Journal of Organometallic Chemistry, 446 (1993) 167–175

JOM 22874

Mixed (μ-alkane- and arenethiolato)(μ-phosphido)hexacarbonyldiiron complexes. Synthesis and P–Cl reactivity *

Dietmar Seyferth, Karen S. Brewer, Gary B. Womack and Colin M. Archer

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139 (USA)

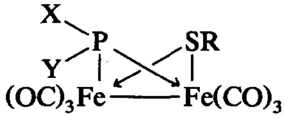
(Received February 14, 1992)

Abstract

Reactions of the Et_3NH^+ or Li^+ salts of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions (R = ^{t}Bu, Et, Ph) with chlorophosphines (PCl_3, Ph_2PCl, $PhPCl_2$, CH_3PCl_2) gave $(\mu\text{-Cl}_2P)(\mu\text{-RS})Fe_2(CO)_6$ (R = ^{t}Bu, Et, Ph), $(\mu\text{-Ph}_2P)(\mu\text{-RS})Fe_2(CO)_6$ (R = ^{t}Bu, Et), $(\mu\text{-PhPCl})(\mu\text{-EtS})Fe_2(CO)_6$ and $(\mu\text{-CH}_3PCl)(\mu\text{-EtS})Fe_2(CO)_6$. Reactions of the complexes that contain P–Cl bonds with NH_3 and amines and with alkanethiols are described.

1. Introduction

In previous papers, we have described the synthesis and diverse reactions of Et_3NH^+ and Li^+ salts of the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions [1,2]. In this paper, we report reactions of these anions (R = Et, ^{t}Bu, Ph, counterion Et_3NH^+) with phosphorus trichloride and some of its organic derivatives. A brief study of the reactivity of some of the (μ-alkane- and arenethiolato)(μ-chlorophosphido)hexacarbonyldiiron complexes, 1, thus prepared is also reported.

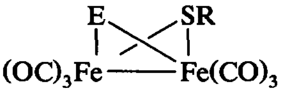


(1)

Complexes of type 1 had been prepared previously by Evertz and Huttner [3] by the reaction of (μ-RClP)(μ-Cl)$Fe_2(CO)_6$ complexes with thiols in the presence of bases at low temperature.

2. Results and discussion

When the $[(\mu\text{-CO})(\mu\text{-RS})Fe_2(CO)_6]^-$ anions react with an electrophile E that is the source of a potential $3e^-$ donor bridging ligand, complexes of type **2** are formed [1].



(2)

When the electrophilic substrate used is a chlorophosphine, a μ-phosphido complex 1 is produced. Such compounds generally are air-stable orange solids and the ones that were prepared are listed in Table 1. While the μ-Cl_2P and μ-Ph_2P complexes were isolated in the form of a single isomer, in the cases of μ-CH_3ClP and the μ-PhClP complexes, two isomers were present according to their ^{31}P NMR spectra (Table 2). For the latter two complexes, four isomers, A–D, are possible (Fig. 1). They are designated with respect to the orientation of the R group on sulfur, and the Cl substituent on P. According to the results of

TABLE 1. (μ-Phosphido)(μ-thiolate)$Fe_2(CO)_6$ complexes prepared

Complex	Yield (%)
$(\mu\text{-Ph}_2P)(\mu\text{-EtS})Fe_2(CO)_6$	80
$(\mu\text{-Ph}_2P)(\mu\text{-Me}_3CS)Fe_2(CO)_6$	91
$(\mu\text{-PhClP})(\mu\text{-EtS})Fe_2(CO)_6$	87
$(\mu\text{-Cl}_2P)(\mu\text{-PhS})Fe_2(CO)_6$	69
$(\mu\text{-Cl}_2P)(\mu\text{-Me}_3CS)Fe_2(CO)_6$	55
$(\mu\text{-Cl}_2P)(\mu\text{-EtS})Fe_2(CO)_6$	78
$(\mu\text{-CH}_3ClP)(\mu\text{-EtS})Fe_2(CO)_6$	89

Correspondence to: Prof. Dr. D. Seyferth.

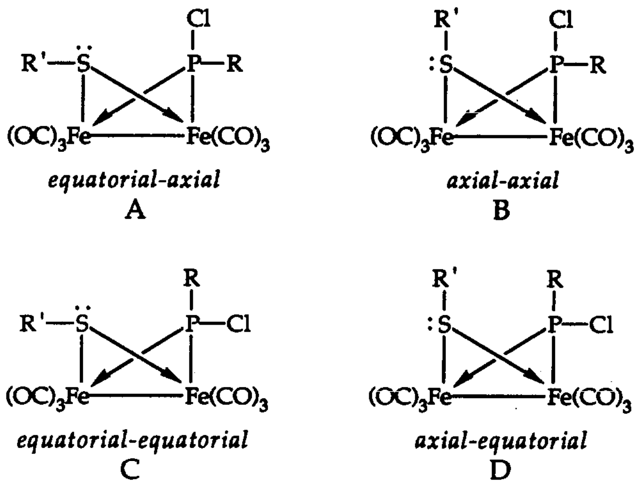
* Dedicated to Professor M.G. Voronkov in recognition of his many contributions to organometallic chemistry.

0022-328X/93/$6.00

TABLE 2. ^{31}P NMR spectra of (μ-phosphido)(μ-thiolate)$Fe_2(CO)_6$ complexes

Complex	^{31}P NMR (δ_P)
(μ-CH_3ClP)(μ-EtS)$Fe_2(CO)_6$	249.6, 265.7 [a]
(μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$	323.1 [a]
(μ-Cl_2P)(μ-t-BuS)$Fe_2(CO)_6$	317.6 [a]
(μ-Cl_2P)(μ-PhS)$Fe_2(CO)_6$	319.5 [c]
(μ-PhClP)(μ-EtS)$Fe_2(CO)_6$	244.4, 271.5 [a]
(μ-Ph_2P)(μ-EtS)$Fe_2(CO)_6$	142.9 [a]
(μ-Ph_2P)(μ-Me_3CS)$Fe_2(CO)_6$	139.8 [b]

[a] In $CDCl_3$. [b] In acetone-d_6. [c] In CD_2Cl_2.



equatorial-axial
A

axial-axial
B

equatorial-equatorial
C

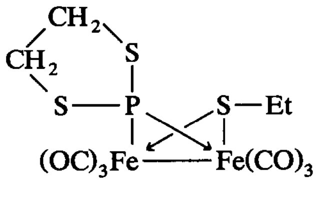
axial-equatorial
D

Fig. 1

Evertz and Huttner, the SR′ group in (μ-RClP)(μ-R′S)$Fe_2(CO)_6$ complexes generally occupies an equatorial position, as in **A** and **C**, and when two isomers are present they are those with the Cl substituent on phosphorus in the axial (**A**) and equatorial (**C**) positions. In all cases, the resonance in the ^{31}P NMR spectrum of **A** occurred at lower field than that of **C**, *e.g.* for (μ-CH_3ClP)(μ-^tBuS)$Fe_2(CO)_6$: **A** isomer, $\delta_P = 262.1$; **C** isomer, 240.0 ppm. These assignments are secure since the X-ray crystal structure of the **A** isomer was determined. Since the environment of the equatorial S^tBu group was somewhat different in the two isomers, the ^1H chemical shifts of the ^tBu protons were different: δ 1.51 for the **A** isomer and 1.40 ppm for the **C** isomer. On this basis, the assignments in the case of (μ-CH_3ClP)(μ-EtS)$Fe_2(CO)_6$ would be: δ_P 265.7 ppm, **A** isomer; δ_P 249.6 ppm, **C** isomer and for (μ-C_6H_5ClP)(μ-EtS)$Fe_2(CO)_6$: δ_P 271.5 ppm, **A** isomer; δ_P 244.4 ppm, **C** isomer.

A brief study was made of the reactivity of the P–Cl bonds in (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ and (μ-CH_3ClP)(μ-EtS)$Fe_2(CO)_6$. The former was very reactive toward amines, giving substitution of both chlorine substituents in high yield (Table 3). The P–Cl bond in (μ-CH_3ClP)(μ-EtS)$Fe_2(CO)_6$ appeared to be less reactive, as might be expected since its phosphorus atom is less electrophilic. Thus this complex did not react with ammonia under conditions which served well in the preparation of (μ-$(H_2N)_2P$)(μ-EtS)$Fe_2(CO)_6$, but it did react with the more nucleophilic methylamine, albeit in only moderate yield.

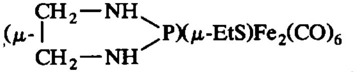
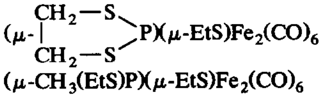
(μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ reacted with ethanethiol and with 1,2-ethanedithiol in the presence of triethylamine to give (μ-$(EtS)_2P$)(μ-EtS)$Fe_2(CO)_6$ and **3**, respectively.



(**3**)

The use of EtSLi resulted in a higher (63% *vs.* 44%)

TABLE 3. Reactions of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ and (μ-CH_3ClP)$Fe_2(CO)_6$

Complex	Reaction with	Product	Yield (%)
(μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$	NH_3	(μ-$(H_2N)_2P$)(μ-EtS)$Fe_2(CO)_6$	81
	CH_3NH_2	(μ-$(CH_3NH)_2P$)(μ-EtS)$Fe_2(CO)_6$	99
	$(CH_3)_2NH$	(μ-$[(CH_3)_2N]_2P$)(μ-EtS)$Fe_2(CO)_6$	100
	$H_2NCH_2CH_2NH_2$	 (μ-$\begin{matrix}CH_2-NH\\ CH_2-NH\end{matrix}$$>$P)($\mu$-EtS)$Fe_2(CO)_6$	100
(μ-CH_3ClP)(μ-EtS)$Fe_2(CO)_6$	$(CH_3)_2NH$	(μ-$[(CH_3)_2N][CH_3]P$)(μ-EtS)$Fe_2(CO)_6$	43
(μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$	EtSH	(μ-$(EtS)_2P$)(μ-EtS)$Fe_2(CO)_6$	44
	EtSLi	(μ-$(EtS)_2P$)(μ-EtS)$Fe_2(CO)_6$	63
	$HSCH_2CH_2SH$	 (μ-$\begin{matrix}CH_2-S\\ CH_2-S\end{matrix}$$>$P)($\mu$-EtS)$Fe_2(CO)_6$	87
(μ-CH_3ClP)(μ-EtS)$Fe_2(CO)_6$	EtSLi	(μ-$CH_3(EtS)P$)(μ-EtS)$Fe_2(CO)_6$	66

product yield. In the case of (μ-CH_3ClP)(μ-EtS)$Fe_2(CO)_6$, the use of EtSLi, but not of EtSH/Et_3N, gave (μ-CH_3(EtS)P)(μ-EtS)$Fe_2(CO)_6$. Similar complexes had been prepared by Evertz and Huttner [3] by reactions of (μ-RClP)(μ-Cl)$Fe_2(CO)_6$ with thiols.

After this work was completed, Song and co-workers reported syntheses of complexes of type (μ-Ph_2P)(μ-RS)$Fe_2(CO)_6$, [μ-(p-$CH_3C_6H_4$)$_2$P](μ-RS)$Fe_2(CO)_6$, and (μ-p-$CH_3C_6H_4PCl$)(μ-RS)$Fe_2(CO)_6$ by the reaction of [(μ-CO)(μ-RS)$Fe_2(CO)_6$]$^-$ reagents with the respective arylchlorophosphines [4].

3. Experimental section

3.1. General comments

All reactions were carried out under an inert atmosphere of pre-purified nitrogen or argon. Solvents (tetrahydrofuran, diethyl ether) were purified by standard methods and purged with inert gas prior to use. Trichlorophosphine and triethylamine were distilled and stored at room temperature under an inert atmosphere. Triiron dodecacarbonyl was prepared by the literature method [5] and stored under inert atmosphere at −10°C. Ammonia, monomethylamine, and dimethylamine were obtained from the Matheson Co. and used without further purification. n-Butyllithium was obtained from Alfa Products, Inc. and RLi content was determined by the Gilman double titration method. Diphenylchlorophosphine, phenyldichlorophosphine and methyldichlorophosphine were obtained from Strem Chemicals, Inc. and used as received, with storage under argon at room temperature. The thiols and ethylenediamine were degassed immediately prior to use.

The progress of all reactions was monitored by thin layer chromatography (Baker Flex–Silica Gel IB-F). Purification of the compounds was effected by filtration chromatography in which the reaction products, after removal of the reaction solvent by trap-to-trap distillation, were dissolved in pentane/methylene chloride and chromatographed on a bed of 200 ml silicic acid (100–300 mesh, Sigma or Mallinkrodt) in a 350 ml glass fritted funnel. In some cases (as noted in the experimental details), further purification was effected by medium pressure column chromatography using a 450 × 25 mm gravity column with Sigma 230–400 mesh silica gel. All chromatographic separations were carried out without the exclusion of either atmospheric oxygen or moisture. Solid products were recrystallized from deoxygenated solvents at −20°C.

Infrared spectra (NaCl solution cells) were obtained using a Perkin–Elmer Model 1430 double beam grating infrared spectrometer and are referenced to polystyrene film. Proton NMR spectra were recorded on either a Bruker WM-250 or Varian XL-300 spectrometer operating at 250 and 300 MHz, respectively. $^{31}P\{H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer operating at 121.64 MHz using an external standard of 85% aqueous H_3PO_4 as a reference. ^{13}C NMR spectra were recorded on either a Bruker WM-270 or a Varian XL-300 spectrometer operating at 67.9 and 75.4 MHz, respectively. Electron impact mass spectra were obtained using a Finnigan-3200 mass spectrometer operating at 70 eV. Masses were correlated using the following isotopes: ^1H, ^{12}C, ^{14}N, ^{16}O, ^{31}P, ^{32}S, ^{35}Cl, and ^{56}Fe. Melting points of analytically pure solid products were determined in air using a Büchi melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytical Laboratory in Herlev, Denmark.

3.2. Synthesis of (μ-Cl_2P)(μ-RS)$Fe_2(CO)_6$ complexes

3.2.1. R = Et

A 300 ml Schlenk flask equipped with a stir bar and septum was charged with 3.00 g (5.96 mmol) of $Fe_3(CO)_{12}$, then degassed and argon-backfilled three times. Diethyl ether (100 ml) was added to the flask by cannula. Triethylamine (0.83 ml, 0.60 g, 5.96 mmol) and ethanethiol (0.44 ml, 0.37 g, 5.96 mmol) were added by syringe. The solution was stirred at room temperature for 3.5 h to generate the red anion salt, [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$]. This solution was added dropwise by cannula to a solution of 0.52 ml (0.80 g, 6.00 mmol) of PCl_3 in 150 ml of diethyl ether. Upon the addition of the anion solution, the solution of trichlorophosphine immediately turned orange and a precipitate formed. After the solution had been stirred for 18 h at room temperature to ensure complete reaction, the solvent was removed by trap-to-trap distillation and the solid, orange–brown residue was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (1 : 9, v/v) afforded an orange–red, crystalline solid which was identified as (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ (2.07 g, 4.68 mmol, 78%) and recrystallized from hot pentane; m.p. 99–100°C.

Anal. Found: C, 22.10; H, 1.28. $C_8H_5Cl_2Fe_2O_6PS$ calc.: C, 21.70; H, 1.14%. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.46 (t, J(H–H) = 6.7 Hz, 3H, CH_3CH_2S); 2.65 (q, J(H–H) = 6.2 Hz, 2H, CH_3CH_2S). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.64 MHz): δ_P 323.1. ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 18.1 (q, J(C–H) = 128.9 Hz, CH_3CH_2S); 34.5 (t, J(C–H) = 141.1 Hz, CH_3CH_2S); 208.1 (s, terminal CO). IR ($CHCl_3$): 2965vw, 2930vw, 1450vw, 1380vw, 1044vw,br, 608s, 590s,br cm^{-1}. Terminal carbonyl region: 2082vs, 2051vs, 2018vs,br, 2003vs,br,sh cm^{-1}. Mass spectrum (EI): m/z (relative intensity) 442

(M^+, 27), 414 (M^+- CO, 9), 386 (M^+- 2CO, 16), 358 (M^+- 3CO, 27), 330 (M^+- 4CO, 31), 302 (M^+- 5CO, 35), 274 (M^+- 6CO, 85), 246 ($Fe_2PCl_2S^+$, 98), 232 ($Fe_2COSPEt^+$, 45), 210 (Fe_2PClS^+, 40), 179 (Fe_2PCl^+, 37), 148 (Fe_2Cl^+, 42), 144 (Fe_2P^+, 35), 119 ($FeSP^+$, 100), 89 (Fe_2PCl^{+2}, 11), 56 (Fe^+, 68), 35 (Cl^+, 15).

3.2.2. $R = {}^tBu$

In this synthesis, the Li[(μ-CO)(μ-^{t}BuS)$Fe_2(CO)_6$] reagent was used. The reagent was generated *in situ* by slowly adding 1.85 ml of a 1.63 M hexane solution of ^{n}BuLi (Alfa, 3.02 mmol) to a cooled solution (−78°C) of 1.50 g of $Fe_3(CO)_{12}$ (2.98 mmol) and 0.27 g of ^{t}BuSH (3.02 mmol) in 50 ml of Et_2O. The reaction mixture was stirred at −78°C for 15 min and the bath was then removed. After the green to red–brown color change had occurred during the course of 30 min, the reaction mixture was added dropwise via cannula to a stirred solution of 0.56 g (4.59 mmol) of PCl_3 in 30 ml of Et_2O at room temperature. An immediate color change from red-brown to orange was observed. The resulting reaction mixture was stirred at room temperature for 2 h. The solvents were removed *in vacuo*, and the residue was taken up in pentane and subjected to filtration chromatography. Elution with pentane gave one major band which yielded an orange–yellow, crystalline, mildly air-sensitive solid which was recrystallized from pentane to give (μ-Cl_2P)(μ-^{t}BuS)$Fe_2(CO)_6$ (0.77 g, 55%); m.p. 81–82°C.

Anal. Found: C, 25.68; H, 1.98. $C_{10}H_9Fe_2O_6PSCl_2$ calc.: C, 25.51; H, 1.93%. ^1H NMR (90 MHz, $CDCl_3$): δ 1.32 (s, ^{t}BuS). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 33.8 (q, J(C–H) = 128.3 Hz, SC($CH_3)_3$); 57.5 (s, SC($CH_3)_3$); 208.5 (s, CO). $^{31}P\{^1H\}$ NMR (36.2 MHz, $CDCl_3$): δ_P 317.6. IR (CCl_4, NaCl): 2980w, 2939w, 2010w, 2878vw, 2078s, 2024vs, 2010vs, 1998s, 1958m, 1468w, 1460w, 1397w, 1371m, 1153m, 1075w, 604m, 579m, 531m, 517m cm^{-1}. Mass spectrum: m/z (relative intensity) 470 (M^+, 3), 442 (M^+- CO, 1), 414 (M^+- 2 CO, 3), 386 (M^+- 3 CO, 2), 358 (M^+- 4 CO, 2), 330 (M^+- 5 CO, 2), 302 (M^+- 6 CO, 4), 56 (Fe^+, 100).

3.2.3. $R = Ph$

The reaction was carried out using the procedure in 3.2.2. and on the same scale with PhSH instead of ^{t}BuSH. After removal of solvent, the residue was taken up in pentane/CH_2Cl_2 (70 : 30, v/v) and subjected to filtration chromatography. Elution with pentane gave one major band which yielded an orange–yellow, crystalline, air-stable solid which was recrystallized from pentane to give 1.01 g (69%) of (μ-Cl_2P)(μ-PhS)$Fe_2(CO)_6$; m.p. 109.5–110°C.

Anal. Found: C, 29.54; H, 1.15. $C_{12}H_5Fe_2O_6PSCl_2$ calc.: C, 29.37; H, 1.03%. ^1H NMR (250 MHz, CD_2Cl_2): δ 7.29–7.50 (m, aromatic Hs). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ_C 128.4–141.5 (m, aromatic Cs), 207.8 (s, carbonyl Cs). ^{31}P NMR (36.2 MHz, CD_2Cl_2): δ_P 319.5. IR (CCl_4, NaCl): 2974w, 2940w, 2868vw, 2082s, 2046vs, 2020vs, 2008vs, 1950w, 1538w, 1469w, 1442w, 1266m, 1074w, 699w, 611w, 600m, 590m, 575m cm^{-1}. Mass spectrum: m/z (relative intensity) 494 (M^+ [^{37}Cl, ^{37}Cl], 0.6), 492 (M^+ [^{37}Cl, ^{35}Cl], 4), 490 (M^+ [^{35}Cl, ^{35}Cl], 5), 462 (M^+- CO, 4), 434 (M^+- 2 CO, 6), 406 (M^+- 3 CO, 5), 378 (M^+- 4 CO, 6), 350 (M^+- 5 CO, 12), 322 (M^+- 6 CO, 18), 196 (?, 100).

3.3. Synthesis of (μ-Ph_2P)(μ-RS)$Fe_2(CO)_6$ complexes

3.3.1. $R = Et$

The standard [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] reagent solution (from 2.98 mmol of $Fe_3(CO)_{12}$, 3.38 mmol of EtSH and 3.50 mmol of Et_3N in 50 ml of THF) was prepared and 0.66 g (3.0 mmol) of diphenylchlorophosphine was added. The mixture was stirred at room temperature for 20 h, during which time it became dark red and a white solid precipitated. Filtration and removal of solvent was followed by filtration chromatography (silicic acid/pentane). Pentane eluted two minor yellow bands which were discarded. Pentane/CH_2Cl_2 (9 : 1, v/v) eluted an orange band which yielded 1.26 g (80%) of an orange, air-stable solid, (μ-Ph_2P)(μ-EtS)$Fe_2(CO)_6$; m.p. 111–112°C (from pentane/CH_2Cl_2).

Anal. Found: C, 45.75; H, 2.93. $C_{20}H_{15}O_6PSFe_2$ calc.: C, 45.66; H, 2.87%. ^1H NMR (CD_2Cl_2, 250 MHz): δ 1.32 (t, J = 7.3 Hz, 3H, CH_3); 2.54 (dq, J = 7.3 Hz, J(P–H) = 1.5 Hz, 2H, CH_2); 7.2–7.7 (m, 10H, Ph). $^{31}P\ \{^1H\}$ NMR ($CDCl_3$, 36.2 MHz): δ_P 142.9. IR ($CHCl_3$): 3077w, 3059w, 3000w, 2984w, 2966w, 1482m, 1454w, 1436m, 1381w, 1332w, 1307w, 1257m, 1189w, 1103m, 1096m, 1085w, 1031w, 1006w, 975w, 699s, 616s, 584s, 523m cm^{-1}; terminal carbonyl region (pentane): 2063s, 2025s, 1990s, 1980s, 1970m, 1943w cm^{-1}. Mass spectrum: m/z (relative intensity) 526 (M^+, 17), 498 (M^+- CO, 11), 470 (M^+- 2 CO, 11), 442 (M^+- 3 CO, 11), 414 (M^+- 4 CO, 6), 386 (M^+- 5 CO, 73), 358 (M^+- 6 CO, 100), 330 (Fe_2PPh_2SH, 84), 252 (Fe_2PPhS, 28), 175 (Fe_2PS, 39), 144 (Fe_2S, 39), 119 (FePS, 28), 112 (Fe_2, 11), 56 (Fe, 6).

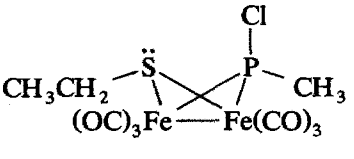
3.3.2. $R = {}^tBu$

The reaction described in (a) (same scale) was carried out as described using ^{t}BuSH in place of EtSH. The same workup procedure gave (μ-$Me_3CS)_2$-$Fe_2(CO)_9$ in 7% yield and (μ-Ph_2P)(μ-^{t}BuS)$Fe_2(CO)_6$, an orange, air-stable solid; m.p. 137–139°C (from pentane/CH_2Cl_2) in 91% yield.

Anal. Found: C, 47.52; H, 3.47. $C_{22}H_{19}Fe_2O_6PS$ calc.: C, 47.69; H, 3.46%. ^{1}H NMR (acetone-d_6, 90 MHz); δ 1.40 (s, 9H, t-butyl CH_3); 7.2–7.7 (m, 5H, Ph). ^{31}P {^{1}H} NMR (acetone-d_6, 36.2 MHz): δ_P 139.8. IR ($CHCl_3$): 3082m, 3065w, 2969m, 2943m, 2930m, 2904m, 2868w, 1479m, 1458m, 1432s, 1394w, 1365s, 1328w, 1304w, 1151s, 1096m, 1069w, 1025w, 999m, 691s, 608s, 585s, 520s cm^{-1}; terminal carbonyl region (pentane): 2060s, 2021vs, 1991vs, 1983vs, 1973m cm^{-1}.

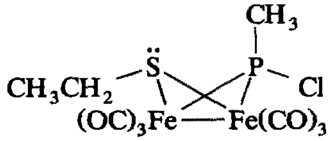
3.4. Synthesis of (μ-CH_3PCl)(μ-EtS)$Fe_2(CO)_6$

A solution of [Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$], prepared as above and on the same scale, was added dropwise to a solution of 0.66 ml (0.86 g, 7.39 mmol) of CH_3PCl_2 in 100 ml of diethyl ether. Upon addition of the anion solution, the solution of methyldichlorophosphine immediately changed to orange in color and a precipitate formed. After stirring for 18 h at room temperature to ensure complete reaction, the solvent was removed by trap-to-trap distillation and the orange-brown solid residue was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (1:9, v/v) afforded 2.26 g (5.35 mmol, 89%) of an orange-red crystalline solid, which was recrystallized from hot pentane and identified as (μ-CH_3PCl)(μ-EtS)$Fe_2(CO)_6$. Two isomers were identified by spectroscopy and their ratio determined by ^{1}H NMR spectroscopy: axial (69%), equatorial (31%). The isomer mixture had m.p. 104.5–105.5°C.



equatorial-axial isomer
"a-isomer"

(A)



equatorial-equatorial isomer
"e-isomer"

(C)

Anal. Found: C, 25.77; H, 1.96. $C_9H_8ClFe_2O_6PS$ calc.: C, 25.60; H, 1.91%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (t, J(H–H) = 7.3 Hz, 0.93H, e-isomer, SCH_2CH_3); 1.45 (t, J(H–H) = 7.7 Hz, 2.07H, a-isomer SCH_2CH_3); 2.02 (d, ^2J(P–H) = 9.8 Hz, 2.07H, a-isomer, PCH_3); 2.48 (q, J(H–H) = 7.3 Hz, ^4J(H–P) = 2.0 Hz, 0.62H, SCH_2CH_3, e-isomer); 2.55 (d, ^2J(H–P) = 9.3 Hz, 0.93H, e-isomer, PCH_3); 2.63 (q, J(H–H) = 7.2 Hz, ^4J(H–P) = 2.2 Hz, 1.38H, a-isomer, SCH_2CH_3). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.64 MHz): δ_P 249.6 (e-isomer), 265.65 (a-isomer). ^{13}C NMR ($CDCl_3$, 72.5 MHz): δ_C 18.0 (q, J(C–H) = 126.5 Hz, SCH_2CH_3); 26.9 (dq, J(C–H) = 134.5 Hz, J(C–P) = 11.7 Hz, μ-PCH_3); 34.8 (t, J(C–H) = 142.2 Hz, J(C–P) = 22.2 Hz, SCH_2CH_3); 209.2, 209.7 (s's, terminal CO). IR ($CHCl_3$): 2990w, 2962w, 2924w, 1603w, 1452w, 1422vw, 1378w, 1279w, 984vw, 898m, 881m, 620sh, 610s, 600s,br cm^{-1}; terminal carbonyl region: 2068s, 2038vs, 2002vs,br, 1988vs, br cm^{-1}. Mass spectrum (EI): m/z (relative intensity) 422 (M^+, 33), 394 (M^+ − CO, 32), 366 (M^+ − 2CO, 28), 338 (M^+ − 3CO, 46), 310 (M^+ − 4CO, 50), 282 (M^+ − 5CO, 66), 254 (M^+ − 6CO, 100), 226 ($Fe_2PClMeSH^+$, 85), 210 (Fe_2PClS^+, 37), 179 (Fe_2ClP^+, 24), 175 (Fe_2SP^+, 5), 145 (Fe_2SH^+, 2), 56 (Fe^+, 3).

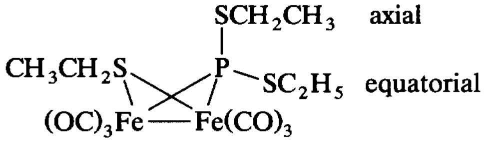
3.5. Synthesis of (μ-PhPCl)(μ-EtS)$Fe_2(CO)_6$

[Et_3NH][(μ-CO)(μ-EtS)$Fe_2(CO)_6$] was generated in 50 ml of Et_2O using 1.50 g (2.98 mmol) of $Fe_3(CO)_{12}$, 0.18 g (2.97 mmol) of EtSH and 0.31 g of Et_3N (3.01 mmol). After the green to red-brown color change had occurred, the reaction mixture was added dropwise via cannula to a stirred solution of 1.32 g (7.37 mmol) of $C_6H_5PCl_2$ in 150 ml of Et_2O at room temperature. After a reaction for 2 h at room temperature, the standard workup used in the experiments above (elution with pentane/CH_2Cl_2 (9:1)) gave 1.25 g (87%) of (μ-PhPCl)(μ-EtS)$Fe_2(CO)_6$, orange–yellow crystals; m.p. 93–94°C.

Anal. Found: C, 34.88; H, 2.16. $C_{14}H_{10}Fe_2O_6PSCl$ calc.: C, 34.72; H, 2.08%. ^{1}H NMR (90 MHz, $CDCl_3$): δ 1.33 (t, J(HH) = 7.3 Hz, e-isomer, $-SCH_2CH_3$); 1.57 (t, J(HH) = 7.3 Hz, a-isomer, $-SCH_2CH_3$); 2.53 (qd, J(HH) = 7.3 Hz, J(HP) = 2.0 Hz, e-isomer, $-SCH_2CH_3$); 2.78 (qd, J(HH) = 7.6 Hz, J(HP) = 1.8 Hz, a-isomer, $-SCH_2CH_3$); 7.46–7.87 (m, 5H, aromatic Hs). ^{13}C NMR 67.9 MHz, $CSCl_3$): δ_C 17.9 (q, J(CH) = 128.5 Hz, e-isomer, $-SACH_2CH_3$); 18.0 (q, J(CH) = 128.6 Hz, a-isomer, $-SCH_2CH_3$); 34.6 (td, J(CH) = 141.7 Hz, J(CP) = 25.6 Hz, a-isomer, $-SCH_2CH_3$); 34.7 (td, J(CH) = 141.7 Hz, J(CP) = 25.4 Hz, e-isomer, $-SCH_2CH_3$); 128.1–140.0 (m, aromatic Cs); 209.3, 209.9 (s's, carbonyl Cs). ^{31}P {^{1}H} NMR (36.2 MHz, $CDCl_3$): δ_P 244.4 (e-isomer), 271.5 (a-isomer). IR (CCl_4, NaCl): 3078w, 3060w, 2984w, 2960w, 2928w, 2857vw, 2079s, 2046vs, 2020vs, 2010vs, 1998s, 1970m, 1580w, 1475w, 1439w, 1264s, 1071w, 1024w, 1002w, 896w, 710m, 698m, 688m, 612m, 585m,br, 539m, 518m cm^{-1}. Mass spectrum: *m/z* (relative intensity) 484 (M^+, 22), 465 (M^+ $-$ CO, 12), 428 ($M^+ - 2$ CO, 14), 400 ($M^+ - 3$ CO, 38), 372 ($M^+ - 4$ CO, 23), 344 ($M^+ - 5$ CO, 31), 316 ($M^+ - 6$ CO, 92), 288 ($(Fe_2[SH][PClC_6H_5]^+$, 100), 252 $[C_6H_5PS]^+$, 29), 210 (Fe_2ClPS^+, 59), 107 ($C_6H_5P^+$, 31), 56 (Fe^+, 100).

3.6. Reaction of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ with two molar equivalents of ethanethiol

Triethylamine (0.30 ml, 0.22 g, 2.15 mmol) and ethanethiol (0.15 ml, 0.126 g, 2.03 mmol) were added by syringe to a diethyl ether (35 ml) solution of 0.31 g (0.70 mmol) of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ and the mixture was stirred at room temperature for 48 h. The solution gradually darkened to brown-orange in color. After removal of the solvent by trap-to-trap distillation, the oily brown residue was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (1:9, v/v) afforded 0.15 g (0.30 mmol, 44%) of an orange-red oil which was identified as (μ-$(EtS)_2P$)(μ-SEt)$Fe_2(CO)_6$.



A satisfactory analysis for C, H could not be obtained for this oil.

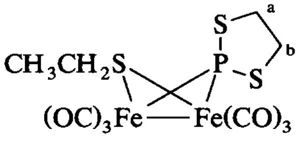
^{1}H NMR ($CDCl_3$, 250 MHz): δ 1.29 (t, *J*(H-H) = 7.6 Hz, 3H, μ-SCH_2CH_3); 1.40 (m, 6H, equatorial- and axial-SCH_2CH_3); 2.55 (qd, *J*(H-H) = 6.8 Hz, *J*(H-P) = 1.7 Hz, 2H, μ-SCH_2CH_3); 2.81 (complex m, 2H, equatorial-SCH_2CH_3); 3.02 (complex m, 2H, axial-SCH_2CH_3). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.64 MHz): δ_P 201.10. ^{13}C NMR ($CDCl_3$, 72.9 MHz): δ_C 15.18 (qd, *J*(C-H) = 128.5 Hz, *J*(C-P) = 19.8 Hz, equatorial- and axial-SCH_2CH_3); 17.95 (q, *J*(C-H) = 130.0 Hz, μ-SCH_2CH_3); 30.05 (td, *J*(C-H) = 140.0 Hz, *J*(C-P) = 31.7 Hz, equatorial-SCH_2CH_3); 30.19 (td, *J*(C-H) = 141.0 Hz, *J*(C-P) = 32.1 Hz, axial-SCH_2CH_3); 34.60 (td, *J*(C-H) = 142.6 Hz, *J*(C-P) = 24.9 Hz, μ-SCH_2CH_3); 209.9 (s, terminal CO). IR ($CHCl_3$): 2982vw, 2960vw, 2925w, 1450w, 1378w, 1100w, 1015w, 923w, 615m,sh, 609m, 579m,br cm^{-1}; terminal carbonyl region: 2063s, 2030vs, 1990vs,br cm^{-1}. Mass spectrum (EI): *m/z* (relative intensity) 494 (M^+, 1), 466 ($M^+ -$ CO, 3), 438 ($M^+ -$ 2CO, 25), 410 ($M^+ -$ 3CO, 43), 382 ($M^+ -$ 4CO, 34), 354 ($M^+ -$ 5CO, 29), 326 ($M^+ -$ 6CO, 100), 298 ($Fe_2SHP(SEt)_2^+$, 31), 270 ($Fe_2SHP(SH)SEt^+$, 90), 241 ($Fe_2SPSSH_2^+$, 47), 240 (Fe_2SHPSS^+, 53), 208 (Fe_2PSSH^+, 42), 207 (Fe_2PSS^+, 54), 177 (Fe_2SSH^+, 32), 176 (Fe_2SS^+, 24), 144 (Fe_2S^+, 15), 57 (FeH^+, 22), 56 (Fe^+, 18).

3.7. Reaction of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ with two molar equivalents of lithium ethanethiolate

Lithium ethanethiolate, generated at -78°C by reaction of 0.09 ml (0.08 g, 1.29 mmol) of ethanethiol with 0.61 mL of a 2.13 M solution of ^{n}BuLi (1.29 mmol) in 10 ml of THF for 15 min, was added by cannula to a stirred THF solution of 0.26 g (0.58 mmol) of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ at -78°C and the reaction mixture was warmed slowly to room temperature. The solution gradually darkened to brown-red upon warming and the progress of the reaction was monitored by TLC analysis. Removal of the solvent by trap-to-trap distillation afforded an oily brown-red residue which was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (1:20, v/v) afforded 0.18 g (0.36 mmol, 63%) of a dark orange oil which was identified as (μ-$(EtS)_2P$)(μ-EtS)$Fe_2(CO)_6$ by comparison of its ^{1}H and ^{31}P NMR spectral data with that of an authentic sample (above).

3.8. Reaction of (μ-PCl_2)(μ-EtS)$Fe_2(CO)_6$ with 1,2-ethanedithiol

Triethylamine (0.12 ml, 0.087 g, 0.86 mmol) and 1,2-ethanedithiol (0.05 ml, 0.056 g, 0.569 mmol) were added by syringe to a diethyl ether solution of 0.26 g (0.59 mmol) of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ and the mixture was stirred at room temperature for 18 h. Within minutes of adding the reagents, the solution had darkened to brown-orange in color. After removal of the solvent by trap-to-trap distillation, the brown-orange oily residue was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (3:7, v/v) afforded 0.24 g (0.52 mmol, 87%) of an orange solid which was recrystallized from hot pentane and identified as (μ-$\overline{SCH_2CH_2SP}$)(μ-EtS)$Fe_2(CO)_6$; m.p. 89–90°C.

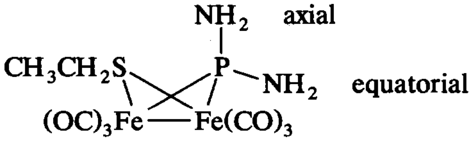


Anal. Found: C, 26.19; H, 2.01. $C_{10}H_9Fe_2O_6PS_3$ calc.: C, 25.87; H, 1.96%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.40 (t, *J*(H-H) = 7.3 Hz, 3H, SCH_2CH_3); 2.54 (q, *J*(H-H) = 7.3 Hz, *J*(H-P) = 2.0 Hz, 2H, SCH_2CH_3); 3.32–3.48 (complex m, 4H, $PSCH_2CH_2S$). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.64 MHz): δ_P 241.76. ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 17.98 (q, *J*(C-H) = 128.0 Hz, SCH_2CH_3); 35.31 (td, *J*(C-H) = 140.2 Hz, *J*(C-P) = 26.9 Hz, SCH_2CH_3); 40.22 (overlapping t, b-

PS*C*H$_2$CH$_2$S); 41.67 (overlapping t, a-PSCH$_2$*C*H$_2$S); 209.82 (s, terminal CO). IR (CHCl$_3$): 2962w, 2923w, 2864vw, 1450w, 1417w, 1378w, 1280w, 1100w,br, 1025w,br, 940w, 618sh, 607m, 592m,br, 530 (w) cm^{-1}; terminal carbonyl region: 2064 (vs), 2025 (vs), 1980 (vs,br) cm^{-1}. Mass spectrum (EI): *m/z* (relative intensity) 464 (M$^+$, 10), 436 (M$^+$ − CO, 13), 408 (M$^+$ − 2CO, 27), 380 (M$^+$ − 3CO, 28), 352 (M$^+$ − 4CO, 30), 324 (M$^+$ − 5CO, 33), 296 (M$^+$ − 6CO, 85), 268 (Fe$_2$SHPSCH$_2$CH$_2$S$^+$, 39), 240 FeEtSPSCH$_2$CH$_2$S$^+$, 100), 207 (Fe$_2$PSS$^+$, 13), 177 (Fe$_2$SSH$^+$, 28), 176 (Fe$_2$SS$^+$, 40), 144 (Fe$_2$SH$^+$, 19), 119 (FeSP$^+$, 5), 89 (FeSH$^+$, 2), 56 (Fe$^+$, 6).

3.9. Reaction of (μ-PCl$_2$)(μ-EtS)Fe$_2$(CO)$_6$ with ammonia

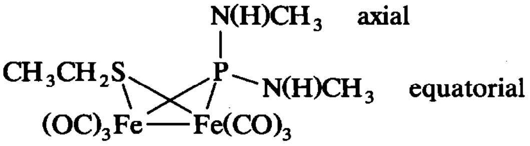
Ammonia was bubbled slowly through a stirred diethyl ether solution of 0.23 g (0.52 mmol) of (μ-Cl$_2$P)(μ-EtS)Fe$_2$(CO)$_6$ at room temperature for 8 h. Diethyl ether was added as necessary to maintain the solution level in the flask. The solution gradually became cloudy with the formation of a precipitate, but remained orange in color. After removal of the solvent by trap-to-trap distillation, the oily orange residue was purified by filtration chromatography. Elution with CH$_2$Cl$_2$/pentane (1:20, v/v) afforded 0.02 g (0.05 mmol, 10%) of starting material which was identified by comparison of its ^{1}H and ^{31}P NMR spectra with those of an authentic sample. Further elution with CH$_2$Cl$_2$/pentane (1:1, v/v) afforded 0.17 g (0.42 mmol, 81%) of an orange-yellow solid which was recrystallized from hot pentane and identified as the equatorial thiolate isomer of (μ-(H$_2$N)$_2$P)(μ-EtS)Fe$_2$(CO)$_6$; m.p. 92.5–93.5°C.



Anal. Found: C, 24.30; H, 2.36. C$_8$H$_9$Fe$_2$N$_2$O$_6$PS calc.: C, 23.79; H, 2.25%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.38 (t, J(H–H) = 7.3 Hz, 3H, C*H*$_3$CH$_2$S); 2.27 (broad s, 2H, equatorial-N*H*$_2$); 2.52 (q, J(H–H) = 7.3 Hz, ^4J(H–P) = 1.4 Hz, 2H, CH$_3$C*H*$_2$S); 2.79 (broad s, 2H, axial-N*H*$_2$). ^{31}P {^{1}H} NMR (CDCl$_3$, 121.64 MHz): δ_P 232.6. ^{13}C NMR (CDCl$_3$, 67.9 MHz): δ_C 18.14 (q, J(C–H) = 128.0 Hz, *C*H$_3$CH$_2$S); 34.77 (t, J(C–H) = 139.9 Hz, J(C–P) = 23.0 Hz, CH$_3$*C*H$_2$S); 211.4 (s, terminal CO). IR (CHCl$_3$): 3461vw (ν(NH)), 3430vw (ν(NH)), 3363w (ν(NH)), 3337w (ν(NH)), 2962w, 2928vw, 1538w,br, 1452vw, 1042vw,br, 1007vw,br, 878vw, 840vw, 612m, 607m, sh, 573m,sh cm^{-1}; terminal carbonyl region: 2060m, 2020vs, 1985vs,br, 1973vs,br cm^{-1}. Mass spectrum (EI): *m/z* (relative intensity) 404 (M$^+$, 17), 376 (M$^+$ − CO, 22), 348 (M$^+$ − 2CO, 28), 320 (M$^+$ − 3CO, 13), 292 (M$^+$ − 4CO, 18), 264 (M$^+$ − 5CO, 65), 236 (M$^+$ − 6CO, 94), 208 (Fe$_2$SHP(NH$_2$)$_2$$^+$, 100), 191 (Fe$_2$SPNH$_2$$^+$, 70), 190 (Fe$_2$SPNH$^+$, 53), 189 (Fe$_2SPN^+$, 40), 175 (Fe$_2SP^+$, 5), 160 (Fe$_2NH_2S^+$ and Fe$_2$NH$_3$P$^+$, 22), 145 (Fe$_2$SH$^+$, 34), 144 (Fe$_2$S$^+$, 52), 56 (Fe$^+$, 14).

3.10. Reaction of (μ-Cl$_2$P)(μ-EtS)Fe$_2$(CO)$_6$ with methylamine

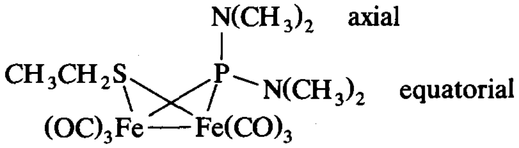
Methylamine was bubbled slowly through a stirred diethyl ether solution of 0.31 g (0.70 mmol) (μ-Cl$_2$P)(μ-EtS)Fe$_2$(CO)$_6$ at room temperature for 3 h. Diethyl ether was added as necessary to maintain the solution level in the flask. The solution quickly became cloudy with precipitate formation, but remained orange in color. The solvent was removed by trap-to-trap distillation and the oily orange residue purified by filtration chromatography. Elution with CH$_2$Cl$_2$/pentane (3:7, v/v) afforded 0.30 g (0.70 mmol, 99%) of an yellow-orange solid which was recrystallized from hot methylene chloride/pentane and identified as the equatorial μ-thiolate isomer of (μ-(MeHN)$_2$P)(μ-EtS)Fe$_2$(CO)$_6$; m.p. 74.5–75.5°C.



Anal. Found: C, 28.10; H, 3.11; N, 6.57. C$_{10}$H$_{13}$Fe$_2$N$_2$O$_6$PS calc.: C, 27.81; H, 3.03; N, 6.49%. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.36 (t, J(H–H) = 7.3 Hz, 3H, C*H*$_3$CH$_2$S); 2.10 (br, 1H, equatorial-PN*H*CH$_3$); 2.47 (br, 1H, axial-PN*H*CH$_3$); 2.49–2.54 (complex pseudo d, 5H, equatorial-PNHC*H*$_3$ and CH$_3$C*H*$_2$S); 2.70–2.75 (pseudo q, 3H, axial-PNCH$_3$*H*). ^{31}P {^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ_P 236.7. ^{13}C NMR (CDCl$_3$, 67.9 MHz): δ_C 18.15 (q, J(C–H) = 126.6 Hz, *C*H$_3$CH$_2$S); 30.87, 3098 (overlapping q's, J(C–H) could not be determined, J(C–P) = 42.3 Hz, complex region, NCH$_3$), 34.77 (qd, J(C–H) = 141.1 Hz, J(C–P) = 22.82 Hz, CH$_3$*C*H$_2$S), 211.6 (s, terminal CO). IR (CHCl$_3$): 3600vw (ν(NH)), 3420w (ν(NH)), 3390vw (ν(NH)), 2960w, 2927w, 2887sh, 2857vw,sh, 1450vw, 1390w, 1110sh, 1068m,br, 1045sh, 610m, 598sh, 575sh cm^{-1}; terminal carbonyl region: 2057s, 2018vs, 1982vs,br, 1970vs,br cm^{-1}. Mass spectrum (EI): *m/z* (relative intensity) 432 (M$^+$, 23), 404 (M$^+$ − CO, 26), 376 (M$^+$ − 2CO, 19), 348 (M$^+$ − 3CO, 20), 320 (M$^+$ − 4CO, 20), 292 (M$^+$ − 5CO, 34), 264 (M$^+$ − 6CO, 99), 236 ($Fe_2SHP(NHMe)_2^+$, 100), 205 ($Fe_2SHPNMe^+$, 41), 204 (Fe_2SPNMe^+, 27), 176 (Fe_2SPH^+, 35), 145 (Fe_2SH^+, 24), 144 (Fe_2S^+ and Fe_2PH^+, 35).

3.11. *Reaction of (μ-PCl_2)(μ-EtS)$Fe_2(CO)_6$ with dimethylamine*

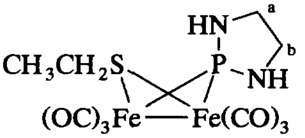
Dimethylamine was slowly bubbled through a stirred diethyl ether solution of 0.28 g (0.62 mmol) of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ at room temperature for 10 h. Diethyl ether was added as necessary to maintain the solution level in the flask. The solution gradually became cloudy with precipitate formation, but remained orange in color. After removal of the solvent by trap-to-trap distillation, the oily orange residue was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (1:1, v/v) afforded 0.29 g (0.62 mmol, 100%) of an orange-yellow solid which was recrystallized from hot dichloromethane/pentane and identified as the equatorial μ-thiolate isomer of (μ-$(Me_2N)_2P$)(μ-EtS)$Fe_2(CO)_6$; m.p. 47.5–49.0°C.



^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.35 (t, J(H–H) = 7.3 Hz, 3H, CH_3CH_2S); 2.44 (dq, J(H–H) = 7.3 Hz, J(P–H) = 2.06 Hz, 2H, CH_3CH_2S); 2.72, 2.74, 2.79, 2.83 (s's, 12H, NCH_3s). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.46 MHz): δ_P 247.3. ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 18.09 (q, J(C–H) = 128.1 Hz, CH_3CH_2S); 29.49 (dt, J(C–H) = 141.6 Hz, J(C–P) = 23.1 Hz, CH_3CH_2S); 44.75, 45.05 (dq, too complex to determine J(C–H), NCH_3s); 211.6 (s, terminal CO). IR ($CHCl_3$): 2944vw, 2928w, 2883w, 2876sh, 2833w, 2795vw, 1450w, 1378vw, 974m, 613m, 602m, 595sh cm^{-1}; terminal carbonyl region: 2060s, 2020vs, 1978vs,br, 1948vs,br cm^{-1}. Mass spectrum (EI): m/z (relative intensity) 460 (M^+, 17), 432 ($M^+ -$ CO, 38), 404 ($M^+ -$ 2CO, 40), 376 ($M^+ -$ 3CO, 19), 348 ($M^+ -$ 4CO, 51), 320 ($M^+ -$ 5CO, 57), 292 ($M^+ -$ 6CO, 100), 264 ($Fe_2SHP(NMe_2)_2^+$, 87), 230 (?, 71), 219 ($Fe_2SEtPNH^+$ and $Fe_2SP(NMe_2)^+$, 41), 187 ($Fe_2P(NMe_2)_2^+$, 66), 175 (Fe_2SP^+, 36), 145 (Fe_2SH^+, 29), 144 (Fe_2S^+, 43), 119 ($FeSP^+$, 17).

3.12. *Reaction of (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ with ethylenediamine*

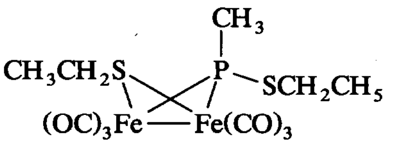
Triethylamine (0.12 ml, 0.09 g, 0.86 mmol) and ethylenediamine (0.06 ml, 0.05 g, 0.90 mmol) were added by syringe to a diethyl ether solution of 0.25 g (0.57 mmol) (μ-Cl_2P)(μ-EtS)$Fe_2(CO)_6$ at room temperature. The solution immediately became cloudy with precipitate formation upon addition of the ethylenediamine, but remained orange in color. The solution was stirred at room temperature for 12 h under argon. After removal of the solvent by trap-to-trap distillation, the orange oily residue was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (2:3, v/v) afforded 0.24 g (0.56 mmol, 100%) of an orange-yellow solid which was recrystallized from hot pentane and identified as (μ-$H\overline{NCH_2CH_2NHP}$)(μ-EtS)$Fe_2(CO)_6$; m.p. 143–144°C (dec).



Anal. Found: C, 28.25; H, 2.75. $C_{10}H_{11}Fe_2N_2O_6PS$ calc.: C, 27.94; H, 2.58%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.38 (t, J(H–H) = 7.3 Hz, 3H, CH_3CH_2S); 2.52 (q, J(H–H) = 7.3 Hz, J(H–P) = 2.1 Hz, 2H, CH_3CH_2S); 3.00 (broad s, 1H, b-NH); 3.08 (broad s, 1H, a-NH); 3.20–3.36 (complex m's, 4H, NCH_2CH_2N). ^{31}P {^{1}H} NMR ($CDCl_3$, 121.64 MHz): δ_P 253.2. ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ_C 18.31 (q, J(C–H) = 127.8 Hz, CH_3CH_2S); 35.22 (dt, J(C–H) = 140.3 Hz, J(C–P) = 22.7 Hz, CH_3CH_2S); 44.02 (dt, J(C–H) = 143.4 Hz, J(C–P) = 32.4 Hz, NCH_2CH_2N), 211.5 (s, terminal CO). IR ($CHCl_3$): 3430w, 2986vw, 2961w, 2924w, 2870w, 1290w, 1272vw, 1072m, 922vw, 860vw,br, 610m cm^{-1}; terminal carbonyl region: 2060s, 2020vs, 1968vs,br, 1938vs,br cm^{-1}. Mass spectrum (EI): m/z (relative intensity) 430 (M^+, 16), 402 ($M^+ -$ CO, 66), 374 ($M^+ -$ 2CO, 56), 346 ($M^+ -$ 3CO, 29), 318 ($M^+ -$ 4CO, 54), 290 ($M^+ -$ 5CO, 100), 262 ($M^+ -$ 6CO, 96), 234 ($Fe_2SHP(N(H)CH_2CH_2N(H))^+$, 86), 232 ($Fe_2SH(NCH_2CH_2N)^+$, 58), 205 ($Fe_2SPNHCH_3^+$, 61), 201 (?, 57), 176 (Fe_2SHP^+, 35), 160 (?, 16), 145 (Fe_2SH^+, 29), 144 (Fe_2S^+ and Fe_2PH^+, 57), 120 ($FeSPH^+$, 8), 89 ($FeSH^+$, 14), 59 ($H_2NCH_2CH_2NH^+$, 29), 56 (Fe^+, 14).

3.13. *Reaction of (μ-CH_3PCl)(μ-EtS)$Fe_2(CO)_6$ with lithium ethanethiolate*

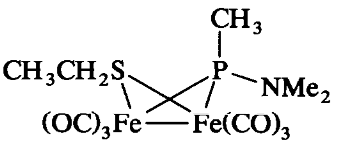
Lithium ethanethiolate, generated at −78°C by reaction of 0.06 ml (0.05 g, 0.81 mmol) of ethanethiol with 0.33 ml (0.78 mmol) of a 2.35 M solution of ^{n}BuLi in hexane in 10 ml of THF for 15 min, was added by cannula to a stirred, solution of 0.33 g (0.77 mmol) of (μ-CH_3PCl)(μ-EtS)$Fe_2(CO)_6$ in THF at −78°C, and warmed slowly to room temperature. The solution slowly darkened to brown–orange upon warming and the progress of the reaction was monitored by TLC analysis. The solvent was removed at reduced pressure and the oily orange-brown residue purified by filtration chromatography. Elution with CH_2Cl_2/pentane (1:20, v/v), afforded a mixture of two products which were separated by column chromatography (with pentane). The first minor yellow band was discarded (starting material). The second orange band afforded 0.23 g (0.513 mmol, 66%) of an orange solid which was recrystallized from hot pentane and identified as the axial methyl isomer of (μ-CH_3PSEt)(μ-EtS)$Fe_2(CO)_6$; m.p. 97–98°C.



Anal. Found: C, 29.66; H, 3.02. $C_{11}H_{13}Fe_2O_6PS_2$ calc.: C, 29.49; H, 2.92%. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.29 (t, J(H–H) = 7.2 Hz, 3H, μ-SCH_2CH_3); 1.39 (t, J(H–H) = 7.3 Hz, 3H, μ-$PMeSCH_2CH_3$); 2.21 (d, J(H–P) = 10.6 Hz, 3H, μ-PCH_3); 2.55 (dq, J(H–H) = 7.3 Hz, J(H–P) = 2.3 Hz, 2H, μ-SCH_2CH_3); 2.74 (p, 2H, μ-$PSCH_2CH_3$). ^{31}P {^1H} NMR ($CDCl_3$, 121.64 MHz): δ_P 165.4. IR ($CHCl_3$): 2990w, 2963w, 2930w, 1451w, 1378w, 1287vw, 894m, 877w, 615m, 595m,br, 573br,sh cm^{-1}; terminal carbonyl region: 2068s, 2034vs, 1988vs,br cm^{-1}. Mass spectrum (EI): m/z (relative intensity): 448 (M^+, 9), 420 ($M^+ - CO$, 18), 392 ($M^+ - 2CO$, 40), 364 ($M^+ - 3CO$, 18), 336 ($M^+ - 4CO$, 19), 308 ($M^+ - 5CO$, 27), 280 ($M^+ - 6CO$, 100), 252 ($Fe_2PMeSHSEt^+$, 80), 224 ($Fe_2PMeSHSH^+$, 63), 207 ($Fe_2S_2P^+$, 50), 177 (Fe_2SHPH^+ and Fe_2SHS^+, 44), 176 (Fe_2SHP^+ and $Fe_2S_2^+$, 65), 144 (Fe_2S^+ and Fe_2PH^+, 32), 112 (Fe_2^+ and Fe^{2+}, 5), 56 (Fe^+, 17), 43 ($CH_3CH_2CH_2^+$, 11).

3.14. Reaction of (μ-CH_3PCl)(μ-EtS)$Fe_2(CO)_6$ with dimethylamine

Dimethylamine was bubbled slowly through a diethyl ether solution of 0.36 g (0.850 mmol) of (μ-CH_3PCl)(μ-EtS)$Fe_2(CO)_6$ at room temperature for 4 h. Diethyl ether was added as necessary to maintain the solution level in the flask. The solution gradually became cloudy with precipitate formation, but remained orange in color. After removal of the solvent by trap-to-trap distillation, the orange oily residue was purified by filtration chromatography. Elution with CH_2Cl_2/pentane (1:20, v/v) afforded a mixture of starting material and product which were separated by medium pressure column chromatography. Elution with pentane afforded 0.06 g (0.145 mmol, 17%) of an orange solid which was identified as starting material by comparison of its ^1H and ^{31}P NMR spectra with those of an authentic sample. Further elution with pentane afforded 0.16 g (0.362 mmol, 43%) of an orange solid which was recrystallized from hot pentane and identified as the axial methyl isomer of (μ-CH_3PNMe_2)(μ-EtS)$Fe_2(CO)_6$; m.p. 95–96°C.



Anal. Found: C, 30.46; H, 3.29. $C_{11}H_{14}Fe_2NO_6PS$ calc.: C, 30.66; H, 3.27%. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, J(H–H) = 7.3 Hz, 3H, SCH_2CH_3); 2.01 (d, J(H–P) = 9.2 Hz, 3H, PCH_3); 2.46 (q, J(H–H) = 6.8 Hz, 2H, SCH_2CH_3); 2.57 (s, 3H, NCH_3); 2.61 (s, 3H, NCH_3). ^{31}P {^1H} NMR ($CDCl_3$, 121.64 MHz): δ_P 209.3. IR ($CHCl_3$): 2963w, 2930w, 2880w, 1451w, 975m, 894w, 868vw, 615m, 600m,br, 578m,sh cm^{-1}; terminal carbonyl region: 2062s, 2023vs, 1982vs,br cm^{-1}. Mass spectrum (EI): m/z (relative intensity) 431 (M^+, 18), 403 ($M^+ - CO$, 36), 375 ($M^+ - 2CO$, 29), 347 ($M^+ - 3CO$, 21), 319 ($M^+ - 4CO$, 23), 291 ($M^+ - 5CO$, 66), 263 ($M^+ - 6CO$, 100), 235 ($Fe_2SHPMeNMe_2^+$, 68), 219 ($Fe_2SPNMe_2^+$, 26), 187 ($Fe_2PNMe_2^+$, 53), 175 (Fe_2SP^+, 25), 145 (Fe_2SH^+, 25), 144 (Fe_2S^+ and Fe_2PH^+, 33), 119 ($FeSP^+$, 4), 90 (?, 16), 69 (?, 11), 56 (Fe^+, 5), 44 (NMe_2^+, 23).

Acknowledgment

The authors are grateful to the National Science Foundation for support of this work.

References

1 D. Seyferth, G. B. Womack, C. M. Archer and J. C. Dewan, *Organometallics, 8* (1989) 430.
2 D. Seyferth, G. B. Womack, C. M. Archer, J. P. Fackler, Jr. and D. O. Marler, *Organometallics, 8* (1989) 443.
3 K. Evertz and G. Huttner, *Chem. Ber., 121* (1988) 143.
4 (a) L.-C. Song, R.-J. Wang, Y. Li, H.-G. Wang and J.-T. Wang, *Youji Huaxue, 9* (1989) 512.
(b) L.-C. Song, Y. Li, Q.-M. Hu, J.-T. Wang, W.-J. Zhao, Y.-Q. Fang and S. Zhang, *Chem. J. Chin. Univ., 11* (1990) 154.
5 W. McFarlane and G. Wilkinson, *Inorg. Synth., 8* (1966) 181.