Chemistry of Metallacyclic Complexes containing the $\overline{\text{FeCSCS}}$ Ring obtained by Metal-promoted CS_2–CS Coupling. *X*-Ray Crystal Structures of [(CO)(cp)$\overline{\text{FeC\{SW(CO)}_5\text{\}SC(FeL}_n\text{)S}}$] and [(CO)(cp)$\overline{\text{FeC(SEt)SC(FeL}_n\text{)S}}$]$SO_3CF_3$ [FeL_n = $Fe(cp)(CO)_2$, cp = η-C_5H_5]†

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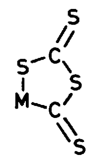
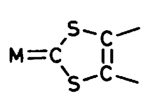
Nucleophilic addition of the thione sulphur atom in the complexes [$FeL_nC(S)SML_n$] [FeL_n = $Fe(cp)(CO)_2$, ML_n = FeL_n or $Re(CO)_5$, cp = η-C_5H_5] at the thiocarbonyl carbon atom in the complex [$FeL_n(CS)$]SO_3CF_3 promotes CS_2–CS coupling to yield five-membered ring metallacycles [(CO)(cp)$\overline{\text{FeC(SML}_n\text{)SC(FeL}_n\text{)S}}$]$SO_3CF_3$, through an unstable open-chain intermediate followed by ring closure at the Fe atom of the dithioester precursor. These derivatives react with nucleophiles to give [(CO)(cp)$\overline{\text{FeC(S)SC(FeL}_n\text{)S}}$] *via* S–$ML_n$ bond cleavage. The thioanhydride-like C_2S_3 grouping disproportionates under u.v. irradiation to restore the CS_2 and CS fragments co-ordinated to the same metal centre in [(CS)(cp)$\overline{\text{FeSC(FeL}_n\text{)S}}$]. The co-ordinating ability of [(CO)(cp)$\overline{\text{FeC(S)SC(FeL}_n\text{)S}}$] is proved by reactions with [$M'(CO)_5$(thf)] (M′ = Cr, Mo, or W; thf = tetrahydrofuran), HgX_2 (X = Cl, Br, or I) and $AgBF_4$ which afford derivatives with a metallacycle:metal ratio of 1:1 in the first two cases and 2:1 in the latter. Other electrophiles (E) such as H^+, R^+ (R = Me or Et), or BF_3 also give addition at the thionic end of the molecule, forming [(CO)(cp)$\overline{\text{FeC(SE)SC(FeL}_n\text{)S}}$]. Hydrogen-1 and ^{13}C n.m.r. and i.r. spectra of the complexes are presented and discussed. The i.r. analyses reveal the presence of conformers arising from restricted rotation around C(sp^2)–Fe(*exo*). The crystal structures of the complexes [(CO)(cp)$\overline{\text{FeC\{SW(CO)}_5\text{\}SC(FeL}_n\text{)S}}$] [monoclinic, *a* = 13.162(2), *b* = 13.156(1), *c* = 14.029(3) Å, β = 93.66(1)°, *Z* = 4, space group $P2_1/a$] and of [(CO)(cp)$\overline{\text{FeC(SEt)SC(FeL}_n\text{)S}}$]$SO_3CF_3$ [monoclinic, *a* = 14.565(4), *b* = 10.369(2), *c* = 16.176(2) Å, β = 101.73(1)°, *Z* = 4, space group $P2_1/n$] have been determined. Both species contain a planar, five-membered metallacyclic ring. Corresponding bond distances in the two species do not show great differences and reveal the carbenic character of both the endocyclic carbon atoms. Extensive delocalization of electrons promotes charge equalization on all the atoms and minimizes the differences between the neutral and cationic species.

It is well known that bidentate CS_2 derivatives of transition metals (M) promote a large variety of cycloaddition reactions. The complexes so obtained invariably contain a five-membered ring moiety in which the CS_2 grouping displays various anchoring modes within the cyclic unit and to the metals.

The reactivity pattern yielding stable compounds analogous to (I), in which two CS_2 units are coupled head-to-tail,[1] is quite general among CO_2-like heterocumulenes and has been observed for CO_2 itself,[2] isothiocyanates,[3] allenes,[4] and ketenes.[5] The reaction with activated acetylenes has been shown to result in the 1,3-dithiol-2-ylidene derivatives (II) for iron,[6] manganese,[6] chromium,[7] nickel,[8] and rhodium[8] complexes, whereas another type of five-membered metallacycle (III) has been observed for rhodium compounds.[9] Finally, a [3 + 2] cycloaddition reaction recently communicated was shown to give type (IV) heterocyclic compounds from [$W(CO)_3\{Ph_2(CH_2)_2Ph_2\}(CS_2)$] and $Ph\overset{+}{N}$–N≡CPh.[10]


(I)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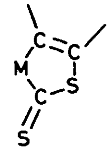
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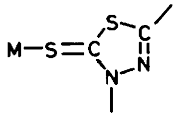
(IV)

Despite this rich chemistry, no example of a cycloaddition reaction involving σ-CS_2 compounds has been reported so far; moreover no metal-promoted CS_2–CS coupling was known. For these reasons we were prompted to explore such a possibility.

A more general interest in this chemistry stems from the

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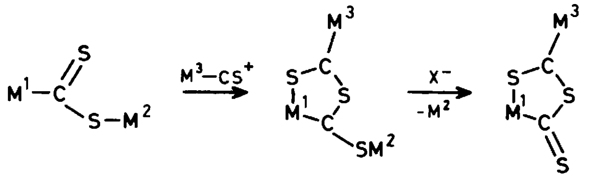
† 1,1,2-Tricarbonyl-1,2-di(η-cyclopentadienyl)-μ-[3-(pentacarbonyl-tungstenio)thio-1-thioxo-2-thiapropan-1-yl-3-ylidene-C^1(Fe^1)C^3(Fe^2)-C=*S*(Fe^2)]-di-iron and 1,1,2-tricarbonyl-1,2-di(η-cyclopentadienyl)-μ-[3-ethylthio-1-thioxo-2-thiapropan-1-yl-3-ylidene-C^1(Fe^1)C^3-(Fe^2)C=*S*(Fe^2)]-di-iron trifluoromethanesulphonate respectively.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

importance of the homogeneous- as well as heterogeneous-catalyzed transformation of CO_2 into CO.[11] It is believed that studies of CS_2 chemistry will lead to a better understanding of CO_2 activation.

The 'building-block' chosen for the present work is $[FeL_nC(S)SML_n]$[12] $[FeL_n = Fe(cp)(CO)_2$, cp = η-$C_5H_5]$ because the ML_n moiety $[ML_n = FeL_n$ or $Re(CO)_5]$ acts as a S-protective group and drives the electrophilic addition of the carbon in $[FeL_n(CS)]^+$ at the thione sulphur atom. The closure of a metallacyclic ring eventually affords the new stable species (V). Cleavage of the S–ML_n bond with nucleophiles can finally restore the protected thionic end of the molecules (VI).

In the present paper we describe the sequence (1), leading to type (VI) derivatives. These, in their turn, are transformed in a variety of type (V) species by reacting (VI) with Lewis acids.



(1)

(V) **(VI)**

In order to gain unambiguous information about the stereochemistry of the C_2S_3 anchoring moiety and the type of bonds present in these novel metallacyclic complexes, two structures have been determined and discussed: $[(CO)(cp)FeC(SEt)SC(FeL_n)S]SO_3CF_3$ and $[(CO)(cp)FeC\{SW(CO)_5\}SC(FeL_n)S]$. An important outcome of the structural analysis is the demonstration of the carbenic character of the carbon atoms in the ring. The spectroscopic properties revealing the presence of conformers arising from M^3–C(sp^2) restricted rotation in (V) and (VI) species are reported. Finally, irradiation of type (VI) species, resulting in the disproportionation of the C_2S_3 group into CS_2 and CS co-ordinated fragments is described.

Part of this work has been the subject of a preliminary communication.[13]

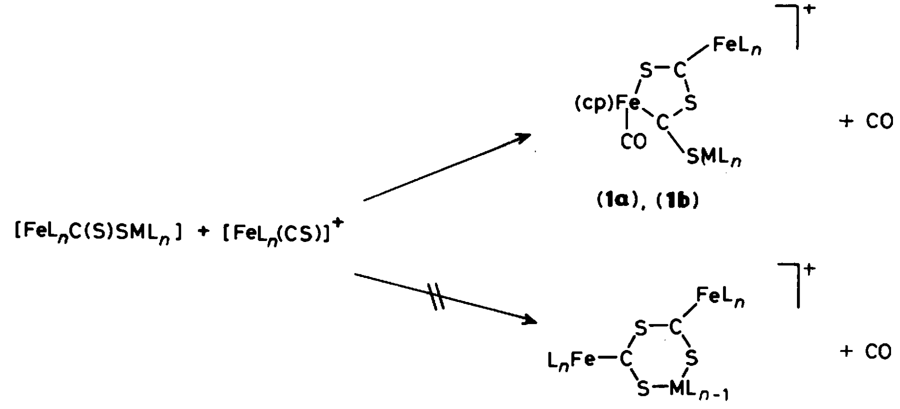
Results and Discussion

Synthesis of Metallacyclic Complexes containing FeSCSC.—The clean reaction of the thiocarbonyl complex $[FeL_n(CS)]SO_3CF_3$ with a slight excess of $[FeL_nC(S)SML_n]$[12] occurs within 1 h in CH_2Cl_2 at room temperature to form the adducts $[(CO)(cp)FeC(SML_n)SC(FeL_n)S]^+$ $[ML_n = FeL_n$ **(1a)** or $Re(CO)_5$ **(1b)**] in high yields, equation (2).

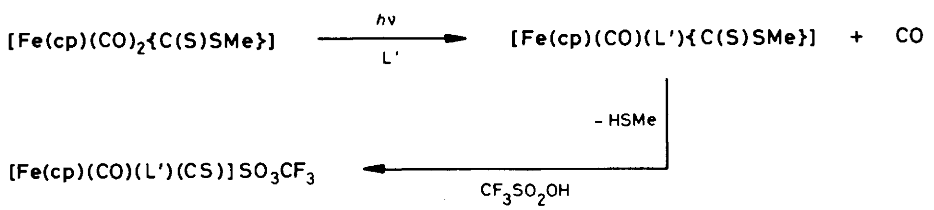
These metallacyclic derivatives are soluble in CH_2Cl_2, from which they are routinely obtained as deep green, **(1a)**, or brown, **(1b)**, crystals by addition of n-hexane at −20 °C. Both compounds are air stable. Their formation clearly results *via* nucleophilic addition of the basic thione sulphur atom in the metallodithioester precursors[14,15] at the electrophilic thiocarbonyl centre of the $[FeL_n(CS)]^+$ complex[16,17] with concomitant loss of one carbonyl ligand and ring formation. The formation of the five-membered ring FeC_2S_2 has been demonstrated in the previously reported *X*-ray structure of **(1a)**.[13]

The total absence of isomers containing six-membered rings MC_2S_3 [equation (2)] suggests the steric pathway of the cycloaddition. In fact the proposed nucleophilic addition forms unstable open-chain intermediates $[FeL_nC(SML_n)SC(S)ML_n]^+$ through a sterically enforced *Z* sulphur-addition step in order to exclusively afford ring closure at the Fe atom [equation (2)], which seems to be unique. In fact neither type (1) nor open-chain nor six-membered ring complexes have been observed starting from more hindered cations such as $[Fe(cp)(CO)(L')(CS)]SO_3CF_3$ (L′ = PPh_3 or PMe_2Ph) which are known to undergo easy nucleophilic addition at the thiocarbonyl carbon centre.[18] In view of the general stability of the few MCSCS metallacycles so far reported,[1,3,19,20] the lack of cycloadducts derived from phosphine-substituted reactants seems kinetic in nature and suggests that the reaction pathway is largely governed by steric factors.

The metallodithioester derivatives $[FeL_nC(S)SML_n]$ fail to react at the carbonyl carbon of $[Fe(cp)(CO)_3]^+$ and $[Mn(cp)(CO)_2(NO)]^+$ to form addition products. The expected acyclic derivatives, *i.e.* $[FeL_nC(SML_n)SC(O)ML_n]^+$ cannot be detected in these reactions probably because of their instability. This observation is in agreement with the unsuccessful attempt to acylate the thione sulphur atom with acetyl halides or trifluoroacetic anhydride.[21]



(2)



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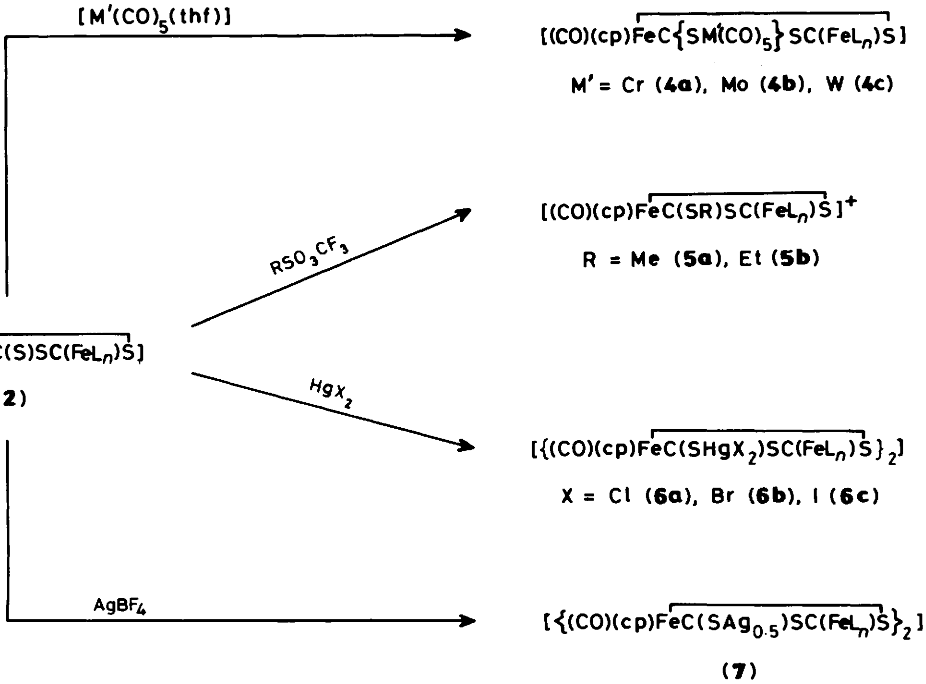
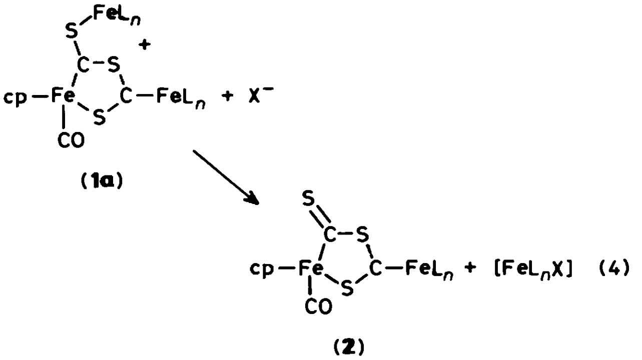


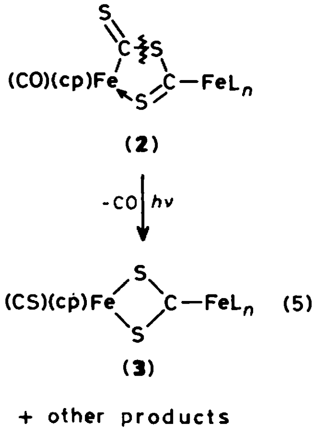
Scheme.



The thiocarbonyl complexes $[Fe(cp)(CO)(L')(CS)]SO_3CF_3$ are easily prepared by the new method described by equation (3).

Because of the novelty of type (**1**) complexes, the only related precedent being $[Mo_2(S_2CNEt_2)_3\{\mu\text{-}CSC(S)S\}(\mu\text{-}S_3C_2NEt_2)]$,[22] we aimed to prepare a variety of derivatives in order to study their chemistry and properties. The obvious candidate for this purpose was $[(CO)(cp)FeC(S)SC(FeL_n)S]$ (**2**) in which the unco-ordinated exocyclic sulphur atom should react with electron-deficient species. In line with the reported easy cleavage of the $S{\rightarrow}ML_n$ bond[14,15] in $[FeL_nC\{S(ML_n)\}S\text{-}FeL_n]$ and $[FeL_nC(SMe)SFeL_n]^+$, demonstrating its polar nature, the desired complex (**2**) has been obtained by reacting (**1a**) with nucleophiles such as Br^-, I^-, MeS^-, and $PhC(O)S^-$ [equation (4)]. The use of NaI in refluxing acetone turned out to be the most convenient method because (*i*) it produces (**2**) in the highest yield, (*ii*) it gives a reaction mixture easily separable by chromatography, and (*iii*) it affords $[FeL_nI]$ which can be reused to form the $[FeL_nC(S)SFeL_n]$[23] for preparing (**1a**). It is worth noting that (**2**) cannot be prepared from $Na[FeL_n(CS_2)]$ and $[FeL_n(CS)]SO_3CF_3$.

The deep green air-stable complex (**2**) decomposes within a few hours in toluene solution at 60 °C whereas u.v. irradiation yields a complicated reaction mixture from which only the new thiocarbonyl complex $[(CS)(cp)FeSC(FeL_n)S]$ (**3**) can be isolated in *ca.* 10% yield after column chromatography [equation (5)].



The red air-stable complex (**3**) has been characterized by elemental analysis, i.r. and ^1H n.m.r. spectra in $CDCl_3$. In the ^1H n.m.r. spectrum, two sharp singlets of equal intensity appear at δ 4.97 and 4.77. Equally consistent with the proposed structure is the i.r. spectrum which shows, in addition to the two CO stretching modes at 2 030 and 1 987 cm^{-1}, a strong absorption at 1 263 cm^{-1} attributable to terminal $\nu(CS)$ in the region found for related neutral thiocarbonyl complexes.[24] Furthermore, two bands are observed at 913 and 880 cm^{-1} which are due to $\nu_{asym}(CS_2)$ and $\nu_{sym}(CS_2)$ stretchings and are characteristic for all the CS_2-bridged binuclear complexes containing the $\overline{MSC(Fe)S}$ unit.[14]

The production of (**3**) probably derives from the intermediate $[(CO)(CS)(cp)FeSC(S)FeL_n]$ generated by cleavage of one of the two longer C–S bonds in the C_2S_3 unit [equation (5)]. This intermediate rapidly undergoes ring closure *via* Fe–S bond formation in agreement with the properties of the three known

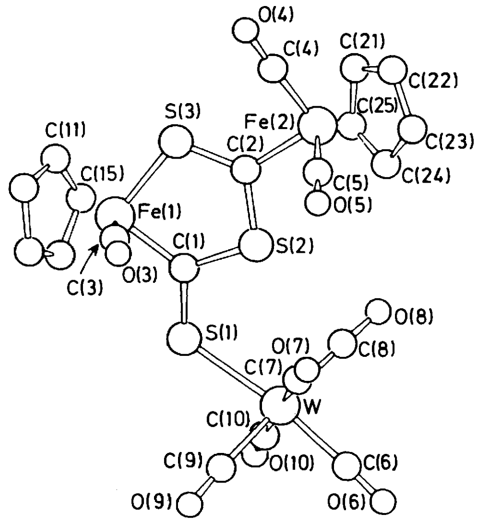
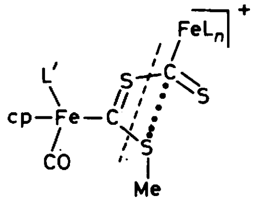


Figure 1. Perspective drawing of the molecule (**4c**)



(VII)

complexes $[FeL_nC(S)SML_n]$ $[ML_n = FeL_n$ or $Re(CO)_5]$ [14] and $[(CO)_5ReSC(S)Sn(PPh_3)]$ [25] which can be isolated only if the conditions are sufficiently mild to avoid formation of chelate species. The rather low yield observed in the C_2S_3 disproportionation [reaction (5)] may be attributed to formation of other not yet identified products derived from rupture of the other long C–S bond.

The reactions presented here are the CS_2–CS coupling to give the C_2S_3 grouping and its photochemical fragmentation to give back CS_2 and CS co-ordinated to the same metal centre. This reactivity pattern fits well the mechanism of 'heteroallene' disproportionation in which type (**2**) complexes have been proposed to be the unstable intermediates.[26] Our findings, however, indicate that acyclic intermediates should be invoked in these head-to-tail metal-promoted condensation–disproportionations of heteroallenes.

Reactions of $[(CO)(cp)FeC(S)SC(FeL_n)S]$ *with Electrophiles.*—In agreement with our prediction (**2**) reacts with electrophiles (E) to give exocyclic S-addition products $[(CO)(cp)FeC(SE)SC(FeL_n)S]$ which may be neutral or cationic depending on the nature of E (Scheme). Treating (**2**) with photogenerated $[M'(CO)_5(thf)]$ in tetrahydrofuran (thf) solution at room temperature readily produces the violet compounds (**4a**)—(**4c**) which can be crystallized from CH_2Cl_2–hexane at −20 °C. All these compounds are air stable in the solid state. Their stability in solution is much greater than that of the related μ^3-CS_2 derivatives $[FeL_nC(SFeL_n)SM'(CO)_5]$ (M′ = Cr, Mo, or W),[14] confirming that cyclic CS_2-containing compounds are more stable than acyclic derivatives. Compound (**4b**) was also isolated as the only product by treating $[Mo(\eta^4\text{-}C_7H_8)(CO)_4]$ with (**2**), indicating the inability of the endocyclic C–S–C sulphur to take part in metal complexation. The spectroscopic properties of (**4**) are in agreement with the structure which has been unambiguously determined for (**4c**) by *X*-ray crystallography (Figure 1).

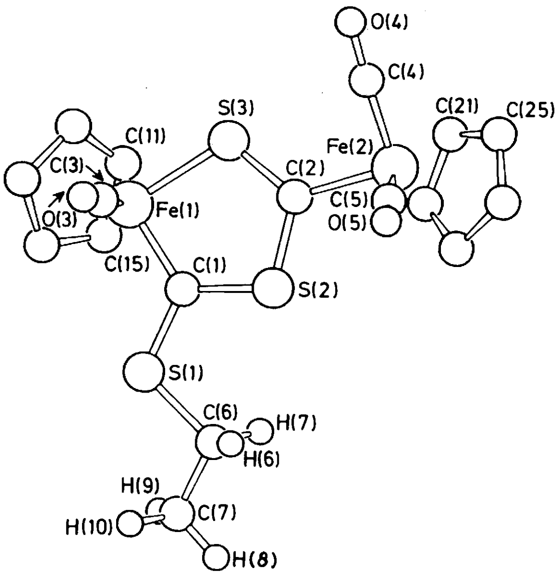


Figure 2. Perspective drawing of the cation of (**5b**)

As communicated earlier[13] (**2**) reacts within 15 min in CH_2Cl_2 with methyl- or ethyl-trifluoromethane sulphonate to quantitatively form the deep green air-stable S-alkyl complexes (**5a**) and (**5b**). The methylated product (**5a**) is also obtained from (**2**) and MeI, requiring a longer reaction time.

The cation $[(CO)(cp)FeC(SMe)SC(FeL_n)S]^+$ cannot be prepared as expected by reacting $[FeL_n\{C(S)SMe\}]$ and $[FeL_n(CS)]SO_3CF_3$. Furthermore the reaction with $[Fe(cp)(CO)(PPh_3)\{C(S)SMe\}]$, in which the presence of the phosphine ligand enhances the basicity of the thione sulphur, gives $[Fe(cp)(CO)(PPh_3)(CS)]^+$ and $[FeL_n\{C(S)SMe\}]$ as the only isolable products after 2 h at room temperature in CH_2Cl_2. This result strongly confirms our feeling that both steric factors and the instability of open-chain thioanhydride-like derivatives are decisive in determining the nature of the sulphur-adducts and the reaction products. In fact where the addition step is likely to occur in the *E* position because of the presence of the bulky ligand PPh_3, the unstable open-chain intermediate (**VII**) (L′ = PPh_3) is probably formed which undergoes rearrangement to give the observed products in a transesterification type reaction. The bis-carbene nature of the alkylated cyclic adducts was confirmed by crystal structure of $[(CO)(cp)FeC(SEt)SC(FeL_n)S]SO_3CF_3$ (see Figure 2).

Reaction of (**2**) with the molecular Lewis acid HgX_2 in CH_2Cl_2 produces the bright green air-stable 1:1 adducts (**6a**)—(**6c**). Presumably all these compounds are dimeric; preliminary results from the *X*-ray study of the $HgBr_2$ adduct have indicated that bromine atoms bridge tetrahedrally co-ordinated mercury(II) ions.[27] While derivatives such as $[FeL_nC(SHgX_2)SFeL_n]$ [15] and $[(CO)_3(cp)_2Fe_2(CS{\cdot}HgX_2)]$ [28] are very labile in solution and are largely dissociated in the absence of HgX_2 in excess, (**6a**)—(**6c**) are stable in solution. No dissociation of (**6a**) into (**2**) and $HgCl_2$ was detected in the ^1H n.m.r. spectra after standing for 24 h in chlorinated solvents.

Silver ion has been already shown to form labile adducts with electron-rich thiocarbonyl complexes.[29] Similarly (**2**) reacts with $AgBF_4$ to form an isolable green complex. A stoicheiometric study has shown that only 0.5 mol of Ag^+ is required per mol of complex and elemental analyses indicate a

Table 1. Relevant bond distances (Å) and angles (°) with e.s.d.s in parentheses

	(5b)	**(4c)**		**(5b)**	**(4c)**
Fe(1)–S(3)	2.190(1)	2.181(3)	C(8)–S(4)	1.78(1)	
Fe(1)–C(1)	1.862(5)	1.891(8)	S(4)–O (av.)	1.42	
Fe(2)–C(2)	1.940(4)	1.933(8)	C(8)–F (av.)	1.30	
C(1)–S(1)	1.686(5)	1.671(8)			
C(2)–S(2)	1.722(5)	1.714(8)	C(1)–Fe(1)–S(3)	89.1(1)	89.9(3)
C(1)–S(2)	1.739(5)	1.75(1)	Fe(1)–S(3)–C(2)	108.3(2)	108.0(3)
C(2)–S(3)	1.653(5)	1.65(1)	S(3)–C(2)–S(2)	116.8(3)	116.8(5)
W–S(1)		2.557(2)	C(2)–S(2)–C(1)	102.5(2)	103.8(4)
C(6)–S(1)	1.818(6)		S(2)–C(1)–Fe(1)	123.0(3)	119.2(4)
C(6)–C(7)	1.52(1)		C(1)–S(1)–W		119.6(3)
Fe(1)–C(3)	1.744(5)	1.73(1)	C(1)–S(1)–C(6)	110.1(3)	
C(3)–O(3)	1.149(7)	1.18(2)	S(3)–C(2)–Fe(2)	124.8(3)	126.6(5)
Fe(2)–C(4)	1.746(7)	1.77(1)	S(2)–C(2)–Fe(2)	118.3(3)	116.6(5)
C(4)–O(4)	1.15(1)	1.15(1)	Fe(1)–C(1)–S(1)	121.0(3)	126.8(5)
Fe(2)–C(5)	1.774(6)	1.75(1)	S(2)–C(1)–S(1)	116.0(3)	113.7(5)
C(5)–O(5)	1.129(8)	1.13(1)	Fe(1)–C(3)–O(3)	178.9(5)	177(1)
W–CO (av.)		2.01	Fe(2)–C(4)–O(4)	177.2(6)	177(1)
WC–O (av.)		1.14	Fe(2)–C(5)–O(5)	178.3(5)	179(1)

1:2 ratio of Ag^+ : $[(CO)(cp)\overline{FeC(S)SC(FeL_n)S}]$. The crystalline complex (**7**) has spectroscopic properties similar to those of the HgX_2 adducts.

Although $[FeL_nC(S)SML_n]$ react with $HOSO_2CF_3$ to form isolable S-protonated species,[15] the analogous reaction of (**2**) in diethyl ether immediately gives a green solution from which an unstable olive-green oil can be obtained. The formation of (**8**) is indicated only by the ν(CO) pattern in the i.r. spectrum. Similarly no stable BF_3 adducts (**9**) could be isolated, but i.r. spectra clearly indicate its formation in solution.

Description of the Structures of (**5b**) *and* (**4c**).—Crystals of (**5b**) contain discrete anions and cations whose packing shows no unusual features. Crystals of (**4c**) consist of discrete molecules held together by normal van der Waals interactions. Perspective drawings of the two molecules are shown in Figures 1 and 2; selected bond distances and angles are compared in Table 1. Both the cation (**5b**) and the neutral molecule (**4c**) have the same overall stereogeometry except for the sulphur-addition groups Et and $W(CO)_5$. The central unit of both molecules is the planar five-atom ring $\overline{Fe(1)C(1)S(2)C(2)S(3)}$ [maximum deviation from the average plane 0.04 in (**5b**) and 0.11 Å in (**4c**)]. Outer substituents are bonded to C(2), $(CO)_2(cp)Fe$, and to the exocyclic sulphur S(1): Et in (**5b**) and $W(CO)_5$ in (**4c**) [in *E* position to minimize contacts with the ligands on Fe(1)]. The S(1) atoms deviate slightly from the ring planes [0.13 in (**5b**) and 0.3 Å in (**4c**)]. The endocyclic iron, Fe(1), is chiral bearing one CO and one cp group. The CO group bonded to Fe(1) is almost orthogonal to the ring and, in order to compare the molecular conformations, the same configuration at Fe(1) (the crystals are racemic) and angle of view are adopted in the molecular drawings.

The core of the molecules can be looked at as two condensed CS_2 units sharing the S(2) atom and cyclized upon incorporation of an iron atom. The geometry of these CS_2 fragments is comparable to that found in $[FeL_nC(SFeL_n)SW(CO)_5]$[14] in which the CS_2 ligand is tridentate and all its atoms exhibit sp^2 hydridization of their orbitals. The fragment S(2)C(2)S(3) is equivalent in (**5b**) and (**4c**) within experimental error. The bond C(2)–S(3) [average 1.65(1) Å] is shorter than C(2)–S(2) [average 1.72(1) Å] indicating a higher double-bond character for the former and substantial differences between S(3) and S(2). In fact S(2) forms two normal electron pair bonds to C(2) and C(1) and therefore has a filled p_z orbital usable for π interactions. S(3), on the other hand, donates an electron pair to Fe(1) and employs its unpaired electrons in a σ + π double bond to C(2). The C(2)–Fe(2) bond [average 1.935(10) Å] is substantially longer than Fe–CO [average 1.76(1) Å] but is shorter than a formal single Fe–C bond as found in $[Fe(cp)(CO)_2\{C(SMe)_3\}]$, 2.11(1) Å.[30] Therefore there is evidence that C(2) is involved in a significant π interaction with *exo*-Fe(2) and exhibits carbenoid character. As a consequence the conformation of the *exo*-FeL_n fragment with respect to the carbene plane is dictated not only by the optimization of the non-bonded contacts, but also by the condition of maximum overlap of the orbitals involved in π interactions.

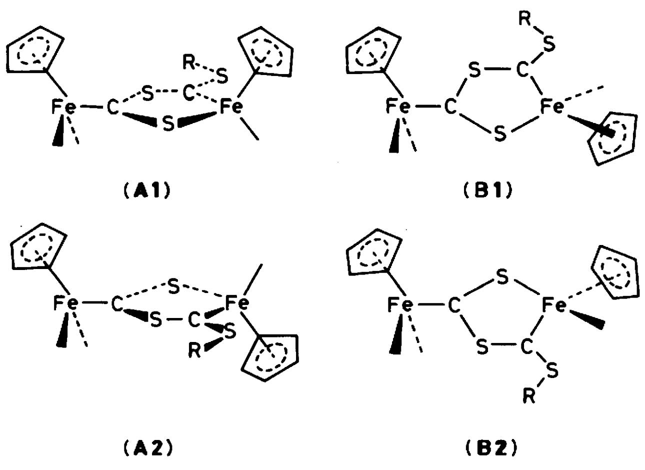


Figure 3. Idealized conformations of cyclic bis-carbene complexes arising from rotation around Fe–C(sp^2) bond

The orientation of the FeL_n group is equivalent in both structures; the CO ligands lie above the carbene ring, on the same side as C(3)–O(3). The angle between the carbene ring plane and the symmetry plane of FeL_n is 73 in (**5b**) and 69° in (**4c**). Due to the asymmetry of the ring fragment, four non-equivalent low-energy conformations can be obtained by rotation around the C(2)–Fe(2) axis (Figure 3). The ring plane and the symmetry plane of FeL_n are orthogonal in two conformations (**A1**, **A2**) and coincident in the other two (**B1**, **B2**). It is reasonable to assume that the **A2** rotamer is very similar in energy to the actual one, **A1**, as confirmed by its occurrence in the species $[(CO)(cp)\overline{FeC(SFeL_n)SC(FeL_n)S}]^+$.[13] The **B1** and **B2** rotamers are probably disfavoured in the present

Table 2. Infrared and ^{1}H n.m.r. data [FeL_n = $Fe(cp)(CO)_2$]

Complex	I.r.		^{1}H N.m.r. (δ)^c
	ν(CO)^a/cm^{-1}	ν(CS)^b/cm^{-1}	
(**1a**) $[(CO)(cp)FeC(SFeL_n)SC(FeL_n)S]SO_3CF_3$	2 048s, 2 006s	998m, 940m, 802m, 750m	5.31, 5.23, 4.94^d
(**1b**) $[(CO)(cp)FeC\{SRe(CO)_5\}SC(FeL_n)S]SO_3CF_3$	2 145m, 2 047vs, 2 006s	997ms, 932m, 804m, 760m	5.54, 5.16
(**2**) $[(CO)(cp)FeC(\dot{S})SC(FeL_n)S]$	2 044s, 1 999s, 1 962s	996ms, 976m, 819m, 755w	5.13, 4.75
(**4a**) $[(CO)(cp)FeC\{SCr(CO)_5\}SC(FeL_n)S]$	2 056ms, *2 046s*, *2 004s* *1 975s*, 1 933vs, 1 897m (sh)	998m, 964m, 810m, 744w	5.13, 4.78
(**4b**) $[(CO)(cp)FeC\{SMo(CO)_5\}SC(FeL_n)S]$	2 066ms, *2 046s*, *2 005s* *1 976s*, 1 936vs, 1 898m (sh)	1 004m, 952m, 818m, 750w	5.10, 4.78
(**4c**) $[(CO)(cp)FeC\{SW(CO)_5\}SC(FeL_n)S]$	2 065ms, *2 046s*, *2 005s* *1 977s*, 1 930vs, 1 892m (sh)	1 003m, 946m, 808m, 746w	5.15, 4.83
(**5a**) $[(CO)(cp)FeC(SMe)SC(FeL_n)S]SO_3CF_3$	2 053s, 2 013s	1 010ms, 934m, 806m, 763w	5.32, 5.17, 3.15 (CH_3)
(**5b**) $[(CO)(cp)FeC(SEt)SC(FeL_n)S]SO_3CF_3$	2 053s, 2 013s	1 010ms, 941m, 805m, 762w	5.38, 5.23, 3.70 (CH_2) 1.53 (CH_3)
(**6a**) $[\{(CO)(cp)FeC(SHgCl_2)SC(FeL_n)S\}_2]$	2 052s, 2 012s	997m, 913m, 806m, 764m	5.53, 5.29^e
(**6b**) $[\{(CO)(cp)FeC(SHgBr_2)SC(FeL_n)S\}_2]$	2 051s, 2 010s	996m, 911m, 806m, 762m	5.55, 5.30^e
(**6c**) $[\{(CO)(cp)FeC(SHgI_2)SC(FeL_n)S\}_2]$	2 049s, 2 008s	997m, 923m, 805m, 757m	5.50, 5.18^e
(**7**) $[\{(CO)(cp)FeC(SAg_{0.5})SC(FeL_n)S\}_2]BF_4$	2 048s, 2 006s	997m, 950m, 809m, 738m	5.14, 4.89
(**8**) $[(CO)(cp)FeC(SH)SC(FeL_n)S]SO_3CF_3$	2 054s, 2 009s		
(**9**) $[(CO)(cp)FeC(SBF_3)SC(FeL_n)S]$	2 053s, 2 014s		

^{a} In CH_2Cl_2; the absorptions due to the precursor (**2**) are italicized. ^{b} As KBr pellets. ^{c} Values in p.p.m., $SiMe_4$ as internal standard; recorded in $CDCl_3$. ^{d} In $CDCl_2$. ^{e} In $(CD_3)_2CO$.

system, even though molecular orbital calculations on $[Mn(cp)(CO)_2(CH_2)]$[31] and both calculations and diffraction studies on $[Mn(cp)(CO)_2\{C(OMe)Ph\}]$[32,33] assigned the lowest energy to type **B** conformations. The present results might depend on the weakness of the π C(carbene)–Fe interaction, the p_z orbital on C(2) being mainly engaged in the π ring orbitals.

The bond interactions of C(1) are of great interest because these are the only significant difference between the two molecules. The C(1) atoms, like C(2), also exhibit carbenic character, but their bonding interactions are formally different in (**5b**) and (**4c**). In the cation (**5b**), in which Fe(1) formally bears the positive charge, C(1) is to be considered a two-electron donor to Fe(1), in order to fulfil the effective atomic number of the metal atom. The other σ bonds, C(1)–S(2) and C(1)–S(1), can be considered primarily as normal electron-pair bonds and therefore the p_z atomic orbital on C(1) is formally empty. The *exo*-S(1) atom, on the other hand, also exhibits sp^2 hybridization of its orbitals and engages its unpaired electrons in σ bonds to C(1) and C(6). The S(1) p_z lone pair can donate to the empty orbital on C(1) and therefore it is involved in the delocalized ring orbitals. As a result the C(1)–Fe(1) interaction [1.862(5) Å] has more double bond character than C(2)–Fe(2) [1.940(4) Å], *i.e.* the carbenic character of C(1) is greater than that of C(2). This bond description is very crude because all bonds show double-bond character, shown by a comparison of the S(1)–C(6) single bond [1.82(1) Å] with all the other C–S bond distances. Thus extensive π-electron delocalization results in efficient charge equalization over the whole cation.

In (**4c**) no formal charge resides on Fe(1), and C(1) could be considered [*cf.* C(2)], as a one-electron donor to Fe(1) leaving its p_z orbital singly occupied; S(1) donates one electron pair to $W(CO)_5$ and its p_z orbital is also singly occupied. Therefore the two p_z orbitals on S(1) and C(1) overlap in a π bond that is expected to be more localized than in (**5b**), confirmed by the slight shortening of C(1)–S(1) [1.671(8) *vs.* 1.686(5) Å in (**5b**)]. Consequently C(1)–Fe(1) in (**4c**) is slightly longer than in (**5b**) [1.891(8) *vs.* 1.862(5) Å].

Another difference between the cation (**5b**) and the neutral (**4c**) is that the Fe–CO interactions are equivalent in the $Fe(cp)(CO)_2$ fragments [average 1.76(1) for Fe–C, 1.14(1) Å for C–O], while significant variations are found for the Fe(1)–C(3)–O(3) interactions [1.73(1) and 1.18(2) in (**4c**), 1.744(5) and 1.149(7) Å in (**5b**)]. This effect indicates that CO bonded to endocyclic iron is particularly affected by the electronic effects of the substituents at S(1).

In spite of the different schemes of electron allocation around C(1) in (**5b**) and (**4c**), these differences are more formal than real. In conclusion the most significant differences are not between the cation (**4c**) and the neutral (**5b**), but between Fe(1) and Fe(2) within either species. They arise from the substitution at Fe(1) of the better donor S for one CO. The elimination of a strong π competitor on Fe(1) enhances the donor ability of this atom towards C(1) compared to Fe(2) towards C(2).

Infrared Spectra.—The CO stretching absorptions in CH_2Cl_2 solution are reported in Table 2. Three equally intense bands are observed for (**2**) whereas two bands have been found for the cationic species (**1a**), (**1b**), (**5a**), (**5b**), (**7**), and (**8**), and the adducts (**6a**)—(**6c**) and (**9**). In (**4a**)—(**4c**) the number of terminal ν(CO) absorptions is the sum of those attributable to the $M(CO)_5$ fragment and those of the precursor (**2**). The lowest band in (**2**), attributed to CO bonded to the endocyclic iron, shifts to a higher wavenumber in complexes having two ν(CO) bands and superimposes on the lowest ν(CO) of the exocyclic FeL_n group. Such a shift indicates a lower iron–carbonyl back-donation upon co-ordination of acidic fragments at the thione sulphur. This effect suggests that a significant amount of electron density resides in delocalized ring orbitals involving the endocyclic Fe(1) and C(1) and the exocyclic S(1). Its variations can be measured by the differences, Δν(CO), in the adducts and in the precursor; increase of Δν(CO) indicates higher electron-withdrawing abilities of the groups linked to the exocyclic sulphur in the order $BF_3 \approx R^+$ (R = Me or Et) (*ca.* 52) > HgX_2 (*ca.* 48) > $M'(CO)_5$ (*ca.* 15 cm^{-1}).

The i.r. spectrum of (**2**) in cyclohexane (Figure 4) displays some unusual features, *i.e.* the splitting of the lowest ν(CO) band

Table 3. I.r. spectroscopic data in the CO stretching region (cyclohexane solution)

Complex	$\nu(CO)^a/cm^{-1}$
(**2**) $[(CO)(cp)FeC(S)SC(FeL_n)S]$	2 043s, 2 002s, 1 973m, 1 963ms
(**4a**) $[(CO)(cp)FeC\{SCr(CO)_5\}SC(FeL_n)S]$	2 055m, *2 048*s, *2 010*s, *1 986*ms (sh), *1 977*ms 1 939vs, 1 928s, 1 914s
(**4b**) $[(CO)(cp)FeC\{SMo(CO)_5\}SC(FeL_n)S]$	2 065m, *2 049*s, *2 010*s, *1 985*s (sh), *1 978*s 1 942vs, 1 932s, 1 914s
(**4c**) $[(CO)(cp)FeC\{SW(CO)_5\}SC(FeL_n)S]$	2 063ms, *2 049*s, *2 011*ms, *1 985*s (sh), *1 975*s 1 938vs, 1 924s, 1 910s
$[(CO)(cp)FeSC(FeL_n)S]^b$	2 039ms, 2 036s, 1 995ms, 1 991s, 1 957ms, 1 949s
$[(NO)(cp)MnSC(FeL_n)S]^b$	2 039ms, 2 036s, 1 995ms, 1 990s, 1 723s (NO)

[a] The absorptions due to the precursor (**2**) are italicized. [b] For i.r. spectra in CH_2Cl_2 see ref. 14.

of the pair at 1 973m and 1 963ms cm^{-1} (Figure 4). The same effect is true for the cyclohexane-soluble adducts (**4a**)—(**4c**) (Table 3). Repeated recrystallizations of the complexes do not alter the spectra. A high-resolution i.r. spectrum of (**2**) shows the two bands at highest wavenumbers to be actually unresolved pairs. The band at 2 002 cm^{-1} shows significant asymmetry and the one at 2 043 cm^{-1} is shouldered. This indicates presence of different conformers in solution. Conformational isomerism about the M–C(sp^2) bond has been observed previously by a doubling of all terminal ν(CO) bands in the Fischer-type pseudo-octahedral carbene complexes $[Mn(cp)(CO)_2\{C(OEt)Ph\}]$[34] and $[CrR'(CO)_2\{C(OMe)Ph\}]$ (R' = η-C_6H_6 or η-C_6H_5Me).[35] To our knowledge, no example of such conformers has been reported for related dithiocarbene derivatives.

The observed ν(CO) i.r. pattern of (**2**) and (**4a**)—(**4c**) is evidence for the existence in solution of type **A** and **B** conformers (Figure 3) in non-equivalent concentrations. The two conformations of each type are indistinguishable by i.r. spectroscopy. The ν(CO) doubling cannot be attributed to *E–Z* conformers at *exo*-S in (**4a**)—(**4c**) because it is present also in (**2**) in which the thionic end is free. The i.r. spectra of $[(L')(cp)M'SC(FeL_n)S]$ (M' = Fe, L' = CO; M' = Mn, L' = NO)[14] in cyclohexane similarly show doubling of the terminal ν(CO) bands (Table 3). Again only two of the three possible idealized conformations can be detected: the indistinguishable mixture **A3**, **A4** and the electronically favoured **B3** form.

An indication that the energy differences between conformations **A** and **B** cannot be large is found in the actual orientation of the FeL_n fragment in the crystals of (**5b**) and (**4c**) which is some 20° off the **A1** ideal conformation. The structural findings also suggest that type **A** conformers are the predominant form in solution.

The ν(CS) i.r. spectrum (Table 2) shows four bands for (**2**); the highest and most intense absorption, assigned to the exocyclic thione group stretching mode, is comparable with those of the related metallodithioesters.[12,23] A characteristic ν(CS) band pattern is found in all the S-adducts (Table 2) and the band at 911—950 cm^{-1} may be assigned to the exocyclic ν[C(1)–S(1)] stretching mode, due to its greater dependence on the different electron-withdrawing abilities of the Lewis acids bonded to S(1). A similar effect is observed for $[Fe_2(cp)_2(CO)_2(L')(CSHgCl_2)]$ (L = CO[36] or CS[37]). Consequently the highest ν(CS), practically unaffected by HgX_2, may be related to the C(2)–S(3) bond, the shortest in both (**4c**) and (**5b**).

*Hydrogen-*1 *and Carbon-*13 *N.M.R. Spectra.*—The room-temperature ^1H n.m.r. spectra are as expected. The lack of doubling of the sharp ^1H signals both in the precursor (**2**) and in the S-adduct derivatives indicates that conformers arising from Fe(2)–C(2) restricted rotation or *E–Z* isomerism derived from rotation around exocyclic C(1)–S(1) or from inversion at S(1) cannot be detected on the n.m.r. time-scale. Low-temperature n.m.r. analyses have been frustrated by sample precipitation.

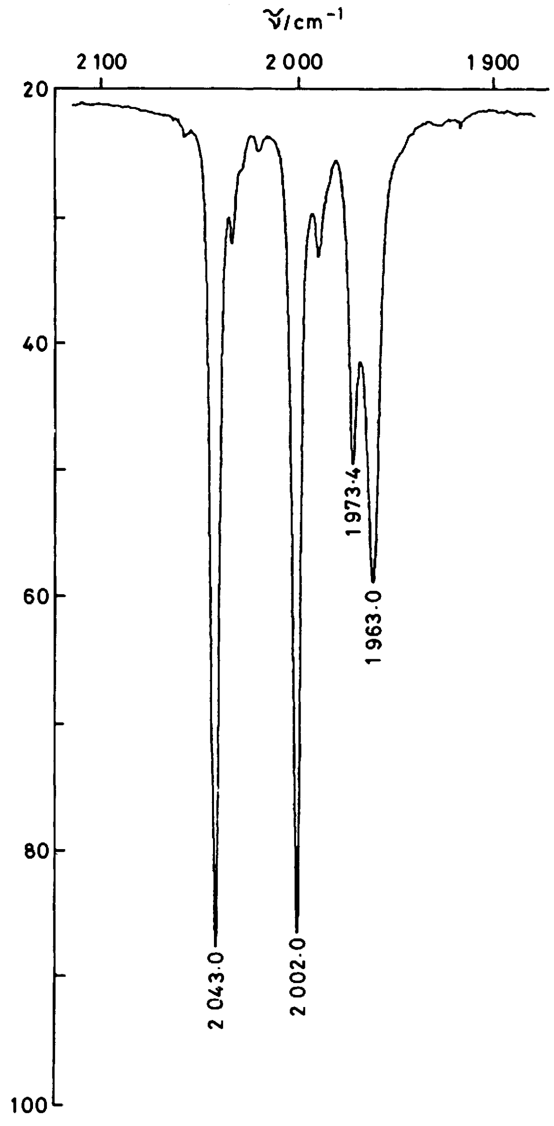
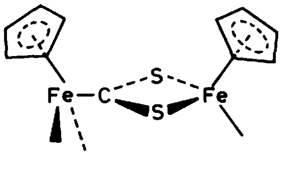


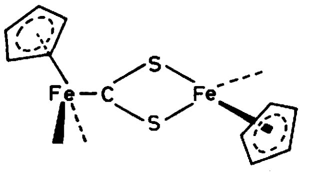
Figure 4. Infrared spectrum of (**2**) in the CO-stretching region (cyclohexane solution)

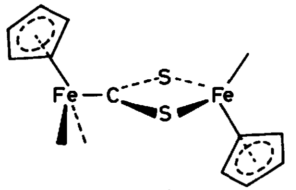
Conclusive evidence for the presence of carbene type carbons within the FeC_2S_2 five-membered-ring complexes is the rather

Table 4. Carbon-13 n.m.r. data (in CD_2Cl_2)

Complex	C(1)	C(2)	CO	Others
(1a)	329.23	284.23	211.25, 210.92, 210.72 (1:2:2)	87.95, 87.87, 87.21 (C_5H_5)
(2)	329.49	279.24	213.51, 211.23 (1:2)	87.83, 87.70 (C_5H_5)
(4c)	321.51	280.29	211.54, 210.17, 210.08 198.54 [*trans*-$W(CO)_5$], 198.20 [*cis*-$W(CO)_5$]	86.86, 86.56 (C_5H_5)
(5a)	312.12	286.11	210.21, 210.12, 209.24	88.21, 87.94 (C_5H_5); 29.82 (CH_3)
(5b)	311.21	286.21	210.32, 210.29, 210.20	88.38, 88.00 (C_5H_5); 41.07 (CH_2), 12.41 (CH_3)
(6b)	326.95	285.08	211.18, 210.74 (1:2)	89.19, 87.78 (C_5H_5)


(A3)


(B3)


(A4)

low-field ^{13}C n.m.r. signals (Table 4). Two distinct ^{13}C ($\delta_{carbene}$) resonances are displayed, one at higher (279—286 p.p.m.) and the other at lower field (311—329 p.p.m.). We assign the high-field signal to C(2) because it falls in a range typical of cyclic dithiocarbene complexes [$W(CO)_5\{CS(CH_2)_2S\}$] (282.6 p.p.m.),[38] [$FeL_n\{CS(CH_2)_2S\}]^+$ (294.7 p.p.m.)[39] and is surprisingly similar to that of [$Cr(CO)_2(\eta$-$C_6H_3Me_3$-1,3,5)-$\{CSC(R)C(R')S\}$] (R,R′ = CO_2Me) (279—281 p.p.m.)[7] in which high π-delocalization is present within the 1,3-dithiol-2-ylidene ring.[6] The lowest field signal, assigned to C(1), is in good agreement with that reported for a carbon in similar environment that is bonded to an iron atom on which a CO group is (*i*) replaced by a ligand with high σ/π ratio, *e.g.* [$Fe(cp)(CO)(L')\{C(SMe)_2\}]^+$ [L′ = $P(OMe)_3$ (314) or pyridine (319 p.p.m.)],[40] or (*ii*) linked to two S atoms in a non-cyclic dithiocarbene, *e.g.* [$FeL_nC(SMe)SML_n]^+$ [ML_n = FeL_n (315.4) or $Re(CO)_5$ (321.4 p.p.m.)][15,41] and [$(CO)_5WC(SMe)SFeL_n$] (323.4 p.p.m.).[38]

The ^{13}CO chemical shifts are in the range expected for this type of complex. In agreement with the diastereotopic nature of the carbonyls bonded to the exocyclic iron two ^{13}CO signals for FeL_n are present in the spectra of (**4c**), (**5a**), and (**5b**). These δ(CO) resonances are superimposed in (**2**) and in (**6b**). The differences between δ(CO) for CO bonded to exocyclic and endocyclic iron atoms are very small (1—2 p.p.m.), compared with those for δ(carbene) bonded to the same metal centre (40—60 p.p.m.). Thus a change in the electronic environment causes a greater shift in δ(carbene) than in δ(CO).

The other ^{13}C resonances fall in the range expected.

Experimental

All solvents were appropriately dried and degassed prior to use under dinitrogen and reactions were routinely carried out by using standard Schlenk techniques under dinitrogen. All reagent-grade chemicals were used as received. The compounds [$FeL_nC(S)SFeL_n$],[23] [$FeL_nC(S)SRe(CO)_5$],[12] [$FeL_n\{C(S)SMe\}$],[15] [$FeL_n(CS)]SO_3CF_3$[37] were prepared by the reported procedures. Infrared spectra were recorded on a Perkin-Elmer 983G spectrometer as KBr pellets or in solution using a pair of matched 1.0-mm NaCl cells. The observed frequencies (± 1 cm^{-1}) were calibrated with the 1 673 cm^{-1} band of water vapour. Higher resolution (±0.5 cm^{-1}) i.r. spectra [ν(CO)] were recorded on a Bruker IFS 113V instrument. Hydrogen-1 and ^{13}C-$\{^1H\}$ n.m.r. spectra were recorded on a Varian XL100 spectrometer using $SiMe_4$ as internal standard (positive shifts are downfield). Elemental analyses were determined by Pascher Microanalytical Laboratorium (Bonn, Germany). Conductivity measurements were performed with a LKB 5300B conductivity bridge (1 × 10^{-4} mol dm^{-3} solutions in acetone). Melting points were determined using a Büchi instrument and are uncorrected.

Syntheses.—[$(CO)(cp)FeC(SFeL_n)SC(FeL_n)S]SO_3CF_3$ (**1a**). A mixture of the dimetallodithioester [$FeL_nC(S)SFeL_n$] (3.00 g, 6.98 mmol) and [$FeL_n(CS)]SO_3CF_3$ (2.41 g, 6.50 mmol) was stirred in CH_2Cl_2 (50 cm^3) for 60 min. The solution was then evaporated to dryness under vacuum and the residue washed with Et_2O (200 cm^3). Crystallization of the crude product from CH_2Cl_2–Et_2O at −20 °C afforded (**1a**) as deep green crystals. Yield 72% (3.61 g, 4.68 mmol); m.p. 179—181 °C (decomp.) (Found: C, 35.4; H, 1.90; S, 16.8. Calc. for $C_{23}H_{15}F_3Fe_3O_8S_4$: C, 35.75; H, 1.95; S, 16.6%). $\Lambda_m(Me_2CO)$ = 137 S cm^2 mol^{-1}.

[$(CO)(cp)FeC\{SRe(CO)_5\}SC(FeL_n)S]SO_3CF_3$ (**1b**). This was prepared analogously to (**1a**), starting with a solution of [$FeL_nC(S)SRe(CO)_5$] (0.50 g, 0.86 mmol) in CH_2Cl_2 (30 cm^3) and [$FeL_n(CS)]SO_3CF_3$ (0.20 g, 0.79 mmol). The solution was evaporated to dryness after being stirred for 60 min. The resulting residue was washed with Et_2O (100 cm^3) and dried under vacuum. The green complex was crystallized from a CH_2Cl_2–Et_2O mixture at −20 °C. Yield 69% (0.54 g, 0.60 mmol); m.p. 140—145 °C (decomp.) (Found: C, 27.4; H, 1.10; S, 13.9. Calc. for $C_{21}H_{10}F_3Fe_2O_{11}ReS_4$: C, 27.35; H, 1.10; S, 13.9%). $\Lambda_m(Me_2CO)$ 151 S cm^2 mol^{-1}.

[$(CO)(cp)FeC(S)SC(FeL_n)S$] (**2**). The complex (**1a**) (2.00 g, 2.60 mmol) and a two-fold excess of NaI (0.80 g, 5.20 mmol) were allowed to react in boiling acetone (50 cm^3) for 30 min. The solution was then evaporated to dryness and the residue chromatographed on an alumina column (3 × 35 cm). Elution with light petroleum (b.p. 40—70 °C throughout)–CH_2Cl_2 (2:1) gave first a fraction which contained [FeL_nI], and a second green fraction which was collected and evaporated to dryness. Crystallization of the residue at −20 °C from light petroleum–CH_2Cl_2 gave deep green crystals of (**2**). Yield 67% (0.77 g, 1.74 mmol); m.p. 144—145 °C (decomp.) (Found: C, 40.15; H, 2.25; S, 20.7. Calc. for $C_{15}H_{10}Fe_2O_3S_3$: C, 40.4; H, 2.25; S, 21.55%).

[$(CS)(cp)FeSC(FeL_n)S$] (**3**). A tetrahydrofuran (thf) solution (20 cm^3) containing (**2**) (0.30 g, 0.67 mmol) was irradiated with a Hanovia ultraviolet lamp for 1 h. The resulting solution was evaporated to dryness under vacuum and the residue

Table 5. Summary of crystal data and intensity collection parameters

Complex	**(5b)**	**(4c)**
Formula	$C_{18}H_{15}F_3Fe_2O_6S_4$	$C_{20}H_{10}Fe_2O_8S_3W$
M	624.26	770.04
Crystal size (mm)	0.2 × 0.05 × 0.2	0.15 × 0.05 × 0.03
System	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
a/Å	14.565(4)	13.162(2)
b/Å	10.369(2)	13.156(1)
c/Å	16.176(2)	14.029(3)
β/°	101.73(1)	93.66(1)
U/Å^3	2 391.9	2 424.3
Z	4	4
D_c/g cm^{-3}	1.73	2.11
μ(Mo-K_α)/cm^{-1}	16.0	63.1
Scan mode	ω–2θ	ω
θ Range/°	2.5—27	2—25
ω Scan width/°	0.7 + 0.35 tan θ	1.2 + 0.35 tan θ
Prescan rate/° min^{-1}	5	4
Prescan acceptance, σ(I)/I	0.3	0.3
Required σ(I)/I	0.01	0.01
Maximum scan time (s)	150	150
Octants explored in the reciprocal space	$\pm h, k, l$	$h, k, \pm l$
Measured reflections	5 696	4 664
Unique observed reflections $[F_o > 5\sigma(F_o)]$	2 302	2 142
R, R'	0.042, 0.042	0.033, 0.029

chromatographed on an alumina column (2 × 30 cm). Elution with light petroleum–CH_2Cl_2 (3:1) gave first a red fraction which was dried under vacuum. Crystallization from light petroleum–CH_2Cl_2 at −20 °C gave orange needles of **(3)**. Yield 11% (0.030 g, 0.07 mmol); m.p. 117—120 °C (decomp.) (Found: C, 40.75; H, 2.00; S, 23.0. $C_{14}H_{10}Fe_2O_2S_3$ requires C, 40.2; H, 2.40; S, 23.0%). I.r.: ν(CO) (n-hexane) 2 030s, 1 987s; ν(CS) (KBr) 1 263s, 913m, 880m; $\delta_H(CDCl_3)$ 4.97 (5 H, s, C_5H_5) and 4.77 (5 H, s, C_5H_5).

$[(CO)(cp)FeC\{SM'(CO)_5\}SC(FeL_n)S]$ [M′ = Cr **(4a)**, Mo **(4b)**, *or* W **(4c)**].—To a solution of $[M'(CO)_5(thf)]$ prepared by irradiation of $[M'(CO)_6]$ (0.50 mmol), in freshly distilled thf (20 cm^3) was added **(2)** (0.134 g, 0.30 mmol). The resulting violet solution was then chromatographed on an alumina column (2 × 20 cm) with light petroleum–CH_2Cl_2 (1:1) to separate the first fraction containing $[M'(CO)_6]$. The second violet fraction was collected, evaporated to dryness and the residue crystallized from light petroleum–CH_2Cl_2 at −20 °C to give dark purple crystals. **(4a)**: yield 54% (0.10 g, 0.16 mmol); m.p. 135—139 °C (decomp.) (Found: C, 37.2; H, 1.85; S, 15.0. Calc. for $C_{20}H_{10}CrFe_2O_8S_3$: C, 37.6; H, 1.60; S, 15.05%). **(4b)**: yield 40% (0.082 g, 0.12 mmol); m.p. 137—140 °C (decomp.) (Found: C, 35.25; H, 1.50; S, 13.95. Calc. for $C_{20}H_{10}Fe_2MoO_8S_3$: C, 35.2; H, 1.50; S, 14.1%). **(4c)**: yield 78% (0.18 g, 0.23 mmol); m.p. 154 °C (decomp.) (Found: C, 31.2; H, 1.35; S, 11.9. Calc. for $C_{20}H_{10}Fe_2O_8S_3W$: C, 31.2; H, 1.30; S, 12.5%).

$[(CO)(cp)FeC(SR)SC(FeL_n)S]SO_3CF_3$ [R = Me **(5a)** *or* Et **(5b)**]: Stoicheiometric amounts of CF_3SO_2OR were added by a syringe to a CH_2Cl_2 solution (20 cm^3) of **(2)** (0.60 g, 1.35 mmol). The mixture, which immediately turned bright green, was stirred for 15 min at room temperature. The solution was concentrated to 10 cm^3 and the green complexes **(5a)** and **(5b)** were crystallized by addition of Et_2O (5 cm^3) and cooling to −20 °C. **(5a)**: yield 88% (0.73 g, 1.19 mmol); m.p. 130—133 °C (decomp.) (Found: C, 33.35; H, 2.15; S, 20.8. Calc. for $C_{17}H_{13}F_3Fe_2O_6S_4$: C, 33.45; H, 2.15; S, 21.0%). $\Lambda_m(Me_2CO)$ 135 S cm^2 mol^{-1}. **(5b)**: yield 91% (0.77 g, 1.23 mmol); m.p. 119—121 °C (decomp.) (Found: C, 34.6; H, 2.40; S, 20.6. Calc. for $C_{18}H_{15}F_3Fe_2O_6S_4$: C, 34.65; H, 2.40; S, 20.55%). $\Lambda_m(Me_2CO)$ 132 S cm^2 mol^{-1}.

$[\{(CO)(cp)FeC(SHgX_2)SC(FeL_n)S\}_2]$ [X = Cl **(6a)**, Br **(6b)**, *or* I **(6c)**].— A dichloromethane solution (20 cm^3) of **(2)** (0.22 g, 0.50 mmol) was stirred with a slight excess of HgX_2 (0.55 mmol) for 20 min. The resulting solution was filtered and concentrated to *ca.* 4 cm^3. Cooling to −20 °C gave dark green crystals. **(6a)**: yield 52% (0.18 g, 0.13 mmol); m.p. 132—134 °C (decomp.) (Found: C, 26.4; H, 1.45; S, 14.0. $C_{30}H_{20}Cl_4Fe_4Hg_2O_6S_6$ requires C, 26.4; H, 1.50; S, 14.1%). **(6b)**: yield 81% (0.30 g, 0.21 mmol); m.p. 150—152 °C (decomp.) (Found: C, 24.8; H, 1.35; S, 13.2. $C_{30}H_{20}Br_4Fe_4Hg_2O_6S_6$ requires C, 24.8; H, 1.40; S, 13.25%). **(6c)**: yield 77% (0.30 g, 0.19 mmol); m.p. 141—143 °C (decomp.) (Found: C, 23.4; H, 1.30; S, 12.2. $C_{30}H_{20}Fe_4Hg_2I_4O_6S_6$ requires C, 23.3; H, 1.30; S, 12.45%).

$[\{(CO)(cp)FeC(SAg_{0.5})SC(FeL_n)S\}_2]BF_4$ **(7)**. Stoicheiometric amounts of **(2)** (0.22 g, 0.50 mmol) and $AgBF_4$ (0.048 g, 0.25 mmol) were allowed to react in CH_2Cl_2 (20 cm^3) for 30 min. The solution was then filtered through a Celite pad (3 × 3 cm) and dried under vacuum. Crystallization of the residue from CH_2Cl_2–Et_2O at −20 °C afforded dark green crystals of **(7)**. Yield 68% (0.18 g, 0.17 mmol); m.p. 92—95 °C (decomp.) (Found: C, 33.25; H, 1.85; S, 17.5. $C_{30}H_{20}AgBF_4Fe_4O_6S_6$ requires C, 33.15; H, 1.85; S, 17.7%). $\Lambda_m(Me_2CO)$ 129 S cm^2 mol^{-1}.

$[(CO)(cp)FeC(SH)SC(FeL_n)S]SO_3CF_3$ **(8)**. A rapidly stirred Et_2O solution (15 cm^3) of **(2)** (0.22 g, 0.50 mmol) was treated with an equimolar amount of CF_3SO_2OH. The solution, which immediately turned bright green, was dried under vacuum and the olive-green oily residue was characterized by its i.r. spectrum. Attempted crystallization of the oil failed because of decomposition.

$[(CO)(cp)FeC(SBF_3)SC(FeL_n)S]$ **(9)**. A vigorously stirred Et_2O solution (15 cm^3) of **(2)** (0.22 g, 0.50 mmol) was treated with one equivalent of $BF_3{\cdot}Et_2O$ (0.071 g, 0.50 mmol). The resulting solution was evaporated under vacuum and the olive-green residue was characterized by its i.r. spectrum. Substantial decomposition of the residue rapidly occurs, preventing any further characterization.

$[Fe(cp)(CO)(L')(CS)]SO_3CF_3$ (L′ = PPh_3 *or* PMe_2Ph). These complexes were prepared by a modification of a previous method.[37]

A thf solution (40 cm^3) of $[Fe(cp)(CO)_2\{C(S)SMe\}]$ (0.30 g, 1.13 mmol) and an excess of L′ (4:1) were irradiated in thf for 30 min. The solvent was then removed under vacuum and the residue chromatographed on an alumina column (3 × 20 cm). Elution with light petroleum–CH_2Cl_2 (3:1) gave first an orange fraction which contained small amounts of unreacted dithioester. The second orange fraction was collected, dried under vacuum and the residue crystallized from a light petroleum–CH_2Cl_2 mixture affording orange needles of $[Fe(cp)(CO)(L')\{C(S)SMe\}]$. L′ = PPh_3: yield 64% (Found: C, 62.1; H, 4.55; S, 12.8. Calc. for $C_{26}H_{23}FeOPS_2$: C, 62.15; H, 4.60; S, 12.75%). ν(CO) (cyclohexane) 1 940s; ν(CS) (KBr) 1 002m cm^{-1}; $\delta_H(CDCl_3)$ 7.36 (15 H, m, Ph), 4.50 (5 H, s, C_5H_5), 2.32 (3 H, s, Me). L′ = PMe_2Ph: yield 43% (Found: C, 51.5; H, 3.55; S, 17.2. Calc. for $C_{16}H_{14}FeOPS_2$: C, 51.5; H, 3.80; S, 17.2%). ν(CO) (cyclohexane) 1 931s; ν(CS) (KBr) 986m cm^{-1}; $\delta_H(CDCl_3)$, 7.55 (5 H, m, Ph), 4.43 [5 H, d, J(PH) 1.0, C_5H_5], 2.55 [3 H, s, SMe], 1.97 [3 H, d, J(PH) 10, Me], 1.50 [3 H, d, J(PH) 10 Hz, Me].

These methyl dithioester complexes were treated with slight excess of CF_3SO_2OH in Et_2O affording, after filtration and crystallization from CH_2Cl_2–Et_2O, the title complexes. L =

Table 6. Fractional atomic co-ordinates for (**4c**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	0.645 60(3)	0.587 00(1)	0.338 60(3)	O(7)	0.423 2(7)	0.498 3(7)	0.327 0(7)
Fe(1)	0.667 96(10)	0.342 55(9)	0.021 95(8)	C(8)	0.699 3(9)	0.465 9(9)	0.418 8(8)
Fe(2)	0.545 83(10)	0.106 25(9)	0.271 03(8)	O(8)	0.731 2(8)	0.403 1(6)	0.467 7(6)
S(1)	0.696 5(2)	0.517 8(2)	0.178 1(2)	C(9)	0.590 9(8)	0.706 7(8)	0.264 3(7)
S(2)	0.607 2(2)	0.330 3(2)	0.234 8(2)	O(9)	0.556 3(6)	0.776 1(6)	0.224 4(6)
S(3)	0.632 7(2)	0.193 5(2)	0.079 5(2)	C(10)	0.783 5(9)	0.654 1(8)	0.350 3(7)
C(1)	0.662 8(6)	0.399 9(6)	0.145 2(6)	O(10)	0.859 1(7)	0.695 1(8)	0.356 2(6)
C(2)	0.596 9(6)	0.209 7(6)	0.188 8(6)	C(11)	0.762 0(10)	0.278 2(8)	−0.074 7(9)
C(3)	0.538 8(10)	0.368 0(8)	0.007 8(8)	C(12)	0.683 8(11)	0.334 5(13)	−0.124 1(7)
O(3)	0.450 0(8)	0.383 1(7)	0.002 3(8)	C(13)	0.699 7(12)	0.433 9(11)	−0.091 2(10)
C(4)	0.507 0(7)	0.026 1(7)	0.174 1(7)	C(14)	0.780 3(10)	0.436 4(8)	−0.026 0(10)
O(4)	0.482 1(6)	−0.029 7(5)	0.114 3(5)	C(15)	0.818 0(10)	0.339 3(10)	−0.011 5(9)
C(5)	0.430 3(8)	0.1725(8)	0.269 4(7)	C(21)	0.657 8(8)	0.006 6(8)	0.325 3(7)
O(5)	0.356 6(6)	0.216 2(7)	0.267 6(7)	C(22)	0.565 2(8)	−0.012 7(7)	0.367 4(7)
C(6)	0.608 7(8)	0.657 7(8)	0.456 9(8)	C(23)	0.539 0(10)	0.075 3(8)	0.416 6(7)
O(6)	0.586 2(7)	0.700 4(7)	0.521 7(5)	C(24)	0.614 8(10)	0.148 8(9)	0.403 1(7)
C(7)	0.505 1(9)	0.525 9(8)	0.330 6(8)	C(25)	0.689 4(9)	0.105 8(8)	0.348 2(8)

Table 7. Fractional atomic co-ordinates for (**5b**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe(1)	0.738 86(5)	−0.052 12(7)	0.107 91(5)	O(6)	0.347 6(4)	0.013 6(5)	0.234 4(4)
Fe(2)	0.695 18(5)	0.368 53(6)	−0.051 01(4)	O(7)	0.328 6(3)	0.215 7(5)	0.165 5(3)
S(1)	0.871 56(10)	−0.156 97(12)	−0.002 94(9)	O(8)	0.439 5(4)	0.060 3(6)	0.132 7(3)
S(2)	0.804 84(10)	0.105 49(12)	−0.037 16(8)	F(1)	0.526 9(4)	0.266 0(7)	0.245 0(5)
S(3)	0.677 63(10)	0.138 81(12)	0.075 84(9)	F(2)	0.538 4(4)	0.095 2(6)	0.309 8(3)
S(4)	0.389 75(11)	0.112 70(15)	0.191 48(10)	F(3)	0.440 7(4)	0.230 9(8)	0.333 4(4)
C(1)	0.804 5(3)	−0.035 6(4)	0.021 0(3)	C(11)	0.606 0(5)	−0.135 6(7)	0.086 1(6)
C(2)	0.725 8(3)	0.201 0(4)	0.000 7(3)	C(12)	0.637 7(6)	−0.120 8(7)	0.172 1(6)
C(3)	0.833 4(4)	0.012 0(5)	0.179 9(3)	C(13)	0.720 3(6)	−0.193 2(7)	0.194 6(4)
C(4)	0.659 2(5)	0.426 8(5)	0.038 6(4)	C(14)	0.737 7(5)	−0.252 3(6)	0.122 9(5)
C(5)	0.811 4(5)	0.428 3(5)	−0.021 3(4)	C(15)	0.667 1(5)	−0.216 2(6)	0.056 4(4)
C(6)	0.914 1(4)	−0.118 5(6)	−0.098 1(3)	C(21)	0.559 7(4)	0.365 7(5)	−0.123 1(4)
C(7)	0.960 5(5)	−0.239 9(6)	−0.123 1(4)	C(22)	0.612 1(4)	0.269 2(5)	−0.150 9(3)
C(8)	0.475 7(6)	0.178 1(9)	0.275 1(6)	C(23)	0.687 8(4)	0.327 4(6)	−0.178 0(3)
O(3)	0.895 7(3)	0.055 8(5)	0.226 5(3)	C(24)	0.680 0(5)	0.462 9(5)	−0.166 5(3)
O(4)	0.632 5(6)	0.467 1(5)	0.095 3(4)	C(25)	0.601 8(4)	0.485 6(5)	−0.133 4(4)
O(5)	0.884 4(3)	0.469 5(5)	−0.002 6(4)				

PPh_3: yield 74% (0.30 g, 0.53 mmol) (Found: C, 51.6; H, 3.50; S, 10.4. Calc. for $C_{26}H_{20}F_3FeO_4PS_2$: C, 51.65; H, 3.35; S, 10.6%). Spectroscopic properties were identical with those previously reported.[18] L = PMe_2Ph: yield 68% (0.15 g, 0.33 mmol) (Found: C, 40.1; H, 3.35; S, 13.3. Calc. for $C_{16}H_{16}F_3FeO_4PS_2$: C, 40.0; H, 3.35; S, 13.35%). ν(CO) (CH_2Cl_2) 2 033s; ν(CS) (KBr) 1 319ms cm^{-1}; δ_H(CD_2Cl_2) 7.7 (5 H, m, Ph), 5.33 (5 H, s, br, C_5H_5), 2.24 [3 H, d, *J*(PH) 4, Me], 2.06 [3 H, d, *J*(PH) 4 Hz, Me].

X-Ray Data Collection.—Crystal data and experimental details are listed in Table 5. The diffraction experiments for both compounds were carried out on a fully automated Enraf-Nonius CAD-4 diffractometer at room temperature using Mo-K_α radiation. The unit-cell parameters were determined by least-squares refinement of the setting angles of 25 well centred high-angle reflections. The diffraction intensities were corrected for Lorentz and polarization factors. An empirical absorption correction was applied to the intensity data using the azimuthal scan method for compound (**4c**).[42] The calculations were performed using the SHELX system of programs.[43]

Structure Determination and Refinement.—The two structures were solved by direct methods which allowed location of Fe and S in the case of complex (**5b**) and W, Fe, and S in the case of complex (**4c**). The remaining non-hydrogen atoms were located in a Fourier map phased with the heavy atoms. The structures were refined by full-matrix least-squares methods in the space group $P2_1/a$ (no. 14) for (**4c**) and $P2_1/n$ (no. 14) for (**5b**). In the least-squares calculations the weighting factor used was $w = k/[\sigma^2(F) + |g|F^2]$ [where $k = 1.132$ and $g = 0.0016$ for (**5b**), $k = 1.088$ and $g = 0.0004$ for (**4c**)]. Hydrogen atoms were added in calculated positions (d_{CH} = 1.08 Å) and their positions were not refined but continuously updated with respect to their carbon atoms. Bond length constraints for the C–C distances in the cyclopentadienyl rings were introduced (distances equal within an estimated error of 0.01 Å). The final refinement of all positional and thermal parameters proceeded using anisotropic thermal parameters. The final difference Fourier map showed peaks not exceeding 0.60 e Å^{-3} due to the thermal motion of the cyclopentadienyl C atoms. Atomic co-ordinates are reported in Tables 6 and 7.

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References

1 H. Werner, O. Kolb, R. Feser, and U. Schubert, *J. Organomet. Chem.*, 1980, **191**, 283; M. Cowie and S. K. Dwight, *ibid.*, 1981, **214**, 233.
2 T. Herskovitz and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1976, **98**, 1615.
3 M. Cowie and J. A. Ibers, *Inorg. Chem.*, 1976, **15**, 552; H. Werner, S. Lotz, and B. Heiser, *J. Organomet. Chem.*, 1981, **209**, 197; H. Werner, *Coord. Chem. Rev.*, 1982, **43**, 165; D. H. M. W. Thewissen and H. L. M. Van Gaal, *J. Organomet. Chem.*, 1979, **172**, 69.
4 J. R. Schmidt and D. M. Duggan, *Inorg. Chem.*, 1981, **20**, 318.
5 G. Facchinetti, C. Biran, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1978, **17**, 2995.
6 H. Le Bozec, A. Gorgues, and P. H. Dixneuf, *Inorg. Chem.*, 1981, **20**, 2486; J. Y. Le Marouille, C. Le Lay, A. Benoit, D. Grandjean, D. Touchard, H. Le Bozec, and P. H. Dixneuf, *J. Organomet. Chem.*, 1980, **191**, 133.
7 C. C. Frazier, N. D. Magnusen, L. N. Osuji, and K. O. Parker, *Organometallics*, 1982, **1**, 903.
8 C. Bianchini, A. Meli, and G. Scapacci, *Organometallics*, 1985, **4**, 264; C. Bianchini, C. Mealli, A. Meli, and M. Sabat, *ibid.*, p. 421.
9 Y. Wakatsuky, H. Yamazaki, and H. Iwasaki, *J. Am. Chem. Soc.*, 1973, **95**, 5781.
10 W. A. Schenk and D. Kummerle, *J. Organomet. Chem.*, 1986, **303**, C25-28.
11 R. P. A. Sneeden, 'Comprehensive Organometallic Chemistry,' Pergamon Press, London, 1982 and refs. therein; R. Eisenberg and D. E. Endriksen, *Adv. Catal.*, 1979, **28**, 79; D. J. Darensbourg and R. A. Kudaroski, *Adv. Organomet. Chem.*, 1983, **22**, 129.
12 L. Busetto, A. Palazzi, and M. Monari, *J. Chem. Soc., Dalton Trans.*, 1982, 1631.
13 V. G. Albano, D. Braga, L. Busetto, M. Monari, and V. Zanotti, *J. Chem. Soc., Chem. Commun.*, 1984, 1257.
14 L. Busetto, M. Monari, A. Palazzi, V. G. Albano, and F. Demartin, *J. Chem. Soc., Dalton Trans.*, 1983, 1849.
15 H. Stolzenberg, W. P. Fehlhammer, M. Monari, V. Zanotti, and L. Busetto, *J. Organomet. Chem.*, 1984, **272**, 73.
16 L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, 1971, **10**, 78.
17 M. M. Singh and R. J. Angelici, *Inorg. Chem.*, 1984, **23**, 2691.
18 L. Busetto and A. Palazzi, *Inorg. Chim. Acta*, 1976, **19**, 23
19 M. G. Mason, P. N. Swepston, and J. A. Ibers, *Inorg. Chem.*, 1983, **22**, 411.
20 D. Catheline, E. Roman, and D. Astruc, *Inorg. Chem.*, 1984, **23**, 4508.
21 L. Busetto, V. Zanotti, and S. Bordoni, unpublished work.
22 S. J. N. Burgmajer and J. L. Templeton, *Inorg. Chem.*, 1985, **24**, 3939.
23 J. E. Ellis, R. W. Fennel, and E. A. Flom, *Inorg. Chem.*, 1976, **15**, 2031.
24 M. A. Andrews, *Inorg. Chem.*, 1977, **16**, 496.
25 T. Hattich and U. Kunze, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 364.
26 J. A. Ibers, *Chem. Soc. Rev.*, 1982, **11**, 57 and refs. therein.
27 L. Busetto, unpublished work.
28 M. H. Quick and R. J. Angelici, *Inorg. Chem.*, 1982, **21**, 1674.
29 D. B. Dombek and R. J. Angelici, *Inorg. Chem.*, 1976, **15**, 2397.
30 F. B. McCormick, R. J. Angelici, R. A. Pickering, and R. E. Wagner, *Inorg. Chem.*, 1981, **20**, 4108.
31 B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.
32 N. M. Kostic and R. F. Fenske, *J. Am. Chem. Soc.*, 1982, **104**, 3879.
33 U. Schubert, *Organometallics*, 1982, **1**, 1087.
34 E. O. Fischer, E. W. Meineke, and R. Kreizl, *Chem. Ber.*, 1977, **110**, 1140.
35 H. J. Beck, E. O. Fischer, and C. G. Kreiter, *J. Organomet. Chem.*, 1971, **26**, C41.
36 M. H. Quick and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 1123.
37 R. J. Angelici and J. W. Dunker, *Inorg. Chem.*, 1985, **24**, 2209.
38 R. A. Pickering and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 2977.
39 F. B. McCormick and R. J. Angelici, *Inorg. Chem.*, 1981, **20**, 1111.
40 F. B. McCormick and R. J. Angelici, *J. Organomet. Chem.*, 1981, **205**, 79.
41 L. Busetto, A. Palazzi, and M. Monari, *J. Organomet. Chem.*, 1982, **228**, C19—20.
42 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
43 G. M. Sheldrick, SHELX 76 System of computer programs, University of Cambridge, 1976.

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