $|^2J(P\text{-}H)|$ coupling constants of 129 and 8 Hz, respectively. The most notable spectroscopic property of $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII) is its proton-coupled phosphorus-31 NMR spectrum, which exhibits a complicated second-order spectrum not inconsistent with an $A_2M_2X_4$ spin system (A = P, M = P-bonded H, X = C-bonded H). A detailed NMR study of the related complex $(MePH)_2Fe_2(CO)_6$ (an $A_2M_2X_6$ spin system) has been reported by Treichel and Berg,[18] who obtain three chemical shifts and nine coupling constants for that complex by simulating the proton-coupled phosphorus-31 and proton NMR spectra with and without phosphorus-31 decoupling.

The reactivities of the complexes $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) and $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII) toward hydrogen halides are of interest. No reaction was observed upon treatment of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ with HBr in hexane for 5 min in accord with the stability of diisopropylamino groups bonded to terminal phosphorus atoms in $(i\text{-}Pr_2NP)_2P(X)Fe_2(CO)_6$ derivatives (II) toward hydrogen halide cleavage. However, reaction of $(i\text{-}Pr_2NPH)_2Fe_2(CO)_6$ (VII) with HBr in hexane resulted in the immediate formation of a precipitate. The latter reaction is complicated as indicated by the phosphorus-31 NMR spectrum of the reaction mixture.

(C) Heterometallic Derivatives. The conversion of $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (I) to $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (II, X = Cl) has the following two important consequences: (1) the lone pair on the central phosphorus atom becomes accessible owing to the much smaller size of Cl relative to i-Pr_2N; (2) the P-Cl bond provides a reactive site for nucleophilic attack. Reaction of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with $(THF)Cr(CO)_5$ results in displacement of the weakly coordinated tetrahydrofuran in $(THF)Cr(CO)_5$ by the center phosphorus lone pair in $(i\text{-}Pr_2NP)_2P(Cl)Fe(CO)_6$ to give $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (III). Reaction of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ with $NaMn(CO)_5$ results in nucleophilic displacement of the chlorine atom by $Mn(CO)_5^-$ to give the heterometallic complex $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (IV). Reactions of $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) with $(THF)Cr(CO)_5$ and with $Fe_2(CO)_9$ also result in complexation of the central phosphorus lone pair to the metal carbonyl moiety to give $(i\text{-}Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$ (VIII), and $(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$ (IX), respectively. Reaction of $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (II, X = Cl) with $Fe_2(CO)_9$ in tetrahydrofuran gave a mixture of two products. One of these products was $(i\text{-}Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$ (IX) identical (^{31}P NMR) to the product from $(i\text{-}Pr_2NP)_2P(H)Fe_2(CO)_6$ and $Fe_2(CO)_9$. The other product was a presently unidentified orange compound with an unexpected AXY rather than AX_2 phosphorus-31 NMR spectrum showing resonances at δ 457.3 dd (319, 268 Hz), 180.0 dd (319, 26 Hz), and 172.7 dd (268, 26 Hz). Most notable is the unusually small apparent $|^1J(P\text{-}P)|$ coupling constant of 26 Hz. Attempts to determine the structure of this complex by X-ray diffraction failed owing to disorder problems.



VIII



IX

The structure of $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (III) is shown in Figure 1. The $Cr(CO)_5$ group is bonded to the central phosphorus atom P3: P3–Cr1 = 2.341 (2) Å. The geometry at P3 is a distorted tetrahedron with the P2-P3-P1 angle compressed to 70.94 (8)°, the P2–P3–Cr1 and P1–P3–Cr1 angles opened to 130.84 (11) and 128.52 (9)°, respectively, and the remaining three angles within 4° of the ideal tetrahedral angle 109.5°. The P1,P2,P3 plane nearly bisects the Fe–Fe bond as indicated by the angles P3–P1–Fe1 = 93.90 (8), P3–P2–Fe1 = 93.78 (8), P3–P1–Fe2 = 99.40 (8), and P3–P2–Fe2 = 99.24 (9)°.

The structure of $(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (IV) is shown in Figure 2. The $Mn(CO)_5$ group is bonded to the central phosphorus atom P3: P3–Mn1 = 2.492 (3) Å. The geometry at P3 is pyramidal rather than planar (P2–P3–P1 = 68.5 (1), P2–P3–Mn1 = 118.1 (1), P1–P3–Mn1 = 115.9 (1)°), indicating that the lone pair on P3 is stereochemically active. The plane P1–P2–P3 is tilted about 4.5° about the P1–P2 axis from the idealized plane perpendicular to and bisecting the Fe1–Fe2 bond (P3–P1–Fe1 = 103.8 (1), P3–P2–Fe1 = 103.8 (1), P3–P1–Fe2 = 94.8 (1), P3–P2–Fe2 = 94.7 (1)°).

The infrared ν(CO) spectra of the complexes $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (III) and $(i\text{-}Pr_2NP)_2P(H)[M(CO)_n]Fe_2(CO)_6$ (n = 5, M = Cr; n = 4, M = Fe) can be readily resolved into bands arising from the $Fe_2(CO)_6$ group with local C_{2v} symmetry (five bands) and the $Cr(CO)_5$ (four bands, $2A_1 + B_1 + E$) or $Fe(CO)_4$ group (three bands, $2A_1 + E$) with the E modes being split and the B_1 modes being infrared active for the $Cr(CO)_5$

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derivatives (Table I). The assignments of the latter peaks are based on their characteristic numbers, frequency ranges, and relative intensities.[19] The infrared ν(CO) spectrum of (i-$Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (IV) consists of only seven bands, which is not inconsistent with the observations that the E mode of the $Mn(CO)_5$ group remains unsplit, the B_1 mode is infrared inactive, and one of the weak A_1 modes of the $Mn(CO)_5$ group is obscured by the strong bands of the $Fe_2(CO)_6$ group around 1960 cm^{-1}. These infrared ν(CO) data suggest that the effective local symmetries of the ideal C_{3v} $Fe(CO)_4$ group in IX and the ideal C_{4v} $Cr(CO)_5$ groups in III and IV are considerably lowered by the effective local symmetry of the $Mn(CO)_5$ group in IV remains close to the ideal C_{4v}.

The phosphorus-31 NMR spectra of (i-$Pr_2NP)_2P(H)[Cr(CO)_5]Fe_2(CO)_6$ (VIII) and (i-$Pr_2NP)_2P(H)[Fe(CO)_4]Fe_2(CO)_6$ (IX) exhibit the following interesting features when compared with that of their precursors (i-$Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI).

(1) Upon coordination the central phosphorus atoms of VIII and IX undergo only small chemical shift changes (19 ppm downfield for VIII and 5 ppm upfield for IX) whereas the terminal phosphorus atoms undergo much larger downfield chemical shifts (36 and 46 ppm for VIII and IX, respectively). The greater effect of the $Cr(CO)_5$ or $Fe(CO)_4$ group on the terminal phosphorus chemical shift rather than that of the center phosphorus to which it is directly bonded suggests that an effect of metal carbonyl complexation to the phosphorus lone pair in (i-$Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) is a change in the P–P–P bond angles involving the terminal phosphorus atoms. At the present time X-ray structural data are not available to test this idea.

(2) The one-bond $|^1J(P-H)|$ coupling constant of (i-$Pr_2NP)_2P(H)Fe_2(CO)_6$ (VI) increases as expected from 129 to 253 and 278 Hz for VIII and IX, respectively, whereas the two-bond $|^2J(P-H)|$ coupling constant of VI (8 Hz) decreases below the limits of detectability upon coordination of VI to $M(CO)_n$ groups to give VIII and IX, respectively.

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Registry No. I, 101997-82-4; II (X = Cl), 101997-84-6; II (X = Br), 101997-85-7; II (X = OMe), 101997-86-8; II (X = OEt), 101997-87-9; II (X = H), 101997-88-0; III, 112863-59-9; IV, 112895-70-2; VII, 102046-52-6; VIII, 112895-69-9; IX, 112863-60-2; $Cr(CO)_6$, 13007-92-6; $Fe_2(CO)_9$, 15321-51-4; $Mn_2(CO)_{10}$, 10170-69-1; (i-$Pr_2NPH)_2PN(Pr$-$i)_2$, 101997-89-1; (i-$Pr_2NPH)_2PCl$, 102046-53-7.

Supplementary Material Available: Listings of positional parameters, anisotropic thermal parameters, and bond angles and distances for (i-$Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ and (i-$Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$ (11 pages); listings of observed and calculated structure factors (132 pages). Ordering information is given on any current masthead page.

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The Balance of Steric and Electronic Factors in Co_3 Cluster Geometry: Synthesis, Structure, Computations, and Electrochemistry of $[Co(\mu\text{-}Cy_2P)(CO)_2]_3$ (Cy = Cyclohexyl)

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Reaction of $Co_2(CO)_8$ with Cy_2PH (Cy = cyclohexyl) (1/2) in toluene under reflux (8 h) yields $[Co(\mu\text{-}Cy_2P)(CO)_2]_3$ (**1**) in 65% yield. The complex has been studied spectroscopically and electrochemically. The solid-state structure has been determined by X-ray diffraction and the electronic structure probed by extended Hückel molecular orbital calculations on the model complex $[Co(\mu\text{-}H_2P)(CO)_2]_3$. Crystal data: $C_{40}H_{66}Co_3O_6P_3$, $M_r = 912.69$, monoclinic, $P2_1/a$ (No. 14), $a = 18.912$ (7) Å, $b = 13.081$ (5) Å, $c = 20.253$ (7) Å, $\beta = 108.08$ (3) Å, $V = 4762.9$ (5) Å^3, $D_{calcd} = 1.273$ g cm^{-3}, $Z = 4$, λ(Mo Kα) = 0.71073 Å (graphite monochromator), μ(Mo Kα) = 11.68 cm^{-1}. Methods: MULTAN, difference Fourier, full-matrix least squares. Refinement of 3788 reflections ($I > 3\sigma(I)$) out of 8992 unique observed reflections ($2° < 2\theta < 50°$) gave R and R_w values of 0.0710 and 0.0800, respectively. The data/parameter ratio = 7.471. The molecular structure of **1** consists of a Co_3 triangle with three edge-bridging Cy_2P^- units. Each Co atom bears two terminal CO ligands. There is considerable distortion of the structure from an idealized D_{3h} geometry. The three phosphido groups lie above, in, and below the Co_3 plane. In addition, each pair of terminal CO ligands adopts a configuration such that each C–Co–C plane is skewed from an orthogonal, idealized (D_{3h}) geometry. The overall geometry is roughly C_2. In solution, ^{31}P NMR spectra indicate a rapid fluxional motion that results in the phosphido ligands becoming equivalent. Extended Hückel calculations show that this cannot occur via a D_{3h} geometry. An analysis of possible reaction paths is given. The cyclic voltammetry of **1** in THF displays a reversible one-electron oxidation at 0.49 V (vs SCE), a reversible one-electron reduction (–0.96 V vs SCE), and a further quasi-reversible one-electron reduction (–1.56 V vs SCE) to give a dianion. The dianion of **1** can be generated chemically by reduction with Na/Hg in THF although the extreme air sensitivity of this brick red material has so far precluded its full characterization.

Introduction

Several di- and trinuclear diphenylphosphido (Ph_2P^-) bridged cobalt complexes have recently been described by Geoffroy and co-workers.[4] These complexes undergo some interesting dimer/trimer interconversions as well as ligand-exchange reactions. In contrast, the reaction of t-Bu_2PH with $Co_2(CO)_8$ produces the dinuclear Co=Co doubly bonded complex $[Co(\mu\text{-}t\text{-}Bu_2P)(CO)_2]_2$, which appears to be relatively inert to reaction with CO or phosphines.[5] The large steric bulk of the t-Bu_2P groups is no doubt at least partially responsible for the lack of reactivity. In order to gain more insight into these systems, we investigated the reaction of Cy_2PH (Cy = cyclohexyl) with $Co_2(CO)_8$. If the differences in reactivity are due to steric factors, we expected to observe complexes of intermediate reactivity between those of Ph_2P^- and t-Bu_2P^- since Cy is not as large as t-Bu but considerably

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