An Improved Route to the Synthesis of μ-(Alkane- or arene-thiolato)(μ-ethenyl)di-iron Complexes. Crystal Structure of μ-Phenylmethanethiolato-μ-(1,2-diphenylethenyl)-hexacarbonyldi-iron(*Fe–Fe*) †

Josep Ros * and Josep M. Viñas
Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain
René Mathieu
Laboratoire de Chimie de Coordination du C.N.R.S., Unité no. 8241 liée par convention à l'Université Paul Sabatier, 205 Route de Narbonne, 31077 Toulouse, France
Xavier Solans and Mercé Font-Bardía
Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, Gran Vía 585, 08007 Barcelona, Spain

The reactions of $[Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}CPh{=}CHPh)]$ with LiSR (R = Et, Pr^i, cyclo-C_6H_{11}, Ph, or CH_2Ph) lead to the complexes $[Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}CPh{=}CHPh)]$. The structure of the benzyl derivative has been established by *X*-ray diffraction methods; crystals are monoclinic, space group $P2_1/n$ with a = 21.383(3), b = 7.098(2), c = 16.856(3) Å, β = 95.49(2)°, and Z = 4. The structure was solved and refined on the basis of 2 197 significant counter data, to a final R value of 0.056. The structure consists of $Fe_2(CO)_6$ units with benzylthiolato and $\sigma:\eta^2$-diphenylethenyl ligands bridging the two metal centres.

In a recent communication we reported the synthesis and structure of $[Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}CPh{=}CHPh)]$ (**1**) which contains diphenylethenyl and chloride ligands bridging the two metal centres.[1] Here we present a generalized route to (**1**) and the reactions of complexes of this type with some lithium thiolates which lead to complexes $[Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}CPh{=}CHPh)]$ (R = Et, Pr^i, cyclo-C_6H_{11}, Ph, or CH_2Ph) in good yield. This type of complex has been reported previously by reaction of vinyl sulphides with $[Fe_3(CO)_{12}]$ in a maximum yield of 10%.[2] Recently, the synthesis and structure of dinuclear iron complexes containing allyl or 2-propynyl groups as bridging ligand, and a bridging thiolate group, have been published.[3] The synthetic route that we propose is based on the easy access to dinuclear anionic iron complexes with alkenyl bridges[4] which allow the introduction of anionic bridging ligands such as halides,[1] thiolates, or phosphides.[5]

Experimental

The reactions were performed under a nitrogen atmosphere using standard Schlenk techniques and solvents deoxygenated and dried by standard methods. Infrared spectra were recorded on a Beckman IR 20 A spectrophotometer in cyclohexane solutions in the ν(CO) region. ^1H N.m.r. spectra were recorded on a Bruker WP80 spectrometer in $CDCl_3$ solutions. The mass spectra were measured on a Hewlett-Packard 2985 GC/MS spectrometer. Elemental analysis (C and H) was performed on a Perkin-Elmer 240-B analyzer. The synthesis of (**1**) was as described previously.[1]

Synthesis of $[Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}CR{=}CHPh)]$ [R = Ph (**1**) *or* H (**4**)].—To a dichloromethane solution of $PPh_4[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CR{=}CHPh)]$ (R = Ph or H[4]), a stoicheiometric amount of solid $[Me_3O][SbCl_6]$ was slowly added with stirring. After 5 min the reaction was complete and the solvent evaporated to dryness. The residue was extracted with hexane. Evaporation of solvent gave dark violet crystals which were recrystallized from dichloromethane–methanol. Yield 40—45%.

The same procedure as above, but using an equimolar amount of freshly prepared $[PPh_4][SbCl_6]$ (obtained by mixing stoicheiometric amounts of $SbCl_5$ and $[PPh_4]Cl$ in CH_2Cl_2) dissolved in dichloromethane, leads to a solid which was chromatographed on silica using hexane as eluant. The dark violet fraction collected was evaporated and the residue recrystallized from dichloromethane–methanol. Yield 20—25%.

Synthesis of $[Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}CPh{=}CHPh)]$ [R = Et (**5**), Pr^i (**6**), *cyclo*-C_6H_{11} (**7**), Ph (**8**), *or* CH_2Ph (**9**)].—The corresponding lithium thiolates were prepared by addition of an equimolar amount of a 1.6 mol dm^{-3} solution of butyl-lithium in hexane to a solution of the thiol in the same solvent. The hexane was evaporated and the lithium thiolate dissolved in dichloromethane (5 cm^3). This solution was slowly added to an equimolar solution of (**1**) in dichloromethane and stirred for 2 h. The resulting reaction mixture was evaporated to dryness. The residual solid was extracted with benzene, filtered and evaporated to dryness. Crystallizations from dichloromethane–methanol gave the complexes (**5**)—(**9**) in *ca.* 50% yield.

X-*Ray Crystal Structure of* $[Fe_2(CO)_6(\mu\text{-}SCH_2Ph)(\mu\text{-}CPh{=}CHPh)]$.—*Crystal data.* $C_{27}H_{18}Fe_2O_6S$, M = 582.2, monoclinic, a = 21.383(3), b = 7.098(2), c = 16.856(3) Å, β = 95.49(2)°, U = 2 537.1(8) Å^3, D_c = 1.524 g cm^{-3}, Z = 4, $F(000)$ = 1 184, space group $P2_1/n$, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 69 Å, $\mu(\text{Mo-}K_\alpha)$ = 12.89 cm^{-1}, T = 288 K.

Intensity measurements. A tabular crystal (0.1 × 0.1 × 0.08 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. The ω-scan technique was used with scan width 0.8°; unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by least-squares methods. Scan speed 0.03° s^{-1}, graphite-monochromated Mo-K_α radiation; 2 324 independent reflections measured ($2 \leqslant \theta \leqslant 25°$), 2 197 unique [$I \geqslant 2.5\sigma(I)$]. Significant decay was not observed; the data were corrected for Lorentz-polarization effects, but not for absorption.

Structure solution and refinement. Direct methods were employed using the MULTAN 80 system of computer programs.[6] Full-matrix least-squares refinement was carried out using the SHELX 76 computer program.[7] The H-atom positions were computed, with the exception of H(1), which was determined from

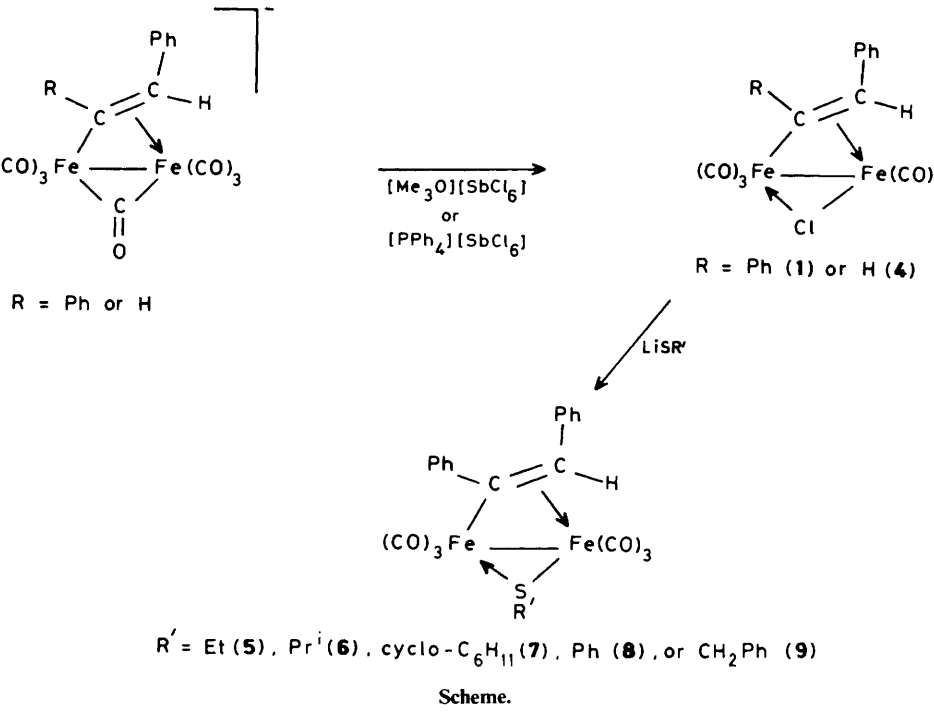
---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Analytical[a] and spectroscopic data for the synthesized complexes

	Complex	ν(CO)[b]/cm^{-1}	^{1}H N.m.r. (δ/p.p.m.)[c]	M^{+}[d]	Yield[e] (%)	Analysis (%) C	H
(4)	$[Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}CH{=}CHPh)]$	2 078m, 2 048vs, 2 016s, 2 000s, 1 996m	5.01 (d, J = 13.8, 1 H) 7.35 (br, 5 H) 9.17 (d, J = 13.8, 1 H)	418	40	40.2 (40.5)	1.7 (1.6)
(5)	$[Fe_2(CO)_6(\mu\text{-}SEt)(\mu\text{-}CPh{=}CHPh)]$	2 056m, 2 038s, 1 998s, 1 992s	1.67 (t, J = 7.0, 3 H) 2.42 (q, J = 7.0, 2 H) 3.65 (s, 1 H) 7.07 (br, 10 H)	520	45	49.9 (50.8)	3.0 (3.1)
(6)	$[Fe_2(CO)_6(\mu\text{-}SPr^i)(\mu\text{-}CPh{=}CHPh)]$	2 056m, 2 038s, 1 998s, 1 992s	1.40 (d, J = 6.0, 6 H) 2.54 (m, 1 H) 3.60 (s, 1 H) 7.08 (br, 10 H)	534	50	51.3 (51.7)	3.2 (3.4)
(7)	$[Fe_2(CO)_6(\mu\text{-}C_6H_{11})(\mu\text{-}CPh{=}CHPh)]$	2 058m, 2 038s, 1 996s, 1 990s	1.55 (m, 11 H) 3.61 (s, 1 H) 7.19 (br, 5 H) 7.25 (br, 5 H)	574	50	53.9 (54.4)	3.8 (3.9)
(8)	$[Fe_2(CO)_6(\mu\text{-}SPh)(\mu\text{-}CPh{=}CHPh)]$	2 064m, 2 038s, 1 998s, br	3.70 (s, 1 H) 7.88 (br, 15 H)	568	60	54.4 (54.9)	2.8 (2.8)
(9)	$[Fe_2(CO)_6(\mu\text{-}SCH_2Ph)(\mu\text{-}CPh{=}CHPh)]$	2 056m, 2 038s, 1 996s, 1 990s	3.59 (s, 1 H) 3.70 (s, 1 H) 7.21 (br, 10 H) 7.36 (br, 5 H)	582	75	55.5 (55.0)	2.9 (3.1)

[a] Required values are in parentheses. [b] Cyclohexane solution. [c] $CDCl_3$ solution. Coupling constants are given in Hz. [d] Parent ion. [e] Based on dinuclear iron complexes.



Scheme.

a difference synthesis. The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.031(F_o)^2]^{-1}$; final $R = 0.056$, $R' = 0.060$. The largest peak in the final difference synthesis was only 0.04 e Å^{-3}. The maximum shift/e.s.d. was 0.4 in U_{22} of Fe(2).

Results and Discussion

The analytical and spectroscopic data for the synthesized compounds are in Table 1.

The synthesis of $[Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}CPh{=}CHPh)]$ (**1**) in good yield (*ca.* 40%) prompted us to attempt to expand the number of similar compounds and investigate new pathways for their preparation. We found that the reaction of $[Fe_2(CO)_6(\mu\text{-}CO)(\mu\text{-}CPh{=}CHPh)]^-$ (**2**) with $[Me_3O][SbCl_6]$ takes place through methylation of the bridging carbonyl ligand and subsequent attack by $[SbCl_6]^-$. Since the anionic complex (**2**) undergoes oxidation by reaction with electrophiles in the same manner as the methylated complex $[Fe_2(CO)_6(\mu\text{-}COMe)(\mu\text{-}CPh{=}CHPh)]$ (**3**),[8] some chlorinating agents were treated

Table 2. Fractional atomic co-ordinates (× 10^4), with e.s.d.s in parentheses, for $[Fe_2(CO)_6(\mu\text{-}SCH_2Ph)(\mu\text{-}CPh{=}CHPh)]$ (**9**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Fe(1)	5 090(1)	1 993(2)	6 511(1)	C(31)	7 009(4)	2 264(15)	8 100(5)
Fe(2)	5 174(1)	3 984(2)	7 790(1)	C(32)	7 316(5)	706(17)	8 485(6)
S	5 782(1)	1 437(3)	7 581(1)	C(33)	7 727(5)	989(23)	9 151(7)
C(1)	4 560(4)	1 655(13)	8 093(5)	C(34)	7 845(5)	2 765(22)	9 469(6)
C(2)	4 442(3)	2 297(12)	7 282(5)	C(35)	7 557(5)	4 265(20)	9 089(6)
C(11)	4 155(4)	1 856(12)	8 745(5)	C(36)	7 138(4)	4 035(17)	8 417(6)
C(12)	4 260(5)	555(13)	9 374(5)	C(4)	4 618(4)	3 150(14)	5 717(5)
C(13)	3 912(6)	687(17)	10 027(6)	O(4)	4 357(3)	3 814(12)	5 166(4)
C(14)	3 485(5)	2 079(18)	10 070(6)	C(5)	5 724(4)	2 143(15)	5 896(5)
C(15)	3 364(5)	3 333(16)	9 462(6)	O(5)	6 127(3)	2 156(13)	5 482(4)
C(16)	3 705(4)	3 199(15)	8 810(6)	C(6)	4 827(5)	−326(17)	6 277(5)
C(21)	3 778(4)	2 779(14)	6 983(5)	O(6)	4 648(4)	−1 806(11)	6 137(5)
C(22)	3 315(5)	1 410(17)	7 053(6)	C(7)	4 643(4)	5 848(15)	7 892(5)
C(23)	2 701(5)	1 753(24)	6 794(7)	O(7)	4 321(3)	7 144(10)	7 979(5)
C(24)	2 520(6)	3 430(27)	6 456(7)	C(8)	5 475(5)	4 102(13)	8 823(6)
C(25)	2 980(6)	4 815(21)	6 387(6)	O(8)	5 619(4)	4 106(12)	9 492(5)
C(26)	3 606(4)	4 518(14)	6 622(5)	C(9)	5 661(5)	5 548(14)	7 272(6)
C(3)	6 589(5)	2 034(16)	7 358(6)	O(9)	5 970(4)	6 559(11)	6 971(5)

with (**2**). The reagents used were $[SbCl_6]^-$, $[PCl_6]^-$, and $[SnCl_6]^{2-}$; however, the yield was always low (*ca.* 25%). The reaction of (**2**) with freshly prepared $[PPh_4][SbCl_6]$ is the best chlorinating method to obtain (**1**) and similar complexes, as well as using $[Me_3O][SbCl_6]$. Chlorinating reactions with $[SbCl_6]^-$, $[PCl_6]^-$, and $[SnCl_6]^{2-}$ yielded mixtures which were chromatographed on silica gel in order to separate other oxidation products.

The complex $[Fe_2(CO)_6(\mu\text{-}Cl)(\mu\text{-}CH{=}CHPh)]$ (**4**) was prepared by the same method as complex (**1**) and was identified by elemental analysis, i.r., and ^1H n.m.r. spectra. The i.r. spectrum of (**4**) in the ν(CO) region in cyclohexane solution shows the same pattern as for (**1**) while the ^1H n.m.r. spectrum in $CDCl_3$ solution at room temperature shows two doublets at 5.01 (1 H) and 9.17 p.p.m. (1 H) (J = 13.8 Hz), and one broad signal at 7.35 p.p.m. (5 H) characteristic of the 2-phenylethenyl bridge with the protons in a *trans* configuration.

The reactions of (**1**) with equimolar amounts of lithium thiolates in dichloromethane solution at room temperature, monitored by i.r. spectroscopy, lead to products formulated as $[Fe_2(CO)_6(\mu\text{-}SR)(\mu\text{-}CPh{=}CHPh)]$ (Scheme). All are air stable and undergo decomposition in solution only after several days. The products (**5**)—(**9**) can be recrystallized from dichloromethane–methanol. Elemental analysis, i.r., ^1H n.m.r., and mass spectra confirm the presence of two bridges (diphenylethenyl and thiolate) in a $Fe_2(CO)_6$ system. In order to determine the structural features of these complexes, a single-crystal *X*-ray diffraction study of (**9**) was undertaken.

The structure of $[Fe_2(CO)_6(\mu\text{-}SCH_2Ph)(\mu\text{-}CPh{=}CHPh)]$ (**9**) is shown in the Figure. Fractional atomic co-ordinates are given in Table 2 and bond lengths and angles are in Table 3. Two $Fe(CO)_3$ units are linked by a single metal–metal bond [2.569(2) Å]. This short distance seems to correspond to a formally dative $Fe \leftarrow SCH_2Ph$ bond assuming that the two bridging ligands are three-electron donors. The 1,2-diphenylethenyl ligand is σ-bonded to Fe(1) and unsymmetrically η^2-bonded to Fe(2). The phenyl groups are in a *cis* configuration forming a torsion angle of −17.60°; this value is larger than those normally observed in dinuclear iron complexes with 1,2-diphenylethenyl and ethoxymethylidyne[9] or chloride[1] bridges. The orientation of both ligands in this molecular structure forms a cisoid configuration with a dihedral angle between the planes formed by Fe(1)Fe(2)C(2) and Fe(1)Fe(2)S of 115.53°. A similar value is observed in the molecular structure of complex (**1**) (115.73°). This angle seems to be increased by the bulk of the bridging ligands: thus in the complex $[Mn_2(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}CH{=}CH_2)]$[10] the angle is significantly greater (125.7°). It is interesting to note that the calculated distance between the vinyl hydrogen H(1) and the sulphur atom is 2.3 Å. This distance is shorter than the sum of the van der Waals radius for both atoms,[11] suggesting a hydrogen-bonding interaction. This situation could be favoured by the particular orientation of the benzyl group which is turned around the $S\text{–}CH_2Ph$ bond, minimizing interactions with the diphenylethenyl ligand. The geometry around Fe(1) may be considered octahedral while Fe(2) is pseudo-six-co-ordinate considering the π system of the ethenyl group to occupy one co-ordination site.

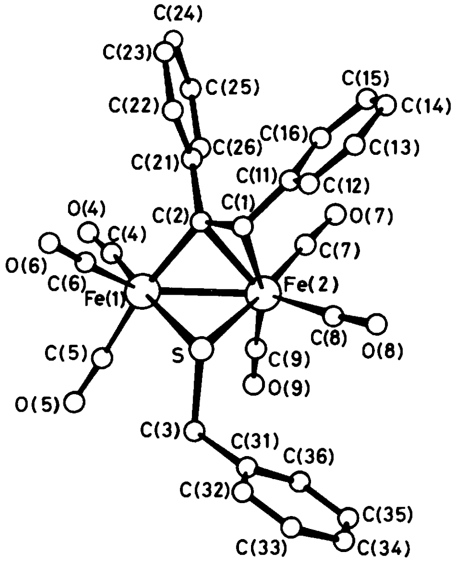


Figure. Structure of complex $[Fe_2(CO)_6(\mu\text{-}SCH_2Ph)(\mu\text{-}CPh{=}CHPh)]$ (**9**) showing the atomic numbering scheme

The Fe–CO bond lengths average 1.787(11) Å but the apical Fe(2)–C(7) distance *trans* to sulphur is shorter than the others [1.762(10) Å]. The Fe–C–O angles average 176.1(1)° and no incipient semi-bridging carbonyl is observed, indicating that the two metallic centres are electronically saturated. This contrasts with the situation observed in $[Mn_2(CO)_7(\mu\text{-}PPh_2)(\mu\text{-}CH{=}CH_2)]$ where an electronic imbalance is confirmed by the

Table 3. Selected bond distances (Å) and angles (°) for [$Fe_2(CO)_6(\mu$-$SCH_2Ph)(\mu$-$CPh{=}CHPh)$] (**9**)

Fe(2)–Fe(1)	2.569(2)	S–Fe(2)	2.274(2)	C(3)–S	1.851(9)	O(5)–C(5)	1.159(10)
S–Fe(1)	2.256(2)	C(1)–Fe(2)	2.202(8)	C(2)–C(1)	1.440(10)	O(6)–C(6)	1.135(11)
C(2)–Fe(1)	2.000(7)	C(2)–Fe(2)	2.088(7)	C(11)–C(1)	1.470(11)	O(7)–C(7)	1.167(10)
C(4)–Fe(1)	1.797(9)	C(7)–Fe(2)	1.762(10)	C(21)–C(2)	1.500(10)	O(8)–C(8)	1.140(10)
C(5)–Fe(1)	1.787(10)	C(8)–Fe(2)	1.800(9)	C(31)–C(3)	1.478(12)	O(9)–C(9)	1.128(10)
C(6)–Fe(1)	1.772(11)	C(9)–Fe(2)	1.804(10)	O(4)–C(4)	1.139(9)		
S–Fe(1)–Fe(2)	55.8(1)	C(6)–Fe(1)–C(5)	99.7(4)	C(8)–Fe(2)–C(2)	127.4(4)	C(11)–C(1)–C(2)	128.1(7)
C(2)–Fe(1)–Fe(2)	52.6(2)	S–Fe(2)–Fe(1)	55.1(1)	C(8)–Fe(2)–C(7)	92.6(4)	Fe(2)–C(2)–Fe(1)	77.9(3)
C(2)–Fe(1)–S	86.6(2)	C(1)–Fe(2)–Fe(1)	77.6(2)	C(9)–Fe(2)–Fe(1)	86.0(3)	C(1)–C(2)–Fe(1)	120.9(5)
C(4)–Fe(1)–Fe(2)	111.3(3)	C(1)–Fe(2)–S	78.5(2)	C(9)–Fe(2)–S	92.8(3)	C(1)–C(2)–Fe(2)	74.7(4)
C(4)–Fe(1)–S	162.7(3)	C(2)–Fe(2)–Fe(1)	49.5(2)	C(9)–Fe(2)–C(1)	163.6(4)	C(21)–C(2)–Fe(1)	119.9(5)
C(4)–Fe(1)–C(2)	93.4(3)	C(2)–Fe(2)–S	84.1(2)	C(9)–Fe(2)–C(2)	126.8(4)	C(21)–C(2)–Fe(2)	131.0(6)
C(5)–Fe(1)–Fe(2)	117.2(3)	C(2)–Fe(2)–C(1)	39.1(3)	C(9)–Fe(2)–C(7)	89.6(4)	C(31)–C(3)–S	110.8(6)
C(5)–Fe(1)–S	89.9(3)	C(7)–Fe(2)–Fe(1)	120.0(3)	C(9)–Fe(2)–C(8)	105.7(4)	O(4)–C(4)–Fe(1)	173.5(7)
C(5)–Fe(1)–C(2)	169.0(4)	C(7)–Fe(2)–S	174.4(3)	Fe(2)–S–Fe(1)	69.1(1)	O(5)–C(5)–Fe(1)	176.7(9)
C(5)–Fe(1)–C(4)	86.8(4)	C(7)–Fe(2)–C(1)	97.9(3)	C(3)–S–Fe(1)	110.5(3)	O(6)–C(6)–Fe(1)	178.5(10)
C(6)–Fe(1)–Fe(2)	133.9(3)	C(7)–Fe(2)–C(2)	90.3(3)	C(3)–S–Fe(2)	114.0(3)	O(7)–C(7)–Fe(2)	176.0(8)
C(6)–Fe(1)–S	100.7(3)	C(8)–Fe(2)–Fe(1)	145.8(3)	C(2)–C(1)–Fe(2)	66.2(4)	O(8)–C(8)–Fe(2)	174.3(9)
C(6)–Fe(1)–C(2)	91.2(4)	C(8)–Fe(2)–S	91.7(3)	C(11)–C(1)–Fe(2)	120.5(6)	O(9)–C(9)–Fe(2)	177.7(9)
C(6)–Fe(1)–C(4)	96.6(4)	C(8)–Fe(2)–C(1)	80.6(3)				

presence of an asymmetric phosphido ligand and one incipient semi-bridging carbonyl group.[10] The presence of the plane formed by Fe(1), C(1), C(2), and C(11) accounts for the shortening of the C(1)–C(11) bond [1.470(11) Å] compared with the homologous C(2)–C(21) [1.500(10) Å].

The i.r. spectra of the thiolato complexes in the ν(CO) region in cyclohexane solution are very similar to those observed for (**1**) and (**4**), showing the same patterns of bands but shifted to lower energies. This effect could originate from the lower electronegativity of the thiolato group. The ^1H n.m.r. spectra at room temperature in $CDCl_3$ solution show the presence of 1,2-diphenylethenyl and thiolato groups in a 1:1 ratio. Only one signal for the vinylic proton is observed at *ca.* 3.6 p.p.m., suggesting the formation of one isomeric form; the simplicity of the ν(CO) region in the i.r. spectra supports this hypothesis. For the majority of alkane- or arene-thiolato $Fe_2(CO)_6(SR)_2$ complexes, the *syn* and *anti* isomers are formed.[12] A point of interest is the short distance between sulphur and the ethenylic proton observed in the molecular structure of the benzyl derivative (**9**). This suggests an interaction that could originate from a shielding effect on the vinylic proton in the same manner as in the anionic complex [$Fe_2(CO)_6(\mu$-$CO)(\mu$-$CPh{=}CHPh)]^-$ (**2**). In the μ-chloro complex (**1**), the vinylic proton appears at 4.73 p.p.m.[1] The mass spectra of compounds (**5**)—(**9**) show the parent ion M^+ and the successive loss of six molecules of CO groups, thus confirming the formulation for the thiolato complexes. Furthermore, other observed fragments in all of them are: m/z = 112 (Fe_2), 144 (Fe_2S), 178 (PhCCPh), 221 (Fe_2SPh), and 323 ($Fe_2CPhCHPhS$).

In conclusion, the reactivity of the μ-chloro ligand toward lithium thiolates in neutral, dinuclear μ-diphenylethenyl–iron complexes appears an easy method for the synthesis of complexes with alkane- or arene-thiolato bridges. In the reaction of (**1**) with the bulky lithium 2-methylpropane-2-thiolate only the dithiolato complex [$Fe_2(CO)_6(\mu$-$SBu^t)_2$] is obtained,[13] certainly caused by steric hinderance between the groups.

Acknowledgements

We are grateful to C.A.I.C.Y-T. of Spain and Universitat de Barcelona for financial support and Fluka AG for reagents.

References

1 J. Ros, J. M. Viñas, R. Mathieu, X. Solans, and M. Font-Bardía, *J. Organomet. Chem.*, 1986, **307**, C7.
2 R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, 1961, **83**, 3600.
3 D. Seyferth, G. B. Womack, and J. C. Dewar, *Organometallics*, 1985, **4**, 398.
4 M. Lourdichi and R. Mathieu, *Nouv. J. Chim.*, 1982, **6**, 231.
5 J. Ros, R. Yañez, and R. Mathieu, unpublished work.
6 P. Main, S. E. Fiske, S. L. Hull, L. Lessinger, G. Germain, J. P. Declerq, and M. M. Woolfson, MULTAN, Automatic System of Computer Programs for Crystal Structure Determination from X-ray Diffraction Data, Universities of York and Louvain, Belgium, 1980.
7 G. M. Sheldrick, 'SHELX 76. Program for Crystal Structure Determinations,' University of Cambridge, 1976.
8 R. Yañez, J. Ros, R. Mathieu, and J. Suades, *J. Organomet. Chem.*, 1986, **299**, 357.
9 X. Solans, M. Font-Altaba, J. Ros, R. Yañez, and R. Mathieu, *Acta Crystallogr., Sect. C*, 1985, **41**, 1186.
10 J. A. Iggo, M. J. Mays, P. R. Raithby, and K. Henrick, *J. Chem. Soc., Dalton Trans.*, 1983, 205.
11 L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, 1960.
12 C. F. Campana, F. Y. Lo, and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1236.
13 J. A. de Beer and R. J. Haines, *J. Organomet. Chem.*, 1970, **24**, 757.

Received 15*th December* 1986; *Paper* 6/2413