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Dialkylaminophosphorus metal carbonyls. 12. Insertion of phosphorus, sulfur, and selenium into the $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ unit and a novel product from the reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with PhBCl_2 ☆

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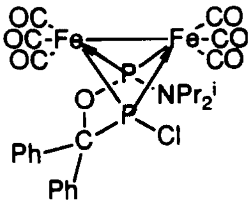
Abstract

Reactions of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with RPCl_2 (R = ^{t}Bu and Ph but not $^i\text{Pr}_2\text{N}$) in boiling toluene give the corresponding yellow $(^i\text{Pr}_2\text{NP})_2(\text{RP})\text{Fe}_2(\text{CO})_6$ derivatives. Similar reactions of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with PX_3(X = Cl, Br) give the corresponding $(^i\text{Pr}_2\text{NP})_2(\text{PX})\text{Fe}_2(\text{CO})_6$ derivatives. Reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with elemental sulfur in boiling toluene gives yellow $(^i\text{Pr}_2\text{NP})_2\text{SFe}_2(\text{CO})_6$. Reactions of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with E_2Cl_2 (E = S, Se) give $(^i\text{Pr}_2\text{NP})_2\text{E}_2\text{Fe}_2(\text{CO})_6$. Treatment of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with boiling CCl_4 results in chlorination to give light yellow $(^i\text{Pr}_2\text{N})_2\text{P}_2\text{Cl}_2\text{Fe}_2(\text{CO})_6$. Reaction of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with PhBCl_2 in boiling toluene gives yellow $[(^i\text{Pr}_2\text{NP})(\text{ClP})\text{OCPh}_2]\text{Fe}_2(\text{CO})_6$. An X-ray diffraction study reveals that the structure of $[(^i\text{Pr}_2\text{NP})(\text{ClP})\text{OCPh}_2]\text{Fe}_2(\text{CO})_6$ is analogous to that of products previously obtained from reactions of $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ with aldehydes or ketones in which expulsion of the phosphorus-bridging carbonyl is followed by addition of the phosphorus atoms across the aldehyde or ketone carbonyl, leading to a central $\text{Fe}_2\text{P}_2\text{OC}$ unit.

Keywords: Iron; Carbonyl; Phosphorus; Sulfur; Selenium; Boron

1. Introduction

Phosphorus-bridging carbonyl expulsion from $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (**I** in Fig. 1) at ~ 110° results in a reactive $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ unit, possibly the diradical **II** (Fig. 1), which was shown in previous papers of this series [1,2] to add across the carbon–oxygen double bonds of aldehydes, ketones, or anhydrides, the carbon–nitrogen triple bonds of nitriles, and the carbon–carbon double bond of acrylonitrile. In addition, alcohols (ROH: R = Me, Et) were shown [3] to add across the $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ unit to form the corresponding $(^i\text{Pr}_2\text{NPOR})(^i\text{Pr}_2\text{NPH})\text{Fe}_2(\text{CO})_6$ derivatives. This paper reports a new type of reaction of the $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ unit generated from $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$, namely the insertion of a third phosphorus atom, one or two sulfur atoms, or two selenium atoms between the two phosphorus atoms of the $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ unit to give $(^i\text{Pr}_2\text{NP})_2(\text{PR})\text{Fe}_2(\text{CO})_6$ with a P–P–P chain (**III** in Fig. 1), $(^i\text{Pr}_2\text{NP})_2\text{SFe}_2(\text{CO})_6$ with a P–S–P chain (**IV** in Fig. 1), or $(^i\text{Pr}_2\text{NP})_2\text{E}_2\text{Fe}_2(\text{CO})_6$ (E = S, Se) with a P–E–E–P chain (**V** in Fig. 1), respectively. This paper also reports the corresponding reaction of PhBCl_2 with $(^i\text{Pr}_2\text{NP})_2\text{COFe}_2(\text{CO})_6$ (**I** in Fig. 1), which follows a totally different course, giving $[(^i\text{Pr}_2\text{NP})(\text{ClP})\text{OCPh}_2]\text{Fe}_2(\text{CO})_6$ (**VI**) closely related to the $[(^i\text{Pr}_2\text{NP})_2\text{OCPh}_2]\text{Fe}_2(\text{CO})_6$ (**VII**: R = R′ = Ph) obtained by heating $(^i\text{Pr}_2\text{NP})_2\text{Fe}_2(\text{CO})_6$ with benzophenone [2].



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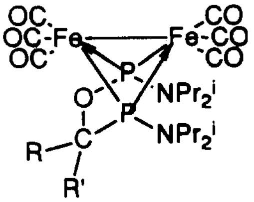

VII

☆ This paper is dedicated to Prof. Fausto Calderazzo in recognition of his many contributions to inorganic and organometallic chemistry.

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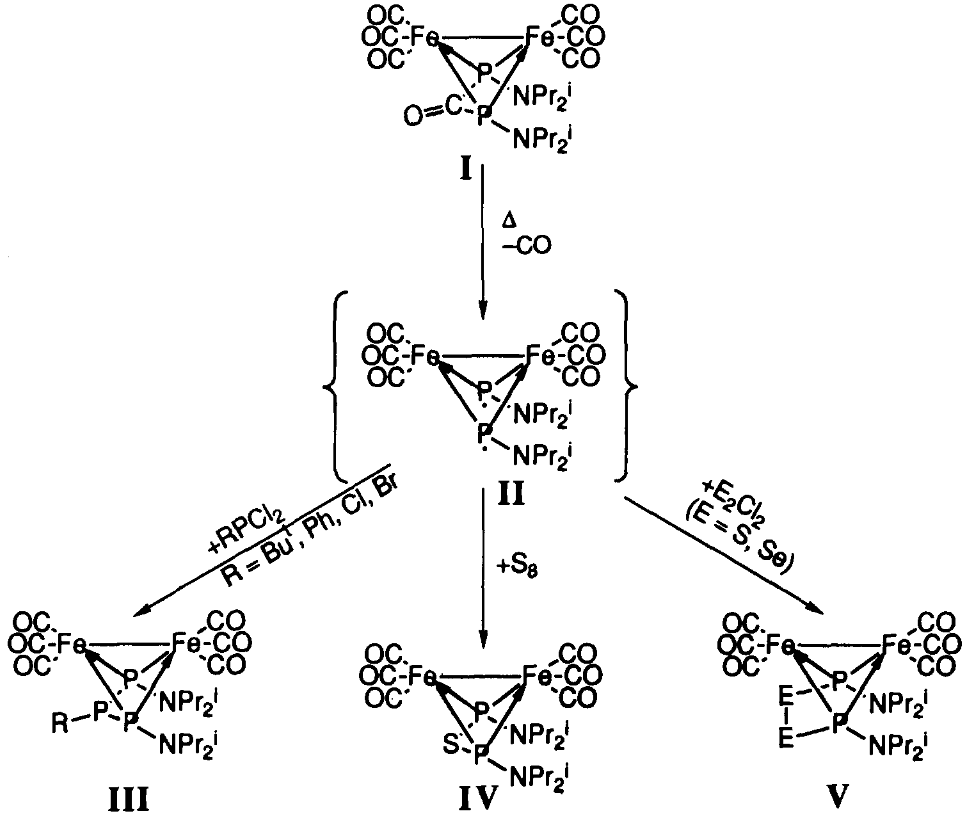

Fig. 1. General scheme for the reactions of $(^iPr_2NP)_2COFe_2(CO)_6$ with $RPCl_2$ (R = ^{t}Bu, Ph, Cl, Br), S_8, and E_2Cl_2(E = S, Se).

2. Experimental section

The general experimental conditions are the same as described the previous paper in this series [1]. IR ν(CO) frequencies and ^{31}P NMR spectra of the products are given in Table 1, proton-decoupled ^{13}C NMR spectra are given in Table 2, and proton NMR spectra are given in Table 3.

2.1. Preparation of $(^iPr_2NP)_2(^tBuP)Fe_2(CO)_6$

A solution of 4.5 g (7.9 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$ and 1.2 g (7.5 mmol) of $^tBuPCl_2$ [4] in 100 ml of toluene was boiled under reflux for 4 h. After removal of solvent in vacuum from the filtered solution, the residue was chromatographed on a silica gel column, with 1 : 1 hexane/dichloromethane being used to elute

Table 1
IR ν(CO) frequency and phosphorus-31 NMR spectra of insertion products into the $(^iPr_2NP)_2Fe_2(CO)_6$ unit and related compounds

Compound [a]	IR ν(CO) (cm^{-1}) [a]	Phosphorus-31 NMR (δ) [b]		
		Middle P	End P	J(P–P) Hz
$(^tBuP)_3Fe_2(CO)_6$ [c]	2050s, 2012s, 1982s, 1971s, 1960s, 1932w	249.0t	99.9d	176
$(^iPr_2NP)_3Fe_2(CO)_6$ [d]	2048s, 2008s, 1986s, 1958s, 1947m	292.2t	170.3d	264
$(^iPr_2NP)_2(PCl)Fe_2(CO)_6$ [d]	2062m, 2023s, 1996s, 1982s, 1967s	318.7t	147.8d	254
$(^iPr_2NP)_2(PBr)Fe_2(CO)_6$ [d]	2059m, 2020s, 1993s, 1984m, 1967s	302.9t	142.2d	257
$(^iPr_2NP)_2(^tBuP)Fe_2(CO)_6$	2044m, 2001s, 1977s, 1957s, 1940s	334.5t	127.1d	212
$(^iPr_2NP)_2(PhP)Fe_2(CO)_6$	2047m, 2007s, 1981s, 1961s, 1945s	285.6t	131.5d	201
$(^iPr_2NP)_2SFe_2(CO)_6$	2052m, 2011s, 1988s, 1970s, 1950m	–	143.0	–
$(^iPr_2NP)_2S_2Fe_2(CO)_6$	2056m, 2018s, 1990s, 1978s, 1956m	–	278.3s	–
$(^iPr_2NP)_2Se_2Fe_2(CO)_6$	2056m, 2020s, 1990s, 1980s, 1961m	–	274.3s	–
$(^iPr_2N)_2P_2Cl_2Fe_2(CO)_6$	2066m, 2032s, 1990s	278.2d	268.4d	123
$[(^iPr_2NP)_2OCPh_2]Fe_2(CO)_6$ [e]	2052m, 2013s, 1987s, 1974m, 1957m	288.6d	259.1(d)	128
$[(^iPr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$	2063m, 2024s, 2000s, 1983s, 1968s	289.5d	279.0d	116

[a] These IR ν(CO) frequencies were measured in CH_2Cl_2 solution. Me = methyl; ^{i}Pr = isopropyl, ^{t}Bu = *tert*-butyl, Ph = phenyl.
[b] The ^{31}P NMR spectra were taken in $CDCl_3$ solution: s = singlet, d = doublet, t = triplet.
[c] Data from Y.W. Li, M.G. Newton, N.K. Bhattacharyya and R.B. King, *Inorg. Chem., 31* (1992) 2069.
[d] Data from R.B. King, F.-J. Wu and E.M. Holt, *J. Am. Chem. Soc., 109* (1987) 7764.
[e] Data from R.B. King, N.K. Bhattacharyya and E.M. Holt, *J. Organomet. Chem., 421* (1991) 247.

Table 2
Proton-decoupled carbon-13 NMR spectra [a] of insertion products into the $(^iPr_2NP)_2Fe_2(CO)_6$ unit and related compounds

Compound	Isopropyl groups		Terminal CO	Other
	CH	CH_3		
$(^iPr_2NP)_2(^tBuP)Fe_2(CO)_6$	53.8	22.6	212.8	*tert*-butyl C: 43.5d(6); Me: 29.8
$(^iPr_2NP)_2(PhP)Fe_2(CO)_6$	53.7	22.5	212.2	phenyl: 130.8, 129.5, 128.1
$(^iPr_2NP)_2SFe_2(CO)_6$	54.8	22.2	209.9	–
$(^iPr_2NP)_2S_2Fe_2(CO)_6$	56.3	24.2	213.1	–
$(^iPr_2NP)_2Se_2Fe_2(CO)_6$	57.0	24.5	212.6	–
$(^iPr_2NP)_2P_2Cl_2Fe_2(CO)_6$	58.1	23.5	210.7	–
$[(^iPr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$	54.8	23.6	211.0	C–O bonded to P_2: 140.6; phenyl: 127.9–127.1

[a] These spectra were taken in $CDCl_3$ solutions using Me_4Si as an internal standard; d = doublet; other resonances appear as singlets.

the black-yellow band. Evaporation of the filtered eluates gave 0.86 g (18% yield) of yellow, air-sensitive $(^iPr_2NP)_2(^tBuP)Fe_2(CO)_6$ (**III**: R = ^{t}Bu in Fig. 1), m.p. 166–167°C. Anal. Calcd. for $C_{22}H_{37}Fe_2N_2O_6P_3$: C, 41.9; H, 5.9; N, 4.4: Found: C, 41.9; N, 5.9; N, 4.4%.

2.2. Preparation of $(^iPr_2NP)_2(PhP)Fe_2(CO)_6$

A solution of 1.85 g (3.25 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$ and 0.60 g (3.25 mmol) of $PhPCl_2$ in 100 ml of toluene was boiled under reflux for 7 h. Examination of the reaction mixture by ^{31}P NMR at this point revealed a minor singlet at δ 170.3 assigned to $^iPr_2NPCl_2$ (lit. [5] δ 167.7). Solvent was removed from the filtrate in vacuo and the residue was chromatographed on silica gel with 1:1 hexane/dichloromethane as eluent. Evaporation of the eluate from the red-yellow band gave 1.13 g (54% yield) of yellow, air-sensitive $(^iPr_2NP)_2(PhP)Fe_2(CO)_6$ (**III** in Fig. 1: R = Ph), m.p. 111–113°C. Anal. Calcd. for $C_{24}H_{33}Fe_2N_2O_6P_3$: C, 44.3; H, 5.1; N, 4.3. Found: C, 44.6; H, 5.1; N, 4.1%.

2.3. Reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ with PCl_3

A solution of 1.0 g (1.75 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$ and 0.16 ml (1.82 mmol) of 99% phosphorus trichloride in 120 ml of toluene was boiled under reflux for 16 h. Removal of solvent gave a residue shown by its ^{31}P NMR spectrum in $CDCl_3$ to be the previously reported [6] $(^iPr_2NP)_2(PCl)Fe_2(CO)_6$ (**III** in Fig. 1: R = Cl) as well as an additional species showing an AX_2 pattern at δ 149.6 and 319.1 with $|J| = 255$ Hz.

2.4. Reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ with PBr_3

A solution of 1.0 g (1.75 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$ and 0.18 ml (1.89 mmol) of phosphorus tribromide in 150 ml of toluene was boiled under reflux for 8 h. The ^{31}P NMR spectrum of the crude reaction mixture at this point indicated the presence of the known [6] $(^iPr_2NP)_2(PBr)Fe_2(CO)_6$ (**III** in Fig. 1: R = Br) and $^iPr_2NPBr_2$ as well as an unknown complex exhibiting a singlet at $\delta - 304.52$, which was presented in too limited quantities for isolation.

2.5. Reaction of $(^iPr_2NP)_2COFe_2(CO)_6$ with $Cl_2PCH_2CH_2PCl_2$

A solution of 2.83 g (4.96 mmol) of $(^iPr_2NP)_2COFe_2(CO)_6$ and 1.0 g (4.30 mmol) of $Cl_2PCH_2CH_2PCl_2$ in 120 ml of toluene was boiled under reflux for 12 h. The ^{31}P NMR spectrum of the crude product mixture showed only $^iPr_2NPCl_2$ with no evidence for the formation of any iron carbonyl complexes with P_3Fe_2 structural units.

Table 3
Proton NMR spectra of insertion products into the $(^iPr_2NP)_2Fe_2(CO)_6$ unit [a]

Compound	Isopropyl Groups		Other
	CH	CH_3	
$(^iPr_2NP)_2(^tBuP)Fe_2(CO)_6$	3.41sp(7)	1.19dd(9.7)	Me: 1.44d(10)
$(^iPr_2NP)_2(PhP)Fe_2(CO)_6$	3.43sp(7)	1.11dd(19.7)	Ph: 7.5–7.9
$(^iPr_2NP)_2SFe_2(CO)_6$	3.68sp(7)	1.19d(7)	–
$(^iPr_2NP)_2S_2Fe_2(CO)_6$	4.04sp(7)	1.46d(7)	–
$(^iPr_2NP)_2Se_2Fe_2(CO)_6$	4.09sp(6)	1.48d(7)	–
$(^iPr_2NP)_2P_2Cl_2Fe_2(CO)_6$	4.01	1.43, 1.35	–
$[(^iPr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$	3.97	1.42d(7)	Ph: 7.62–7.26 (not resolved)

[a] The proton NMR spectra were obtained in $CDCl_3$ solutions using tetramethylsilane as an internal standard; d = doublet, dd = double doublet, t = triplet, sp = septet. Coupling constants are given in parentheses.

2.6. Reactions of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with ${}^{i}Pr_2NPCl_2$ and with $MeP(O)Cl_2$

A solution of 0.50 g (0.88 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ and 0.40 g (1.98 mmol) of ${}^{i}Pr_2NPCl_2$ in 70 ml of toluene was heated for 16 h under reflux in a 135°C oil bath. The ^{31}P NMR spectrum of the crude reaction mixture revealed no evidence for the formation of any of the known [7] $({}^{i}Pr_2NP)_3Fe_2(CO)_6$ (**III** in Fig. 1: $X = {}^{i}Pr_2N$).

A similar procedure for the reaction of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with $MeP(O)Cl_2$ failed to give any evidence by ^{31}P NMR for the formation of any P_3Fe_2 complex.

2.7. Preparation of $({}^{i}Pr_2NP)_2SFe_2(CO)_6$

A mixture of 1.40 g (2.46 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ and 0.10 g (3.13 mmol) of elemental sulfur (S_8) in 70 ml of toluene was heated under reflux at 100°C for 5 h. Solvent was removed in vacuo from the filtered reaction mixture. The residue was extracted with hexane. Concentration and cooling of the filtered hexane extract gave 1.26 g (89% yield) of yellow $({}^{i}Pr_2NP)_2SFe_2(CO)_6$ (**IV** in Fig. 1), m.p. 131–132°C. Anal. Calcd. for $C_{18}H_{18}Fe_2N_2P_2S$: C, 37.6; H, 4.9; N, 4.9; S, 5.6. Found: C, 37.7; H, 4.9; N, 4.9; S, 5.6%.

The reaction of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with commercially available elemental gray selenium was also investigated using a similar procedure. The ^{31}P NMR spectrum of the reaction mixture indicated only the presence of unreacted $({}^{i}Pr_2NP)_2COFe_2(CO)_6$. Increasing the reaction temperature led only to the decomposition of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with no evidence for the formation of any new soluble organophosphorus iron carbonyl complexes.

2.8. Preparation of $({}^{i}Pr_2NP)_2S_2Fe_2(CO)_6$

A solution of 2.56 g (4.49 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ and 0.5 ml (6.1 mmol) of unredistilled commercial 97% disulfur dichloride (S_2Cl_2) in 120 ml of hexane was boiled under reflux. The ^{31}P NMR spectrum after 2.5 h of heating exhibited only unreacted $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ as well as ${}^{i}Pr_2NP(S)Cl_2$. The heating was continued for one week. At that point the ^{31}P NMR spectrum indicated consumption of all of the $({}^{i}Pr_2NP)_2COFe_2(CO)_6$. Solvent was removed from the filtered reaction mixture in vacuum and then the ${}^{i}Pr_2NP(S)Cl_2$ by sublimation at 80°C/0.02 mm. The residue was chromatographed on silica gel using hexane to elute the broad yellow-brown band. Evaporation of the filtered eluate in vacuum followed by crystallization from a mixture of hexane and dichloromethane gave a mixture of $({}^{i}Pr_2NP)_2SFe_2(CO)_6$ and $({}^{i}Pr_2NP)_2S_2Fe_2(CO)_6$. Repeated chromatography and recrystallization by similar procedures ultimately separated 0.32 g (12% yield) of pure yellow $({}^{i}Pr_2NP)_2S_2Fe_2(CO)_6$ (**V** in Fig. 1: E = S). Anal. Calcd. for $C_{18}H_{28}Fe_2N_2P_2S_2$: C, 35.6; H, 4.7; N, 4.6; S, 10.6. Found: C, 35.6; H, 4.6; N, 4.6; S, 10.7%.

2.9. Isolation of ${}^{i}Pr_2NP(S)Cl_2$

A yellow solution containing 3.0 ml (37.5 mmol) of disulfur dichloride (redistilled over P_4O_{10}) and 6.67 g (11.7 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ in 250 ml of toluene was boiled under reflux for 16 h. Removal of solvent from the filtered reaction mixture followed by sublimation of the residue at 70°C/0.01 mm gave 1.63 g (59% yield) of ${}^{i}Pr_2NP(S)Cl_2$. Anal. Calcd. for $C_6H_{14}NPSCl_2$: C, 30.8; H, 6.0; N, 6.0; S, 13.7. Found: C, 31.4; H, 5.8; N, 5.7; S, 15.7%.

2.10. Reaction of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with sulfur dichloride

A solution of 1.0 g (1.75 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ and 0.20 g (1.91 mmol) of sulfur dichloride (redistilled over P_4O_{10}) in 70 ml of toluene was stirred at room temperature for 16 h. The ^{31}P NMR spectrum of the reaction mixture at this point exhibited resonances for unchanged $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ as well as a δ 51 resonance assigned to ${}^{i}Pr_2NP(S)Cl_2$. The reaction mixture was then boiled under reflux for 16 h. The ^{31}P NMR spectrum of the resulting mixture indicated the presence of ${}^{i}Pr_2NP(S)Cl_2$, $({}^{i}Pr_2NP)_2SFe_2(CO)_6$, and $({}^{i}Pr_2NP)_2S_2Fe_2(CO)_6$ by resonances at δ 51, 143, and 278, respectively, and the complete consumption of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$. Two minor components exhibiting ^{31}P NMR singlets at δ 70 and δ 208 were also observed; these products were present in only small quantities and were not isolated.

2.11. Preparation of $({}^{i}Pr_2NP)_2Se_2Fe_2(CO)_6$

A solution of 3.53 g (6.18 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ and 1.43 g (6.18 mmol) of 99% commercial diselenium dichloride (Se_2Cl_2) in 70 ml of toluene was boiled under reflux for 10 h. The ^{31}P NMR spectrum of the crude reaction mixture exhibited two singlets at δ 105 and δ 274. A product isolation procedure similar to that given above for $({}^{i}Pr_2NP)_2S_2Fe_2(CO)_6$ including repeated chromatography on silica gel and recrystallization gave 0.22 g (5% yield) of brown $({}^{i}Pr_2NP)_2Se_2Fe_2(CO)_6$ (V in Fig. 1: E = Se), m.p. 137–138°C. Anal. Calcd. for $C_{18}H_{28}Fe_2N_2P_2Se_2$: C, 30.9; H, 4.0; N, 4.0. Found: C, 31.0; H, 4.1; N, 4.1%.

2.12. Reaction of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ with carbon tetrachloride

A solution of 1.1 g (1.93 mmol) of $({}^{i}Pr_2NP)_2COFe_2(CO)_6$ in 150 ml of carbon tetrachloride was boiled under reflux for 48 h. The ^{31}P NMR spectrum of the reaction mixture indicated the presence of $^{i}Pr_2NPCl_2$ as well as $(^{i}Pr_2N)_2P_2Cl_2Fe_2(CO)_6$ as the principal product. Solvent was removed from the filtered reaction mixture in vacuum. The residue was extracted with hexane. Concentrating and cooling the filtered hexane solution gave 0.86 g (45% yield) of light yellow $(^{i}Pr_2N)_2P_2Cl_2Fe_2(CO)_6$, m.p. 134–135°C. Anal. Calcd. for $C_{18}H_{28}Cl_2Fe_2N_2O_6P_2$: C, 35.3; H, 4.6; Cl, 11.6. Found: C, 35.5; H, 4.6; Cl, 11.6%.

2.13. Reaction of $(^{i}Pr_2NP)_2COFe_2(CO)_6$ with phenyldichloroborane

A solution of 3.0 g (5.26 mmol) of $(^{i}Pr_2NP)_2COFe_2(CO)_6$ and 0.70 ml (5.26 mmol) of commercial 95% phenyldichloroborane ($C_6H_5BCl_2$) in 130 ml of toluene was heated under reflux to 105°C in an oil bath for 50 h. The ^{31}P NMR spectrum of the reaction mixture exhibited a pair of doublets at δ 290.5, 280.3 ($|J|$ = 115 Hz) assigned to $[(^{i}Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$ (**VI**), a second pair of doublets at δ 266, and 143 ($|J|$ = 122 Hz), and a singlet at δ 170.3 assigned to $^{i}Pr_2NPCl_2$. Solvent was removed from the reaction mixture under reduced pressure and the residue was extracted with a mixture of hexane and dichloromethane. The filtered and concentrated extract was chromatographed on a silica gel column. The resulting yellow band was eluted with hexane. Concentration and cooling the filtered eluate gave 0.20 g (12% yield) of yellow $[(^{i}Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$ (**VI**), m.p. 175–176°C. Anal. Calcd. for $C_{25}H_{24}ClFe_2NO_7P_2$: C, 45.5; H, 3.7; Cl, 5.4; N, 2.1. Found: C, 46.2; H, 3.9; Cl, 5.5; N, 2.1%.

2.14. Structure determination of $[(^{i}Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$

An orange needle crystal of $Fe_2P_2ClC_{24}O_6NH_{24}$ = $[(^{i}Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$ from hexane was fixed in a random orientation on a glass fiber and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator. Cell dimensions were determined by least squares refinement of the angular positions of 25 carefully centered independent reflections for each sample in the 10–40° 2θ range during the normal alignment procedure. Intensity data using Cu K_α radiation (λ = 1.54184 Å) were collected at a temperature of 23 ± 1°C over a θ range of 2–75° using the ω-2θ technique. Of the 5899 reflections which were collected, 5691 were unique (R_{int} = 0.313). The intensities of three representative reflections were measured after every 120 min of X-ray exposure time. No decay correction was applied. The linear absorption coefficient, μ, for Cu Kα radiation is 105.6 cm^{-1}. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.35 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 7.45028×10^{-8}).

The structure was solved by direct methods [8] and expanded using Fourier techniques [9]. All non-hydrogen atoms were refined anisotropically except C5 which consistently refined to non-positive definite anisotropic factors. C5 was refined isotropically. Hydrogen atoms were included by calculation of estimated coordinates but not refined. The final cycle of full-matrix least squares refinement was based on 2770 observed reflections ($I > 3\sigma(I)$) and 339 variable parameters and converged (largest parameter shift was 0.06 times its esd) with unweighted and weighted agreement factors of $R = 0.110$ and $R_w = 0.129$. These R values are higher than those from typical structure determinations probably because of the rather large empirical absorption correction coupled with the fact that only 49% of the possible data was observed. Neutral atom scattering factors were taken from Cromer and Waber [10]. Anomalous dispersion effects were included in F_{calc} [11]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [12]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [13]. All calculations were performed using the teXsan [14] crystallographic software package of Molecular Structure Corporation.

The crystal data for $[(^{i}Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$ (**VI**) are summarized in Table 4 and its structure is depicted in Fig. 2. Selected bond distances and angles are given in Tables 5 and 6, respectively, and atom coordinates in Table 7. Complete lists of bond lengths and angles and a table of anisotropic displacement

Table 4
Crystal data for $[(^{i}Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$

molecular weight	631.55
crystal dimensions (mm)	0.20 × 0.30 × 0.45 mm
crystal system	monoclinic
space group	$P2_1/a$ (non-standard No. 14)
a (Å)	15.467(1)
b (Å)	10.589(1)
c (Å)	17.263(2)
β (deg)	96.124(9)
V(Å^3)	2811.3(4)
F(000)	1288
μ(Cu Kα) (cm^{-1})	105.57
D_{calcd} (g cm^{-3})	1.492
Z	4
no of total reflections	5691
no of observed reflections	2770
octants collected	$+h, +k, \pm l$
R	0.110
R_w	0.129

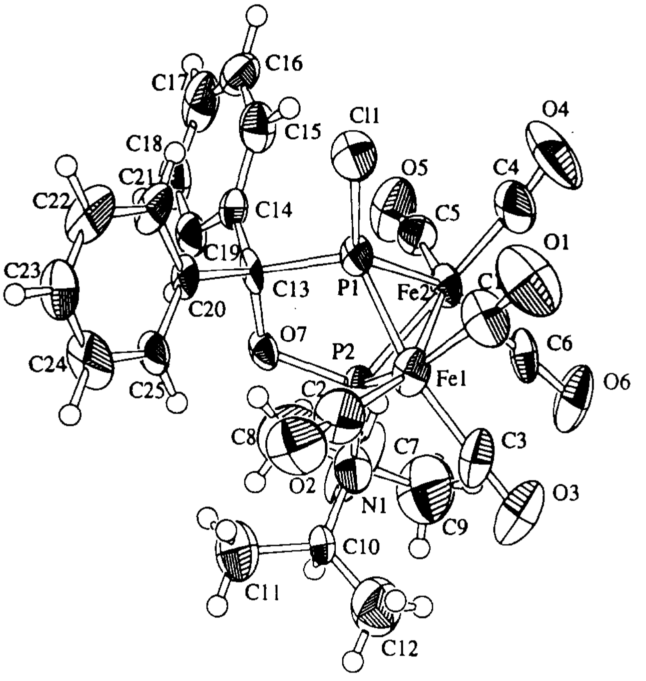

Fig. 2. ORTEP diagram for the structure of $[(^i\mathrm{Pr_2NP})(\mathrm{ClP})\mathrm{OCPh_2}]\mathrm{Fe_2(CO)_6}$ (**VI**).

parameters have been deposited at the Cambridge Crystallographic Data Center.

Table 6
Selected bond angles (°) for $[(^i\mathrm{Pr_2NP})(\mathrm{ClP})\mathrm{OCPh_2}]\mathrm{Fe_2(CO)_6}$ (**VI**)

Fe2–Fe1–P1	52.9(1)	Fe2–Fe1–P2	53.6(1)
Fe2–Fe1–C1	93.0(7)	Fe2–Fe1–C2	151.8(6)
Fe2–Fe1–C3	101.3(5)	P1–Fe1–P2	70.9(2)
P1–Fe1–C1	91.8(8)	P1–Fe1–C2	104.5(7)
P1–Fe1–C3	154.2(6)	P2–Fe1–C1	146.6(7)
P2–Fe1–C2	106.3(7)	P2–Fe1–C3	93.2(6)
C1–Fe1–C2	105.6(9)	C1–Fe1–C3	91.2(10)
C2–Fe1–C3	99.3(9)	Fe1–Fe2–P1	53.5(1)
Fe1–Fe2–P2	53.2(1)	Fe1–Fe2–C4	105.8(7)
Fe1–Fe2–C5	150.3(6)	Fe1–Fe2–C6	94.1(5)
P1–Fe2–P2	71.0(2)	P1–Fe2–C4	93.4(6)
P1–Fe2–C5	105.9(6)	P1–Fe2–C6	147.6(5)
P2–Fe2–C4	158.6(6)	P2–Fe2–C5	102.6(6)
P2–Fe2–C6	90.9(5)	C4–Fe2–C5	95.6(9)
C4–Fe2–C6	95.5(8)	C5–Fe2–C6	104.2(8)
Fe1–P1–Fe2	73.5(2)	Fe1–P1–Cl1	122.3(3)
Fe1–P1–P2	54.5(1)	Fe1–P1–C13	112.2(5)
Fe2–P1–Cl1	127.5(2)	Fe2–P1–P2	55.0(1)
Fe2–P1–C13	108.2(4)	Cl1–P1–P2	176.0(3)
Cl1–P1–C13	109.0(5)	P2–P1–C13	71.5(5)
Fe1–P2–Fe2	73.1(2)	Fe1–P2–P1	54.6(1)
Fe1–P2–O7	110.4(4)	Fe1–P2–N1	130.1(6)
Fe2–P2–P1	54.0(1)	Fe2–P2–O7	110.4(4)
Fe2–P2–N1	127.3(5)	P1–P2–O7	72.3(4)
P1–P2–N1	174.9(6)	O7–P2–N1	103.6(6)
P2–O7–C13	115.9(8)	P2–N1–C7	122(1)
P2–N1–C10	118(1)	Fe1–C1–O1	173(2)
Fe2–C2–O2	177(1)	Fe1–C3–O3	177(1)
Fe4–C4–O4	175(2)	Fe5–C5–O5	172(1)
Fe6–C6–O6	179(1)	P1–C13–O7	99.7(9)
P1–C13–C14	113.0(10)	P1–C13–C20	113(1)

3. Results

3.1. *Atom insertion reactions into the* $(^i\mathit{Pr_2NP})_2\mathit{Fe_2(CO)_6}$ *unit generated by carbonyl extrusion from* $(^i\mathit{Pr_2NP})_2\mathit{CO}$-$\mathit{Fe_2(CO)_6}$

Reactions of $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ (**I**) with $\mathrm{RPCl_2}$ derivatives (R = ^{t}Bu and Ph) in boiling toluene resulted in extrusion of the phosphorus-bridging carbonyl group followed by insertion of an RP unit to give the corresponding $(^i\mathrm{Pr_2NP})_2(\mathrm{RP})\mathrm{Fe_2(CO)_6}$ derivatives (**III**) as yellow air-sensitive solids. These new compounds were characterized by elemental analyses and the similarity of their infrared ν(CO) and ^{31}P NMR spectra to the known [3] $(^i\mathrm{Pr_2NP})_3\mathrm{Fe_2(CO)_6}$ (**III**: R = $^i\mathrm{Pr_2N}$) prepared by a different method, namely the reaction of $\mathrm{Na_2Fe(CO)_4}$ with $^i\mathrm{Pr_2NPCl_2}$ in tetrahydrofuran solution. Interestingly enough, the known $(^i\mathrm{Pr_2NP})_3\mathrm{Fe_2(CO)_6}$ could not be prepared by the analogous reaction of $^i\mathrm{Pr_2NPCl_2}$ with $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ in boiling toluene possibly owing to the greater steric hindrance of $^i\mathrm{Pr_2NPCl_2}$ relative to $\mathrm{PhPCl_2}$ or even to $^t\mathrm{BuPCl_2}$. Reactions of $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ (**I**) with the phosphorus (III) halides, $\mathrm{PX_3}$(X = Cl, Br) in boiling toluene proceeded analogously to the $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$/$\mathrm{RPCl_2}$ (R = ^{t}Bu and Ph) reactions to give the corresponding $(^i\mathrm{Pr_2NP})_2(\mathrm{PX})\mathrm{Fe_2(CO)_6}$ derivatives (**III**: R = Cl, Br in Fig. 1), which were identified by comparison of their ^{31}P NMR spectra with those of authentic materials prepared by reactions of $(^i\mathrm{Pr_2NP})_3\mathrm{Fe_2(CO)_6}$ with the corresponding hydrogen halides, HX (X = Cl, Br) [6]. Similar reactions of $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ with $\mathrm{Cl_2PCH_2CH_2PCl_2}$ and with $\mathrm{MeP(O)Cl_2}$ failed to give any ^{31}P NMR evidence for $(^i\mathrm{Pr_2NP})_2(\mathrm{RP})\mathrm{Fe_2(CO)_6}$ products.

Table 5
Selected bond distances (Å) for $[(^i\mathrm{Pr_2NP})(\mathrm{ClP})\mathrm{OCPh_2}]\mathrm{Fe_2(CO)_6}$ (**VI**)

Fe1–Fe2	2.616(3)	Fe1–P1	2.193(5)
Fe1–P2	2.190(5)	Fe1–C1	1.83(2)
Fe1–C2	1.80(2)	Fe1–C3	1.79(2)
Fe2–P1	2.176(4)	Fe2–P2	2.201(5)
Fe2–C4	1.80(2)	Fe2–C5	1.72(2)
Fe2–C6	1.82(2)	Cl1–P1	2.029(6)
P1 ··· P2	2.542(6)	P1–C13	1.91(1)
P2–O7	1.68(1)	P2–N1	1.66(1)
O1–C1	1.10(2)	O2–C2	1.13(2)
O3–C3	1.14(2)	O4–C4	1.12(2)
O5–C5	1.18(2)	O6–C6	1.12(2)
O7–C13	1.45(2)		

Some related chalcogen insertion reactions were also investigated. Heating $(^i\mathrm{Pr_2NP})_2\mathrm{COFe_2(CO)_6}$ with

Table 7
Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
Fe(1)	0.2726(1)	0.1155(3)	0.1819(1)	3.63(6)
Fe(2)	0.1028(1)	0.1181(3)	0.1573(1)	3.19(6)
Cl(1)	0.1876(3)	0.3563(4)	0.3092(3)	5.0(1)
P(1)	0.1814(3)	0.1804(4)	0.2624(2)	3.01(9)
P(2)	0.1849(2)	−0.0397(4)	0.2041(2)	2.77(9)
O(1)	0.281(1)	0.373(2)	0.122(1)	8.7(5)
O(2)	0.4370(8)	0.070(2)	0.2791(9)	7.1(4)
O(3)	0.3205(10)	0.006(2)	0.0365(8)	7.8(5)
O(4)	0.054(1)	0.376(1)	0.112(1)	9.5(6)
O(5)	−0.0621(7)	0.039(1)	0.2054(7)	6.1(4)
O(6)	0.0979(8)	0.017(1)	−0.0021(7)	6.3(4)
O(7)	0.1790(6)	−0.0557(9)	0.3002(5)	2.9(2)
N(1)	0.1826(10)	−0.187(1)	0.1726(8)	4.3(4)
C(1)	0.283(1)	0.275(2)	0.143(1)	5.5(6)
C(2)	0.373(1)	0.087(2)	0.243(1)	5.8(6)
C(3)	0.301(1)	0.047(2)	0.093(1)	4.8(5)
C(4)	0.074(1)	0.277(2)	0.127(1)	5.5(5)
C(5)	0.003(1)	0.080(2)	0.1857(10)	3.5(3)
C(6)	0.100(1)	0.054(2)	0.0589(9)	3.8(4)
C(7)	0.103(2)	−0.258(2)	0.159(1)	9.6(9)
C(8)	0.061(1)	−0.303(2)	0.219(2)	7.9(8)
C(9)	0.069(2)	−0.283(3)	0.080(1)	8.6(8)
C(10)	0.264(2)	−0.261(3)	0.182(1)	11.3(9)
C(11)	0.295(1)	−0.304(2)	0.258(1)	7.7(7)
C(12)	0.306(1)	−0.282(2)	0.116(1)	7.5(7)
C(13)	0.1684(10)	0.061(1)	0.3428(8)	3.0(3)
C(14)	0.0762(10)	0.059(2)	0.3687(8)	3.0(3)
C(15)	0.026(1)	0.167(2)	0.3739(10)	4.4(5)
C(16)	−0.056(1)	0.160(2)	0.3966(10)	4.5(5)
C(17)	−0.092(1)	0.045(3)	0.412(1)	5.7(6)
C(18)	−0.042(1)	−0.059(2)	0.4096(9)	4.6(5)
C(19)	0.040(1)	−0.054(2)	0.3873(8)	3.4(4)
C(20)	0.2377(10)	0.070(2)	0.4112(8)	3.1(3)
C(21)	0.2342(10)	0.160(2)	0.4681(9)	4.3(4)
C(22)	0.298(1)	0.166(2)	0.532(1)	5.7(5)
C(23)	0.365(1)	0.083(2)	0.537(1)	5.2(5)
C(24)	0.371(1)	−0.008(2)	0.482(1)	5.8(6)
C(25)	0.308(1)	−0.013(2)	0.4186(9)	3.8(4)
H(1)	0.0509	0.2497	0.3599	5.4148
H(2)	−0.0892	0.2394	0.4018	5.4101
H(3)	−0.1521	0.0408	0.4240	6.7741
H(4)	−0.0666	−0.1393	0.4253	5.5957
H(5)	0.0751	−0.1316	0.3833	4.3800
H(6)	0.1853	0.2212	0.4640	5.3088
H(7)	0.2958	0.2294	0.5722	6.5105
H(8)	0.4092	0.0872	0.5815	5.9714
H(9)	0.4208	−0.0672	0.4850	6.9707
H(10)	0.3119	−0.0770	0.3777	4.5656
H(11)	0.2310	−0.3417	0.1718	12.2970
H(12)	0.2477	−0.3176	0.2890	8.7246
H(13)	0.3281	−0.3792	0.2577	8.7246
H(14)	0.3313	−0.2387	0.2834	8.7246
H(15)	0.3386	−0.3605	0.1192	8.5474
H(16)	0.2661	−0.2866	0.0693	8.5474
H(17)	0.3462	−0.2153	0.1098	4.5656
H(18)	0.0636	−0.1773	0.1578	11.0060
H(19)	0.0708	−0.2507	0.2648	8.9170
H(20)	−0.0012	−0.3125	0.2078	8.9170
H(21)	0.0843	−0.3852	0.2326	8.9170
H(22)	0.0072	−0.2949	0.0710	10.2437
H(23)	0.0853	−0.2203	0.0448	10.2437
H(24)	0.0952	−0.3626	0.0651	4.5656

$B_{eq} = \frac{8}{3}\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + iU_{23}bb^*cc^* \cos\alpha)$.

elemental sulfur in boiling toluene resulted in extrusion of the phosphorus-bridging carbonyl group followed by sulfur insertion to give (^{i}Pr$_2$NP)$_2$SFe$_2$(CO)$_6$ (**IV** in Fig. 1) in relatively good yield (89% isolated product). However, a corresponding reaction of (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ with gray selenium failed to give a corresponding product, apparently because of the much lower reactivity of polymeric gray selenium relative to the oligomeric cyclooctasulfur, S_8.

The chalcogens sulfur and selenium could be introduced pairwise as E_2(E = S, Se) units into the (^{i}Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit by reactions of commercially available E_2Cl_2 (E = S, Se) derivatives with (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$. The (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$/S_2Cl_2 reaction gave a 12% yield of (^{i}Pr$_2$NP)$_2$S$_2$Fe$_2$(CO)$_6$ (**V**:E = S in Fig. 1) in boiling hexane but led to decomposition to give ^{i}Pr$_2$NP(S)Cl$_2$ in boiling toluene. The corresponding reaction of (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ with Se_2Cl_2 was performed in boiling toluene but gave only a 5% yield of the insertion product (^{i}Pr$_2$NP)$_2$Se$_2$Fe$_2$(CO)$_6$ (**V**:E = Se in Fig. 1). Reaction of (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ with SCl_2 gave a complicated mixture of (^{i}Pr$_2$NP)$_2$SFe$_2$(CO)$_6$, (^{i}Pr$_2$NP)$_2$S$_2$Fe$_2$(CO)$_6$, and ^{i}Pr$_2$NP(S)Cl$_2$.

An attempt was made to prepare a dichlorocarbene insertion product such as (^{i}Pr$_2$NP)$_2$CCl$_2$Fe$_2$(CO)$_6$ by reaction of (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ in boiling carbon tetrachloride. However, the resulting product had the stoichiometry (^{i}Pr$_2$NP)$_2$Cl$_2$Fe$_2$(CO)$_6$ and more significantly exhibited two coupled doublets rather than a singlet in the ^{31}P NMR spectrum (Table 1) excluding formulation as (^{i}Pr$_2$NP)$_2$CCl$_2$Fe$_2$(CO)$_6$. Suitable X-ray quality crystals of this product have not yet been obtained.

3.2. The reaction of (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ with PhBCl$_2$

The reaction of (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$ with PhBCl$_2$ was originally investigated in an attempt to effect insertion of PhB into the (^{i}Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ unit to give (^{i}Pr$_2$NP)(PhB)Fe$_2$(CO)$_6$ analogous to (^{i}Pr$_2$NP)(PhP)Fe$_2$(CO)$_6$ (**III**: R = Ph in Fig. 1) discussed above. However, the (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$/PhBCl$_2$ reaction followed a different course than the (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$/PhPCl$_2$ reaction in accord with the Lewis acidity of trivalent boron contrasted with the Lewis basicity of trivalent phosphorus. The yellow crystalline product from the (^{i}Pr$_2$NP)$_2$COFe$_2$(CO)$_6$/PhBCl$_2$ reaction contained no boron and was shown by X-ray diffraction to be [(^{i}Pr$_2$NP)(ClP)OCPh$_2$]Fe$_2$(CO)$_6$ (**VI**) analogous to [(^{i}Pr$_2$NP)$_2$OCPh$_2$]Fe$_2$(CO)$_6$ (**VII**: R = R′ = Ph) from (^{i}Pr$_2$NP)$_2$Fe$_2$(CO)$_6$ and benzophenone [2]. The spectroscopic properties of **VI** and **VII** (R = R′ = Ph) are very similar, particularly the AX patterns in the ^{31}P NMR and the positions and relative intensities of the five terminal ν(CO) frequencies in the infrared spectrum. The dimensions of the central Fe$_2$P$_2$OC units in

Table 8
comparison of the geometries of the Fe_2P_2OC units in $[(^i Pr_2NP)_2OCHPh]Fe_2(CO)_6$ (**VII**: R = Ph, R′ = H) and $[(^i Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$ (**VI**)

	$[(^i Pr_2NP)_2OCHPh]Fe_2(CO)_6$	$[(^i Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$
Fe–Fe	2.589(4), 2.609(6)	2.616(3)
Fe–P	2.190(6), 2.231(7), 2.198(8), 2.229(5), 2.199(7), 2.244(1), 2.194(5), 2.243(7)	2.193(5), 2.190(5), 2.176(4), 2.201(5)
P···P	2.614(8), 2.628(6)	2.542(6)
P–C	1.93(3), 1.90(2)	1.91(1)
P–O	1.62(2), 1.64(1)	1.68(1)
P–Fe–P	72.5(2), 72.4(2), 72.5(2), 72.6(2)	70.9(2), 71.0(2)
Fe–P–Fe	73.3(2), 70.8(2), 72.8(2), 71.1(2)	73.5(2), 73.1(2)
Fe–P–C	102.3(8), 90.3(7), 110.6(6), 84.0(4)	112.2(5), 108.2(4)
Fe–P–O	111.9(4), 111.4(7), 110.4(6), 110.5(4)	110.4(6), 110.5(4)
P–C–O	103(1), 103(1)	99.7(9)
P–O–C	115(1), 115.2(12)	115.9(8)

the benzaldehyde adduct [2] $[(^i Pr_2NP)_2OCHPh]Fe_2(CO)_6$ (**VII**: R = Ph, R′ = H) and $[(^i Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$ (**VI**) are very similar (Table 8).

4. Discussion

The reactions of $(^i Pr_2NP)_2COFe_2(CO)_6$ (**I** in Fig. 1) with $RPCl_2$ (R = ^{t}Bu, Ph), PX_3 (X = Cl, Br) and E_2Cl_2 (E = S, Se) most likely consume some of the $(^i Pr_2NP)_2COFe_2(CO)_6$ as a dehalogenating agent and thus proceed in only low to modest yields (5 to 54%) based on $(^i Pr_2NP)_2COFe_2(CO)_6$. However, halogenation products of $(^i Pr_2NP)_2COFe_2(CO)_6$ are not consistently detected in the ^{31}P NMR spectra of the reaction mixtures. Nevertheless, resonances assignable to $^i Pr_2NPX_2$ degradation products are found in some reaction mixtures. Our experimental results do not exclude the possibility that the phosphorus-bridging CO group acts as a dehalogenating agent upon extrusion being converted to the corresponding carbonyl halide $O=CX_2$(X = Cl, Br).

The dehalogenating ability of $(^i Pr_2NP)_2COFe_2(CO)_6$ (**I**) is also indicated by its reaction with carbon tetrachloride to give the chlorinated product $(^i Pr_2NP)_2P_2Cl_2Fe_2(CO)_6$. However, this product has not been found in the ^{31}P NMR spectra of any of the mixtures obtained from reactions of $(^i Pr_2NP)_2COFe_2(CO)_6$ with other chlorides such as $^t BuPCl_2$, $PhPCl_2$, PCl_3, SCl_2, S_2Cl_2, or Se_2Cl_2.

The reaction of $(^i Pr_2NP)_2COFe_2(CO)_6$ (**I**) with elemental sulfur proceeds in essentially quantitative yield after allowing for losses in product isolation. This reaction necessarily involves no dehalogenation and thus can proceed according to the following equation

$$8\ (^i Pr_2NP)_2COFe_2(CO)_6 + S_8 \longrightarrow 8\ (^i Pr_2NP)_2SFe_2(CO)_6 + 8\ CO \qquad (2)$$

This reaction can incorporate all of the Fe_2P_2 units from the starting material into the product thereby leading to efficient conversion of $(^i Pr_2NP)_2COFe_2(CO)_6$ to $(^i Pr_2NP)_2SFe_2(CO)_6$.

The most unusual reaction found in this work is the $(^i Pr_2NP)_2COFe_2(CO)_6/PhBCl_2$ reaction to give $[(^i Pr_2NP)(ClP)OCPh_2]Fe_2(CO)_6$ (**VI**), which is formally derived by addition of benzophenone to the $(^i Pr_2NP)(ClP)Fe_2(CO)_6$ unit derived by CO extrusion from the hypothetical phosphorus-bridging carbonyl derivative $(^i Pr_2NP)(ClP)COFe_2(CO)_6$. In the $(^i Pr_2NP)_2COFe_2(CO)_6/PhBCl_2$ reaction the $PhBCl_2$ reagent serves two functions:

(1) double arylation of the phosphorus-bridging carbonyl group similar to the alkylation and arylation of free carbon monoxide with trialkyl- and triarylboranes, R_3B, to give the corresponding $(-R_2C-O-BR-)_3$ heterocyclic derivatives [15,16];

(2) cleavage of a P–N bond to give a P–Cl bond similar to the reaction of $(^i Pr_2NP)_2COFe_2(CO)_6$ with HBr to give $(^i Pr_2NPBr)(HBr)Fe_2(CO)_6$ [3].

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[1] (a) For part 11 of this series see Y.W. Li, M.G. Newton, and R.B. King, *Inorg. Chem., 32* (1993) 5720; (b) portions of the present paper were presented at the XVth International Conference on Organometallic Chemistry, Warsaw, Poland, August, 1992, abstracts p. 83.

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