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PREPARATION OF THE MONODENTATE DITHIOPHOSPHATE COMPLEXES $Cp^{\star}Fe(CO)_2(\eta^1\text{-}SP(S)(OR)_2)$, ($Cp^{\star}$ = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4Me$, $\eta\text{-}C_5Me_5$)

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Summary

The dithiophosphate complexes of the type $Cp^{\star}Fe(CO)_2(\eta^1\text{-}SP(S)(OR)_2)$, ($Cp^{\star}$ = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4Me$, $\eta\text{-}C_5Me_5$; R = Et, ^{i}Pr) can be conveniently prepared by reaction between $[Cp^{\star}Fe(CO)_2]_2$ and $[SP(S)(OR)_2]_2$ in cyclohexane. The influence of the donor capacity of the substituted cyclopentadienyl rings on the spectral properties of the complexes is discussed.

Introduction

A large number of dinuclear derivatives of iron cyclopentadienyl-carbonyls containing organic sulphur ligands have been prepared by reactions between organic disulphides and $[CpFe(CO)_2]_2$ [1–5]. However, derivatives with terminal sulphur organic groups are relatively rare. In general, the only mononuclear compounds of this type have been obtained by reaction between the halogenated derivatives $CpFe(CO)_2X$ (X = Cl, Br) and the sodium salts of dithiocarbamate and trithiocarbonate ligands [6,7]. A recent method describes the preparation of $CpFe(CO)_2(\eta^1\text{-}SC(S)NR_2)$ by reaction between $[CpFe(CO)_3]^+$ PF_6^- and Na^+ $SC(S)NR_2^-$ [8].

We have found that the reactions between the dimers $[Cp^{\star}Fe(CO)_2]_2$ ($Cp^{\star}$ = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4Me$ and $\eta\text{-}C_5Me_5$) and the disulphides $[SP(S)(OR)_2]_2$, (R = Et, ^{i}Pr) give the stable, 18 electron diamagnetic complexes $\eta\text{-}Cp^{\star}Fe(CO)_2(\eta^1\text{-}SP(S)(OR)_2)$, via oxidative cleavage of the Fe–Fe bond in the dimer and homolytic fragmentation of the S–S bond in the disulphide, which leads to the $(RO)_2P(S)S$ ligand, which is bonded to the iron atom in monodentate form.

The same disulphides $[SP(S)(OR)_2]_2$ (R = Et, ^{i}Pr) react with the halides $TiCl_4$, $TiBr_4$ and $VOCl_3$ in a different way, the ligands not being changed in structure [9].

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Results and discussion

The reactions between the disulphides $[SP(S)(OR)_2]_2$ (R = Et, ^iPr) and $[Cp^\star Fe(CO)_2]_2$ ($Cp^\star = \eta$-C_5H_5, η-C_5H_4Me and η-C_5Me_5) in cyclohexane at 50–60°C lead to the formation of red-orange crystals of $Cp^\star Fe(CO)_2(\eta^1$-$SP(S)(OR)_2)$ in very high yields. When the reaction takes place at reflux temperature a mixture of ferrocene (characterized by IR and NMR spectra) and other solid substances (which do not show the carbonyl bands in the IR and have not been characterized) are obtained in addition to the desired compounds.

It is of interest that in all cases, independent of the ring substituent, complexes in which the dithiophosphate ligand behaves as monodentate are obtained; this result differs from that observed in the reactions of iron cyclopentadienyl-carbonyls with dithiocarbamate ligands, structurally and electronically similar to dithiophosphate, in which, depending on the method used and the substituents, complexes with mono- or bi-dentate dithiocarbamate ligand are obtained [5,8].

The IR spectra of the obtained complexes show the characteristic bands of the η-C_5H_5 ring at 3120–3010m, 1445–1400m, 1100m, 1015–980m, 860vs cm^{-1} [10]; η-C_5H_4Me at 3100–2900m, 1500–1430m, 1300–1250m, 1040m, 860–830s cm^{-1} [11]; and also η-C_5Me_5 at 2990–2930m, 2760m, 1480–1380m, 1060w, 1020w, 740–720w cm^{-1} [12], although some of them are marked due to the presence of the dithiophosphate ligands, which give strong stretching bands in the range 1065–905 cm^{-1}, ν(P)–O–C; 875–730 cm^{-1}, νP–O–(C) and 1240–1080 cm^{-1} δ(CC) [13,14].

The frequencies corresponding to ν(CO) vibrations, either in the solid or in CS_2 and $CHCl_3$ solutions, are listed in Table 1. The assignments are based on a local C_s symmetry. The presence of shoulders in the bands which correspond to ν(CO) in Nujol, may be due to solid state interactions, because they disappear when the spectra are recorded in solution, two strong bands, which correspond to A' and A'' vibrational modes, then being observed. The k and k_i force constants expected for this symmetry have been calculated by the Cotton–Kraihanzel method [15]. The calculated values are in the range k: 16.13–16.49 mdyn $Å^{-1}$ and k_i: 0.36–0.37 mdyn $Å^{-1}$ (Table 1), and are very similar to those found in other iron cyclopentadienyl-carbonyls of the same symmetry as $CpFe(CO)_2X$ (X = halide, $SiCl_3$, . . .), [16,17].

The electron-donating capacity of the methylcyclopentadienyl and pentamethylcyclopentadienyl ligands is reflected in the values of ν(CO), which are smaller than in the corresponding complexes of non-substituted cyclopentadienyl complexes as shown in Table 1. Figure 1 shows that there is a linear relationship between ν(CO) and the number of methyl groups substituted in the ring. Along with this decrease of the ν(CO) stretching, there is a corresponding decrease in the values of the carbonyl force constant k, (see Table 1), and also an increase in the antibonding orbital occupancy [OCC.] of the carbonyl ligand, as indicated in Table 1. (This OCC was calculated from the equations developed by Fenske [18,19] for carbonyl metal complexes.)

On the other hand, the ν(CO) band frequencies are sensitive to change in the solvent. From data in Table 1 several features can be observed. First, the ν(CO) values are, in all cases and for both vibration modes A' and A'' higher in chloroform than in carbon disulphide; furthermore, the splitting between A' and A'' modes is greater in chloroform than in carbon disulphide in all cases. These results are consistent with the observations by other authors [20] and are similar to those found

TABLE 1

ν(CO) (cm^{-1}) VIBRATIONS IN η-Cp* Fe(CO)$_2$L COMPOUNDS

Complex [a]	Nujol		CS_2		$CHCl_3$		$\Delta\nu$($CHCL_3$-CS_2)		k [b]	k_i	[OCC] [c]
	A'	A''	A'	A''	A'	A''	A'	A''			
η-$C_5H_5Fe(CO)_2L^1$	2040.5	1999.8	2043.0	1998.5	2047.0	2001.5	4	3	16.49	0.36	1.648
η-$C_5H_5Fe(CO)_2L^2$	2034.9	1991.5	2043.0	1998.7	2048.0	2003.0	5	4.3	16.49	0.36	1.647
η-$C_5H_4CH_3Fe(CO)_2L^1$	2032.9	1993.1	2039.2	1994.1	2043.0	1997.0	3.8	2.9	16.42	0.36	1.653
η-$C_5H_4CH_3Fe(CO)_2L^2$	2031.6	1990.4	2039.5	1994.8	2042.5	1996.8	3.0	2.0	16.43	0.36	1.654
η-$C_5(CH_3)_5Fe(CO)_2L^1$	2021.0	1970.2	2021.5	1976.0	2025.3	1978.0	3.8	2.0	16.13	0.36	1.678
η-$C_5(CH_3)_5Fe(CO)_2L^2$	2019.6	1936.7	2021.4	1975.7	2025.4	1978.0	4	2.3	16.13	0.36	1.678

[a] $L^1 = SP(S)(O^iPr)_2$, $L^2 = SP(S)(OEt)_2$. [b] k is mdyn Å^{-1}. [c] [OCC] = antibonding orbital occupancy.

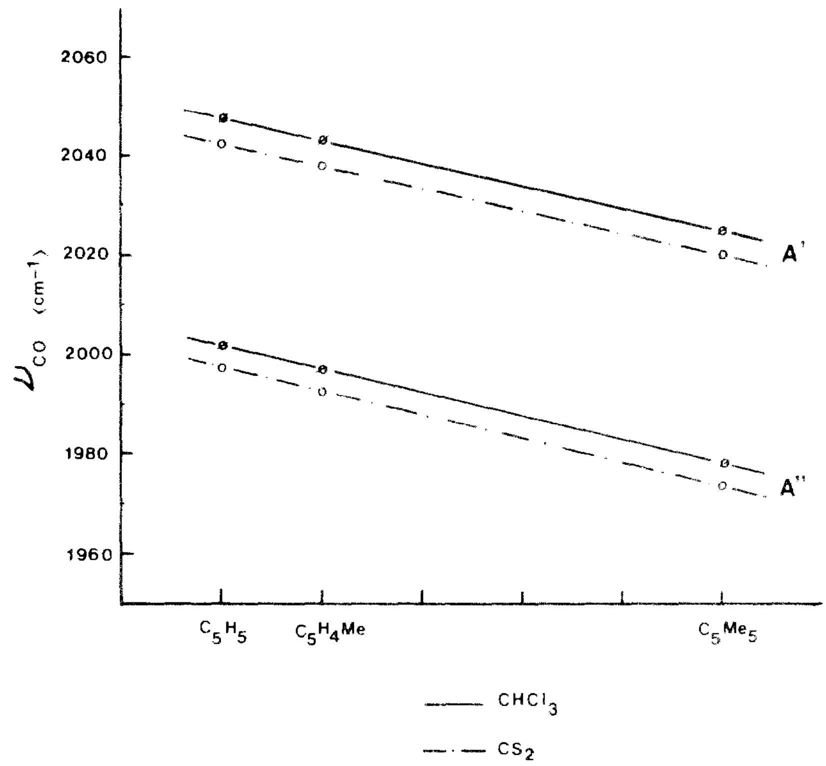

Fig. 1. Variation of ν(CO) with the number of methyl substitutents on the ring for the complexes Cp* Fe(CO)$_2$(η^1-SP(S)(O^{i}Pr)$_2$). (Cp* = η-C_5H_5, η-C_5H_4Me, η-C_5Me_5).

for η-CpFe(CO)$_2$X (X = Cl, Br and I) [21]. It follows that in our complexes the interaction between the solvent and the dithiophosphate ligand is stronger than that between the solvent and the dipoles of the carbonyl group, in keeping with observations on the halide carbonyl derivatives [20,21].

The low symmetry of these complexes in which the two carbonyl groups are not aligned *, implies that all the overtones and combination bands of the A' and A'' modes of ν(CO) will be IR active. In Fig. 2 are shown the IR spectra of η-C_5H_5Fe(CO)$_2$(η^1-SP(S)(O^{i}Pr)$_2$) and η-C_5Me_5Fe(CO)$_2$(η^1-SP(S)(O^{i}Pr)$_2$) in the 4200–3800 cm^{-1} region; the three sharp bands in the spectra may be assigned to the doubly excited carbonyl stretchings, $2A'$, $A' + A''$ and $2A''$, in order of decreasing frequency (Table 2).

In the IR spectrum of η-C_5H_5Fe(CO)$_2$(η^1-SP(S)(O^{i}Pr)$_2$), there is a broad band at 3943.7 cm^{-1} which is absent in the IR spectrum of the pentamethylcyclopentadienyl derivative, and this can be assigned to second overtones or ternary combination bands arising from the η-C_5H_5 ring; a similar effect was observed in the IR spectra of ferrocene and [η-C_5H_5Fe(CO)$_2$]$_2$ [22]. For the other studied complexes the position and relative intensities of the observed bands are consistent with this assignment (Table 2).

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* Preliminary data from a structure study confirms this.

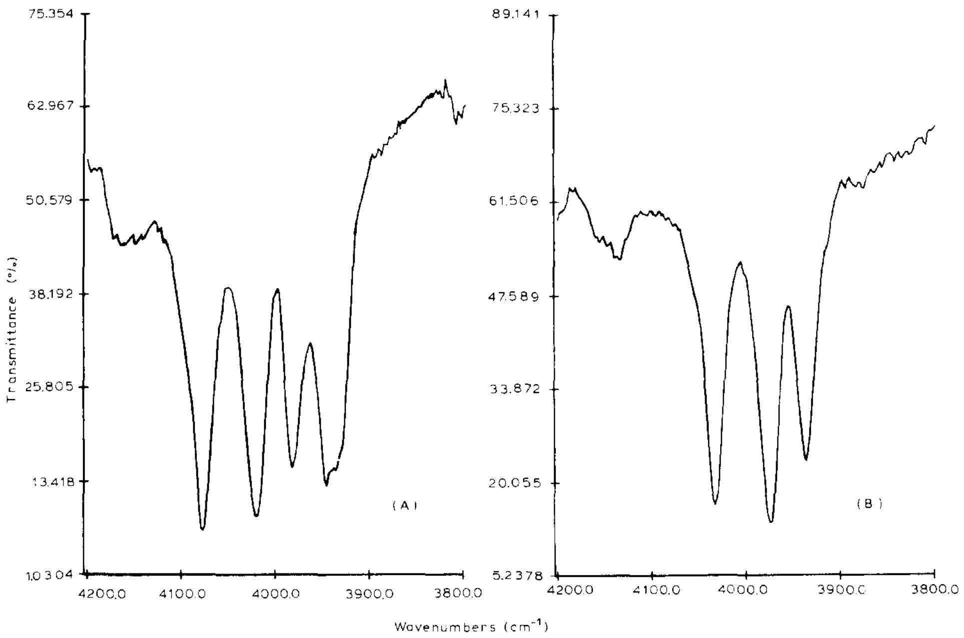

Fig. 2. The IR spectra of (A) η-$C_5H_5Fe(CO)_2(\eta^1$-$SP(S)(O^iPr)_2)$; (B) η-$C_5Me_5Fe(CO)_2(\eta^1$-$SP(S)(O^iPr)_2)$, in the 4200–3800 cm^{-1} region (CS_2 solution).

In all cases, the frequencies at which these $2A'$, $A' + A''$ and $2A''$ bands appear are lower than those theoretically expected. In the overtones, the differences change between 10–11 cm^{-1} for $2A'$, 15–16 cm^{-1} for $2A''$, while in the binary carbonyl combination bands the difference is higher, (23–25 cm^{-1}). These discrepancies between the predicted and observed band positions probably result from the importance of anharmonicity in the carbonyl stretching vibrations of binary metal carbonyls, in agreement with Jones's conclusions [23].

TABLE 2

CALCULATED AND OBSERVED BINARY CARBONYL FREQUENCIES (cm^{-1}) [a]

Complex	Expected			Observed		
	$2A'$	$A' + A''$	$2A''$	$2A'$	$A' + A''$	$2A''$
η-$C_5H_5Fe(CO)_2L^1$	4086.0	4041.5	3997.0	4076.1	4018.5	3982.0
η-$C_5H_5Fe(CO)_2L^2$	4086.0	4041.7	3997.4	4075.9	4019.7	3982.1
η-$C_5H_4(CH_3)Fe(CO)_2L^1$	4078.4	4033.3	3988.2	4068.6	4010.3	3972.7
η-$C_5H_4(CH_3)Fe(CO)_2L^2$	4079.0	4034.3	3989.6	4069.0	4012.3	3975.1
η-$C_5(CH_3)_5Fe(CO)_2L^1$	4043.0	3997.5	3952.0	4032.7	3973.5	3937.0
η-$C_5(CH_3)_5Fe(CO)_2L^2$	4042.8	3997.1	3951.4	4032.0	3974.0	3935.6

[a] In CS_2 solution. $L^1 = SP(S)(O^iPr)_2$; $L^2 = SP(S)(OEt)_2$.

TABLE 3

IR SPECTRA OF THE $Cp^{\star}Fe(CO)_2SP(S)(OR)_2$ IN THE 700–400 cm^{-1} REGION [a]

Complex	δ(FeCO)				ν(FeCO)		ν(P=S)	ν(P–S)
η-$C_5H_5Fe(CO)_2L^1$	607m (607s)	598sh (598sh)	570vs (570vs)	555s (560w)	483w	442w	651vs	540s
η-$C_5H_5Fe(CO)_2L^2$	608m (607f)	599sh (599sh)	575vs (570vs)	558s	484w	443w	658vs	542s
η-$C_5H_4CH_3Fe(CO)_2L^1$	615sh (616sh)	609m (605m)	569s (570s)	555m (554w)	486w	444w	651vs	541s
η-$C_5H_4CH_3Fe(CO)_2L^2$	613sh (610sh)	610m (607w)	570s (570s)	556m (558w)	487w	444w	657vs	541s
η-$C_5(CH_3)_5Fe(CO)_2L^1$	612m (611m)	588sh (590sh)	576vs (576vs)	564s (562s)	492w	445w	652vs	541s
η-$C_5(CH_3)_5Fe(CO)_2L^2$	611m (612m)	589sh (598sh)	576vs (575vs)	555m (557w)	491w	444w	655vs	540m

[a] $L^1 = SP(S)(O^iPr)_2$, $L^2 = SP(S)(OEt)_2$; values in parentheses were measured in CS_2 solution.

The frequencies corresponding to δ(FeCO), ν(FeCO), and ν(PS) vibrations, appear in the 700–400 cm^{-1} range. (Table 3). If we assume that the group $Fe(CO)_2$ has a C_{2v} local symmetry, four δ(FeCO) vibrations (a_1, a_2, b_1, b_2), and two ν(FeCO) stretching vibrations are expected.

In agreement with the results obtained in other metal dicarbonyls [24], the bands corresponding to the δ(FeCO) are more intense and appear at higher frequency than those due to ν(FeCO) vibration modes. It is thus possible to assign the δ(FeCO) bending bands in the 612–550 cm^{-1} range, and those for ν(FeCO) at 492–440 cm^{-1} (see Table 3). As expected there is an increase in the ν(FeCO) frequency with increase of the number of the methyl groups in the cyclopentadienyl ring, due to the increase of the strength of the FeCO bond as a consequence of the greater electron donation by the pentamethylcyclopentadienyl rings. (Compare the previously considered decrease observed in ν(CO).)

The bands corresponding to ν(P=S) appear at 650–658 cm^{-1} and ν(P–S) at 540 cm^{-1} (Table 3), and are found in the frequency ranges as is the case in which the corresponding dithiophosphate ligands are monodentate [25,26].

The signals observed in the ^1H and ^{13}C NMR spectra are shown in Table 4. The signals due to the dithiophosphate ligands $SP(S)(OR)_2$, (R = Et, ^iPr) appear as doublets, as a consequence of the coupling with the phosphorus atoms. The values of J(PH) and J(PC) are shown in Table 4; as expected, since the phosphorus atom is not directly bonded to the metal there is no splitting of the signals from the cyclopentadienyl ring. Thus in the ^1H NMR spectra of the η-$C_5H_5Fe(CO)_2(\eta^1$-$SP(S)(OR)_2)$, complexes there is only one signal in the δ 5 region indicating the equivalence of the five protons of the ring. However, the methylcyclopentadienyl complexes present more complex spectra, comprising two asymmetric pseudotriplets in the range δ 5–6 ppm, characteristic of the A_2X_2 systems [27,28]. For the pentamethylcyclopentadienyl complexes there is only one signal, at δ 1.2 ppm, which must be due to the five methyl groups of the ring.

TABLE 4

^{1}H AND ^{13}C NMR SPECTRA OF THE COMPLEXES [a]

Complex	$\delta(^1H)$	$\delta(^{13}C)$
η-$(C_5H_5)Fe(CO)_2SP(S)(OEt)_2$	1.32 (t, 6H, CH_3, J(HH) 7.0)	15.92 (d, CH_3, J(PC) 34)
	4.12 (m, 4H, CH_2, J(HH) 6.0; J(PH) 12.1)	63.00 (d, CH_2, J(PC) 28)
		85.63 (s, C_5H_5)
	5.13 (s, 5H, C_5H_5)	211.50 (s, CO)
η-$(C_5H_5)Fe(CO)_2SP(S)(O^iPr)_2$	1.37 (dd, 12H, CH_3, J(HH) 6.1; J(PH) 2.3)	23.70 (d, CH_3, J(PC) 22)
		72.00 (d, CH, J(PC) 30)
	4.82 (m, 2H, CH, J(HH) 6.0; J(PH) 11.2)	85.66 (s, C_5H_5)
		211.20 (s, CO)
	5.16 (s, 5H, C_5H_5)	
η-$(MeC_5H_4)Fe(CO)_2SP(S)(OEt)_2$	1.29 (s, 3H, CH_3-Cp)	12.85 (s, CH_3-Cp)
	1.40 (t, 6H, CH_3, J(HH) 7.2)	15.91 (d, CH_3, J(PC) 20)
	4.11 (m, 4H, CH_2, J(HH) 6.1; J(PH) 11.8)	62.40 (d, CH_2, J(PC) 18)
		74.60 (s, $C_{2,5}$Cp)
		84.70 (s, $C_{3,4}$Cp)
	4.80 (t, 4H, CH, Cp, J 2)	104.40 (s, C_1Cp)
	5.12 (t)	211.80 (s, CO)
η-$(MeC_5H_4)Fe(CO)_2SP(S)(O^iPr)_2$	1.32 (s, 3H, CH_3Cp)	12.95 (s, CH_3-Cp)
	1.42 (dd, 12H, CH_3, J(HH) 6.3; J(PH) 2.5)	23.60 (d, CH_3, J(PC) 12)
		71.80 (d, CH, J(PC) 20)
	4.80 (m, 2H, CH, J(HH) 6.2; J(PH) 12.6)	74.70 (s, $C_{2,5}$Cp)
		84.70 (s, $C_{3,4}$Cp)
	4.88 (t, 4H, CH, Cp, J 2)	104.60 (s, C_1Cp)
	5.10 (t)	212.00 (s, CO)
η-$(C_5Me_5)Fe(CO)_2SP(S)(OEt)_2$	1.26 (s, 15H, $(CH_3)_5C_5$)	9.38 (s, Me_5Cp)
	1.40 (t, 6H, J(HH) 6)	15.80 (d, CH_3, J(PC) 30)
	4.21 (m, 4H, CH_2, J(HH) 6; J(PH) 12)	62.40 (d, CH_2, J(PC) 34)
		96.40 (s, C_5)
		214.00 (s, CO)
η-$(C_5Me_5)Fe(CO)_2SP(S)(O^iPr)_2$	1.23 (s, 15H, $(CH_3)_5C_5$)	9.40 (s, Me_5C_5)
	1.53 (dd, 12H, CH_3, J(HH) 7.0; J(PH) 2.8)	23.60 (d, CH_3, J(PC) 26)
		71.40 (d, CH, J(PC) 35)
	4.70 (m, 2H, CH, J(HH) 6.3; J(PH) 12.5)	96.30 (s, C_5)
		214.00 (s, CO)

[a] In $CDCl_3$ solution; δ in ppm, J in Hz.

On the other hand, when the electronic density around the metal is increased as a consequence of the increase in the number of methyl substituents on the cyclopentadienyl ring, a decrease in the carbon–oxygen bond order and an increase in the screening of the ^{13}C nucleus are expected, shifting the CO signal to higher δ values. There is thus a linear correlation between ν(CO) and δ(CO), as can be seen from Fig. 3; this is similar to that found for complexes such as η-$C_5H_5Fe(CO)_2X$ (X = σ-ligand type) [29,30].

There is similar correlation between δ(CO) ppm and the anodic oxidation potential * (Fig. 4). It can be inferred that the increase in the electronic density on

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* The electrochemical behaviour of the new complexes will be considered in a subsequent publication.

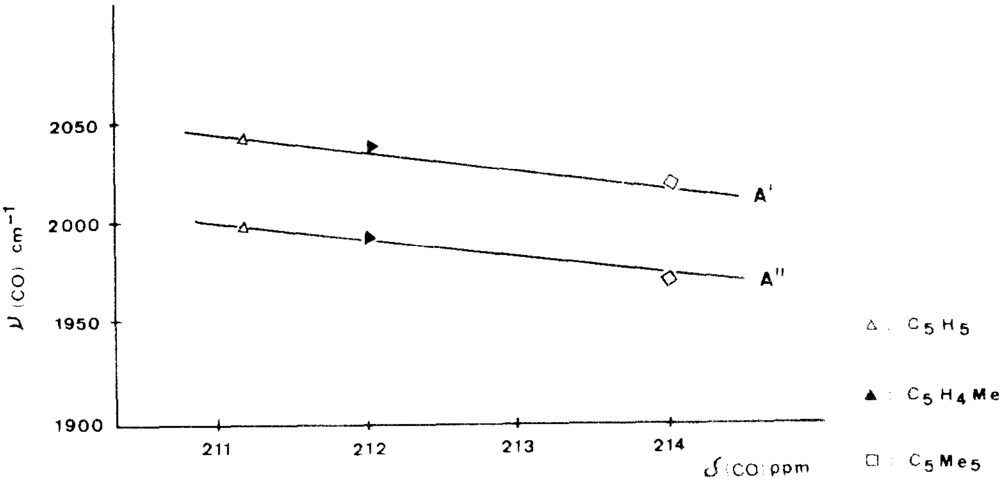

Fig. 3. Plot of carbonyl chemical shifts against carbonyl stretching frequencies for the complexes $Cp^{\star}Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$, ($Cp^{\star}$ = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4Me$, $\eta\text{-}C_5Me_5$).

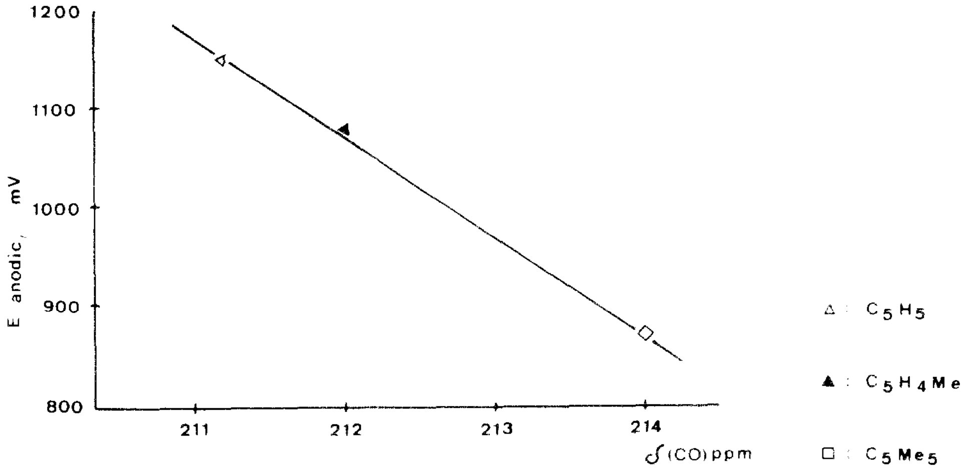

Fig. 4. Plot of carbonyl chemical shifts against anodic oxidation potential for the complexes $Cp^{\star}Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$, $Cp^{\star}$ = $\eta\text{-}C_5H_5$, $\eta\text{-}C_5H_4Me$, C_5Me_5).

the metal caused by the introduction of methyl groups in the ring, and which shows up as an increase in δ(CO), correlates with the decrease in the oxidation potential, as was expected.

Experimental

All reactions were carried out under oxygen-free N_2 using Schlenck techniques. The disulphides $[SP(S)(OR)_2]_2$ (R = Et, ^{i}Pr), were prepared by oxidation of the $(RO)_2P(S)SNa$ precursor with I_2 [31]. Pentamethylcyclopentadiene [32], and the

TABLE 5

PREPARATIVE AND ANALYTICAL DATA FOR THE COMPLEXES η-Cp*Fe(CO)$_2$(η^1-SP(S)(OR)$_2$) [a] (Solvent: cyclohexane (60 ml))

Complex	[Cp*Fe(CO)$_2$]$_2$ (g (mmol))	[L]$_2$ [b] (g (mmol))	T (°C)	t (h)	Colour	Yield (%)	Analysis (Found (calcd.) (%))		
							C	H	Fe
η-C$_5$H$_5$Fe(CO)$_2$L^1	2 (5.6)	3 (7.1)	50–60	4	Orange	88	39.6 (40.0)	4.8 (4.8)	14.0 (14.3)
η-C$_5$H$_5$Fe(CO)$_2$L^2	2 (5.6)	2.6 (7.1)	50–60	4	Red	85	36.9 (36.4)	4.2 (4.1)	15.2 (15.4)
η-C$_5$H$_4$CH$_3$Fe(CO)$_2$L^1	0.9 (2.3)	1.6 (3.8)	50–60	5	Orange	73	41.2 (41.6)	5.3 (5.2)	13.5 (13.8)
η-C$_5$H$_4$CH$_3$Fe(CO)$_2$L^2	0.9 (2.3)	1.4 (3.8)	50–60	4	Orange	70	38.5 (38.3)	4.7 (4.5)	14.7 (14.9)
η-C$_5$(CH$_3$)$_5$Fe(CO)$_2$L^1	1 (2)	1.5 (3.5)	50–60	5	Red	84	46.7 (46.9)	6.3 (6.3)	12.0 (12.2)
η-C$_5$(CH$_3$)$_5$Fe(CO)$_2$L^2	1 (2)	1.3 (3.5)	50–60	3	Red	82	44.0 (44.4)	5.7 (5.7)	13.0 (12.9)

[a] η-Cp* = η-C$_5$H$_5$, η-C$_5$H$_4$CH$_3$ and η-C$_5$(CH$_3$)$_5$. [b] L^1 = SP(S)(O^{i}Pr)$_2$; L^2 = SP(S)(OEt)$_2$.

dimer carbonyls $[\eta\text{-}C_5H_5Fe(CO)_2]_2$, $[\eta\text{-}C_5H_4MeFe(CO)_2]_2$ [33] and $[\eta\text{-}C_5Me_5Fe(CO)_2]_2$ [34] were obtained by published methods. The last one was made by a modification of the King synthesis involving use of n-decane as solvent.

The IR spectra were recorded at 4000–200 cm^{-1} on a Nicolet 5DX FT-IR spectrophotometer using Nujol and hexachlorobutadiene mulls between CsI windows. The solution spectra ($CHCl_3$ or CS_2) were examined in a liquid cell with CsBr windows. In the range 4200–3800 cm^{-1} the spectra were recorded on CS_2 solutions in 4-cm quartz cells. In all cases the solvent absorptions was substracted by use of the software of the spectrophotometer.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker WH-200-5Y (200 MHz, FT mode) spectrometer.

Preparation of complexes

The preparation of $\eta\text{-}C_5Me_5Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$ is described in detail below. The procedures for the other complexes were essentially similar (Table 5).

$\eta\text{-}C_5Me_5Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$. A mixture of 1 g (2 mmol) of $[C_5Me_5Fe(CO)_2]_2$ and 1.5 g (3.5 mmol) of $[SP(S)(O^iPr)_2]_2$ in 60 cm^3 of cyclohexane contained in a 100 cm^3 two-necked flask fitted with N_2 inlet, magnetic stirrer and reflux condenser was kept between 50–60°C. The formation of $\eta\text{-}C_5Me_5Fe(CO)_2(\eta^1\text{-}SP(S)(O^iPr)_2)$ was monitored by IR spectroscopy. (The initial bands of the dimer $[\eta\text{-}C_5Me_5Fe(CO)_2]_2$ at 1940 and 1970 cm^{-1} give way to new bands at 2040 and 1980 cm^{-1} corresponding to the complex.) The solids initially present in the reaction mixture dissolved and an intense red coloured solution was formed. After 5 h the reaction was complete, and cooling to room temperature gave red crystals. These were filtered off, washed several times with cyclohexane, and dried in vacuo. The solid was recrystalized from cyclohexane/hexane or CH_2Cl_2/hexane.

The complexes are soluble in CH_2Cl_2, THF, CH_3CN slightly soluble in benzene and cyclohexane, and insoluble in n-hexane and CCl_4.

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