inversion of **3b** ought to be nontrivial since the phosphorus atom in this compound is still four-coordinate. Without having further proof for this, we propose as an inversion pathway a rotation of the Fe–W unit around the FePW three-center bond, thereby formally considering the phosphorus atom as three-coordinate. At the moment there is, however, no obvious way of testing this hypothesis.

Conclusions

The cluster types 1 and 2 extend the series of clusters that can be opened by addition of donor ligands.[3,7,9] They differ from the previously studied μ_3-PR-bridged trimetal systems in that they add two PR_3 ligands showing no noticeable intermediate and that reversal to the closed cluster framework is possible by loss of CO only or by loss of CO and PR_3. For the one case studied kinetically an associative mechanism is indicated for the rate-determining step in complete analogy to dinuclear $FeCo(\mu\text{-}AsMe_2)$ systems. A significant stereochemical information has been obtained in the observation that optical activity is maintained in this type of cluster opening but that the open cluster framework sustains slow inversion. This puts a serious limitation on the transfer of stereochemical information in conversions that may involve cluster framework reactions.

Although the cluster types 1 and 2 demonstrate again that ligand substitution on clusters can occur by an addition–elimination sequence, this will certainly not be the case for all custers. Future investigations should elucidate which factors (besides just metal–metal bond strengths) determine the preference of clusters for "internal" or "external" substitution mechanisms that in turn should offer a better understanding for the still ill-defined area of cluster catalysis.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Alexander von Humboldt-Stiftung, and the Fonds der Chemischen Industrie. We thank Mr. C. de Meric de Bellefon and Mr. J.-L. Richert, Strasbourg, for ^{31}P NMR measurements, Dr. K. Steinbach, Marburg, for mass spectra, and the Rechenzentrum der Universität Freiburg for computer time.

Supplementary Material Available: Tables containing all distances and angles for **3a** (7 pages); a listing of F_o/F_c for **3a** (13 pages). Ordering information is given on any current masthead page.

Use of Organolithium Reagents in the Synthesis of Diiron Complexes with Bridged and Terminal Carbene Ligands. X-ray Structures of $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4NMe_2\}Fe(CO)_3$ and $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)Ph\}$

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Received August 21, 1986

Reaction of iron pentacarbonyl with $o\text{-}MeXC_6H_4Li$ (X = O, NMe), followed by alkylation of the acylmetalate with $[Et_3O]BF_4$, gave the methylene-bridged complexes $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4XMe\}Fe(CO)_3$. Substitution of two carbonyls from the complex where X = O with $P(OMe)_3$ yielded $(CO)_2\{P(OMe)_3\}Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4OMe\}Fe\{P(OMe)_3\}(CO)_2$ as the main product. The complexes $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)R\}$ (R = *n*-Bu, Me, Ph), which have terminal carbene ligands, were synthesized from $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$ and organolithium reagents. The structures of $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4NMe_2\}Fe(CO)_3$ (II) and $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)Ph\}$ (VII) were confirmed by X-ray crystallography. The crystals of II are monoclinic, space group $P2_1/n$, with $a = 9.180\ (3)$ Å, $b = 18.636\ (4)$ Å, $c = 10.890\ (5)$ Å, $\beta = 95.62\ (4)°$, and $Z = 4$. The crystals of VII are monoclinic, space group $P2_1/c$, with $a = 8.909\ (2)$ Å, $b = 15.028\ (3)$ Å, $c = 15.203\ (13)$ Å, $\beta = 102.39\ (4)°$, and $Z = 4$. The final R factors are $R = 4.7\%$ and $R_w = 3.0\%$ for II and $R = 9.3\%$ and $R_w = 4.8\%$ for VII.

Introduction

Five-coordinate metallacyclic complexes of iron-containing carbene–carbon and hetero donor atoms in five-membered chelate rings are scarce (Chart I). In a reaction of $Fe(CO)_5$ with $LiN\text{-}i\text{-}Pr_2$ and subsequent treatment with $[Et_3O]BF_4$, the cyclic carbene complex $Fe(CO)_3\{C(N\text{-}i\text{-}Pr_2)OC(O)Et\}$ was found as a minor product in low yield.[3]

Chart I

By contrast, chelates of this kind are well-known for chromium with heteroatoms O, S, N, and P.[4-7] Since

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complexes of the type $Fe(CO)_3(L)\{C(OR)R^1\}$ (L = $P(OR)_3$ and PR_3; R = alkyl and aryl) are found, the synthesis of such chelates seems likely.[8]

α-Thiocarbanions react with $Fe(CO)_5$ and then with methyl iodide to give β-keto sulfides.[9] The question of metal alkylation instead of O-alkylation has been dealt with in a number of papers.[10-15] Fischer-type carbene complexes of iron are not as easily accessible with organolithium reagents as are their chromium analogues. The chromium chelates $Cr\{C(OEt)C(OEt)C(SR)R^1\}(CO)_4$, however, are also obtainable from $Cr\{S(CH_2R)R^1\}(CO)_5$ and butyllithium via a different route.[16] Thioether compounds undergo decarbasulfurization reactions with $Fe_2(CO)_9$ to give complexes of general formula $Fe_2(CO)_6(SR)_2$.[17] The reactivity of diiron complexes with bridged phosphido and alkylthio ligands toward metalation reactions has been studied.[18,19]

In our efforts to prepare an iron chelate with a metallacyclic carbene ligand, we have employed organolithium reagents with heteroatoms in the β-position. In this paper we describe the use of such reagents to synthesize methylene bridged diiron complexes. An unusual structure of a compound with a η^2-coordinated benzene ligand is of particular interest. We also wish to report on the synthesis of dithio-bridged diiron complexes with terminal carbene ligands and the X-ray structure determination of one of these compounds.

Experimental Section

General Comments. All reactions and manipulations were carried out routinely under nitrogen with dried solvents. Reagent grade chemicals were used without further purification. Organolithium reagents were purchased (Aldrich) and o-$MeOC_6H_4Li$ and o-$Me_2NC_6H_4Li$ prepared as previously reported.[20,21] Column chromatography on SiO_2 (0.063–0.200 mm) was performed on 2 cm × 40 cm columns cooled by recycling cold methanol through column jackets. Microanalyses were obtained from F. Pascher and E. Pascher, Microanalytical Laboratories, Bonn. Infrared spectra were recorded by using a Beckman IR4250 spectrometer and calibrated against polystyrene. Proton NMR spectra were recorded on a Bruker WP 80-MHz instrument and mass spectra on a Perkin-Elmar RMU-6H instrument operating at 70 eV. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

Synthesis. Preparation of $(CO)_3Fe\{\mu$-$C(OEt)$-η^2-$C_6H_4OMe\}Fe(CO)_3$ (I). A freshly prepared solution of o-$MeOC_6H_4Li$ (10 mmol) was added to a cooled (−100 °C) solution of $Fe(CO)_5$ (1.97 g, 10 mmol) in 30 cm^3 of THF. The reaction mixture immediately changed color and became dark brown. After the mixture was stirred for 2 h at room temperature, $[Et_3O]BF_4$ (1.9 g, 10 mmol) was added followed with 250 cm^3 of water 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 and stripped of solvent. The residue was chromatographed with ether/hexane (1/5), and two main bands were collected. The first, a green zone, was the well-known $Fe_3(CO)_{12}$. The second, a red band, was collected and the solvent removed in vacuo. This compound (III) was unstable and rapidly decomposed in solution. It was possible to crystallize 1.02 g of I from this residue by extracting with pentane.

I: yield 46%; mp 86 °C dec; MS, M^+ not observed; IR (ν_{CO}, hexane) 2056 (m), 2026 (s), 1990 (s), 1968 (s), 1948 (m) cm^{-1}. Anal. Calcd for $Fe_2C_{16}H_{12}O_8$: C, 43.28; H, 2.73; Fe, 25.16. Found: C, 43.81, H, 3.07; Fe, 25.79.

Preparation of $(CO)_3Fe\{\mu$-$C(OEt)$-η^2-$C_6H_4NMe_2\}Fe(CO)_3$ (II). Freshly prepared o-$Me_2NC_6H_4Li$ (10 mmol) was added to 1.97 g of $Fe(CO)_5$ (10 mmol) in THF, and the same procedures as above were followed. Column chromatography was performed with dichloromethane/hexane (1/5), and the main product, an orange band, was collected and stripped of solvent. Recrystallization from pentane yielded 1.23 g of II.

II: yield 54%; mp 115 °C; MS, m/e 457 $\{M^+\}$, 429 $\{M^+ - CO\}$, 401 $\{Me^+ - 2CO\}$, 373 $\{M^+ - 2CO\}$, 373 $\{M^+ - 3CO\}$, 345 $\{M^+ - 4CO\}$, 317 $\{M^+ - 5CO\}$, 289 $\{M^+ - 6CO\}$, 261 $\{Fe\{\mu$-$C(OH)C_6H_4NMe_2\}Fe^+\}$; IR (ν_{CO}, hexane) 2055 (m), 2008 (s), 1983 (s), 1976 (sh), 1960 (w), 1942 (m) cm^{-1}. Anal. Calcd for $Fe_2C_{17}H_{15}NO_7$: C, 44.68; H, 3.31; N, 3.07. Found: C, 44.93, H, 3.58; N, 3.23.

Reaction of I with $P(OMe)_3$. $P(OMe)_3$ (0.68 cm^3, 7.7 mmol) was added to 1.0 g (2.25 mmol) of the methylene-bridged diiron complex I, which was dissolved in 50 cm^3 benzene, and the solution stirred for 1 h at room temperature. The red solution changed to yellow, after which the solvent was removed. The residue was chromatographed with benzene/hexane (5/3) yielding three bands. The first red band yielded 0.43 g (0.68 mmol, 30%) of $(CO)_2\{P(OMe)_3\}Fe\{\mu$-$C(OEt)$-$\eta^2$-$C_6H_4OMe\}Fe\{P(OMe)_3\}(CO)_2$ (IV) after recrystallization from CH_2Cl_2/hexane. The second yellow zone was collected and after recrystallization from CH_2Cl_2/hexane afforded 0.41 g (1.1 mmol, 24%) $Fe\{P(OMe)_3\}_2(CO)_3$.[22,23] A third red zone, representing a product in very low yield, was not collected.

IV: red crystals; mp 74 °C dec; MS, M^+ not observed; IR (ν_{CO}, hexane) 2065 (w), 1996 (m), 1955 (vs) cm^{-1}. Anal. Calcd for $Fe_2C_{20}H_{30}O_{12}P_2$: C, 37.77; H, 4.75; P, 9.74. Found: C, 38.23; H, 5.11; P, 9.20.

$Fe\{P(OMe)_3\}_2(CO)_3$:[22,23] yellow crystals; mp 74 °C; MS, m/e 388 $\{M^+\}$, 360 $\{M^+ - CO\}$, 332 $\{M^+ - 2CO\}$, 304 $\{M^+ - 3CO\}$, 180 $\{Fe[P(OMe)_3]^+\}$, 56 $\{Fe^+\}$; IR (ν_{CO}, hexane) 1918 (br) cm^{-1}; ^1H NMR (δ, $CDCl_3$) 3.72 ($P(OMe)_3$, "Harris triplet").[24]

Preparation of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$. A solution of 1.2 g (10 mmol) of 1,3-dithiane in 20 cm^3 (150 mmol) of $Fe(CO)_5$ was irradiated for 2 h after it was positioned 6–8 cm from the mercury lamp. The solution was then refluxed for 1 h at 150 °C and finally irradiated and refluxed simultaneously for another 2 h. The excess $Fe(CO)_5$ was removed in vacuo and the residue dissolved in 20–50 cm^3 of THF. After filtration through Al_2O_3, the solvent was again removed and the residue chromatographed on SiO_2 (−10 °C) with hexane as the eluent. The red fraction was crystallized from hexane and yielded 1.6 g of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$: yield 42%; mp 90 °C; MS, m/e 386 $\{M^+\}$, 358 $\{M^+ - CO\}$, 330 $\{M^+ - 2CO\}$, 302 $\{M^+ - 3CO\}$, 274 $\{M^+ - 4CO\}$, 246 $\{M^+ - 5CO\}$, 218 $\{M^+ - 6CO\}$, 190 $\{FeSCH_2SFe^+\}$; IR (ν_{CO}, hexane) 2075 (m), 2031 (s), 2003 (s), 1987 (sh), 1958 (w), 1942 (w) cm^{-1}; ^1H NMR ($CDCl_3$, δ values) 2.25–2.06 (m, 4), 1.94–1.69 (m, 2). Anal. Calcd for $Fe_2C_9H_6O_6S_2$: C, 27.65; H, 1.55; S, 16.40. Found: C, 27.94; H, 1.82; S, 16.17.

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Table I. Experimental Data for X-ray Diffraction Study of II and VII

	II	VII
formula	$Fe_2C_{17}H_{15}NO_7$	$Fe_2C_{17}H_{16}O_6S_2$
mol wt	456.9	492.1
space group	$P2_1/n$	$P2_1/c$
a, Å	9.180 (3)	8.909 (2)
b, Å	18.636 (4)	15.028 (3)
c, Å	10.890 (5)	15.203 (13)
β, deg	95.62 (4)	102.39 (4)
V, Å^3	1854 (1)	1988 (1)
Z	4	4
d(calcd), g cm^{-3}	1.64	1.55
d(measd), g cm^{-3}	1.63	1.53
cryst size, mm	0.12 × 0.18 × 0.24	0.10 × 0.15 × 0.07
μ(Mo Kα), cm^{-1}	15.0	16.9
radiation	Mo Kα, λ = 0.7107 Å	Mo Kα, λ = 0.7107 Å
scan method (ω:2θ)	1:$^1/_3$	1:1
scan speed, deg min^{-1}	var, max 5.49	var, max 3.30
scan range	$+h,+k,\pm l$; $3 \leq \theta \leq 25°$	$+h,+k,\pm l$; $3 \leq \theta \leq 25°$
no. of data measd	3363	3868
no. of unobsd data [$I \leq 2\sigma(I)$]	825	1385
no. of unique reflctns used	2949	3210
no. of parameters refined	292	250
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.047	0.093
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.030	0.048

Reaction of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$ with RLi (R = *n*-Bu, Me, Ph). Preparation of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)Bu\}$ (V). A solution of 3.86 g (10 mmol) of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$ in 100 cm^3 THF was cooled to −70 °C and 6.4 cm^3 of a 1.6 M (10 mmol) BuLi in hexane solution added dropwise. The mixture was stirred for 1 h at −70 °C. $[Et_3O]BF_4$ (1.89 g, 10 mmol) was added to the mixture at room temperature followed by 250 cm^3 of water, while stirring vigorously. The products were extracted into 25-cm^3 portions of hexane and filtered through SiO_2 and anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue chromatographed with benzene/hexane (2/5). The first red zone was collected and after removal of the solvent yielded 2.12 g (4.5 mmol) red oil of V.

V: yield 45%; MS, *m/e* values 472 {M$^+$}, 444 {M$^+$ − CO}, 416 {M$^+$ − 2CO}, 388 {M$^+$ − 3CO}, 360 {M$^+$ − 4CO}, 332 {M$^+$ − 5CO}; IR (ν_{CO}, hexane) 2043 (s), 1995 (vs), 1970 (vs), and 1945 (s) cm^{-1}. Anal. Calcd for $Fe_2C_{15}H_{20}O_6S_2$: C, 38.16; H, 4.27; S, 13.55. Found: C, 39.01; H, 4.74; S, 14.04.

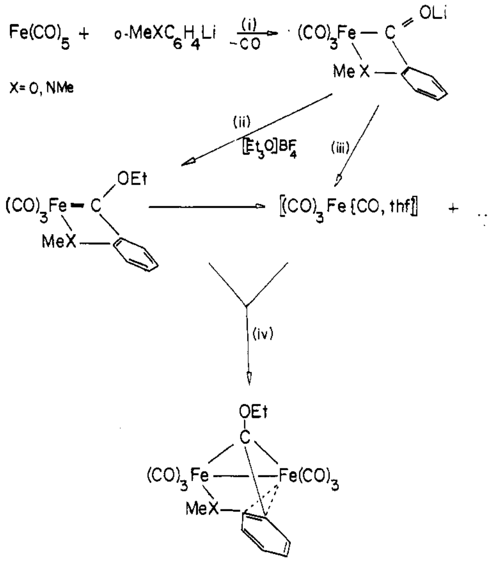
Preparation of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)Me\}$ (VI). The same procedures as above were followed. The reaction was carried out at −30 °C and on 10-mmol scale. Products were chromatographed with CH_2Cl_2/hexane (2/5) as eluent, and the last red zone was collected. Recrystallization from pentane yielded 0.69 g (1.60 mmol) red crystals of VI.

VI: yield 18%; mp 86 °C; MS, *m/e* values 430 {M$^+$}, 402 {M$^+$ − CO}, 374 {M$^+$ − 2CO}, 346 {M$^+$ − 3CO}, 318 {M$^+$ − 4CO}, 290 {M$^+$ − 5CO}; IR (ν_{CO}, hexane) 2040 (s), 1998 (vs), 1972 (vs), 1942 (s) cm^{-1}. Anal. Calcd for $Fe_2C_{12}H_{14}O_6S_2$: C, 33.52; H, 3.28; S, 14.91. Found: C, 33.91; H, 3.57; S, 14.68.

Preparation of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)Ph\}$ (VII). The same procedures used above for V was followed. The reaction was carried out on 10-mmol scale. Recrystallization of the first red zone from pentane yielded 1.69 g (3.43 mmol) of red crystals of VII.

VII: yield 42%; mp 96 °C; MS, *m/e* values 492 {M$^+$}, 464 {M$^+$ − CO}, 436 {M$^+$ − 2CO}, 408 {M$^+$ − 3CO}, 380 {M$^+$ − 4CO}, 352 {M$^+$ − 5CO}; IR (ν_{CO}, hexane) 2050 (s), 1995 (vs), 1972 (vs), 1948 (s) cm^{-1}. Anal. Calcd for $Fe_2C_{17}H_{16}O_6S_2$: C, 41.49%; H, 3.27%; S, 13.03%. Found: C, 41.71%; H, 3.43%; S, 12.84%.

Scheme I



X-ray Analysis. All diffraction measurements were performed at room temperature on an Enraf-Nonius CAD-4F diffractometer using graphite-monochromatized Mo Kα radiation. Both unit cells were determined from 25 randomly selected reflections for each, using the automatic search, index, and least-squares routines. The refined cell constants and other relevant crystal data for the orange crystals of $Fe_2C_{17}H_{15}NO_7$ (II) and $Fe_2C_{17}H_{16}O_6S_2$ (VII), together with the details of the intensity measurements, are listed in Table I. For both crystals the data were corrected for Lorentz and polarization effects and empirical absorption corrections were applied by measuring the intensities of nine reflections with χ near 90° and for different ψ values ($0 \leq \psi \leq 360°$, every 10°), using the EAC program from the Enraf-Nonius packages. The maximum and minimum transmission factors were 1.00 and 0.95 for II and 1.00 and 0.79 for VII, respectively. Three standard reflections were measured periodically to check orientation and crystal stability in each case, and the decay during data collections was less than 3%.

The structures were solved by conventional Patterson and Fourier methods and refined by blocked-matrix least-squares techniques using SHELX.[25] The position of all the hydrogen atoms were obtained from a difference electron density map for II, and these were refined isotropically with a common temperature factor (U = 0.074 (4) Å^2). For VII the hydrogen atoms were placed in calculated positions with a common temperature factor that refined to (U = 0.088 (9) Å^2). All the non-hydrogen atoms were refined anisotropically by using all the data and $\sigma^{-2}(F)$ weights. The final difference map showed residual electron densities of 0.3 and 0.9 e/Å^3 (close to Fe) for II and VII, respectively. Scattering factors for iron were taken from the literature.[26]

Results and Discussion

Synthesis. Reaction of $Fe(CO)_5$ with *o*-$MeXC_6H_4Li$. Iron pentacarbonyl reacts with organolithium reagents *o*-$MeXC_6H_4Li$ (X = O, NMe) in THF to give a red-brown acylate salt. Alkylation of this salt with $[Et_3O]BF_4$ affords the bridged methylene complex $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4XMe\}Fe(CO)_3$ (X = O (I), NMe (II)). The mechanism whereby the dimers are formed was not studied, and different pathways are possible. The formation of these complexes involving dimeric acylates was not

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Table II. Proton NMR Data of $(CO)_2(L)Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4XMe\}Fe(CO)_2(L)$ (X = O, L = CO (I), L = $P(OMe)_3$ (IV); X = NMe, L = CO (II)), $Fe\{C(OEt)C_6H_4OMe\}(CO)_3$ (III), and $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)R\}$ (R = *n*-Bu (V), Me (VI), Ph (VII))

	chemical shifts,[a] δ				
	$COCH_2$	OCH_2CH_3	X*Me*	C_6H_4[b]	L or R
I	4.36 (q)	1.38 (t)	3.83 (s)	7.84–7.73 (m)	
				7.07–6.83 (m)	
II	4.30 (q)	1.32 (t)	2.86 (s)	7.76–7.60 (m)	
			1.69 (s)	6.79–6.50 (m)	
III[c]	4.74 (q)	1.55 (t)	3.90 (s)	7.70–7.22 (m)	
IV	4.36 (q)	1.38 (t)	3.90 (s)	7.86–7.73 (m)	$P(OMe)_3$ 3.73 (d)[d]
				7.06–6.87 (m)	
			SCH_2	SCH_2CH_2	
V	5.19 (q)	1.60 (t)	2.29–2.07 (m)	1.98–1.80 (m)	*n*-Bu 1.69–1.11 (m)
VI	5.06 (q)	1.60 (t)	2.23–2.07 (m)	1.98–1.81 (m)	Me 2.93 (s)
VII	5.15 (q)	1.67 (t)	2.16–1.92 (m)	1.67–1.49 (m)	*Ph* 7.80–7.65 (m), 7.45–7.31 (m)

[a] Measured in $CDCl_3$ relative to internal Me_4Si. The number of protons established by integration are in accord with the given structures. Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet. [b] Two distinct regions of signals, both integrating for two protons were found for I, II, and IV. [c] Unstable compound. [d] J_{PH} = 12.64 Hz.

considered.[27,28] Instead, a pathway based on an unstable metallacyclic carbene intermediate is presented in Scheme I. Step i represents the formation of a monoiron acylate salt. The formyl and acetyl acylates $[Fe\{P(OPh)_3\}(CO)_3C(O)R]^-$ (R = H, Me) were isolated as stable tetraethylammonium salts and studied structurally.[29] Enhanced stability was found due to the five-membered chelate ring systems for the compounds $(CO)_4M\{C(OLi)C(OH)C(R^1)SR^2\}$ (M = W, Cr; R^1 = Ph; R^2 = Me, Ph) and a five-membered ring tricarbonyl acylate salt is preferred.[5] Step ii represents the formation of a metallocyclic carbene complex following alkylation of the oxygen with $[Et_3O]BF_4$. Although insufficient, evidence for the existence of such a mononuclear carbene intermediate can be found from a ^1H NMR study of the unstable compound III, the presence of the chelate ring in the final dimers and the fact that a similar product, $(CO)_3Fe\{C(N^iPr_2)CO(O)Et\}$, was fully characterized.[3] Metal alkylation and/or the decomposition of the proposed mononuclear carbene chelate leads to the formation of organic compounds and unstable, coordinatively unsaturated iron carbonyl species (step iii), which also acts as precursors in the formation of triiron dodecacarbonyl. The simultaneous presence of the proposed mononuclear carbene intermediate and unstable iron species are used to explain the formation of the bridged methylene complexes in step iv. Reactions of low-valent coordinatively unsaturated metal species with metal carbene complexes represent a novel route for synthesizing bridged methylene complexes.[30,31] The classical carbene synthesis, yielding μ-methylene complexes instead of the corresponding mononuclear compounds, supports the idea that carbenes preferentially adopt, where possible, a bridged rather than a terminal position.[32,33]

The oxygen diiron complex I is less stable in solution than the nitrogen analogy II and slowly decomposes. The bridged carbene and η^2-coordinated benzene were subjected to possible substitution by adding excess $P(OMe)_3$. Substitution with $P(OMe)_3$ proceeded smoothly at room temperature in benzene for I, and two products were isolated. It was found for the main product that, instead of the methylene bridge or the η^2-coordinated benzene, two carbonyls were displaced, yielding $(CO)_2\{P(OMe)_3\}Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4OMe\}Fe\{P(OMe)_3\}(CO)_2$. The second product was the well-known $Fe\{P(OMe)_3\}_2(CO)_3$ (V), which may form as a result of the decomposition of I.[22,23] By contrast, no substitution took place for II at room temperature in benzene. On heating the solution turned green, but only the starting methylene-bridged complex could be isolated.

Reaction of $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$ with RLi. Iron pentacarbonyl and 1,3-dithiane was first heated to reflux (150 °C), then irradiated with UV light, and subsequently heated and irradiated to afford $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$. The deprotonation of bridged phosphido and alkylthio ligands in diiron complexes has been studied extensively.[18,19,34] The reaction of $(CO)_3Fe\{SCH_2S\}Fe(CO)_3$ with lithium diisopropylamide at −78 °C led unexpectedly, via an intramolecular nucleophilic substitution reaction, to the complex $(CO)_3Fe\{SCHS(Li)\}Fe(CO)_3$.[18] Analogous products were reported for different phosphido-bridged diiron complexes under similar reaction conditions.[19,34] Bearing this in mind and with our interest lying in the nucleophilic attack on a carbonyl, we treated $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_3$ with RLi (R = *n*-Bu, Me, Ph) in THF at low temperatures. Alkylation in THF with $[Et_3O]BF_4$ yielded a number of products, one of them being $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{C(OEt)R\}$, which has a terminal carbene ligand. The alkylation of the dianionic diiron compound $Na_2Fe_2(PPh_2)_2(CO)_6$ with $ICH_2CH_2CH_2I$ resulted in the formation of the diiron carbene complex $Fe_2(\mu\text{-}PPh_2)_2(CO)_5\{C(CH_2)_3O\}$.[35]

Spectroscopic Studies. The ^1H NMR chemical shifts

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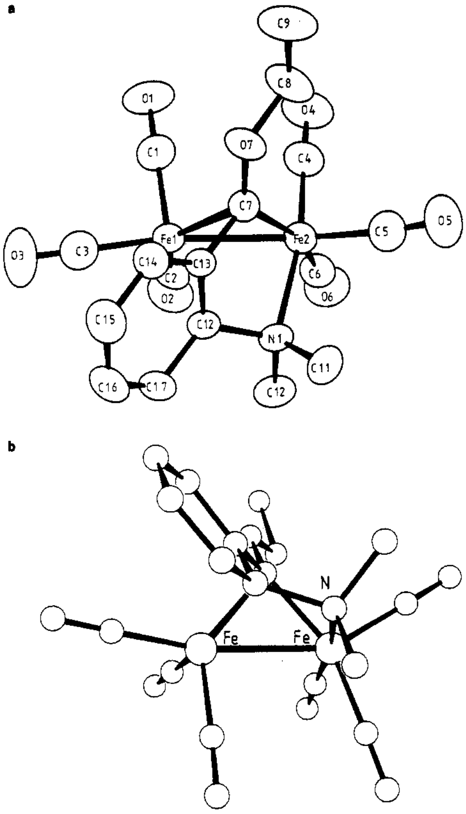

Figure 1. Two different views of $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4NMe_2\}Fe(CO)_3$ (II): (a) with the atomic numbering scheme used and (b) a projection showing the displacement of the nitrogen atom.

of the methylene-bridged complexes $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4XMe\}Fe(CO)_3$ (X = O (I), NMe (II)), $Fe\{C(OEt)C_6H_4OMe\}(CO)_3$ (III), and $(CO)_2\{P(OMe)_3\}Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4OMe\}Fe\{P(OMe)_3\}(CO)_2$ (IV) and carbene complexes $(CO)_3Fe\{S(CH_2)_3S\}Fe(CO)_2\{(OEt)R\}$ (R = *n*-Bu (V), Me (VI), Ph (VII)) are given in Table II. Two distinct regions of signals were observed for the aromatic protons of the methylene-bridged complexes, each integrating for two protons. This can be ascribed to the different chemical environments of the protons in positions 3 and 6 and those in positions 4 and 5 with respect to the η^2-coordinated carbon atoms of the benzene ring. Inconclusive evidence for the existence of the proposed mononuclear carbene intermediate $Fe\{C(OEt)C_6H_4OMe\}(CO)_3$ (III) was found in the resonances of the aromatic protons and a downfield shift of the ethoxy protons. The value of 4.74 ppm for the methylene protons in III was shifted downfield by 0.38 ppm compared with that in $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4OMe\}Fe(CO)_3$. A survey of ^{13}C and ^1H NMR data has shown that signals of mononuclear carbene carbon atoms, and to a lesser extent those of the attached protons, are shifted downfield compared with the corresponding signals of the analogous dinuclear methylene-bridged complexes.[32,36] The ethoxy protons of the diiron complexes with terminal carbene ligands (V–VII) give rise to signals that are found even further downfield. Attempts to measure a ^{13}C spectrum of III failed due to instability.

The ^1H NMR spectrum of $(CO)_2\{P(OMe)_3\}Fe\{\mu\text{-}C(OEt)C_6H_4OMe\}Fe\{P(OMe)_3\}(CO)_2$ has similar features to that of I and II and shows three infrared-active bands in the $\nu(CO)$ stretching region (Experimental Section). From these observations a structure similar to that found for $[\mu\text{-}(SMe)Fe(CO)_2L]_2$ is proposed for IV with the phosphite ligands and sulfur atoms on the same side of a plane through the metal–metal bond.[37,38]

Table III. Selected Bond Lengths (Å) for II and VII

	II		
Fe(1)–C(1)	1.768 (4)	Fe(1)–C(2)	1.792 (4)
Fe(1)–C(3)	1.778 (5)	Fe(1)–Fe(2)	2.570 (1)
Fe(1)–C(7)	2.120 (3)	Fe(1)–C(12)	2.106 (3)
Fe(1)–C(13)	2.089 (3)	Fe(2)–C(5)	1.792 (4)
Fe(2)–C(4)	1.746 (5)	Fe(2)–C(7)	1.965 (3)
Fe(2)–C(6)	1.815 (4)	C(7)–C(13)	1.417 (5)
Fe(2)–N(1)	2.087 (3)	N(1)–C(11)	1.493 (5)
C(7)–O(7)	1.363 (4)	C(12)–C(13)	1.409 (5)
O(7)–C(8)	1.400 (6)	C(13)–C(14)	1.444 (5)
N(1)–C(10)	1.495 (6)	C(15)–C(16)	1.433 (7)
N(1)–C(12)	1.487 (5)	C(14)–C(15)	1.341 (6)
C(12)–C(17)	1.454 (6)	C(16)–C(17)	1.340 (7)
	VII		
Fe(1)–Fe(2)	2.552 (1)	Fe(1)–C(1)	1.721 (9)
Fe(1)–C(2)	1.823 (9)	Fe(1)–C(3)	1.823 (9)
Fe(1)–S(1)	2.255 (2)	Fe(1)–S(2)	2.255 (2)
Fe(2)–C(4)	1.835 (8)	Fe(2)–C(5)	1.779 (9)
Fe(2)–S(1)	2.256 (2)	Fe(2)–S(2)	2.284 (3)
Fe(2)–C(6)	1.850 (7)	S(2)–C(11)	1.825 (9)
S(1)–C(9)	1.836 (9)	O(6)–C(7)	1.475 (10)
C(6)–O(6)	1.331 (8)	C(9)–C(10)	1.461 (12)
C(10)–C(11)	1.516 (12)		

Table IV. Selected Bond Angles (deg) for II and VII

	II		
C(1)–Fe(1)–C(2)	99.3 (2)	C(3)–Fe(1)–Fe(2)	166.8 (1)
C(2)–Fe(1)–C(3)	98.2 (2)	Fe(2)–Fe(1)–C(7)	48.4 (1)
C(3)–Fe(1)–C(7)	123.7 (2)	Fe(2)–Fe(1)–C(12)	71.7 (1)
C(1)–Fe(1)–C(12)	157.1 (2)	C(1)–Fe(1)–C(13)	118.9 (2)
C(7)–Fe(1)–C(12)	67.8 (1)	C(7)–Fe(1)–C(13)	39.4 (1)
C(2)–Fe(1)–C(13)	139.3 (2)	Fe(1)–Fe(2)–C(5)	151.3 (1)
Fe(2)–Fe(1)–C(13)	73.8 (1)	C(5)–Fe(2)–C(6)	102.6 (2)
C(12)–Fe(1)–C(13)	39.3 (1)	C(4)–Fe(2)–C(7)	94.7 (2)
Fe(1)–Fe(2)–C(7)	53.7 (1)	C(6)–Fe(2)–C(7)	159.1 (2)
C(5)–Fe(2)–C(7)	98.1 (2)	C(4)–Fe(2)–N(1)	169.0 (2)
Fe(1)–Fe(2)–N(1)	75.4 (1)	Fe(1)–C(7)–O(7)	128.6 (2)
C(7)–Fe(2)–N(1)	82.6 (1)	Fe(1)–C(7)–C(13)	69.2 (2)
Fe(1)–C(7)–Fe(2)	77.9 (1)	O(7)–C(7)–C(13)	113.0 (3)
Fe(2)–C(7)–O(7)	133.5 (2)	Fe(2)–N(1)–C(12)	100.1 (2)
Fe(2)–C(7)–C(13)	112.2 (2)	Fe(1)–C(12)–C(13)	69.7 (2)
Fe(1)–C(12)–N(1)	105.0 (2)	Fe(1)–C(13)–C(12)	71.0 (2)
N(1)–C(12)–C(13)	112.1 (3)	C(7)–C(13)–C(12)	112.9 (3)
Fe(1)–C(13)–C(7)	71.5 (2)	C(7)–C(13)–C(14)	126.6 (3)
	VII		
Fe(2)–Fe(1)–C(1)	103.6 (3)	Fe(2)–Fe(1)–C(2)	105.2 (3)
Fe(2)–Fe(1)–S(1)	55.6 (1)	Fe(2)–Fe(1)–C(3)	144.6 (3)
C(2)–Fe(1)–S(1)	160.1 (3)	C(1)–Fe(1)–S(1)	87.0 (3)
Fe(2)–Fe(1)–S(2)	56.3 (1)	C(3)–Fe(1)–S(1)	102.7 (3)
C(2)–Fe(1)–S(2)	87.2 (3)	C(1)–Fe(1)–S(2)	159.2 (3)
S(1)–Fe(1)–S(2)	85.2 (1)	C(3)–Fe(1)–S(2)	98.2 (3)
Fe(1)–Fe(2)–C(5)	146.4 (3)	Fe(1)–Fe(2)–C(4)	99.2 (3)
Fe(1)–Fe(2)–S(1)	55.5 (1)	C(4)–Fe(2)–S(1)	152.8 (3)
C(5)–Fe(2)–S(1)	110.2 (2)	Fe(1)–Fe(2)–S(2)	55.3 (1)
C(4)–Fe(2)–S(2)	88.2 (3)	C(5)–Fe(2)–S(2)	96.1 (3)
S(1)–Fe(2)–S(2)	84.6 (1)	Fe(1)–Fe(2)–C(6)	110.9 (2)
S(1)–Fe(2)–C(6)	89.8 (2)	S(2)–Fe(2)–C(6)	165.7 (2)
Fe(1)–S(2)–Fe(2)	68.4 (1)	Fe(1)–S(1)–Fe(2)	68.9 (1)
S(1)–C(9)–C(10)	120.0 (6)	Fe(2)–C(6)–O(6)	129.3 (5)
S(2)–C(11)–C(10)	117.6 (7)	C(9)–C(10)–C(11)	114.2 (7)
Fe(2)–C(6)–C(12)	126.5 (5)	Fe(2)–C(6)–O(6)	129.3 (5)

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Table V. Fractional Coordinates (×10^4; ×10^3 for H) and Equivalent Isotropic Temperature Factors (Å^2, ×10^3) for II

	x/*a*	*y*/*b*	*z*/*c*	*U*(eq)[a]
Fe(1)	2952 (1)	752 (1)	8271 (1)	38 (1)
C(1)	4833 (5)	775 (2)	8045 (4)	53 (3)
O(1)	6057 (3)	792 (2)	7904 (3)	71 (2)
C(2)	3009 (4)	1237 (2)	9695 (3)	51 (3)
O(2)	3110 (3)	1533 (2)	10615 (2)	69 (2)
C(3)	3091 (5)	−131 (3)	8892 (4)	58 (3)
O(3)	3175 (4)	−704 (2)	9258 (3)	86 (3)
Fe(2)	2185 (1)	1921 (1)	7134 (1)	40 (1)
C(4)	3979 (5)	2194 (2)	6981 (4)	51 (3)
O(4)	5149 (3)	2404 (2)	6905 (3)	72 (2)
C(5)	1447 (5)	2395 (2)	5782 (4)	52 (3)
O(5)	1070 (4)	2681 (2)	4891 (3)	78 (2)
C(6)	2161 (5)	2598 (2)	8331 (4)	51 (3)
O(6)	2227 (3)	3028 (2)	9071 (3)	70 (2)
C(7)	2408 (4)	977 (2)	6373 (3)	37 (2)
O(7)	3088 (3)	747 (1)	5387 (2)	46 (2)
C(8)	4011 (6)	1190 (3)	4772 (5)	63 (3)
C(9)	4373 (5)	809 (4)	3649 (5)	68 (4)
N(1)	226 (3)	1475 (2)	7594 (3)	37 (2)
C(10)	−385 (5)	1772 (3)	8711 (4)	52 (3)
C(11)	−970 (5)	1513 (3)	6562 (4)	50 (3)
C(12)	679 (4)	713 (2)	7770 (3)	36 (2)
C(13)	1442 (4)	459 (2)	6796 (3)	33 (2)
C(14)	1235 (4)	−268 (2)	6355 (4)	42 (2)
C(15)	338 (5)	−709 (2)	6897 (4)	54 (3)
C(16)	−387 (5)	−466 (3)	7927 (4)	52 (3)
C(17)	−284 (4)	215 (3)	8326 (4)	45 (2)
H(8A)	500 (4)	120 (2)	535 (3)	74 (4)*
H(8B)	351 (4)	160 (2)	458 (4)	74 (4)*
H(9A)	354 (4)	74 (2)	317 (4)	74 (4)*
H(9B)	502 (4)	110 (2)	316 (3)	74 (4)*
H(9C)	511 (4)	48 (2)	390 (4)	74 (4)*
H(10A)	28 (4)	173 (2)	942 (3)	74 (4)*
H(10B)	−135 (4)	154 (2)	886 (3)	74 (4)*
H(10C)	−66 (4)	228 (2)	850 (3)	74 (4)*
H(11A)	−60 (4)	135 (2)	576 (3)	74 (4)*
H(11B)	−126 (4)	194 (2)	640 (4)	74 (4)*
H(11C)	−184 (4)	123 (2)	668 (3)	74 (4)*
H(14)	169 (4)	−43 (2)	567 (3)	74 (4)*
H(15)	20 (4)	−123 (2)	657 (3)	74 (4)*
H(16)	−103 (4)	−80 (2)	826 (3)	74 (4)*
H(17)	−86 (4)	36 (2)	892 (3)	74 (4)*

[a] An asterisk indicates the isotropic temperature factor. Equivalent isotropic temperature factor: defined as the geometric mean of the diagnoal elements of the diagonalized matrix of $U_{i,j}$.

Crystal and Molecular Structure of $(CO)_3Fe\{\mu\text{-}C(OEt)\text{-}\eta^2\text{-}C_6H_4NMe_2\}Fe(CO)_3$ (II). The atomic numbering scheme used for molecule II is shown in Figure 1 along with another view of the molecule showing the displacement of the N atom. Selected bond lengths (Å), the most relevant bond angles (deg), and fractional atomic coordinates are shown in Tables III, IV, and V, respectively.

Two important aspects of this structure need to be accentuated. Whereas the heteroatom of the aromatic ring is bonded to one iron, two of the carbons of the aromatic ring are μ-bonded to the other iron. The five-membered metallacyclic chelate we set out to synthesize is found as a fragment of the dimer.

Common features found for the symmetrical triangular framework of the $[\mu\text{-}C(R)R^1]Fe_2$ moiety of reported methylene-bridged diiron complexes include metal–metal bond lengths in the range 2.49–2.58 Å, typical internal angles of 77–81° around the methylene carbon, and external values of 108–113°.[39–42] According to Tables IV and V, the geometry of the methylene bridge of II correlates closely with this structural data, and bond distances and angles fall within the ranges given.

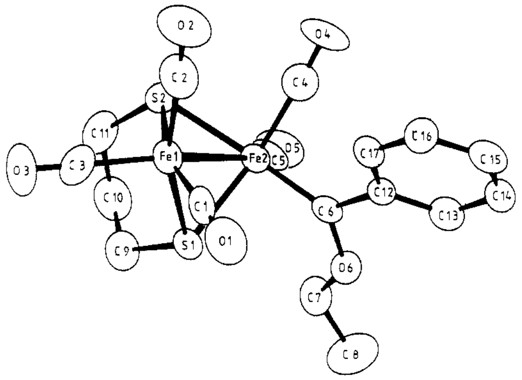

Figure 2. A perspective view of the molecular structure of VII.

An interesting feature of the crystal structure of II is the interaction of the C(12) and C(13) carbons of the phenyl group with the Fe(1) center. These distances of 2.106 (3) and 2.089 (3) Å are very short compared with corresponding values of 2.433 (7) and 2.468 (8) Å for $(CO)_3Fe\{\mu\text{-}(C_6H_4CHC_6H_5)\}Fe(CO)_3$, 2.431 (7) and 2.433 (7) Å for $(CO)_3Fe\{\mu\text{-}C(OEt)C(Ph)C(Ph)H\}Fe(CO)_3$, and 2.404 (4) and 2.401 (4) Å for $(CO)_3Fe\{\mu\text{-}C_3Ph_3H\}Fe(CO)_3$.[43–45] The Fe–C($\eta^2$-benzene) distances in II are in fact comparable to the Fe–C values of 2.120 (3) and 1.965 (3) Å found for the methylene bridge. The η^2-coordination of the benzene induces a localization of the bonds in the phenyl ring, which are alternately long and short. The C(12)–C(13) bond length is significantly shorter than the three longer distances and longer than the two shorter distances in the phenyl ring, due to the effect of coordination of these two carbons to Fe(1). A similar situation was found for $(CO)_3Fe\{\mu\text{-}C(OEt)C(Ph)C(Ph)H\}Fe(CO)_3$ and $(CO)_3Fe\{\mu\text{-}C_3Ph_3H\}Fe(CO)_3$.[44,45]

While the Fe–C bond lengths of the carbonyls are on average the same around Fe(1), 1.779 (5) Å and Fe(2), 1.784 (5) Å, a significantly shorter distance of 1.746 (5) Å is found for the carbonyl opposite the nitrogen donor atom (Fe(2)–C(11)).

The other striking feature of the crystal structure of II is found in the position of the coordinating nitrogen atom. The nitrogen is displaced from the plane of the benzene ring by +0.82 (2) Å, while the methylene carbon C(7) is only −0.11 (2) Å from this plane. This displacement of the N atom results in a torsion angle for C(7)–C(13)–C(12)–N(1) of 39.1 (5)°. The benzene ring remained in a planar conformation with the largest deviation from the plane being that of −0.03 (2) Å for C(16). There are no other significant structural features observable in the benzene ring. The Fe(2)–N(1) distance of 2.087 (3) Å is, however, very similar to the 2.100 (2) Å found for the coordinating nitrogen atom in the five membered chelate ring of $(CO)_3Fe\{\mu\text{-}C(H)CH_2CH_2NCH_2CH_2\}Fe(CO)_4$.[46]

Crystal and Molecular Structure of $(CO)_3Fe\{S$-

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Table VI. Fractional Coordinates (×10⁴) and Equivalent Isotropic Temperature Factors (Å², ×10³) for VII

	x/a	y/b	z/c	U(eq)[a]
Fe(1)	6596 (1)	1065 (1)	7070 (1)	41 (1)
Fe(2)	8313 (1)	2439 (1)	7359 (1)	36 (1)
C(1)	6518 (8)	825 (5)	5954 (6)	41 (5)
O(1)	6436 (6)	674 (4)	5185 (4)	69 (4)
C(2)	7856 (10)	129 (6)	7475 (7)	65 (6)
O(2)	8602 (7)	−446 (4)	7740 (5)	84 (5)
C(3)	4831 (10)	559 (5)	7259 (6)	56 (6)
O(3)	3754 (7)	260 (4)	7391 (5)	74 (5)
C(4)	10172 (9)	1890 (5)	7761 (6)	52 (5)
O(4)	11283 (6)	1564 (4)	8049 (4)	65 (4)
C(5)	8763 (8)	3437 (6)	7989 (5)	45 (5)
O(5)	9106 (6)	4053 (4)	8434 (4)	66 (4)
S(1)	5833 (2)	2453 (1)	6618 (1)	40 (1)
S(2)	7408 (2)	1682 (1)	8440 (1)	49 (1)
C(6)	8904 (7)	2797 (4)	6318 (5)	31 (4)
O(6)	8473 (5)	3510 (3)	5807 (3)	47 (3)
C(7)	7576 (9)	4244 (5)	6083 (6)	57 (6)
C(8)	7459 (12)	4926 (6)	5382 (6)	76 (7)
C(9)	4539 (8)	2886 (5)	7309 (5)	54 (5)
C(10)	5112 (10)	3041 (6)	8271 (6)	66 (6)
C(11)	5800 (10)	2225 (6)	8792 (6)	64 (6)
C(12)	10061 (7)	2339 (5)	5874 (4)	34 (4)
C(13)	10970 (8)	2844 (5)	5420 (5)	49 (5)
C(14)	12085 (8)	2438 (6)	5031 (5)	51 (5)
C(15)	12244 (8)	1519 (6)	5060 (5)	51 (5)
C(16)	11323 (8)	1032 (5)	5510 (5)	49 (5)
C(17)	10260 (7)	1424 (5)	5915 (5)	38 (4)

[a] Equivalent isotropic temperature factor: defined as the geometric mean of the diagonal elements of the diagonalized matrix of $U_{i,j}$.

$\overline{(CH_2)_3S}$}Fe(CO)$_2${C(OEt)Ph} (VII). A perspective view of the structure of molecule VII is given in Figure 2. Selected bond lengths (Å), the most relevant bond angles (deg) and fractional atomic coordinates are shown in Tables III, IV, and VI, respectively.

The Fe_2S_2 skeleton of the $Fe_2(CO)_5(L)S_2$ unit has the well-known butterfly structure, typical for bridging diiron complexes of the type $Fe_2(CO)_6(SR)_2$. Structural data are available for a number of these complexes without a direct bond between the two sulfur atoms e.g., $Fe_2(CO)_6(SEt)_2$, $Fe_2(CO)_6(SCPh)_2$, and $Fe_2(CO)_6(SCH_2S)$.[47-49] These complexes exhibit Fe–Fe distances between 2.50 and 2.55 Å and Fe–S distances over the range 2.22–2.28 Å. The Fe–Fe bond length of 2.55(1) Å and the average directly bonded Fe–S distance of 2.263 (3) Å in VII fall within these ranges. In fact, neither the nature of substituents bonded to the two sulfur atoms, e.g., $Fe_2(CO)_6(S_2CO)$ and $Fe_2(CO)_6\{S_2P(C_6H_4OMe)Fe(CO)_4\}$, nor the substitution of a carbonyl by another ligand, e.g., $Fe_2(CO)_4(PMe_3)_2(SMe)_2$ and $Fe_2(CO)_4(PPh_3)\{CC_6H_6(Me)_4\}\{S_2CC_6H_6(Me)_4\}$, has much effect on the bonding characteristics of the Fe_2S_2 core.[50-53] The S···S nonbonding distance of 3.054 Å is significantly longer than those reported for any of the complexes referred to above.

The relative position of the carbene ligand in VII and other carbon donor ligands, such as vinylidene in $Fe_2(CO)_4(PPh_3)\{CC_6H_6(Me)_4\}\{S_2CC_6H_6(Me)_4\}$ and carbene in $Fe_3(CO)_8(\mu_3\text{-}S)_2(\overline{CSCH_2CH_2S})$, differs from phosphorus ligands, such as PMe_3 in $Fe_2(CO)_4(PMe_3)_2(SMe)_2$.[52-54] Carbon donor ligands are found opposite one of the sulfur atoms, whereas the phosphine ligands are on the same side as both sulfur atoms. Other interesting features concerning the position of the carbene carbon atom in VII are (i) an angle of 104.2 (4)° between the phenyl and alkoxy substituents on the carbene, which is smaller than the 120° found for sp^2-hybridized carbon atoms and (ii) a short iron–carbene cation distance of 1.851 (7) Å, which is comparable with some of the iron–carbonyl carbon distances and only a little longer than the average value of 1.797 (9) Å. The iron–carbene carbon distance of 1.851 (7) Å is longer than the iron–vinylidene carbon distance of 1.79 (1) Å found for $Fe_2(CO)_4\{S_2CC_6H_6(Me)_4\}\{CC_6H_6(Me)_4\}$ and significantly shorter than the 1.948 (3) Å reported for the triiron carbene complex $Fe_3(CO)_8(\mu_3\text{-}S)_2(\overline{CSCH_2CH_2S})$.[53,54]

Registry No. I, 106359-18-6; II, 106375-46-6; IV, 106359-19-7; V, 106359-20-0; VI, 106359-21-1; VII, 106359-22-2; *o*-$MeOC_6H_4Li$, 31600-86-9; $Fe(CO)_5$, 13463-40-6; *o*-$Me_2NC_6H_4Li$, 22608-37-3; $Fe[\{P(OMe)_3\}_2(CO)_3$, 14949-85-0; $(CO)_3\overline{Fe\{S(CH_2)_3S}\}Fe(CO)_3$, 70789-83-2; $HS(CH_{2,3}SH$, 505-23-7.

Supplementary Material Available: Tables of anisotropic temperature factors, bond lengths, and bond angles as well as ORTEP plots of the unit cell contents for both II and VII (11 pages); listings of observed and calculated structure factors for II and VII (27 pages). Ordering information is given on any current masthead page.

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