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Iron carbene complexes

II *. Syntheses and characterization of the iron carbene complexes $[Fe(CO)_3(L)\{C(OEt)R\}]$ (L = CO, PPh_3; R = $C_6H_4NMe_2$, Bu, $CH(SPh)CH_2Bu$)

Simon Lotz *, **Jan L.M. Dillen** and **Marthie M. van Dyk**
Department of Chemistry, University of Pretoria, Pretoria 0002, (South Africa)

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Abstract

The o-lithiated reagent of *N,N*-dimethylaniline reacts with $Fe(CO)_4L$ (L = CO, PPh_3) to yield, after alkylation with $[Et_3O][BF_4]$, $[Fe(PPh_3)(CO)_3\{C(OEt)C_6H_4NMe_2\}]$ (L = PPh_3), the methylene bridged diiron complex $[(CO)_2(L)Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4NMe_2\}Fe(L)(CO)_2]$ (L = CO) and the monoiron butylcarbene complexes $[Fe(L)(CO)_3\{C(OEt)Bu\}]$ (L = CO, PPh_3). The corresponding reaction with lithiated phenylvinylsulphide leads to the formation of iron acyl anions which, after alkylation wit $[Et_3O][BF_4]$, affords the monoiron carbene complexes $[Fe(CO)_3(L)\{C(OEt)CH(SPh)CH_2Bu\}]$. The structure of the complex with L = PPh_3 was confirmed by X-ray crystallography. The crystals are monoclinic, space group $P2_1/n$ with $a = 11.212(2)$, $b = 20.004(3)$, $c = 15.600(3)$ Å, β 107.81(2)° and $Z = 4$.

Introduction

Relatively few iron carbene complexes of the type $[Fe(CO)_3(L)\{C(OR^1)R^2\}]$ have been synthesized from organolithium reagents. Other methods have been developed to prepare mononuclear carbene complexes of iron [2–4]. One of the problems often encountered, deals with preferred alkylation of the metal centre [5–7]. Various studies have been undertaken to control the site of alkylation and in special cases O-alkylation of tetracarbonyl and tricarbonyliron acylates led to the formation of Fischer type carbene complexes [8,9]. A further complication encountered during syntheses of monoiron carbene complexes is the formation of dimers [10]. For example in the reaction of $[Fe(CO)_5]$ and PhLi mainly $[(CO)_3Fe\{\mu\text{-}(C(O)Ph)_2\}\text{-}$

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* For part I see ref. 1.

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$Fe(CO)_3]$ formed and the bridged benzylidene complex, $[(CO)_4Fe\{\mu\text{-}C(H)Ph\}\text{-}Fe(CO)_4]$, was isolated in a very low yield. The use of organolithium reagents for the preparation of methylene bridged dinuclear complexes is therefore not favoured and their preferential formation above terminal carbene complexes has been shown [1,11].

We reported the reaction of α-lithiated sulphides with $[M(CO)_6]$ (M = Cr, W) which, after alkylation with $[Et_3O][BF_4]$, afforded five-membered metallacyclic carbene thioether chelates [12,13]. In contrast, α-thiocarbanions react with iron pentacarbonyl and then with methyl iodide to give β-keto sulfides [14]. Our studies on the formation of metallacyclic complexes were extended to β-lithiated reagents which afforded the chelates $[\overline{M(CO)_4\{C(OEt)C_6H_4}XR\}]$ (M = W, Cr; X = O, S, NMe; R = Me) [15,16].

In this paper we wish to report on progress made towards the syntheses of metallacyclic monoiron carbene heteroatom chelates and the formation of new monoiron carbene complexes is discussed. Due to our interest in the structural features of iron carbene complexes a single crystal X-ray diffraction determination of $[Fe(CO)_3(PPh_3)\{C(OEt)CH(SPh)CH_2Bu\}]$ was carried out.

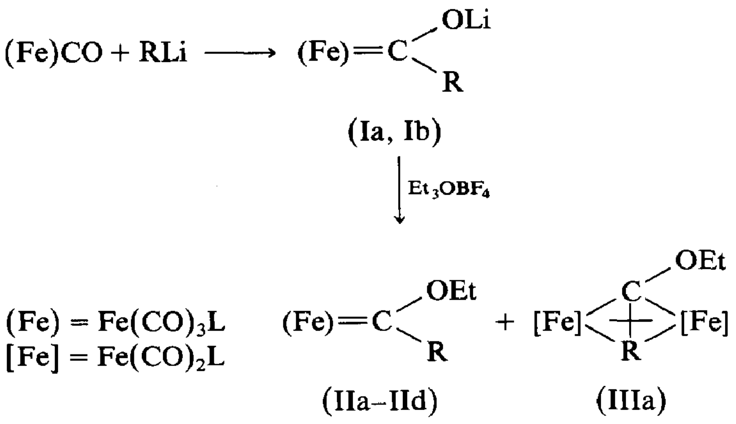
Results and discussion

Syntheses of iron carbene complexes

Organolithium reagents were prepared by treating equimolar amounts of butyllithium and *N,N*-dimethylaniline or thiophenylethylene according to published procedures [17–19]. A problem with these preparations is that lithiation is not accomplished quantitatively. These organolithium solutions reacted with $[Fe(CO)_4L]$ (L = CO, PPh_3) to yield, after subsequent alkylation, $[Fe(CO)_3(L)\{C(OEt)R\}]$ (L = PPh_3, R = Bu (IIb), $o\text{-}C_6H_4NMe_2$ (IIa), $CH(SPh)CH_2Bu$ (IId); L = CO, R = $o\text{-}C_6H_4NMe_2$ (IIc)) and $[(CO)_3Fe\{\mu\text{-}C(OEt)\mu^2\text{-}C_6H_4NMe_2\}Fe(CO)_3]$ (IIIa) which are shown in Scheme 1.

An excess of $C_6H_5NMe_2$ was refluxed with n-BuLi in hexane for 16 h upon which the formation of *o*-Li-*N,N*-dimethylaniline was complete. This was allowed to react with $Fe(CO)_4L$ in THF at low temperature. After removal of the solvent, the acylates $[Fe(L)(CO)_3\{C(OLi)C_6H_4NMe_2\}]$ (L = PPh_3, CO (Ia)) were dissolved in dichloromethane and alkylated with $[Et_3O][BF_4]$. In the case of Ia the acylate was isolated and characterised by means of ^1H NMR spectroscopy (vide infra). The products that formed were isolated by column chromatography and characterized.

Whereas the alkylation of $[Fe(CO)_4\{C(OLi)C_6H_4NMe_2\}]$ (Ia) led to the formation of the bridged dimer $[(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4NMe_2\}Fe(CO)_3]$ (IIIa), alkylation of $[Fe(CO)_3(PPh_3)\{C(OLi)C_6H_4NMe_2\}]$ led to the isolation of the monomer $[Fe(CO)_3(PPh_3)\{C(OEt)C_6H_4NMe_2\}]$ (IIa). The observation of a corresponding red zone during the chromatographic isolation of IIa indicated the probable formation of the analogous PPh_3-dimer. Unfortunately this band decolorized with time on the column. As opposed to the monomer IIa, the corresponding CO-analogue could not be obtained. It appeared that the triphenylphosphine ligand exerted a stabilizing effect, thereby making isolation of the monomer IIa possible. The fact that the dimer IIIa was formed in a much higher yield was therefore attributed to more labile carbonyl ligands promoting dimerization. The formation of the monoiron carbene complexes $[Fe(CO)_3(L)\{C(OEt)Bu\}]$, in fairly high yields, was ascribed



	L	R
Ia	CO	o-$C_6H_4NMe_2$
Ib	PPh_3	$CH(SPh)CH_2Bu$
IIa	PPh_3	o-$C_6H_4NMe_2$
IIb	PPh_3	n-Bu
IIc	CO	$CH(SPh)CH_2Bu$
IId	PPh_3	$CH(SPh)CH_2Bu$
IIIa	CO	η^2-$C_6H_4NMe_2$

Scheme 1

to the presence of unreacted BuLi in the lithiated reaction mixture. Likewise, the presence of excess *N,N*-dimethylaniline in the reaction mixture used for lithiation purposes, resulted in the formation of $[Fe(CO)_4\{N(Me)_2C_6H_5\}]$ (IV) which was identified by ^1H NMR and mass spectroscopy. Product IV was also formed during the decomposition of IIIa in solution in the presence of air. From the distribution of products it could be concluded that the reactive species in the reaction mixture were o-$LiC_6H_4NMe_2$, $C_6H_5NMe_2$ and unreacted BuLi.

Equimolar amounts of butyllithium and thiophenylethylene were treated at −20 °C in THF. This solution was added to $[Fe(CO)_4L]$ ($L = CO, PPh_3$) and after subsequent alkylation yielded $[Fe(CO)_3(L)\{C(OEt)CH(SPh)CH_2Bu\}]$ (L = CO (IIc), PPh_3 (IId)). The attachment of the lithiated reagent through the α-carbon to the carbene carbon atom led us to conclude that the active agent in the lithiated solution was $LiCH(SPh)CH_2Bu$. Usually metallation of vinylic ethers and thioethers occurs by deprotonation of an α-proton to give $LiC(SPh)CH_2$ [18,19]. A possible explanation for this is the fact that our lithiated reagent was prepared at a much higher temperature. It is likely that $LiC(SPh)CH_2$ might have been present in the lithiated mixture, but that the acylate obtained was either alkylated at the metal centre or that it led to unstable carbene compounds. Our attempts to synthesize monoiron carbenes from α-lithiated sulphides $Li\overline{CHS(CH_2)_3S}$ or $LiCH(SPh)SPh$ failed. This was, however, not unexpected as it was reported that α-thiocarbanions and $Fe(CO)_5$ usually lead to β-keto sulphides and thioesters [9,14]. The complex IIc is less stable than IId and slowly decomposed in solution. In addition, the iron

Table 1

NMR spectra of I, II and III

Complex	Solvent	^1H chemical shifts [a], δ(ppm)					$^{13}C/^{31}P$
		OCH_2CH_3	OCH_2CH_3	$N(CH_3)_2$	Aryl	Alkyl	
Ia	$(CD_3)_2SO$	–	–	2.85(s, 6H)	6.70(m, 2H), 7.14(dd, 2H)	–	
Ib	$(CD_3)_2SO$	–	–	–	7.14–7.62(m, 20H)	6.62(t, H), 4.31(m, 2H), 1.75(m, 2H), 1.36(m, 2H), 1.29(m, 2H), 0.85(t, 3H)	
IIa	C_6D_6	5.12(q, 2H)	1.25(t, 3H)	2.53(s, 6H)	7.02–7.88(m, 19H)		
IIb	C_6D_6	5.13(q, 2H)	1.16(t, 3H)	–	6.96–7.06(m, 6H), 7.53(m, 3H), 7.77–7.83(m, 6H)	3.50(t, 2H), 1.75(m, 2H) 1.27(m, 2H), 0.85(t, 3H)	^{13}C: 249.4 ($COCH_2$); 199.7(CO); 133.7, 133.6(PPh_3) ^{31}P: 44.23(PPh_3)
IIc	$CDCl_3$	4.92(q, 2H)	1.37(t, 3H)	–	7.20–7.39(m, 5H)	4.58(t, H), 4.07(m, 2H) 1.60(m, 2H), 1.27(m, 4H) 0.85(t, 3H)	
IId	$CDCl_3$	5.06(q, 2H)	1.46(t, 3H)	–	7.26–7.67(m, 20H)	5.28(t, H), 4.05(q, 2H), 1.73(m, 2H), 1.26(m, 4H), 0.88(t, 3H)	
	$(CD_3)_2CO$	5.14(q, 2H)	1.47(t, 3H)	–	7.24–7.64(m, 20H)	6.62(t, H), 4.06(q, 2H), 1.79(m, 2H), 1.32(m, 4H) 0.85(t, 3H)	^{13}C: 215.8(Fe_2C); 213.1, 211.4, 206.7(CO); 127.7, 126.4, 123.9, 123.3(C_6H_4); 63.2, 50.1 (NMe_2); 71.1(OCH_2); 15.2(OCH_2CH_3)
III	$CDCl_3$	4.30(q, 2H)	1.62(t, 3H)	2.86(s, 3H) 2.69(s, 3H)	6.83–7.07(m, 2H) 7.73–7.84(m, 2H)		
	$(CD_3)_2CO$	4.27(q, 2H)	1.57(t, 3H)	2.88(s, 3H) 1.67(s, 3H)	6.69(m, 2H) 7.09(d, H) 7.61(d, H)		
$C_6H_5NMe_2$	$(CD_3)_2CO$			2.99(s, 6H)	6.28(t, H) 6.34(d, 2H) 6.80(dd, 2H)		

[a] Deuterated solvent was used as internal reference. Chemical shifts are relative to TMS.

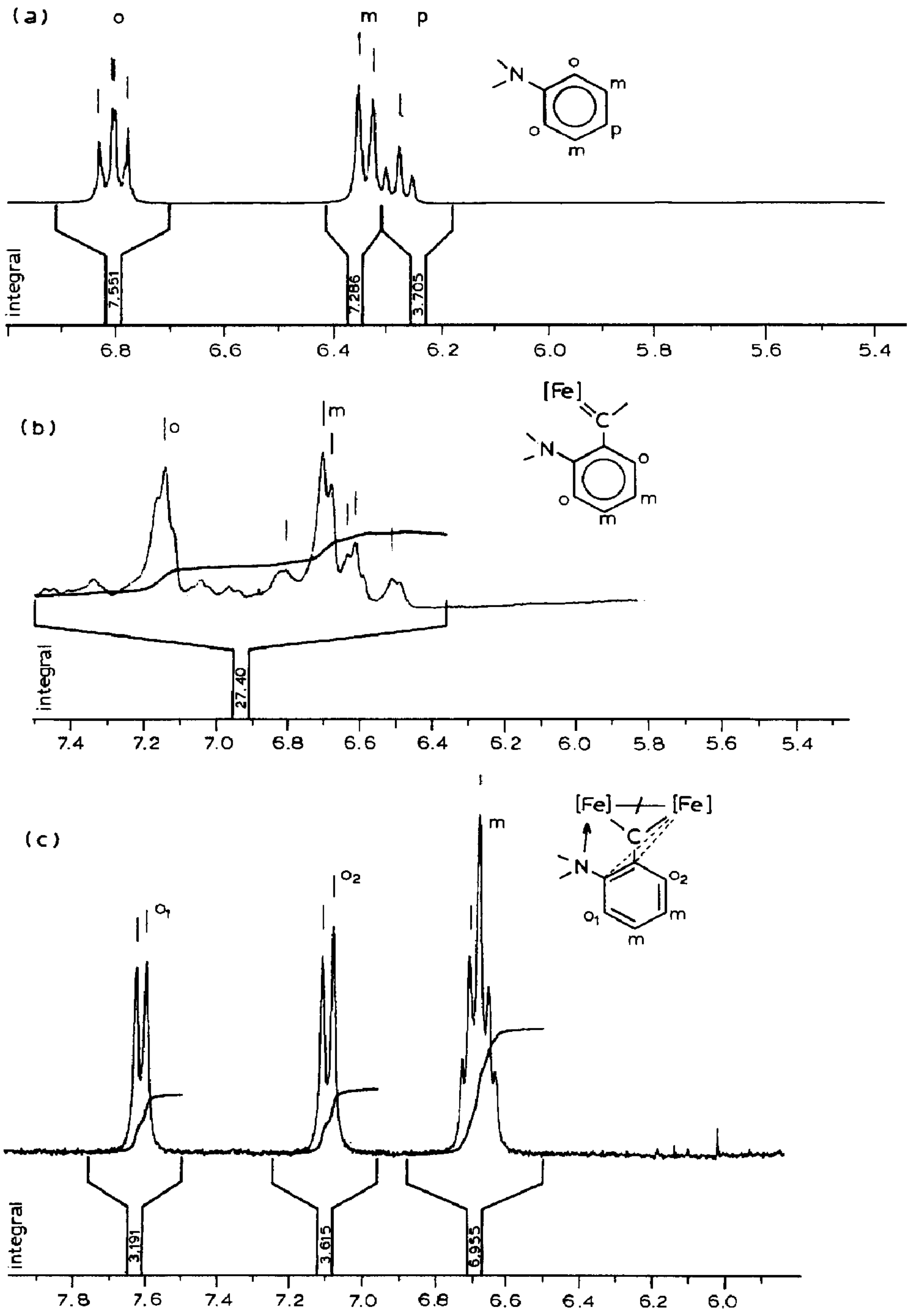


Fig. 1. ^{1}H NMR spectra in the aryl region for (a) $C_6H_5NMe_2$, (b) $[Fe(CO)_4\{C(OLi)C_6H_4NMe_2\}]$ (Ia) and (c) $[(CO)_3Fe\{\mu\text{-}C(OEt)\eta^2\text{-}C_6H_4NMe_2\}Fe(CO)_3$ (IIIa) in $(CD_3)_2SO$.

acylate $[Fe(CO)_3(PPh_3)\{C(OLi)CH(SPh)CH_2Bu\}]$ (Ib) was also isolated and studied by ^1H NMR spectroscopy.

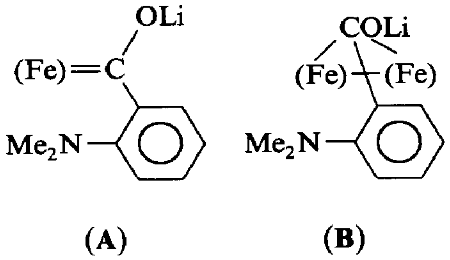
Spectral studies

The IR and mass (*m/e*) spectra for the complexes I, II, III and IV are given in the Experimental Section. The NMR spectral data of complexes Ia, Ib, IIa–IId and IIIa are listed in Table 1 and the spectrà of the aryl proton region of *N,N*-dimethylaniline, Ia and IIIa measured in $(CD_3)_2SO$, illustrated in Fig. 1. The chemical shifts of the methylene protons of the ethoxy group of the monoiron complexes with terminal carbene ligands (IIIa–IIId) occur at higher δ-values than the δ-value found for the diiron complex with a bridged carbene ligand (IIIa). This shift is even more noticeable in the ^{13}C NMR resonance of the carbene carbon. A δ-value of 249.4 ppm was recorded for IIb compared to a value of 215.8 ppm for IIIa. This downfield shift in the ^{13}C and ^1H NMR spectra is very helpful in discriminating between the two forms [11].

The value of 249.4 ppm for the carbene carbon resonance in IIb compares well with reported values of 251.2, 255 and 230.5 ppm for the complexes $[Fe(CO)_4\{\overline{COC(Me)_2C(Me)_2O}\}]$, $[Fe(CO)_4\{C(SMe)NMe_2\}]$ and $[Fe(CO)_4\{C(OEt)N^iPr_2\}]$, respectively [21,22,23].

Two important aspects, with regard to the mechanism whereby the dimer IIIa formed, deal with the nature of the iron acylate and the formation of the metallacycle through nitrogen coordination. Monoiron formyl and acetyl acylates were isolated as stable tetraethylammonium salts and studied structurally [24]. In contrast, structural studies of $[Fe_2(CO)_5\{C(O)R\}(\mu\text{-}PPh_2)_2]^-$ with different counterions, showed binuclear complexes and no coordination of the acyl oxygen to the second iron atom [25]. We experienced considerable difficulty in growing crystals of Ia and efforts to obtain suitable crystals for a single crystal X-ray analysis were unsuccessful. The ^1H NMR spectra presented in Fig. 1 support the fact that cyclization of the carbene-nitrogen ring and the η^2-coordination of the benzene ring to the other iron atom only took place after alkylation. The small change in the pattern of the resonances of the *ortho-* and *meta*-protons on going from $C_6H_5NMe_2$ to the acylate salt Ia, can be ascribed to the fact that the $C_6H_4NMe_2$ group is an aryl substituent on the carbene carbon which is not coordinated through the nitrogen. A dramatic change in the resonance of the proton adjacent to the nitrogen, resulted from coordination of the nitrogen to the iron on the formation of a metallacycle. Further support was found in two sharp singlets at δ 2.86 and 1.69 ppm of equal intensity, indicating two different chemical environments for the methyl protons, observed for IIIa but absent for $C_6H_5NMe_2$ and Ia. Based on this evidence two possible structures remain for Ia (**A** or **B**) and are shown in Scheme 2. The isolation and characterization of $[Fe(CO)_3\{PPh_3\}\{C(OEt)C_6H_4NMe_2\}]$ (IIa) points to a monomeric iron acylate for Ia.

An interesting feature of the mass spectrum of $[Fe(CO)_3(PPh_3)\{C(OEt)C_6H_4NMe_2\}]$ (see Experimental Section) is the initial fragmentation of a fragment with *m/e*-value 121 which represents the carbene substituent, $C_6H_5NMe_2$, followed by five fragments with *m/e*-value 28 which can be assigned to the three CO ligands, a carbene CO and a C_2H_4-fragment leading to the principle ion peak $[Fe(PPh_3)]^+$. On the contrary, initial loss of carbonyls before the fragmentation of the carbene ligand is usually found [26].



(Fe) = Fe(CO)$_4$

Scheme 2

X-Ray structure of [Fe(PPh$_3$)(CO)$_3${C(OEt)CH(SPh)CH$_2$Bu}] (IId)

The conformation and atomic numbering scheme for IId is shown in Fig. 2; selected bond lengths (Å) and angles (°) are listed in Table 2.

The iron atom has a slightly distorted trigonal bipyramidal coordination about the metal centre with the carbene and phosphine occupying the axial sites. The iron atom is displaced out of the equatorial coordination plane by −0.0675 Å away from the phosphine ligand [27]. The triphenylphosphine ligand is located in a staggered arrangement about the Fe–P bond with respect to the three equatorial carbonyl

Table 2

Selected bond lengths (Å) and valence angles (°) for IId

Bond lengths			
C(1)–Fe	1.776(6)	C(1)–O(1)	1.146(6)
C(2)–Fe	1.744(6)	C(2)–O(2)	1.169(6)
C(3)–Fe	1.764(6)	C(3)–O(3)	1.155(6)
C(4)–C(5)	1.498(11)	C(4)–O(4)	1.450(7)
C(6)–C(7)	1.547(7)	C(6)–Fe	1.864(5)
C(6)–O(4)	1.319(5)	C(7)–C(8)	1.552(9)
C(7)–S	1.826(6)	C(13)–S	1.766(6)
C(19)–P	1.825(5)	C(25)–P	1.825(5)
C(31)–P	1.831(5)	Fe–P	2.244(1)
Valence angles			
Fe–C(1)–O(1)	175.2(5)	Fe–C(2)–O(2)	178.4(5)
Fe–C(3)–O(3)	178.2(6)	C(5)–C(4)–O(4)	106.8(6)
C(7)–C(6)–Fe	125.8(4)	C(7)–C(6)–O(4)	104.9(4)
Fe–C(6)–O(4)	129.2(4)	C(6)–C(7)–C(8)	115.4(5)
C(6)–C(7)–S	106.1(4)	C(8)–C(7)–S	109.2(4)
C(14)–C(13)–S	118.9(6)	C(18)–C(13)–S	121.0(6)
C(1)–Fe–C(2)	123.5(3)	C(1)–Fe–C(3)	116.1(3)
C(2)–Fe–C(3)	120.4(3)	C(1)–Fe–C(6)	93.9(2)
C(2)–Fe–C(6)	86.0(2)	C(3)–Fe–C(6)	93.2(2)
C(1)–Fe–P	86.5(2)	C(2)–Fe–P	90.9(2)
C(3)–Fe–P	89.8(2)	C(6)–Fe–P	176.5(2)
C(4)–O(4)–C(6)	123.8(5)	C(19)–P–C(25)	101.7(2)
C(19)–P–C(31)	103.7(2)	C(25)–P–C(31)	102.2(2)
C(19)–P–Fe	115.3(2)	C(25)–P–Fe	116.5(2)
C(31)–P–Fe	115.4(2)	C(7)–S–C(13)	104.3(3)

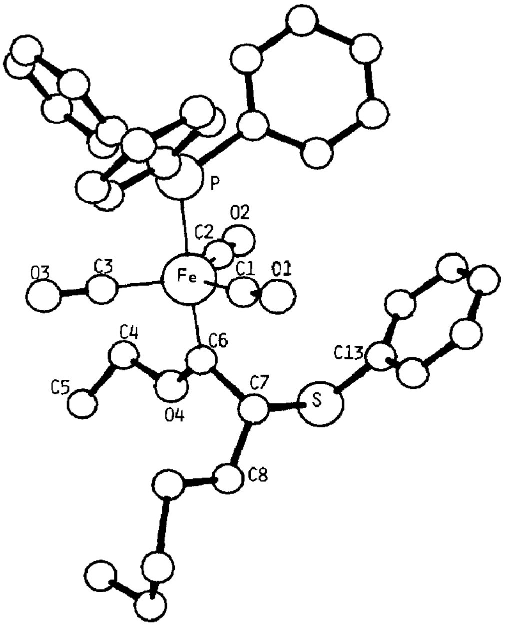


Fig. 2. The molecular structure with atomic numbering for [Fe(PPh_3)($CO)_3${C(OEt)CH(SPh)CH_2Bu}] (IId).

groups. A torsion angle of −44.1° is found for C(31)–P–Fe–C(1) and a value of 75.7° for C(25)–P–Fe–C(1).

The pentyl carbon atoms have large anisotropic temperature factors which probably reflect disorder in this chain and bond lengths are not reliable. Therefore, atoms C(9) to C(12) were refined isotropically, and the bonds C(9)–C(10), C(10)–C(11) and C(11)–C(12) were constrained to have a value of 1.540(5) Å. Notable is the distortion caused by the metal, other ligands and the substituents on the carbene carbon leading to deviations from ideal values for the sp^2-hybridized carbene carbon atom. Angles around the carbene carbon decrease in the order Fe–C(carbene)–heteroatom > Fe–C(carbene)–C(R) ≫ heteroatom–C(carbene)–C(R) (values for IId are 129.2(4), 125.8(4) and 104.9(4)°).

The Fe–C(carbene) bond length of 1.864(5) Å is significantly shorter than the distance of 2.00 Å calculated by ab initio SCF MO methods for [Fe$(CO)_4${C(OH)H}], the 1.915(15) Å reported for [Fe{η^4-$C_{10}H_{16}$}$(CO)_2${C(OEt)C_6H_4Me-*o*}] and the longer values of 1.951(10), 2.013(3) and 2.007(5) Å found for the aminocarbene complexes [Fe(PEt_3)$(CO)_3${$\overline{\text{CN(Me)CH}_2\text{CH}_2\text{N}}$(Me)}], [Fe$(CO)_4${C(OEt)$N^iPr_2$}] and [Fe$(CO)_4${CN(Ph)$CH_2CH_2$N(Ph)}] respectively [28,29,23,30].

In the complexes [Fe$(CO)_4$(L)] the equatorial Fe–C(carbonyl) bond lengths are typically a little longer than the value for the axial carbonyl (L = C(OEt)N^iPr_2 eq: 1.786(4) (av.) vs. ax: 1.763(4) Å or L = CN(Ph)CH_2CH_2N(Ph) eq: 1.789(6) (av.) ax: 1.767(6) Å) [23,30]. Shortening of the Fe–C(carbonyl) bond lengths are found when a carbonyl is substituted by a phosphine ligand. The Fe–C(carbonyl) distances in IId of 1.761(6) Å (av.) compare well with a value of 1.733(12) Å for [Fe(PEt_3)$(CO)_3$-{$\overline{\text{CN(Me)CH}_2\text{CH}_2\text{N}}$(Me)}] [29].

Table 3

Crystal data for IId

Formula	$C_{36}H_{37}FeO_4PS$
M (g/mol)	652.6
Space group	$P2_1/n$
a (Å)	11.212(2)
b (Å)	20.004(3)
c (Å)	15.600(3)
β (°)	107.81(2)
V (Å^3)	3331.1
Z	4
D_c (g/cm^3)	1.30
$F(000)$	1368
μ(Mo-K_α) (1/cm)	5.49
Scan range (°)	$3 \leqslant \theta \leqslant 23$
Reflections, measured	4780
Reflections, used	4120
Variables refined	462
R	0.073
R_w	0.040
Residual density (e/Å^3)	0.89

The bond length of 2.244(1) Å for the Fe–P distance in IId is identical with the value reported for Fe–P in $[Fe(CO)_4\{PPh_3\}]$ [27].

Experimental

All reactions and manipulations were carried out under nitrogen atmosphere and with solvents dried prior to use. Reagent grade chemicals were used without further purification. The organolithium reagent, o-$LiC_6H_4NMe_2$, was prepared as reported previously [17]. Iron pentacarbonyl was filtered before use and $[Fe\{PPh_3\}(CO)_4]$ prepared according to a published method [31]. Column chromatography on SiO_2 (0.063–0.200 mm) was performed on 2 × 35 cm columns at $-10\,°C$. Microanalyses were performed by F. Pascher and E. Pascher, Microanalytical Laboratories, Bonn, West Germany. Infrared spectra were recorded on a Bruker IFS 113 V spectrometer and calibrated against polystyrene. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AC 300 MHz instrument and mass spectra on a Perkin–Elmer RMU-6H instrument operating at 70 eV. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

Synthesis

Reaction of $[Fe(CO)_4(L)]$ ($L = PPh_3$, CO) with o-$LiC_6H_4NMe_2$. A freshly prepared solution of o-$LiC_6H_4NMe_2$ (10 mmol) was added to a cooled ($-80\,°C$) solution of $[Fe(CO)_4(L)]$ (10 mmol) in 30 cm^3 THF. The reaction mixture immediately changed colour and became dark red-brown. After stirring the mixture for 1 h in the cold and another hour at room temperature, the solvent was removed in vacuo. The metalate was washed with hexane and a portion was purified by crystallization from dichloromethane/hexane mixtures (Ia). The residue was dissolved in dichloromethane (50 cm^3), cooled to $-30\,^\circ$C and [Et_3O][BF_4] (10 mmol) added. The reaction mixture was stirred for 2 h, firstly at $-10\,^\circ$C and thereafter at room temperature. The reaction products were filtered through SiO_2 and anhydrous Na_2SO_4 and stripped of solvent. The residue was chromatographed with dichloromethane/hexane (1/5) and several bands were observed and the main ones collected. The first, an orange band, which was collected for the reaction L = PPh_3, was the carbene complex [$Fe(CO)_3(PPh_3)\{C(OEt)Bu\}$] (IIb). The second, a red band, yielded [$(CO)_2(L)Fe\{\mu$-$C(OEt)$-η^2-$C_6H_4NMe_2\}Fe(L)(CO)_2$] (L = CO, IIIa) which was recrystallized from hexane. The corresponding red band for L = PPh_3 faded during column chromatography. For the case L = PPh_3, a brown product which was eluted before the red band, was collected (IIa). Increasing the polarity of the eluant to a 1/1 ratio fo dichloromethane/hexane led to the collection of a brown oil from which [$Fe(CO)_4\{N(Me)_2C_6H_5\}$] (IV) was obtained.

IIa: Yellow-brown crystals, m.p. 130 °C (dec), yield 12%. IR (ν(CO), hexane): 1946s, 1896s cm^{-1}. MS, m/e 579 (M^+, 11%), 458 ([$M-C_6H_5NMe_2$]$^+$, 1%), 430 ([$M-C(OH)C_6H_4NMe_2$]$^+$, 5%), 402 ([$M-C(OEt)C_6H_4NMe_2$]$^+$, 7%), 374 ([$Fe(PPh_3)(CO)_2$]$^+$, 12%), 346 ([$Fe(PPh_3)(CO)$]$^+$, 18%), 318 ([$Fe(PPh_3)$]$^+$, 100%). Anal. Found: C, 66.67; H, 5.69; N, 2.11. $C_{32}H_{30}NO_4PFe$ calcd.: C, 66.34; H, 5.39; N, 2.42%.

IIb: orange crystals, m.p. 142 °C, yield 19%. IR (ν(CO), hexane): 1930s, 1891vs cm^{-1}. MS, m/e 516 (M^+, 7%), 488 ([$M-CO$]$^+$, 2%), 460 ([$M-2CO$]$^+$, 6%), 432 ([$M-3CO$]$^+$, 10%), 318 ([$Fe(PPh_3)$]$^+$, 100%). Anal. Found: C, 65.28; H, 5.89. $C_{28}H_{29}O_4PFe$ calcd.: C, 65.12; H, 5.68%.

IIIa: red crystals, m.p. 115 °C, yield 54%. IR (ν(CO), hexane): 2055m, 2008s, 1983s, 1976sh, 1960w, 1942m cm^{-1}. MS, m/e 457 (M^+, 10%), 429 ([$M-CO$)]$^+$, 9%), 401 ([$M-2CO$]$^+$, 31%), 373 ([$M-3CO$]$^+$, 22%), 345 ([$M-4CO$]$^+$, 16%), 317 ([$M-5CO$]$^+$, 30%), 289 ([$M-6CO$]$^+$, 100%) 261 ([$Fe\{\mu$-$C(OH)C_6H_4NMe_2\}Fe$]$^+$, 70%). Anal. Found: C, 44.93; H, 3.58; N, 3.23. $C_{17}H_{15}NO_7Fe_2$ calcd.: C, 44.68; H, 3.31; N, 3.07%.

IV: red oil, yield 12%. ^{1}H NMR (δ, ppm, CD_3Cl), 7.33–7.19(m, 2H), 6.79–6.61(m, 3H), 2.90(s, 6H). MS, m/e 289 (M^+, 32%), 261 ([$M-CO$]$^+$, 16%), 233 ([$M-2CO$]$^+$, 3%), 205 ([$M-3CO$]$^+$, 4%), 187 ([$M-4CO$]$^+$, 28%). Anal. Found: C, 50.47; H, 3.78; N, 4.5. $C_{12}H_{11}O_4NFe$ calcd.: C, 49.06; H, 3.34; N, 4.85%.

Reaction of [$Fe(CO)_4(L)$] (L = CO, PPh_3) with $LiCH(SPh)CH_2Bu$. A solution of $PhSCHCH_2$ (10 mmol, 1.36 cm^3) in THF (30 cm^3) was allowed to react with n-BuLi for 1 h at $-20\,^\circ$C and thereafter for another hour at room temperature. The colour of the solution changed from orange, at low temperature, to yellow at room temperature. This solution was added to [$Fe(CO)_4(L)$] (L = PPh_3, CO; 10 mmol) in THF and stirred for 1 h at $-80\,^\circ$C. After stirring for 1 h at room temperature, the solvent was removed under reduced pressure. The residue was washed with hexane. A portion of the metalate was purified by repeatedly dissolving the metalate in dichloromethane and adding hexane (L = PPh_3, Ib). The reaction mixture was again cooled (0 °C) and [Et_3O][BF_4] (1.9 g, 10 mmol) added. After stirring for ten minutes, 250 cm^3 water was added while stirring vigorously. The products were extracted into 50 cm^3 portions of hexane which were filtered through SiO_2 and anhydrous Na_2SO_4. The combined fraction was stripped of solvent, the residue chromatographed with dichloromethane/hexane (1/5) and the main red band colleced. Recrystallization from hexane yielded [$Fe(CO)_3(L)\{C(OEt)CH(SPh)CH_2$-$Bu\}$] (L = CO, IIc; L = PPh_3, IId).

IIc: red oil, yield 27%. IR (ν(CO), hexane), 2075m, 2032vs, 2005s, 1949w cm^{-1}. MS, M^+ not observed, Anal. Found: C, 55.32; H, 6.25. $C_{19}H_{22}O_5SFe$ calcd.: C, 54.56; H, 5.30%.

IId: red crystals, m.p. 106 °C, yield 59%, IR (ν(CO), hexane): 1946s, 1902 vs cm^{-1}. MS, M^+ not observed. Anal. Found: C, 66.51; H, 5.91. $C_{36}H_{37}O_4SPFe$ calcd.: C, 66.26; H, 5.72%.

Data collection and structure determination

Diffraction data were collected at room temperature with an Enraf–Nonius CAD4 diffractometer using graphite monochromated Mo-K_α radiation. Lattice constants were obtained from a least squares fit of 25 centred reflections, and are listed in Table 1. An $\theta/2\omega$-scan with a speed ratio of 3/1 was used. Data were collected with a variable scan speed, with a maximum of 3.3/min, and a minimum corresponding to 50 s measuring time per reflection. The ω-scan angle changed as $0.51 + 0.34 \tan\theta(°)$. The horizontal aperture was fixed at 1.42 mm and the vertical slit at 4.0 mm. Intensity checks were carried out every hour and an orientation control every 200 reflections. Data were corrected for Lorentz and polarization effects and for absorption using an empirical method involving ω-scans.

The crystal structure was solved by Patterson and subsequent Fourier methods. All but the hydrogens on three atoms of the butyl chain were located experimentally, the remainder were placed on expected positions. The structure was refined anisotropically with a full matrix method, the hydrogen atoms sharing an isotropic temperature factor, $U = 0.114(3)$ Å^2 [32]. Final residuals were $R = 0.073$ and $R_w = 0.040$ for 462 variables and 4120 data points.

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