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The reaction of [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S)(μ_3-CS)] and related complexes with carbon disulfide. Synthesis, structure and reactivity of [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(L)}(μ_3-S)(μ_3-C$_2$S$_3$)] derivatives (L = PR$_3$ and CNR)

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[{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(L)$_2$}(μ_3-S)(μ_3-CS)] complexes **1** where (L)$_2$ = (**a**) (CO)(PPh$_3$), (**b**) (CO){P(OPh)$_3$}, (**c**) (CO)(PBu$^n_3$), (**d**) (CNMe)$_2$ and (**e**) (CNMes)$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$), but not (CO)(CNMes), react with CS$_2$ under reflux to give [{Co(η^5-C$_5$H$_5$)}$_2${Fe(L)$_2$}(μ_3-S)(μ_3-C$_2$S$_3$)], **2**, in which a CS$_2$ molecule has been incorporated into a FeSC(S*)SC heterocycle with a trithiocarbonate moiety bridging the Fe–C cluster edge. Clusters **2** react with incoming ligands either by simple ligand substitution, or by displacement of CS$_2$ to form clusters of type **1**. The exocyclic sulfur atom S* is nucleophilic and with electrophiles E forms [{Co(η^5-C$_5$H$_5$)}$_2${Fe(L)$_2$}(μ_3-S)(μ_3-C$_2$S$_3$E] adducts which contain S*⟶E bonds where E = Me$^+$ [**3**]$^+$, Et$^+$ [**4**]$^+$, HgCl$_2$ [**5**], and I$_4$ (or I$^+$) [**6**]. The clusters **2a**–**c** and the [**3**]$^+$ and [**4**]$^+$ derived from them are chiral as indicated by their NMR spectra, and do not racemize on the NMR timescale. The structures of **2a**·2C$_6$H$_6$ and [**3a**]I·C$_6$H$_6$·CHCl$_3$ are reported. Cluster **2a** contains a very short Fe–C$_\mu$ bond as compared with **1a**, and it is suggested that in many respects the FeSC(S)SC$_\mu$ ring is best regarded as a metallo-1,3-dithiole-2-thione (or metallovinyl trithiocarbonate) with a Fe–C$_\mu$ double bond which, on alkylation at the exocyclic S*, adopts a more delocalised electronic structure with a longer Fe–C$_\mu$ bond. Spectroscopic and electrochemical data for the new compounds are discussed.

Introduction

Cleavage of the η^2-CS$_2$ ligand in [Fe(PPh$_3$)$_2$(CO)$_2$(η^2-CS$_2$)] by [Co(η^5-C$_5$H$_5$)(PPh$_3$)$_2$] gives [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S)(μ_3-CS)], **1a**, from which can be prepared many [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_{3-n}$(L)$_n$}(μ_3-S)(μ_3-CS)] complexes, **1** (L = PR$_3$ or CNR; n = 1 or 2).[1,2] As would be expected, the S atom of the μ_3-CS ligand in **1** is a powerful nucleophile and forms [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_{3-n}$(L)$_n$}(μ_3-S)(μ_3-CS⟶E)] adducts with electrophiles E.[1,2] More surprisingly, with CS$_2$ it forms similar adducts which also contain a Fe–S bond. Part of this work has been reported previously.[3] Since then there has been a report of the complex Ru$_3$(CO)$_4$(μ-PCy$_2$)$_2$(μ-Ph$_2$CH$_2$PPh$_2$)(μ_3-S)(μ_3-C$_2$S$_3$) which also contains the C$_2$S$_3$ ligand.[4]

Experimental

Literature methods were used to prepare [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$(L)}(μ_3-S)(μ_3-CS)] (L = PPh$_3$, P(OPh)$_3$, PBu$^n_3$ and CNC$_6$H$_2$Me$_3$-2,4,6) and [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(CNR)$_2$}(μ_3-S)(μ_3-CS)] (R = Me and 2,4,6-Me$_3$C$_6$H$_2$).[1,2] Other chemicals were purchased.

Unless stated otherwise, all reactions were carried out at room temperature under an atmosphere of nitrogen in dried and deoxygenated solvents. Where necessary, reactions were monitored by IR spectroscopy.

IR spectra were run on a Perkin Elmer Paragon 2000 FT IR spectrometer. NMR spectra were run on a JEOL JNM-GX-270 MHz spectrometer. Elemental analyses were carried out in the Microanalytical Laboratory of University College Dublin.

Cyclic and square wave voltammetry in CH$_2$Cl$_2$ were performed for all compounds using a three-electrode cell with a polished disk, Pt (2.27 mm^2) as the working electrode; solutions were ~10^{-3} M in electroactive material and 0.10 M in supporting electrolyte (triply recrystallised [Bu$_4$N]PF$_6$). Data was recorded on an AD Instruments Powerlab 4SP computer-controlled potentiostat. Scan rates of 0.05–1 V s^{-1} were typically employed for cyclic voltammetry and for Osteryoung square-wave voltammetry, square-wave step heights of 1–5 mV, a square amplitude of 15–25 mV with a frequency of 30–240 Hz. All potentials are referenced to decamethylferrocene which was chosen as the reference because it shows no variation in reference potential with solvent; to convert to an approximate SCE value in dichloromethane add 0.53 V; $E_{1/2}$ for sublimed ferrocene was 0.55 V.

ESR spectra were measured on a Bruker EMX X-band spectrometer. The compound was dissolved in a 1 : 1 mixture of CH$_2$Cl$_2$–C$_2$H$_4$Cl$_2$ with 0.1 M [Bu$_4$N]PF$_6$. The solution was reduced electrochemically in an *in situ* electrolysis cell in the cavity of the EPR spectrometer at room temperature.

Reaction of [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$(L)}(μ_3-S)(μ_3-CS)] and [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(L)$_2$}(μ_3-S)(μ_3-CS)], 1, with CS$_2$

A solution of [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S)(μ_3-CS)], **1a** (0.5 g, 0.72 mmol), in carbon disulfide (8 cm^3) was refluxed for 12 h. The solution was allowed to cool and stand for 12 h. A brown precipitate was separated by filtration, and the filtrate chromatographed on alumina. Dichloromethane–hexane–tetrahydrofuran mixtures eluted unreacted **1a** (80 mg) and then a brown band. From this was isolated a brown solid which was combined with the brown precipitate (above) and the whole recrystallized from benzene–carbon disulfide mixtures to give brown crystals of [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(PPh$_3$)}(μ_3-S)(μ_3-C$_2$S$_3$)]·½C$_6$H$_6$, **2a**·½C$_6$H$_6$. Yield 0.27 g, 57% (Found: C, 52.9; H, 3.6. C$_{31}$H$_{25}$Co$_2$FeOPS$_4$·½C$_6$H$_6$ requires C, 53.1; H, 3.7%). IR (cm^{-1} in CH$_2$Cl$_2$ with relative peak heights in parentheses) ν_{CO} 1925 (10); ν_{CS} 1020 (5.5), 1009 (3.0). (cm^{-1} in KBr with relative peak heights in parentheses) ν_{CO} 1917 (10); ν_{CS} 1020 (4.0), 1005 (2.5, sh). ^{1}H NMR (δ in CDCl$_3$) 7.40 (m, 18H,

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PPh_3 and C_6H_6), 4.91 (s, 5H, C_5H_5), 4.12 (s, 5H, C_5H_5). ^{13}C NMR (δ in $CDCl_3$) 346.1 (d, J_{PC} = 15.3 Hz, C_μ–S), 243.4 (d, J_{PC} = 18.7 Hz, S–C–S), 218.7 (d, J_{PC} = 22.2 Hz, CO), 135.1 (d, J_{PC} = 42.6 Hz, *ipso*-C_6H_5), 133.6 (d, J_{PC} = 10.2 Hz, *o*-C_6H_5), 130.2 (s, *p*-C_6H_5), 128.3 (d, J_{PC} = 10.3 Hz, *m*-C_6H_5), 86.1 (s, C_5H_5), 84.9 (s, C_5H_5). ^{31}P NMR (δ in $CDCl_3$) 60.36 (s, PPh_3).

A similar procedure starting from $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1b** (0.5 g, 70 mmol) with a reflux time of 15 h gave recovered **1b** (80 mg) and, after a final recrystallization from dichloromethane–hexane, brown crystals of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]\cdot\frac{1}{2}CH_2Cl_2$, **2b**·½$CH_2Cl_2$. Yield 0.345 g, 60% (Found: C, 46.0; H, 3.1. $C_{31}H_{25}Co_2FeO_4PS_4\cdot\frac{1}{2}CH_2Cl_2$ requires C, 45.9; H, 3.1%). IR (cm^{-1} in CH_2Cl_2 with relative peak heights in parentheses) ν_{CO} 1950 (10); ν_{CS} 1024 (7.6), 1007 (3.2). (cm^{-1} in KBr with relative peak heights in parentheses) ν_{CO} 1941 (10); ν_{CS} 1023 (5.0), 1010 (3.8). ^1H NMR (δ in $CDCl_3$) 7.20 (m, 15H, $P(OPh)_3$), 4.68 (s, 5H, C_5H_5), 4.30 (s, 5H, C_5H_5). ^{13}C NMR (δ in $CDCl_3$) 349.3 (d, J_{PC} = 28.0 Hz, C_μ–S), 244.0 (d, J_{PC} = 23.6 Hz, S–C–S), 214.5 (d, J_{PC} = 30.1 Hz, CO), 151.2 (d, J_{PC} = 8.6 Hz, *ipso*-C_6H_5), 129.7 (s, *o*-C_6H_5), 125.2 (s, *p*-C_6H_5), 121.4 (d, J_{PC} = 4.3 Hz, *m*-C_6H_5), 85.9 (s, C_5H_5), 85.3 (s, C_5H_5).

The reaction of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PBu^n{}_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1c** (0.50 g, 0.78 mmol) with CS_2 was carried out in refluxing carbon disulfide (6 cm^3) and pentane (6 cm^3). After 75 h the mixture was evaporated to dryness and the residue chromatographed as above to give recovered **1c** (194 mg) and a brown solid which was crystallized from toluene–hexane mixtures. It was identified as $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PBu^n{}_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]\cdot C_6H_5CH_3\cdot H_2O$, **2c**·$C_6H_5CH_3\cdot H_2O$. Yield 0.278 g, 80% (Found: C, 46.0; H, 3.1. $C_{25}H_{37}Co_2FeOPS_4\cdot C_6H_5CH_3\cdot H_2O$ requires C, 45.9; H, 3.1%). IR (cm^{-1} in CH_2Cl_2 with relative peak heights in parentheses) ν_{CO} 1927 (10); ν_{CS} 1020 (5.0), 1009 (3.5). (cm^{-1} in KBr with relative peak heights in parentheses) ν_{CO} 1919 (10); ν_{CS} 1014 (2.9), 1000 (2.9). ^1H NMR (δ in $CDCl_3$) 4.82 (s, 5H, C_5H_5), 4.59 (s, 5H, C_5H_5), 1.80 (m, 6H, $PBu^n{}_3$), 1.30 (m, 12H, $PBu^n{}_3$), 0.91 (t, 9H, J_{HH} = 6.9 Hz, $PBu^n{}_3$). ^{13}C NMR (δ in $CDCl_3$) 348.4 (d, J_{PC} = 13.6 Hz, C_μ–S), 244.3 (d, J_{PC} = 18.8 Hz, S–C–S), 218.2 (d, J_{PC} = 22.2 Hz, CO), 86.0 (s, C_5H_5), 84.5 (s, C_5H_5), 29.5 (d, J_{PC} = 23.9 Hz, $PBu^n{}_3$), 25.8 (s, $PBu^n{}_3$), 24.4 (d, J_{PC} = 13.7 Hz, $PBu^n{}_3$), 13.8 (s, $PBu^n{}_3$).

A solution of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNMe)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1d** (0.1 g, 0.20 mmol) in carbon disulfide (6 cm^3) and benzene (12 cm^3) was refluxed for 2 h. The solvent was removed from the reaction mixture at reduced pressure and the residue chromatographed as above to give a product which was crystallized from tetrahydrofuran–diethyl ether mixtures to give brown crystals of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CNMe)_2\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, **2d**. Yield 0.071 g, 65% (Found: C, 46.0; H, 3.0; N, 5.1. $C_{16}H_{16}N_2Co_2FeS_4$ requires C, 45.9; H, 3.1; N, 5.2%). IR (cm^{-1} in CH_2Cl_2 with relative peak heights in parentheses) ν_{CN} 2174 (10), 2151 (7.0); ν_{CS} 1019 (2.9, sh), 1012 (4.2). (cm^{-1} in KBr with relative peak heights in parentheses) ν_{CN} 2163 (10), 2140 (8.1); ν_{CS} 1013 (3.8), 999 (4.0). ^1H NMR (δ in $CDCl_3$) 4.62 (s, 10H, C_5H_5), 3.25 (s, 6H, $CNCH_3$). ^{13}C NMR (δ in $CDCl_3$) 344.9 (s, C_μ–S), 244.4 (s, S–C–S), 158.4 (s, *C*NMe), 84.95 (s, C_5H_5), 31.2 (s, $CN\mathit{C}H_3$).

Under the same conditions, $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNMes)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ **1e** (0.08 g, 0.11 mmol) (CNMes = $CNC_6H_2Me_3$-2,4,6), gives $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CNMes)_2\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, **2e**. Yield 0.051 g, 60% (Found: C; 51.1; H, 4.3; N, 3.9. $C_{32}H_{32}N_2Co_2FeS_4$ requires C, 51.5; H, 4.3; N 3.8%). IR (cm^{-1} in CH_2Cl_2 with relative peak heights in parentheses) ν_{CN} 2117 (10), 2084 (7.0); ν_{CS} 1018 (6, sh), 1012 (6.6). (cm^{-1} in KBr with relative peak heights in parentheses) ν_{CN} 2101 (8.0), 2069 (8.1); ν_{CS} 1017 (3.8), 1004 (2.4, sh). ^1H NMR (δ in $CDCl_3$) 6.80 (s, 4H, *m*-C_6H_2) 4.67 (s, 10H, C_5H_5), 2.25 (s, 12H, *o*-CH_3), 2.24 (s, 6H, *p*-CH_3). ^{13}C NMR (δ in $CDCl_3$) 350.2 (s, C_μ–S), 244.8 (s, S–C–S), 171.4 (s, *C*NMes), 138.4 (s, *ipso*-$\mathit{C}_6H_2Me_3$), 134.3 (s, *o*-$\mathit{C}_6H_2Me_3$), 128.9 (s, *m*-$\mathit{C}_6H_2Me_3$), 126.8 (s, *p*-$\mathit{C}_6H_2Me_3$), 85.31 (s, C_5H_5), 21.6 (s, *p*-$C_6H_2(\mathit{CH}_3)_3$), 19.3 (s, *o*-$C_6H_2(\mathit{CH}_3)_3$).

A solution of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(CNMes)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1f** (0.01 g, 0.17 mmol) in carbon disulfide (9 cm^3) and benzene (12 cm^3) was refluxed for 10 h. The products were separated by chromatography as above to give $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CNMes)_2\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$ **2e** (0.017 g, 45% based on CNMes) Some $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNMes)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ was also formed and identified by comparison with an authentic sample.[2]

Reaction of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, 2a, with CNMes

A solution of **2a** (0.053 g, 0.07 mmol) and CNMes (0.25 cm^3) in dichloromethane (20 cm^3) and benzene (15 cm^3) was refluxed for 2 min after which time **2a** was consumed. Two products were separated by chromatography and purified by crystallization. They were shown to be $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(CNMes)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1e** (yield 0.032, 60%, from toluene–diethyl ether) and $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CNMes)_2\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, **2e** (yield 0.018 g, 25%, from tetrahydrofuran–diethyl ether).

Reactions of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PR_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, 2, with alkylating agents

A solution of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PR_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, **2**, (*ca.* 0.1 g) (R = (**a**) Ph, (**b**) OPh and (**c**) Bu^n) in dichloromethane (3 cm^3) was filtered and benzene (25 cm^3) and R^1I (1 cm^3, R^1 = Me or Et) added to it. The mixture was stirred for 16 h. The brown precipitates were then filtered off, washed with benzene and diethyl ether, and recrystallized from dichloromethane–diethyl ether mixtures to give brown crystals of the salts $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PR_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3R^1)]I$, [**3**]I ($R^1$ = Me) and [**4**]I (R^1 = Et) in yields of 70–80%. Under the same conditions $MeOSO_2CF_3$ gave $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PR_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)][SO_3CF_3]$ salts. The salts where PR_3 = $PBu^n{}_3$ were oils which could not be purified further, whilst those derived from **2d** and **2e** were formed but were unstable and could not be purified.

$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)]I$, [**3a**]I. Yield 0.091 g, 80% (Found: C, 42.5; H, 3.4. $C_{32}H_{28}Co_2FeIOPS_4$ requires C, 43.3; H, 3.2). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1947. (cm^{-1} in KBr) ν_{CO} 1925. ^1H NMR (δ in $CDCl_3$) 7.40 (m, 15H, PPh_3), 5.22 (s, 5H, C_5H_5), 4.48 (s, 5H, C_5H_5), 3.08 (s, 3H, CH_3). ^{13}C NMR (δ in $CDCl_3$) 348.5 (d, J_{PC} = 15.3 Hz, C_μ–S), 221.6 (d, J_{PC} = 20.5 Hz, S–C–S), 214.5 (d, J_{PC} = 20.5 Hz, CO), 133.6 (d, J_{PC} = 44.3 Hz, *ipso*-C_6H_5), 133.3 (d, J_{PC} = 10.2 Hz, *o*-C_6H_5), 130.9 (s, *p*-C_6H_5), 128.7 (d, J_{PC} = 10.2 Hz, *m*-C_6H_5), 87.5 (s, C_5H_5), 86.1 (s, C_5H_5), 22.1 (s, CH_3). ^{31}P NMR (δ in $CDCl_3$) 51.8 (s, PPh_3).

$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)][SO_3CF_3]$, [**3a**][$SO_3CF_3$]. Yield 0.086 g, 75% (Found: C, 41.4; H, 2.9; P, 3.5. $C_{33}H_{28}Co_2F_3FeO_4PS_5$ requires C, 41.3; H, 2.9; P, 3.4%). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1948. (cm^{-1} in KBr) ν_{CO} 1933. ^1H NMR (δ in $CDCl_3$) 7.40 (m, 15H, PPh_3), 5.12 (s, 5H, C_5H_5), 4.38 (s, 5H, C_5H_5), 3.04 (s, 3H, CH_3). ^{13}C NMR (δ in $CDCl_3$) 348.6 (d, J_{PC} = 15.3 Hz, C_μ–S), 221.3 (d, J_{PC} = 20.5 Hz, S–C–S), 214.6 (d, J_{PC} = 20.5 Hz, CO), 134.1 (d, J_{PC} = 44.3 Hz, *ipso*-C_6H_5), 133.5 (d, J_{PC} = 10.2 Hz, *o*-C_6H_5), 131.0 (s, *p*-C_6H_5), 128.8 (d, J_{PC} = 10.2 Hz, *m*-C_6H_5), 87.5 (s, C_5H_5), 86.1 (s, C_5H_5), 21.9 (s, 3H, CH_3). ^{31}P NMR (δ in $CDCl_3$) 51.8 (s, PPh_3).

$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)]I\cdot CH_2Cl_2$, [**3b**]I·$CH_2Cl_2$. Yield 0.11 g, 80% (Found: C, 39.1; H, 2.9; I, 12.4. $C_{32}H_{28}Co_2FeIO_4PS_4\cdot CH_2Cl_2$ requires C, 38.8; H, 2.9; I 13.3%). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1969. (cm^{-1} in KBr) ν_{CO} 1956. ^1H NMR (δ in $CDCl_3$) 7.27 (m, 15H, $P(OPh)_3$), 5.05 (s, 5H, C_5H_5), 4.73 (s, 5H, C_5H_5), 3.18 (s, 3H, CH_3). ^{13}C NMR (δ in $CDCl_3$) 353.3 (d, J_{PC} = 25.6 Hz, C_μ–S), 222.6 (d, J_{PC} = 22.1 Hz, S–C–S), 210.4 (d, J_{PC} = 27.3 Hz, CO), 150.8 (d, J_{PC} = 10.2 Hz, *ipso*-C_6H_5), 130.1 (s, *o*-C_6H_5), 125.9 (s, *p*-C_6H_5), 121.0 (d, J_{PC} = 5.1 Hz, *m*-C_6H_5), 87.5 (s, C_5H_5), 86.7 (s, C_5H_5), 22.1 (s, 3H, CH_3).

Table 1 Crystal data and structure refinement for $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]\cdot 2C_6H_6$, **2a**·$2C_6H_6$, and $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)]I\cdot CHCl_3\cdot C_6H_6$, [**3a**]I·$CHCl_3\cdot C_6H_6$

	2a·$2C_6H_6$	[**3a**]I·$CHCl_3\cdot C_6H_6$
Empirical formula	$C_{43}H_{37}Co_2FeOPS_4$	$C_{39}H_{35}Cl_3Co_2FeIOPS_4$
Formula weight	902.65	1085.84
T/K	293(2)	300(2)
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	9.853(13)	12.9130(7)
b/Å	19.97(2)	20.9619(10)
c/Å	20.61(2)	16.2086(8)
β/°	91.79(4)	100.2930(10)
V/Å^3	4055(8)	4316.8(4)
Z	4	4
D_c/g cm^{-3}	1.478	1.671
μ/mm^{-1}	1.440	2.253
F(000)	1848	2160
Crystal size/mm	0.95 × 0.65 × 0.07	0.45 × 0.15 × 0.10
θ Range/°	2.04–25.01	1.60–23.39
Reflections collected	6687	12780
Independent reflections (R_{int})	6380 (0.12960)	4746 (0.0314)
Absorption correction	Empirical	Empirical
Max., min. transmission	0.925, 0.419	1.000, 0.721
Refinement method	Full-matrix least squares on F^2	
Data/restraints/parameters	6380/6/469	4746/36/470
Goodness-of-fit on F^2	0.832	1.078
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0692$, $wR_2 = 0.1575$	$R_1 = 0.0488$, $wR_2 = 0.1283$
R indices (all data)	$R_1 = 0.1488$, $wR_2 = 0.1823$	$R_1 = 0.0576$, $wR_2 = 0.1328$
Largest diff. peak, hole/e Å^{-3}	1.482, −0.620	0.616, −0.627

$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)][SO_3CF_3]$, [**3b**][$SO_3CF_3$]. Yield 0.082 g, 70% (Found: C, 41.3; H, 2.9. $C_{33}H_{28}Co_2F_3FeO_7PS_5$ requires C, 41.4; H, 2.9%). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1969. (cm^{-1} in KBr) ν_{CO} 1956. ^{1}H NMR (δ in $CDCl_3$) 7.25 (m, 15H, $P(OPh)_3$), 4.96 (s, 5H, C_5H_5), 4.64 (s, 5H, C_5H_5), 3.17 (s, 3H, CH_3). ^{13}C NMR (δ in $CDCl_3$) 353.3 (d, $J_{PC} = 27.3$ Hz, C_μ–S), 222.7 (d, $J_{PC} = 22.1$ Hz, S–C–S), 210.4 (d, $J_{PC} = 29.0$ Hz, CO), 150.8 (d, $J_{PC} = 10.2$ Hz, *ipso*-C_6H_5), 130.1 (s, *o*-C_6H_5), 125.9 (s, *p*-C_6H_5), 121.0 (d, $J_{PC} = 5.1$ Hz, *m*-C_6H_5), 87.4 (s, C_5H_5), 86.5 (s, C_5H_5), 21.8 (s, 3H, CH_3).

$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Et)]I\cdot CH_2Cl_2$, [**4a**]I·$CH_2Cl_2$,. Yield 0.098 g, 80% (Found: C, 41.8; H, 3.2; I, 12.9. $C_{33}H_{30}Co_2FeIOPS_4.CH_2Cl_2$ requires C, 41.4; H, 3.3; I, 12.9%). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1947. (cm^{-1} in KBr) ν_{CO} 1933 (10), 1918 (9.0). ^{1}H NMR (δ in $CDCl_3$) 7.35 (m, 15H, PPh_3), 5.22 (s, 5H, C_5H_5), 4.47 (s, 5H, C_5H_5), 3.62 (br s, 2H, CH_2), 1.54 (t, 3H, $J_{HH} = 8.3$ Hz, CH_3). ^{13}C NMR (δ in $CDCl_3$) 348.2 (d, $J_{PC} = 15.3$ Hz, C_μ–S), 220.3 (d, $J_{PC} = 20.5$ Hz, S–C–S), 214.6 (d, $J_{PC} = 22.2$ Hz, CO), 133.6 (d, $J_{PC} = 44.3$ Hz, *ipso*-C_6H_5), 133.4 (d, $J_{PC} = 10.2$ Hz, *o*-C_6H_5), 131,0 (s, *p*-C_6H_5), 128.7 (d, $J_{PC} = 10.2$ Hz, *m*-C_6H_5), 87.6 (s, C_5H_5), 86.2 (s, C_5H_5), 33.9 (s, CH_2),13.3 (s, CH_3).

$[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Et)]I\cdot 2CH_2Cl_2$, [**4b**]I·$2CH_2Cl_2$. Yield 0.099 g, 74% (Found: C, 38.0; H, 3.0. $C_{33}H_{30}Co_2FeIO_4PS_4.CH_2Cl_2$ requires C, 37.5; H, 3.0%). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1968. (cm^{-1} in KBr) ν_{CO} 1947. ^{1}H NMR (δ in $CDCl_3$) 7.25 (m, 15H, $P(OPh)_3$), 5.07 (s, 5H, C_5H_5), 4.73 (s, 5H, C_5H_5), 3.75 (q, 2H, $J_{HH} = 7.6$ Hz, CH_2), 1.66 (t, 3H, $J_{HH} = 7.5$ Hz, CH_2). ^{13}C NMR (δ in $CDCl_3$) 353.3 (d, $J_{PC} = 25.5$ Hz, C_μ–S), 222.0 (d, $J_{PC} = 22.1$ Hz, S–C–S), 210.5 (d, $J_{PC} = 29.0$ Hz, CO), 150.8 (d, $J_{PC} = 8.5$ Hz, *ipso*-C_6H_5), 130.0 (s, *o*-C_6H_5), 125.8 (s, *p*-C_6H_5), 121.0 (d, $J_{PC} = 5.1$ Hz, *m*-C_6H_5), 87.6 (s, C_5H_5), 86.7 (s, C_5H_5), 33.9 (s, CH_2), 22.1 (s, 3H, CH_3).

Reactions of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, 2a, with $HgCl_2$

$HgCl_2$ (0.04 g, 0.15 mmol) was added to a solution of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, **2a**, (0.1 g, 0.13 mmol) in dichloromethane (20 cm^3). After 6 min, the mixture was filtered and the solvent removed at reduced pressure. The residue was crystallized from dichloromethane–diethyl ether to give brown $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3HgCl_2)]\cdot H_2O$, **5a**·$H_2O$. Yield 0.121 g, 90% (Found: C, 36.0; H, 2.5; Cl, 6.9. $C_{31}H_{25}Cl_2Co_2FeHgIOPS_4\cdot H_2O$: C, 35.8; H, 2.6; Cl, 6.9%). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1941. (cm^{-1} in KBr) ν_{CO} 1930. ^{1}H NMR (δ in $CDCl_3$) 7.45 (m, 15H, PPh_3), 5.03 (s, 5H, C_5H_5), 4.28 (s, 5H, C_5H_5).

Reactions of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, 2a, with I_2

A solution of I_2 (0.145 g) in dichloromethane (10 cm^3) was titrated into one of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, **2a**, (0.05 g, 0.067 mmol) in dichloromethane (50 cm^3). The reaction was monitored by IR spectroscopy which showed no further changes after the addition of *ca.* 2.2 molar equivalents of I_2. The reaction mixture was filtered and the solvent removed at reduced pressure. The residue was recrystallized from tetrahydrofuran–diethyl ether mixtures to give $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3I)]I_3$, **6a**. Yield 0.064, 75% (Found: C, 30.2; H, 2.2; P, 2.4; I, 38.8. $C_{31}H_{25}Co_2FeHgI_4OPS_4$ requires C, 29.7; H, 2.0; P, 2.5; I, 40.5%). IR (cm^{-1} in CH_2Cl_2) ν_{CO} 1942. (cm^{-1} in KBr) ν_{CO} 1921.

The structures of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, 2a, and $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)]I$, [3a]I

Crystals of **2a**·$2C_6H_6$ and [**3a**]I·$C_6H_6\cdot CHCl_3$ were grown from $CHCl_3$–benzene. Data were collected from the weakly diffracting crystals of **2a** at 293(2) K on a Siemens diffractometer using graphite monochromated Mo-Kα radiation and the ω-scan technique. Lorentz polarisation and absorption corrections were applied using SHELXTL.[5] For [**3a**]I, collection at 300(2) K used a Bruker SMART CCD diffractometer, data was processed using SMART,[6] and empirical absorption corrections applied using SADABS.[7] Crystal data are summarized for both molecules in Table 1.

Both structures were solved by direct methods using SHELXS-86[8] for **2a** and SHELXS-97[9] for [**3a**]I, and were refined by full-matrix least-squares using SHELXL-97.[10]

Table 2 Selected bond lengths (Å) and bond angles (°)

2a		**3a**		**1a**	
Cluster bond lengths					
Fe(1)–Co(1)	2.624(3)	Fe(1)–Co(2)	2.5965(14)	Fe(1)–Co(1)	2.5099(6)
Fe(1)–Co(2)	2.502(3)	Fe(1)–Co(1)	2.5054(16)	Fe(1)–Co(2)	2.5061(6)
Co(1)–Co(2)	2.461(4)	Co(1)–Co(2)	2.4340(13)	Co(1)–Co(2)	2.4378(5)
Fe(1)–C(1)	1.881(11)	Fe(1)–C(1)	1.894(6)	Fe(1)–C(1)	2.805(2)
Co(1)–C(1)	1.881(10)	Co(2)–C(1)	1.869(7)	Co(1)–C(1)	1.910(3)
Co(2)–C(1)	1.880(10)	Co(1)–C(1)	1.871(8)	Co(2)–C(1)	1.922(3)
Fe(1)–S(1)	2.208(4)	Fe(1)–S(1)	2.186(3)	Fe(1)–S(1)	2.1925(7)
Co(1)–S(1)	2.168(3)	Co(2)–S(1)	2.125(2)	Co(1)–S(1)	2.1266(7)
Co(2)–S(1)	2.186(3)	Co(1)–S(1)	2.148(2)	Co(2)–S(1)	2.1370(7)
Fe(1)–P(1)	2.302(4)	Fe(1)–P(1)	2.279(2)	Fe(1)–P(1)	2.353(7)
Fe(1)–C(3)O	1.758(11)	Fe(1)–C(4)O	1.744(7)	Fe(1)–C(2)O	1.764(3)
C(3)–O(3)	1.173(11)	C(4)–O(4)	1.143(2)	C(2)–O(2)	1.147(3)
C(1)–S(2)	1.774(10)	C(1)–S(2)	1.749(7)	C(1)–S(2)	1.638(2)
Cluster bond angles					
Co(1)–Fe(1)–Co(2)	57.31(8)	Co(1)–Fe(1)–Co(2)	56.95(4)	Co(1)–Fe(1)–Co(2)	58.15(2)
Fe(1)–Co(1)–Co(2)	58.86(9)	Fe(1)–Co(2)–Co(1)	59.64(4)	Fe(1)–Co(1)–Co(2)	60.84(2)
Fe(1)–Co(2)–Co(1)	63.83(6)	Fe(1)–Co(1)–Co(2)	63.41(4)	Fe(1)–Co(2)–Co(1)	61.001(14)
Fe(1)–C(1)–Co(1)	88.4(4)	Fe(1)–C(1)–Co(2)	87.3(3)	Fe(1)–C(1)–Co(1)	77.72(9)
Fe(1)–C(1)–Co(2)	83.4(4)	Fe(1)–C(1)–Co(1)	83.4(3)	Fe(1)–C(1)–Co(2)	77.31(9)
Co(1)–C(1)–Co(2)	81.7(4)	Co(1)–C(1)–Co(2)	81.2(3)	Co(1)–C(1)–Co(2)	79.01(10)
Fe(1)–S(1)–Co(1)	73.68(11)	Fe(1)–S(1)–Co(2)	74.06(8)	Fe(1)–S(1)–Co(1)	71.04(2)
Fe(1)–S(1)–Co(2)	69.43(10)	Fe(1)–S(1)–Co(1)	70.62(7)	Fe(1)–S(1)–Co(2)	70.73(3)
Co(1)–S(1)–Co(2)	68.83(12)	Co(1)–S(1)–Co(2)	69.45(7)	Co(1)–S(1)–Co(2)	69.75(2)
P(1)–Fe(1)–C(3)O	95.6(3)	P(1)–Fe(1)–C(4)O	95.1(2)	P(1)–Fe(1)–C(2)O	95.93(9)
P(1)–Fe(1)–S(4)	88.05(11)	P(1)–Fe(1)–S(4)	88.64(8)	P(1)–Fe(1)–C(3)O	94.12(9)
S(4)–Fe(1)–C(3)O	94.1(3)	S(4)–Fe(1)–C(4)O	93.0(3)	C(2)–Fe(1)–C(3)	97.75(14)
Heterocycle bond lengths					
Fe(1)–C(1)	1.881(10)	Fe(1)–C(1)	1.894(6)		
Fe(1)–S(4)	2.301(4)	Fe(1)–S(4)	2.239(3)		
C(1)–S(2)	1.774(10)	C(1)–S(2)	1.749(7)		
C(2)–S(2)	1.731(11)	C(2)–S(2)	1.700(9)		
C(2)–S(3)	1.680(11)	C(2)–S(3)	1.715(8)		
C(2)–S(4)	1.768(11)	C(2)–S(4)	1.684(7)		
Fe(1)–S(4)	2.301(4)	Fe(1)–S(4)	2.239(3)		
		C(3)–S(3)	1.798(9)		
Heterocycle bond angles					
Fe(1)–C(1)–S(2)	129.1(6)	Fe(1)–C(1)–S(2)	127.9(5)		
C(1)–S(2)–C(2)	99.7(5)	C(1)–S(2)–C(2)	97.5(3)		
S(2)–C(2)–S(4)	123.0(7)	S(2)–C(2)–S(4)	120.3(4)		
S(2)–C(2)–S(3)	121.1(7)	S(2)–C(2)–S(3)	122.6(4)		
S(3)–C(2)–S(4)	123.0(7)	S(3)–C(2)–S(4)	117.1(5)		
C(2)–S(4)–Fe(1)	108.1(4)	C(2)–S(4)–Fe(1)	107.1(3)		
S(4)–Fe(1)–C(1)	83.9(3)	S(4)–Fe(1)–C(1)	84.7(2)		
		C(2)–S(3)–C(3)	104.0(4)		

Hydrogen atoms were included as fixed contributions to F_c with fixed isotropic temperature factors. All non-hydrogen atoms were refined anisotropically.

Difference Fourier synthesis following the location of all atoms revealed additional large peaks in both structures. For **2a** the peaks could be sensibly assigned to the carbon atoms of three benzene solvate molecules, two of which lie about inversion centres, while for [**3a**]I they revealed the presence of both chloroform and benzene solvate molecules. In both cases, inclusion of the solvates, together with H atoms in calculated positions, in the refinements led to significant improvements in the residuals. The relatively high values of R_1 and wR_2 for **2a** can largely be attributed to weakly diffracting crystals; only 2930 of the 6380 reflection were 'observed'.

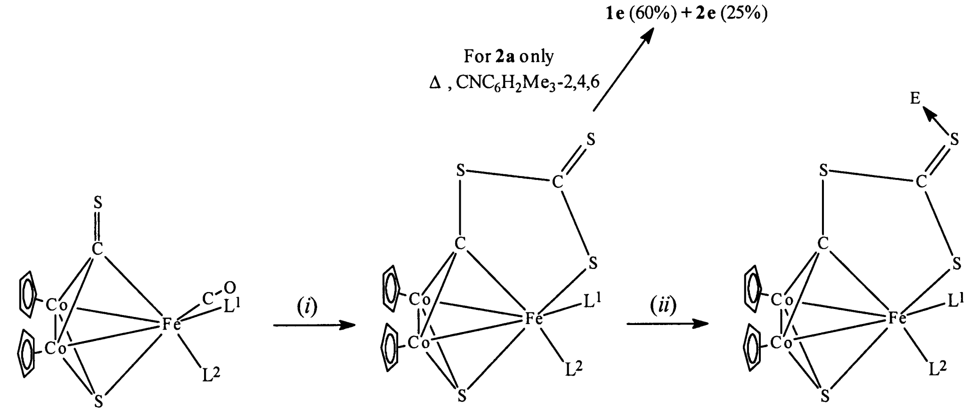
The molecular structure and atom labelling of **2a** is given in Fig. 1, and that of the cation of [**3a**]I in Fig. 2. Selected bond lengths and bond angles are summarised in Table 2 together with those of **1a** for comparison.

CCDC reference numbers 207316 and 215760.

See http://www.rsc.org/suppdata/dt/b3/b308320a/ for crystallographic data in CIF or other electronic format.

Results and discussion

When the μ_3-CS clusters $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(L)_2\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1**, are refluxed in carbon disulfide solution, a molecule of CS_2 is taken up and CO is lost to give the $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(L)_2\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, **2**, clusters where L_2 = (**a**) (CO)(PPh_3), (**b**) (CO){P(OPh)$_3$}, (**c**) (CO)(PBu^n_3), (**d**) (CNMe)$_2$ and (**e**) (CNMes)$_2$ (Mes = 2,4,6-$Me_3C_6H_2$), but not where L_2 = (CO)(CNMes). **2** react with electrophiles E which attack the C_2S_3 ligand to give $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(L)_2\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3E)]$, where E = Me^+ (**3**), Et^+ (**4**), $HgCl_2$ (**5**) and I^+ [**6**]$^+$. These reactions are summarized in Scheme 1. The structures shown in the Scheme for the various complexes are consistent with spectroscopic data and have been confirmed for **2a** and [**3a**]$^+$ by X-ray crystallography.



1

(a) L^1 = PPh$_3$, L^2 = CO
(b) L^1 = P(OPh)$_3$, L^2 = CO
(c) L^1 = PBu$^n_3$, L^2 = CO
(d) L^1 = L^2 = CNMe
(e) L^1 = L^2 = CNMes
(f) L^1 = CNMes, L^2 = CO

2

(a) L^1 = PPh$_3$, L^2 = CO
(b) L^1 = P(OPh)$_3$, L^2 = CO
(c) L^1 = PBu$^n_3$, L^2 = CO
(d) L^1 = L^2 = CNMe
(e) L^1 = L^2 = CNC$_6$H$_2$Me$_3$-2,4,6
(f) L^1 = CNC$_6$H$_2$Me$_3$-2,4,6, L^2 = CO

[3]$^+$ - 6

[3]$^+$X$^-$, E = MeI or MeOSO$_2$CF$_3$
(a) L^1 = PPh$_3$, L^2 = CO
(b)L^1 = P(OPh)$_3$, L^2 = CO
[4]$^+$X$^-$, E = EtI or EtOSO$_2$CF$_3$
(a) L^1 = PPh$_3$, L^2 = CO
(b)L^1 = P(OPh)$_3$, L^2 = CO
5, E = HgCl$_2$, (a) L^1 = PPh$_3$, L^2 = CO
6, E = I$_4$ or I$^+$ I$_3^-$, (a) L^1 = PPh$_3$, L^2 = CO

Scheme 1

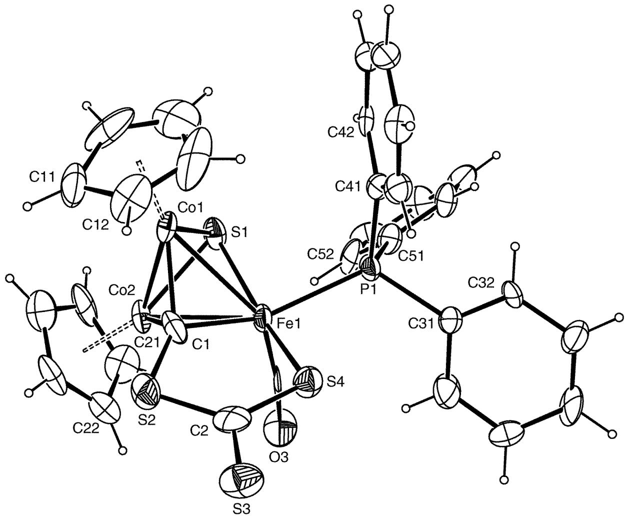


Fig. 1 The molecular structure and atom labelling of [{Co(η^5-C$_5$H$_5$)}$_2$-{Fe(CO)(PPh$_3$)}(μ$_3$-S)(μ$_3$-C$_2$S$_3$)]·2C$_6$H$_6$, **2a**·2C$_6$H$_6$. Displacement ellipsoids are drawn at the 50% probability level. For clarity, only 2 C atoms of the consecutively numbered cyclopentadienyl and phenyl rings are labelled.

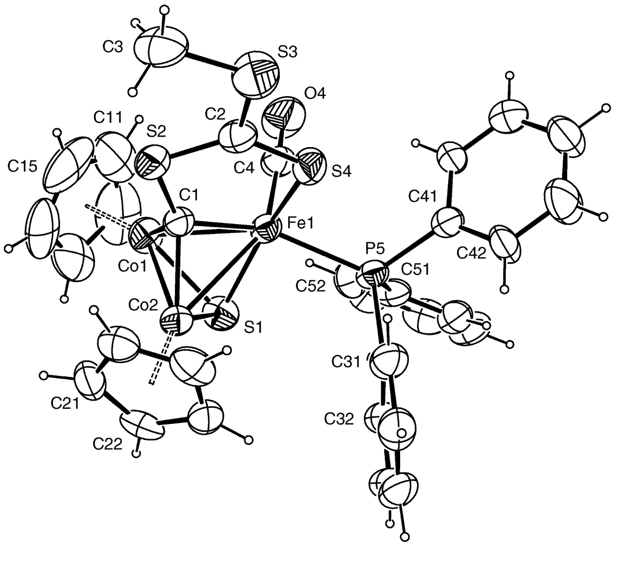


Fig. 2 The molecular structure and atom labelling of the cation of [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(PPh$_3$)}(μ$_3$-S)(μ$_3$-C$_2$S$_3$Me)]I·CHCl$_3$·C$_6$H$_6$, [**3a**]I·CHCl$_3$·C$_6$H$_6$. Displacement ellipsoids are drawn at the 50% probability level. For clarity, only 2 C atoms of the consecutively numbered cyclopentadienyl and phenyl rings are labelled.

Fixation of CS$_2$ by 1

Although CS$_2$ is fixed as the C$_2$S$_3$ ligand by clusters **1a**–**e**, it is not a completely general reaction. [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$-(CNMes)}(μ$_3$-S)(μ$_3$-CS)], **1f**, (CNMes = CNC$_6$H$_2$Me$_3$-2,4,6) reacts with CS$_2$, but it does not give [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)-(CNMes)}(μ$_3$-S)(μ$_3$-C$_2$S$_3$)], **2f**. Instead the only isolable products are [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(CNMes)$_2$}(μ$_3$-S)(μ$_3$-CS)], **1e**, and [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CNMes)$_2$}(μ$_3$-S)(μ$_3$-C$_2$S$_3$)], **2e**. This implies that either **2f** is formed but is unstable or that **1f** is unstable under the reaction conditions used and on thermolysis it gives **1e** which is the true precursor of **2e**.

The overall reaction of **1** + CS$_2$ $\longrightarrow$ **2** is related to that of thiolate anions RS$^-$ with CS$_2$ which is used to prepare organotrithiocarbonate ions [RSCS$_2$]$^-$ and in which the CS$_2$ molecule acts as an electrophile.[11] In the present instance, it takes place because the S atom of the μ$_3$-CS ligand is very nucleophilic. This is illustrated by the ease with which **1** are alkylated to give [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(L)$_2$}(μ$_3$-S)(μ$_3$-CSR)]X salts.[1] However, the μ-CS ligand of [{Co(η^5-C$_5$H$_5$)}$_3$(μ$_3$-S)(μ$_3$-CS)] is alkylated with equal facility,[12,13] but [{Co(η^5-C$_5$H$_5$)}$_3$(μ$_3$-S)(μ$_3$-CS)] does not react with CS$_2$ to give [{Co(η^5-C$_5$H$_5$)}$_3$(μ$_3$-S)(μ$_3$-C$_2$S$_3$)]. This implies that the formation of such adducts is reversible and that the C$_2$S$_3$ ligand in **2** is stabilized because the Fe atoms in the postulated [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(L)$_2$}(μ$_3$-S)-(μ$_3$-CSCS$_2$)] intermediates are able to lose a two-electron ligand and form an Fe–S bond. Surprisingly, CO is the ligand which is replaced by S, whereas if **1a** is reacted with either phosphines, phosphites or isocyanides, triphenylphosphine is substituted preferentially.[2] If this ligation of S is so important in the stabilization of **2**, displacement of the ligating S atom from the coordination shell of Fe by an incoming ligand L should reverse the formation of the μ$_3$-C$_2$S$_3$ to give **1** with the liberation of CS$_2$.

However, such a reaction would compete with the substitution of other ligands at the Fe atoms of **2**. Both of these alternatives have been observed in the reaction of **2a** with CNMes (Mes = $C_6H_2Me_3$-2,4,6). **2e** arises from replacement of PPh_3 and CO by CNMes, but with retention of the C_2S_3 ligand, and **1e** arises from replacement of PPh_3 and CS_2. The second pathway gives the higher reaction yield.

Reactions of 2 with electrophiles

2a–**c** react with electrophiles, E, to give adducts (Scheme 1). These are brown solids soluble in polar organic solvents. They are stable in the solid state but decompose slowly in solution. Similar derivatives are formed by the isocyanide complexes **2d** and **2e**, but they could not be characterized. The structure of one of the adducts, [**3a**]I, has been determined by X-ray crystallography which has confirmed that the nucleophilic site is the exocyclic S* atom of the FeSC(S*)SC_μ ring. All adducts have similar spectra. Consequently it is reasonable to suggest that they have structures similar to [**3a**]I, and that [**3**]X, (E = Me^+), [**4**]X (E = Et^+), **5a** (E = $HgCl_2$) and **6a** (E = $I^+I_3^-$ or I_4) have S⟶C, S⟶Hg or S⟶I bonds. **5a** and **6a** are poorly soluble in organic solvents, which suggests that they have polymeric structures with extensive Hg–Cl–Hg or I–I–I interactions. **6a** has been formulated as a salt containing a $CS{\longrightarrow}I^+$ ligand with an I_3^- counterion because it requires two molar equivalents of I_2 to consume one of **2a**, but even in these circumstances a network of I–I interactions would be expected in the solid state.

The clusters $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ and $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ form $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSE)]$ and $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CSE)]$ adducts with a similar range of electrophiles with the S atom of their μ_3-CS ligand acting as the nucleophilic center. However it is probably more relevant that in the trithiocarbonate complexes $[Co(\eta^5C_5H_5)(PR_3)(\eta^2\text{-}S_2CS)]$ the exocyclic C=S also act as nucleophiles to mercury halides and iodine as well as R^+.[14]

IR spectra

The IR spectra of **2**–**6** show many absorption bands, but the only ones of interest which could be identified with any confidence are those due to the *ν*(CO) and *ν*(CN) vibrations of the coordinated carbonyl and isocyanide ligands, those due to $[SO_3CF_3]^-$ ions of the salts, and, for **2**, some bands at *ca.* 1000 cm^{-1} which we attribute to the *ν*(CS) vibrations of the C_2S_3 ligand

The *ν*(CO) and *ν*(CN) frequencies of [**2**], [**3**]$^+$ and [**4**]$^+$ are a predictable function of the ligand set about Fe. The increase in their frequencies in going from **2** to [**3**]X, [**4**]X, [**5**] or [**6**] is to be anticipated as the presence of a electrophile bonded to S makes the exocyclic CS group a better π-acceptor. This is consistent with electronic communication between the C_2S_3 or $C_2S_3R^+$ ligands and the cluster part of the molecules as strongly indicated by molecular structures of **2a** and [**3a**]I (see below).

There are absorption bands in the IR spectra of **1** having frequencies between *ca.* 1020 and 1050 cm^{-1} which are attributed to the *ν*(CS) vibration of the μ_3-CS ligand.[2] On conversion of **1** to **2** these are replaced by other bands in the same region of the spectrum which are assumed to be due to vibrations of the C_2S_3 moiety. There are usually two of them and they have frequencies between *ca.* 1020 and 950 cm^{-1}. On alkylation of the exocyclic S atoms of **2** these bands disappear and we were not able to identify their counterparts in the spectra of [**3**]$^+$ or [**4**]$^+$. The frequencies of these bands may be compared with those of *ca.* 1035 and 860 cm^{-1} found for the *ν*(C=S) and *ν*(C–S) in the spectra of the trithiocarbonate complexes $[Co(\eta^5C_5H_5)(PR_3)(\eta^2\text{-}S_2CS)]$,[14] and 1067 cm^{-1} for the thione $(MeS)_2C_2S_2CS$.[15] There will probably be much mixing between the various vibrations of the C_2S_3 ligand.

NMR spectra

The ^1H and ^{13}C NMR spectra of **2**–[**4**]X are consistent with the proposed formulae. Resonances due to solvents of crystallization and the organo groups R of phosphine and isocyanide ligands are all present at the expected chemical shifts with the correct integrations and showing the anticipated coupling constants. However, much more important are the resonances due to H and C atoms of the η^5-C_5H_5, $S_2C{=}S$ and S_2CSR^+ groups and the ligating C atoms of CO, CNR and μ_3-C groups.

The Fe atom in **2a**–**c**, [**3a**–**c**]X and [**4a**–**c**]X is chiral. Consequently their two Co(η-C_5H_5) moieties are in different environments so that two η-C_5H_5 resonances are observed in both ^1H and ^{13}C NMR spectra. These observations imply that there is no inversion of configuration of the Fe atoms on the NMR time scale. Both enantiomers are observed in the crystal structures of both **2a** and [**3a**]I (see below). On the other hand, in the NMR spectra of **2d** and **2e** single resonances are observed for η-C_5H_5 and CNR ligands. It is probable that the structures of these compounds is similar to that of **2a** but with $Fe(CO)(PPh_3)$ replaced by $Fe(CNR)_2$. The two CNR ligands are in different environments and consequently the two Co(η-C_5H_5) groups are not equivalent, but they can be made so by a fast oscillation of the $Fe(CNR)_2S$ moiety (Fig. 3) even though free rotation of the FeL_3 group is prevented by the FeSCSC ring.

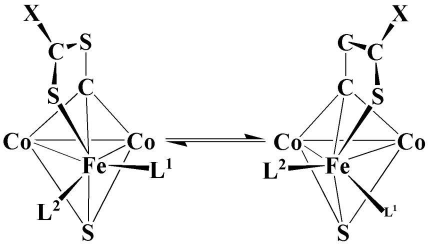


Fig. 3 Equivalencing of the η-C_5H_5 and CNR ligands X = S or SR^+. $L^1 = L^2$ = CNMe or CNMes of **2** and [**3**]$^+$.

As a consequence of ^{13}C–^{31}P coupling the μ_3-C, S–C–S and CO resonances of **2a**–**c**, [**3**]X and [**4**]X are doublets, whilst the μ_3-C, S–C–S and CNR resonances of **2d** and **2e** are singlets. Those due to the μ_3-C atom are readily identified. Their chemical shifts for **2** lie in the range *δ* 344.9–349.3 and depend to a limited extent on the ligands coordinated to Fe. They are *less* deshielded than those of the μ_3-CS ligand of **1**, *e.g.* *δ* 346.1 for **2a** *vs.* *δ* 355.5 for **1a**, whereas the μ_3-C atoms of the corresponding $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2L\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$ salts are *more* deshielded (*δ* 366.6 when L = PPh_3). Furthermore, alkylation of the C_2S_3 ligand deshields this μ_3-C atom to only a limited extent with chemical shifts of *δ* 348.2–353.3 in the [**3**]$^+$ and [**4**]$^+$ salts. In contrast, the chemical shift of the C atom of the SC(S*)S moiety of **2** is almost independent of the ligand L (*δ* 243.4–244.8) but becomes markedly *less* deshielded on alkylation of S* in [**3**]$^+$ and [**4**]$^+$ (*δ* 220.3–222.0). For comparison, the ^{13}C resonance of free CS_2 is found at *δ* 192.6,[16] it shifts downfield to *δ* 205.1 in $[Pt(PPh_3)_2\{SC(S)N(Me)C(O)N(Ph)\}]$ with its six-membered metallocyclic ring,[16] and to *δ* 279.5 when η^2-bonded in $[Fe\{PPh(OEt)_2\}_2(CO)_2(\eta^2\text{-}CS_2)]$.[17] The observed chemical shifts and the way in which they vary indicate fundamental changes in the bonding in both CS_2 and the cluster **1** when they combine to form the C_μSC(S*)SFe heterocycle in **2**, and when this is alkylated at the exocyclic S* to give the C_μSC(S*R^+)SFe heterocycle in [**3**]$^+$ and [**4**]$^+$.

The structure of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$, 2a

The structure of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1a**, is based on a $FeCo_2$ isosceles triangle capped on one face by a μ_3-S ligand and on the other by a μ_3-C atom of a

Table 3 Electrochemical data[a]

	1a	[**1a**Me]I	**2a**	[**3a**]I	Co_3[b]	[Co_3Me]I[b]
E_p^c (A)	−1.10	−0.98	−0.95	−1.25	−1.06	–
E_p^a (B)	−1.00	–	−0.83	irrev.	irrev.	–
E_p^c (C)	–	−0.54	–	−0.58[c]	–	−0.52
E_p^a (D)	–	−0.44	–	irrev.	–	−0.43
E_p^a (E)	0.50	0.42	0.66	–	0.45	0.9
E_p^c (F)	0.02	irrev.	0.02	–	−0.05	−0.2
E_p^a (G)	0.62	0.69	1.30	1.12[d]	1.30	0.96[e]
E_p^c (H)	0.54	0.59	1.19	1.05[d]	irrev.	irrev.

[a] In CH_2Cl_2; volts, 200 mV s^{-1}, Pt, 0.1 M $TBAPF_6$, from cyclic voltammetry; referenced against decamethylferrocene (SCE 0.53 V). Electron transfers assigned as in text and Figs. 5 and 6. irrev. = irreversible. [b] Co_3 = $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ and $[Co_3Me]I$ = $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$. [c] In acetone, –0.54 V. [d] In acetone, 1.03 and 0.96 V. [e] Multi-electron step at 1.33 V.

CS ligand. The two Fe–Co distances are comparable, 2.5061(6) and 2.5099(6) Å, and the molecule possesses a near plane of symmetry which includes S_μ, Fe and CS_μ and bisects the Co–Co bond.[1]

Cluster **2a** has a similar structure (Fig. 1, Table 2) but the μ_3-CS ligand is incorporated into a S–C(S)–S moiety which bridges the μ_3-C atom and Fe(1) to give a near planar C(1)–S(2)–C(2){S(3)}–S(4)–Fe(1) heterocyclic ring with an exocyclic C(1)=S(3). The coordination shell about each Co atom is completed by a η^5-C_5H_5 group and about Fe by terminal CO and PPh_3 ligands. As there are three different ligands coordinated to Fe, the molecule is chiral and both enantiomers are found in the unit cell. The three ligands to Fe1 have interligand bond angles of *ca.* 90°, and are arranged so that the CO ligand lies close to the $FeCo_2$ plane with a Co(1)–Fe(1)–C(3) angle of 144.6°.

In contrast to that of **1a**, the $FeCo_2$ triangle of **2a** is distorted with considerable elongation of Fe(1)–Co(2), 2.624(3) Å, over Fe(1)–Co(1), 2.502(3) Å. This is probably a reflection of their differing electronic environments. The Co–Co distance in **2a**, 2.461(4) Å, is also longer than that in **1a**, 2.4378(5) Å, and the sum of the metal–metal bond lengths in **2a** (7.587 Å) is greater than in **1a** (7.4564 Å). The distortion of the $FeCo_2$ triangle is not reflected in the Co–S(1) and Co–C(1) distances though the former are shorter than in **1a**. The other notable consequence of the formation of the FeSCSC heterocycle is that the Fe(1)–C(1) bond, 1.881(11) Å, is much shorter in **2a** than in **1a**, 2.085(2) Å.

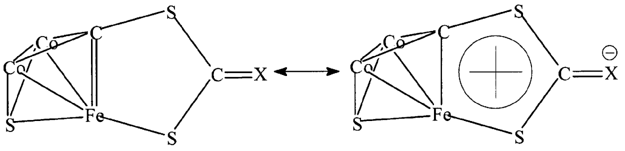
The incorporation of the μ_3-CS ligand into the heterocyclic ring results in an increase in the C_μ–S bond length from 1.638(3) to 1.774(10) Å for C(1)–S(2) These and the other C–S bond lengths, C(2)–S(2) 1.731(11) Å, C(2)–S(4) 1.768(11) Å and the exocyclic C(2)–S(3) 1.680(11) Å, should be compared with 1.55 Å in CS_2, 1.611 Å in the thioketone $PhC_6H_4(Ph)C{=}S$, 1.712 Å in thiophene, 1.819 Å in thioalkanes[18] and the various distances in the potassium salt of the methyltrithiocarbonate ion [C–S 1.6624(14) and 1.7100(15) Å; C–SMe 1.7562(14) Å; S–Me 1.800(2) Å; C–S–Me 106.36(9)°].[19] They indicate that all of the C–S bonds in **2a** have bond orders between one and two, and that even the shortest has much single bond character and the longest some double bond character.

The structure of $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3Me)]I$, [3a]I

The cation of the salt [**3a**]I (Fig. 2, Table 2) has a structure similar to that of **2a**, but with the exocyclic S atom of the FeSC(S)SC heterocycle alkylated by Me^+. This results in a shortening of most bond lengths within the cluster, except for Fe(1)–C(1). Within the heterocyclic moiety most bond lengths decrease except for Fe(1)–C(1) and the exocyclic C(2)–S(3) which lengthen. In the case of the latter, the increase is from 1.680(11) Å to 1.732(10) Å, but it is still much shorter than S(3)–C(3)H_3 which, at 1.798(9) Å, is a normal single bond. The C(2)–S(3)–C(3)H_3 angle of 104.0(4)° is close to the 107.7(4)° found in $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$ [1] (*cf.* also with KS_2CSMe above).

Bonding in the FeSC(S)SC heterocyclic ring of 2a and [3a]$^+$

One of the most puzzling aspects of the structures of **1a**, **2a** and [**3a**]$^+$ is the variation of the Fe(1)–C(1) bond length, 2.085(3), 1.881(11) and 1.895(8) Å, respectively. The distance in **1a** is similar to the Fe–C σ bond length in $(\eta\text{-}C_5H_5)(OC)_2Fe\text{–}CH_2C(O)Mn(CO)_5$, 2.082(4) Å,[20] which suggests that the Fe(1)–C(1) bond order is close to unity. The distance in **2a** is comparable to that in $(\eta\text{-}C_5H_5)(I)(OC)Fe{=}C(Ph)OMe$, 1.849(10) Å,[21] which suggests that in this compound, Fe(1)–C(1) is largely a double bond. If that is so, FeSC(S)SC may be formulated as a metallo-analogue of a 1,3-dithiole-2-thione and its structure described as a resonance hybrid of *A* and *B* (Fig. 4, X = S) where *B* is the conflation of a number of charge separated mesomers in which the positive charge is distributed over the atoms of the FeCSCS heterocyclic ring and, as a consequence, the various C–S bonds have bond orders between one and two. The pattern of bond lengths in **2a** suggests that the major contributor to the overall description of the bonding is mesomer *A*, and *B* is much less important. The lengthening of C(2)–S(3) and the shortening of C(2)–S(2), C(2)–S(4) and Fe(1)–S(4) distances on alkylation of S(4) to give [**3a**]$^+$ suggests that the importance of *B* (Fig. 4, X = SMe^+) has increased compared with *A*.



A *B*

Fig. 4 Resonance forms of **2** (X=S) and [**3**]$^+$ (X = SMe^+).

Spectroelectrochemistry

The electrochemical data for **2a** and [**3a**]$^+$ are given in Table 3 together with those for **1a**, $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$, $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$ and $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ which are included to aid our discussion; the last was taken from ref. 22. The voltammetric profiles for **2a** and [**3a**]I are shown in Fig. 5, and for **1a** and $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$, [**1a**Me]I, in Fig. 6. In the following discussion a couple is denoted by a bold letter, *e.g.* **A**, and the non-isolated species involved in the electron transfer by italicized Roman numerals *e.g. I*. Scheme 2 summarises the proposed electrochemical scheme using **2a** and [**3a**]$^+$ as examples.

Reduction processes. Both neutral clusters, **1a** and **2a**, display a chemically reversible one-electron transfer process **A**/**B** at $E^{0/-}$[**1a**] = −1.05 V and $E^{0/-}$[**2a**] = −0.89 V, respectively (all potentials are referenced against decamethylferrocene). These couples

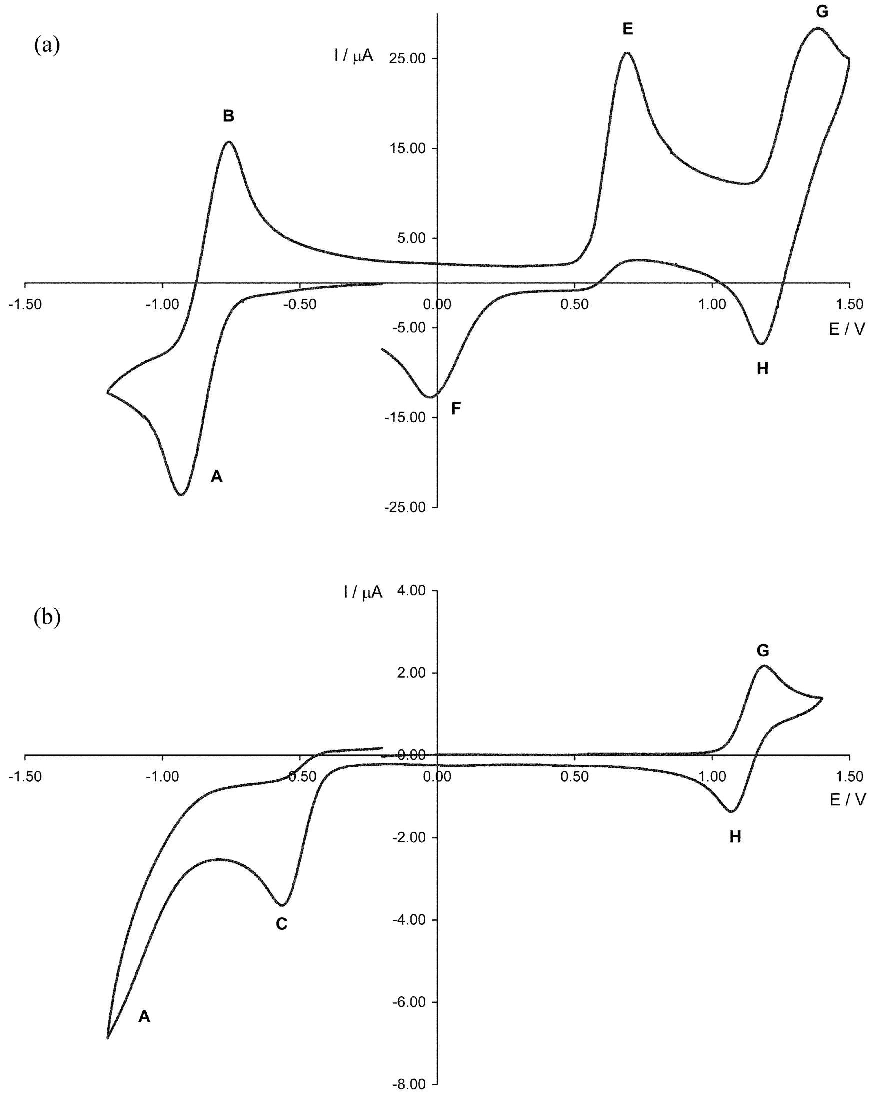


Fig. 5 Voltammetric profiles for (a) [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(PPh$_3$)}(μ$_3$-S)(μ$_3$-C$_2$S$_3$)], **2a**, and (b) [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)(PPh$_3$)}(μ$_3$-S)(μ$_3$-C$_2$S$_3$Me)]I, [**3a**]I.

are clearly due to the formation of the respective radical anions, *I*. There have been electrochemical studies on clusters having the general formula {Co(η-C$_5$H$_5$)}$_3$(μ$_3$-X)(μ$_3$-Y) where a Co$_3$ triangle is capped on one face by X (= O, S, Se, NSiMe$_3$, *etc.*) and on the other by Y (= CO, CS, S, Se, *etc.*) and they all have reduction electron transfers at similar potentials to $E^{0/-}$[**1a**] and $E^{0/-}$[**2a**].[22,23] This suggests that the unpaired electron is in a LUMO dominated by the Co(η-C$_5$H$_5$) groups; a proposal which is supported by an ESR spectrum of **2a**$^{\bullet -}$ which showed ill-defined hyperfine coupling to cobalt. Unfortunately, the ESR spectra were of poor quality even at 77 K despite the apparent stability of the radical anions on the electrochemical timescale. Upon methylation of the μ$_3$-CS ligand of **1a** to give [{Co(η^5-C$_5$H$_5$)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ$_3$-S)(μ$_3$-CSMe)]I, [**1a**Me]$^+$, or the exocyclic sulfur of the C$_2$S$_3$ ligand of **2a** to give [**3a**]$^+$, new one-electron reduction processes **C** giving species *V*, appear at E_p^c = −0.54 and −0.58 V for [**1a**Me]$^+$ and [**3a**]$^+$, respectively. [{Co(η^5-C$_5$H$_5$)}$_3$(μ$_3$-S)(μ$_3$-CSMe)]I also has this feature in its electrochemistry (Table 3). This one-electron step is chemically reversible for [**1a**Me]$^+$, but not for [**3a**]$^+$. Further reduction of *V* leads to decomposition products and multielectron processes at potentials > −1.0 V. The electron transfer step giving rise to *V* is attributed to reduction of the cationic CSMe or S$_2$CSMe moieties, the SOMO being an orbital having a high sulfur content; this infers that the canonical structure *B* in Fig. 4 has a significant contribution to the SOMO.

Oxidation processes. An interesting sequence of electron transfer steps is found in the oxidation electrochemistry of **2a** with its C$_2$S$_3$ ligand. Two anodic one-electron electron transfers **E** and **G** are seen at room temperature and scan rates 50 mV–1 V, Fig. 5(a). The first process **E** (E_p^a = 0.66 V) is irreversible and the radical cation *II*, [**2a**]$^+$, undergoes a fast EC process to form a new species giving rise to feature **F**; this species is oxidized back to **2a** at E_p^c = −0.20 V (Scheme 2). The current ratio i_F/i_E is ~0.5 and is independent of scan rate and temperature but varies with solvent; the potential is temperature-dependent. This is the classical EC profile for an oxidised species undergoing a structural rearrangement. In the anodic scan, **E** is followed by a chemically and electrochemically reversible one-electron couple **G/H** at E_p^o = 1.24 V. A crucial observation is that when exocyclic C=S group of **2a** is methylated, the species giving rise to **F** is no longer formed and the one-electron **G′/H′** couple is the only feature on the anodic scan of [**3a**]$^+$, Fig. 5(b).

Clearly, the structural changes that occur during the EC process cannot be too drastic, nor are **E** and **F** due to decomposition. Furthermore, the electrochemistry shows that the species formed in the fast EC process can be oxidised at **G** as well as the parent **2a**. A clue to the EC mechanism is provided by the work of Moses *et al.*[24] on the electrochemistry of organic cyclic trithiocarbonates, (T). They found that the monomeric radical cations T$^{+\bullet}$ coupled with unchanged T to give dimeric T$_2^{+\bullet}$. The current functions and potentials they reported are

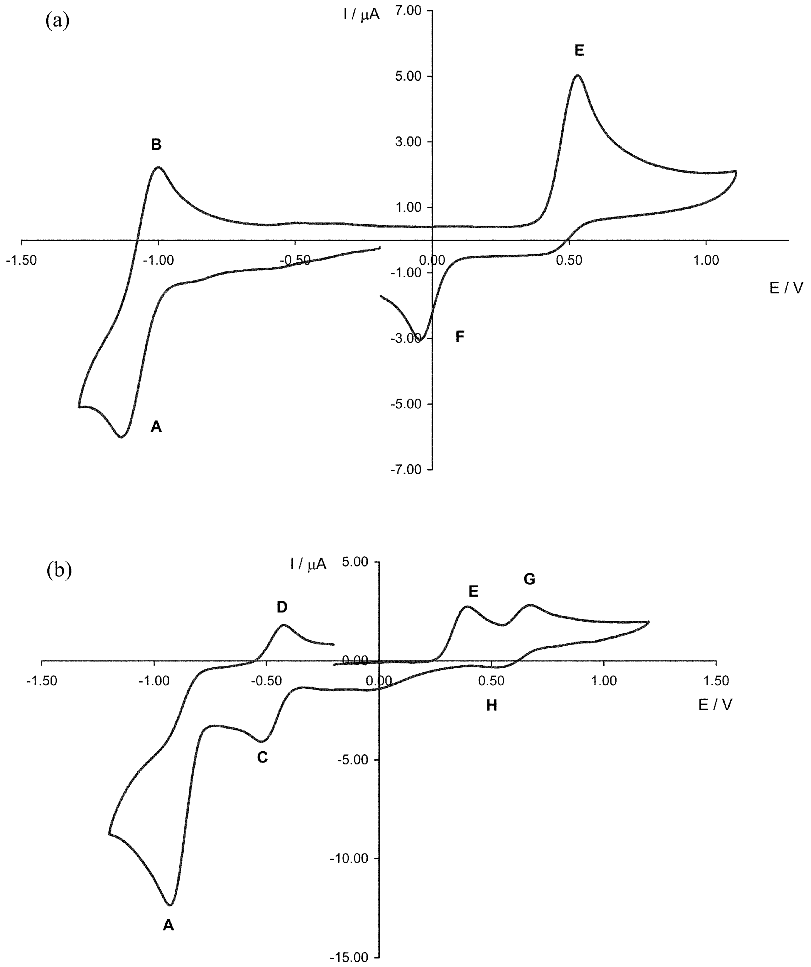
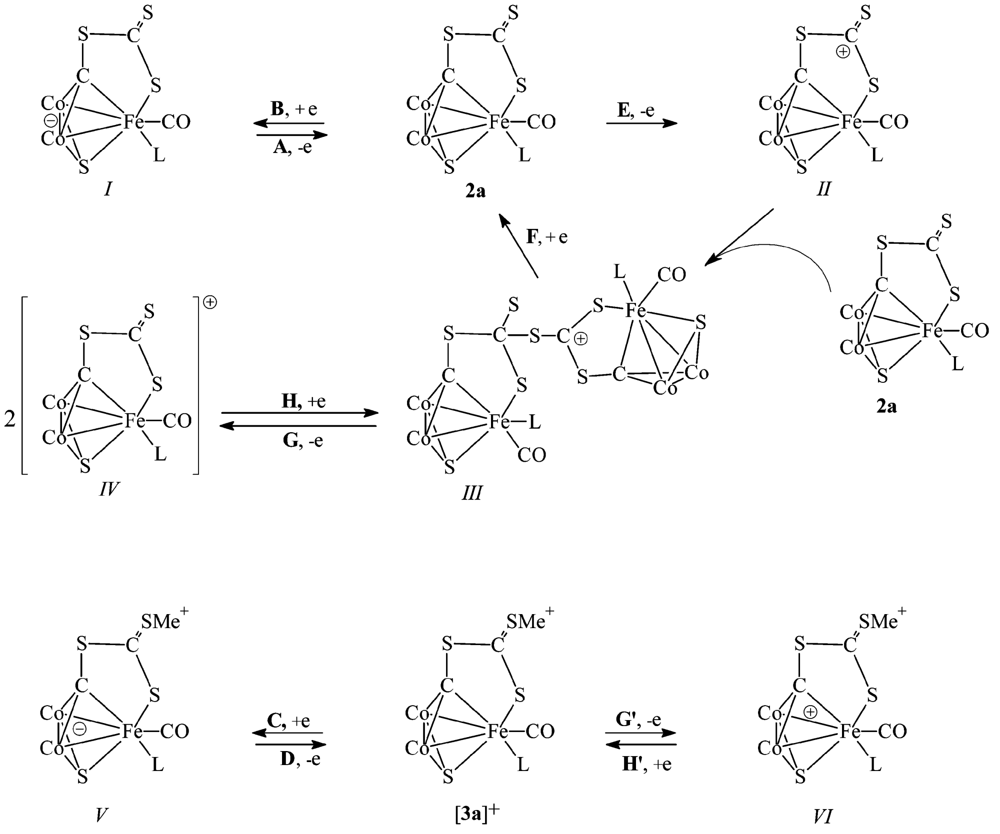


Fig. 6 Voltammetric profiles for (a) [{Co(η^5-C_5H_5)}$_2${Fe(CO)(PPh_3)}(μ_3-S)(μ_3-CS)], **1a**, and (b) [{Co(η^5-C_5H_5)}$_2${Fe(CO)(PPh_3)}(μ_3-S)(μ_3-CSMe)]I, [**1a**Me]I.



Scheme 2 (C_5H_5 ligands omitted for clarity; L = PPh_3.)

similar to those found for **2a** and we propose a similar EC mechanism (Scheme 2). The exocyclic sulfur of **2a** is a good nucleophile and is therefore capable of attacking the radical cation $\mathbf{2a}^{+\bullet}$ at the electrophilic carbon to give the dimer *III* shown in Scheme 2. Because the resultant $FeCS_2CSC(S^{\bullet})S_2CFe$ unit is positively charged, it is reduced at lower potentials (**F**) with cleavage of the S⟶C bond returning **2a** to the electrode surface. The one-electron oxidation **G** is assigned to the formation of the radical cation *IV* from the dimer where the unpaired electron is now in a SOMO largely located on the cluster framework. Overall, the oxidation of **2a** to *IV* is a two-electron transfer as two moles of **2a** are involved. In the case of $[\mathbf{3a}]^+$ the SMe group blocks the dimerisation process and a one electron oxidation **G** gives the radical dication $[\mathbf{3a}]^{2+}$, *VI*, in Scheme 2.

In order to gain more information on the species associated with processes **F** and **G** ν(CO) spectra were recorded during electrochemical (OTTLE) and chemical oxidation. Unfortunately, rapid fouling of the electrode occurred during the OTTLE measurement. Oxidation at 0.60 V gave a new broad ν(CO) band at 1967 cm^{-1} but this species was unstable and decomposed rapidly to another with ν(CO) 1871 cm^{-1}. Chemical oxidation of **2a** with $[(4\text{-}BrC_6H_4)_3N]^+SbCl_6^-$ gave a clean spectrum with a single ν(CO) band at 1951 cm^{-1}, a shift of 26 cm^{-1} from 1925 cm^{-1} for **2a**. As one would have expected a larger shift for a radical cation, it is possible that this spectrum is due to the dimer cation *III*. Under the same conditions, oxidation of $[\mathbf{3a}]^+$ by chemical or electrochemical means led to rapid decomposition.

The cyclic voltammetric responses at room temperature in the anodic direction for **1a** (Fig. 6) are similar to those seen for other $M_3(\mu_3\text{-}S)(\mu_3\text{-}CS)$ clusters, *e.g.* $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$.[22] A one-electron oxidation transfer **E** occurs at E_p^a = 0.50 V and this cation then undergoes a fast EC conversion (*cf.* **2a**) to another species which gives rise to wave **F**; this is then reduced back to original cation at $E_p^c = -0.02$ V. When its μ_3-CS ligand is methylated, [**1a**(Me)]I, this oxidation step is truncated and a new irreversible process **G′** is seen at E_p^a = 0.62 V; this is similar to the electrochemistry of $[\{Co(\eta^5\text{-}C_5H_5)\}_3(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$. The relative current ratio $i(\mathbf{E})/i(\mathbf{G'})$ is dependent on the scan rate and temperature confirming that **G′** is derived from **E**. With its similar electrochemistry to **2a** it is tempting to attribute the EC process for **1a** to a dimerisation reaction.

Conclusions

The fixation of CS_2 by $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(CO)(L)_2(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, **1**, gives $[\{Co(\eta^5\text{-}C_5H_5)\}_2\{Fe(L)_2(\mu_3\text{-}S)(\mu_3\text{-}C_2S_3)]$ complexes, **2**, in which a trithiocarbonate moiety SC(S)S bridges a Fe–C_μ edge of the trigonal bipyramidal $(\mu_3\text{-}C)FeCo_2(\mu_3\text{-}S)$ cluster. On the basis of structural and spectroscopic data it is concluded that the FeSC(S)SC heterocycle is best regarded as a metallovinyl trithiocarbonate or a metallo-1,3-dithiole-2-thione with a Fe–C_μ double bond.

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