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Journal of Organometallic Chemistry 551 (1998) 139–149

Journal of Organo metallic Chemistry

The cleavage of coordinated heterocumulenes. The reactions of $[Fe(CO)_2(PPh_3)_2(\eta\text{-SCY})]$ and their analogues with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ to give heteronuclear $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-S})(\mu_3\text{-CY})]$ $(Y = S \text{ or } SR^+)$ and related clusters [1]

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Received 21 May 1997

Abstract

The reaction of $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)]$ with two equivalents of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ gives $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-S})(\mu_3\text{-CS})]$ $(L = PPh_3)$ as the sole product in good yield. Under the same conditions, $[Fe(CO)_2(L)_2(\eta^2\text{-}CS_2Me)][SO_3CF_3]$ gives $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-S})(\mu_3\text{-CSMe})][SO_3CF_3]$. The PPh_3 ligand of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-S})(\mu_3\text{-CS})]$ $(L = PPh_3)$ may be replaced by $P(OPh)_3$ and $P(OMe)_3$ on UV photolysis to give the complexes where $L = P(OPh)_3$ and $P(OMe)_3$, but no isolable products were formed when L = CO, CNMe, PMe_3 or PBu^n_3. The three clusters react with RI and $ROSO_2CF_3$ (R = Me, Et or allyl) to give $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-S})(\mu_3\text{-CSR})]^+$ salts, and there is spectroscopic evidence for the formation of the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-S})(\mu_3\text{-CSMe}_2)]^{2+}$ cation. The molecular structures of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-S})(\mu_3\text{-CS})]$ and $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-S})\{\mu_3\text{-CSMe}\}][I]$ have been determined by X-ray diffraction methods, and shown to be based on a Co_2Fe triangle capped on one face by a μ_3-S ligand and on the other face by a μ_3-CS or $\mu_3\text{-CSMe}^+$ ligand acting as a two-electron donor to the cluster. In the salt there are two cations whose structures differ slightly. In general, bond lengths are normal, but those to iron are always longer than those to cobalt. © 1998 Elsevier Science S.A.

Keywords: Heterocumulenes; Heteronuclear; Ligands

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1. Introduction

In the presence of transition metal complexes, heterocumulenes X=C=Y (X, Y = O, S, NR) often undergo reactions which involve cleavage of CX or CY bonds. It has been proposed [1] that these reactions proceed via $M(\eta^2\text{-X=CY})$ derivatives which react (a) with excess XCY to give coordinated X_2CY and free or coordinated CY ligands, or with excess M to give coordinated CY and X ligands (M is a transition metal-based fragment). The products from route (a) are usually mononuclear complexes while those from route (b) are usually trinuclear clusters containing μ_3-CY and μ_3-X ligands. If the proposal for route (b) is correct, then preformed $M(\eta^2\text{-XCY})$ complexes may react with a different fragment M′ to give heteronuclear $MM'_2(\mu_3\text{-CY})(\mu_3\text{-X})$ clusters. Not only would this support the proposed reaction pathway, but it is also potentially useful because routes to complexes containing μ_3-CY ligands are not that common.

The first complex to contain a μ_3-CS ligand acting as a two-electron donor through carbon, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-S})(\mu_3\text{-CS})]$, was reported by Werner and Leonard [2] and Werner et al. [3]. Although other and more convenient routes to this and closely related derivatives (i.e., C_5H_5 replaced by MeC_5H_4) have been described [4], the only other compound to be reported which contains a μ_3-CS ligand appears to be $[Fe_4(CO)_{12}(S)(CS)]$ [5]. However, in this the CS ligand which caps the face of a Fe_3 triangle also bonds through

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[1] This paper is dedicated to Professor Peter Maitlis on the occasion of his 65th birthday.

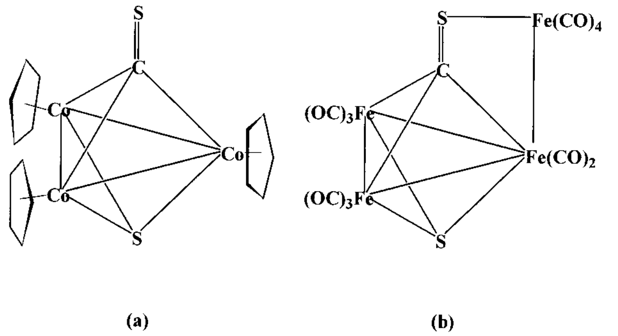

Fig. 1. The structures of: (a) $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ [2,3] and (b) $[Fe_4(CO)_{12}(S)(CS)]$ [5].

S to another $Fe(CO)_4$ moiety. Both molecules are illustrated in Fig. 1.

This paper describes the cleavage of two heterocumulenes, CS_2 and $C(S)SR^+$ in preformed $[Fe(CO)_2(L)_2(\eta^2\text{-}CS_2)]$ ($L = Ph_3P$ and $(PhO)_3P$) and $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2Me)][CF_3SO_3]$ complexes using $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ as source of the electron-deficient M′ fragment. The structures, spectra and some chemistry are reported for the products which contain μ_3-CS or $\mu_3\text{-}CSR^+$ (R = alkyl) ligands and have the general formulae $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CY)]$ (Y = S or SMe^+ and L = P(III) ligand). A preliminary report of part of this work has been published [6].

2. Experimental details

Previously published methods or extensions thereof were used to prepare the $[Fe(CO)_2(L)_2(\eta^2\text{-}CS_2)]$ complexes [7], $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2Me)][CF_3SO_3]$ [7], $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ [8], and $[Co(\eta\text{-}C_5H_4Me)(PPh_3)_2]$ [8]. Other chemicals were purchased.

Reactions were carried out under an atmosphere of nitrogen at room temperature in dried and deoxygenated solvents unless it is stated otherwise. They were monitored by infrared spectroscopy.

Elemental analyses (Table 1) were determined by the Analytical Laboratory of University College, Dublin. IR spectra (Table 1) were run on Perkin-Elmer 1710 and 1720 FTIR spectrometers and NMR spectra (Table 2) on a JEOL JNM-GX270 spectrometer.

2.1. Preparation of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$

$[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)]$ (1.0 g, 1.4 mmol) was added as a solid to a solution of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ (1.83 g, 2.82 mmol) in benzene (30 cm^3). The mixture was stirred for 16 h and filtered. The filtrate was chromatographed on alumina after its volume had been reduced to 8 cm^3. Hexane–dichloromethane (1:1) eluted unreacted $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)]$, dichloromethane eluted PPh_3, and dichloromethane–tetrahydrofuran

Table 1
Melting points, analyses and some IR data for the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ complexes and some of the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CSR)]X$ salts

L	R; $[X]^-$	M.p. (°C)[a]	Analyses[b]			IR spectra (cm^{-1})[c]	
			%C	%H	%S	ν(CO)	ν(CO)
$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$							
PPh_3		162–163	53.3 (53.3)	3.5 (3.6)	9.2 (9.2)	1934 (7)	1986 (10)[e]
PPh_3[d]		dec. 70	54.9 (54.6)	4.0 (4.0)	8.8 (8.8)	1932 (7)	1986 (10)
$P(OPh)_3$		154–155	50.1 (49.9)	3.5 (3.4)	8.5 (8.6)	1948 (6)	1996 (10)[f]
$P(OMe)_3$		149–150	34.2 (34.3)	3.6 (3.4)	11.5 (11.4)	1948 (6)	1996 (10)
$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CSR)]X$							
PPh_3	Me; $[SO_3CF_3]^-$	129–130	46.4 (45.9)	3.5 (3.3)	10.2 (11.1)	1959 (7)	2011 (10)
PPh_3	Et; $[I]^- \cdot 2CH_2Cl_2$[g]	97–98	41.0 (41.0)	3.5 (3.3)	6.8 (6.3)	1959 (8)	2009 (10)
PPh_3	allyl; $[I]^-$	dec. 160	46.8 (47.1)	3.4 (3.4)	7.4 (7.4)	1957 (8)	2011 (10)
PPh_3	$(HgCl_2)_2$	dec. 270	29.3 (30.0)	2.1 (2.0)	5.2 (5.2)	1968 (7)	2014 (10)
$P(OPh)_3$	Me; $[BPh_4]^-$	121–122	61.2 (62.2)	4.5 (4.4)	5.8 (5.9)	1981 (8)	2025 (10)
$P(OPh)_3$	Et; $[BPh_4]^-$	97–98	61.8 (62.5)	4.6 (4.6)	6.0 (5.9)	1981 (9)	2027 (10)
$P(OMe)_3$	Me; $[BPh_4]^-$	119–120	54.8 (55.0)	4.7 (4.7)	7.2 (7.2)	1975 (7)	2024 (10)
$P(OMe)_3$	Et; $[BPh_4]^-$	96–97	55.7 (55.5)	4.7 (4.8)	7.4 (7.0)	1979 (9)	2025 (10)

[a] Determined in sealed tubes; dec. = decomposition.

[b] Found (calculated).

[c] Peak positions with relative peak heights in parentheses; run in chloroform solution.

[d] C_5H_5 replaced by MeC_5H_4.

[e] $\nu(\mu_3\text{-}CS) = 1020\ cm^{-1}$ (KBr disc).

[f] $\nu(\mu_3\text{-}CS) = 1040,\ 1072\ cm^{-1}$.

[g] $2CH_2Cl_2$ of crystallization confirmed by ^1H NMR spectroscopy.

Table 2
NMR spectra of the complexes and some of the salts described in Section 3

L	R; $[X]^-$	Solvent	^{1}H resonances[a]			^{13}C resonances[a]			
			C_5H_5	L	R	C_5H_5	CO	L	R
$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$									
PPh_3		C_6D_6	4.52	7.1–7.8 (m)		88.4			
PPh_3[b]		C_6D_6	4.7 (m)	7.1–7.8 (m)					
$P(OPh)_3$		C_6D_6	4.34	7.1–7.8 (m)		88.3	215.7 (d, $J = 32.8$)	120–135	
$P(OMe)_3$[c]		C_6D_6	4.68	3.60 (d, $J = 11.9$)		88.65	215.9 (d, $J = 23.8$)	52.65 (d, $J = 3.4$)	
$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CSR)]X$									
PPh_3	Me; $[SO_3CF_3]^-$	CD_3CN	5.02	7.3–7.7 (m)	3.74	88.4	212.0 (d, $J = 20.5$)	129–135	33.9
PPh_3	Et; $[I]^-$	CD_3CN	5.03	7.4–7.8 (m)	4.35 (q) 1.93 (t, $J = 7.5$) 5.4 (d, J = 8.2), 6.9 (m), 4	88.4	212.0 (d, $J = 10.5$)	129–135	46.2, 13.6
PPh_3	$(HgCl_2)_2$	CD_3CN	5.07	7.4–7.7 (m)		87.9			
$P(OPh)_3$	Me; $[BPh_4]^-$	$(CD_3)_2CO$	4.90	6.7–7.6 (m)	3.70	88.9			
$P(OPh)_3$	Et; $[BPh_4]^-$	CD_3CN	4.75	6.7–7.6 (m)	4.01 (q) 1.77 (t, $J = 7.5$)	88.6		121–131	46.3, 13.9
$P(OMe)_3$	Me; $[BPh_4]^-$	CD_3CN	5.03	3.63 (d, $J = 11.9$)	3.65	88.1	210.5 (d, $J = 32.6$)	54.2 (d, $J = 6.8$)	34.1
$P(OMe)_3$	Et; $[BPh_4]^-$	$(CD_3)_2CO$	5.11	3.68 (d, $J = 11.9$)	4.20 (q) 1.79 (t, $J = 7.4$)	88.5	210.4 (d, $J = 30.7$)	54.4 (d, $J = 608$)	46.5, 14.0

[a] Chemical shifts given as ppm downfield from Me_4Si as an internal standard. All resonances are singlets unless it is stated otherwise. In parentheses, d = doublet, t = triplet, q = quartet, m = multiplet, coupling constants J in Hertz. For ^{1}H NMR spectra, integrations are as required by formulae. Where relevant, spectra show resonances due to $[BPh_4]^-$ anion at e.g., 6.84, 7.00 and 7.27 ppm (^{1}H spectra in CD_3CN solution) and 122.3, 126.0, 126.1 and 137.0 ppm (^{13}C spectra in $(CD_3)_2CO$).
[b] C_5H_5 replaced by MeC_5H_4 for which δ Me = 2.35 ppm (^{1}H spectra). Complex too unstable for ^{13}C NMR spectrum to be obtained.
[c] ^{13}C NMR spectrum run in $(CD_3)_2CO$ solution.

eluted the product. The solvent was removed at reduced pressure, and the residue crystallized from tetrahydrofuran–hexane or ethanol–ether mixtures to give dark green crystals of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ in 70% yield.

If $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ is replaced by $[Co(\eta\text{-}C_5H_4Me)(PPh_3)_2]$, a similar procedure gives $[\{Co(\eta\text{-}C_5H_4Me)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)$ as an unstable green solid in 50% yield.

If $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)]$ is replaced by $[Fe(CO)_2\{P(OPh)_3\}_2(\eta^2\text{-}CS_2)]$, a similar procedure gives a ca. 1:1 mixture of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ where $L = PPh_3$ and $P(OPh)_3$. They were not separated, but were identified by spectroscopic techniques.

$[Fe(CO)_2(L)_2(\eta^2\text{-}CS_2)]$ where $L = PMe_3$ or PBu^n_3 did not react with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ under the above conditions, and when L = CNMe, a black unidentifiable precipitate was formed.

If $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)]$ is replaced by $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2Me)][SO_3CF_3]$ (1 g, 1.14 mmol), the reaction with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ (1.47 g, 2.28 mmol) in benzene (30 cm^3) gives a green-brown precipitate. After 2 h, it was filtered off and recrystallized from tetrahydrofuran–hexane mixtures to give green-brown crystals of $[(Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)][SO_3CF_3]$ in 70% yield.

2.2. Phosphine substitution reactions of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$

A solution of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ (0.25 g, 0.36 mmol) and $P(OPh)_3$ (0.56 g, 1.8 mmol) in chloroform (20 cm^3) was irradiated with a Philips HPR 125 W UV lamp until reaction was completed (ca. 2 h). The solution was filtered and chromatographed on alumina after its volume was reduced to 3 cm^3. Unreacted $P(OPh)_3$ and PPh_3 were eluted with dichloromethane. A green band was eluted with tetrahydrofuran. Removal of the solvent and recrystallization of the residue from tetrahydrofuran–hexane mixtures gave dark green crystals of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ in 80% yield.

If $P(OPh)_3$ is replaced by $P(OMe)_3$, the same procedure gave $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(P(OMe)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ in 85% yield.

Under the same conditions, $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ gave decomposition products with PMe_3, PBu^n_3, CNMe or CO.

2.3. Reactions of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ with alkyl iodides, alkyl trifluoromethanesulphonates and related reagents

MeI (0.5 g, 3.6 mmol) was added to a solution of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ (0.25 g, 0.36 mmol) in benzene (20 cm^3). After 2 h, a black precipitate formed. It was filtered off, and washed with benzene and hexane. It was identified as $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$ and required no further purification. The same procedure was used to prepare $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSEt)]I$, $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSC_3H_5)]I$ (C_3H_5 = allyl), $[\{Co(\eta\text{-}$

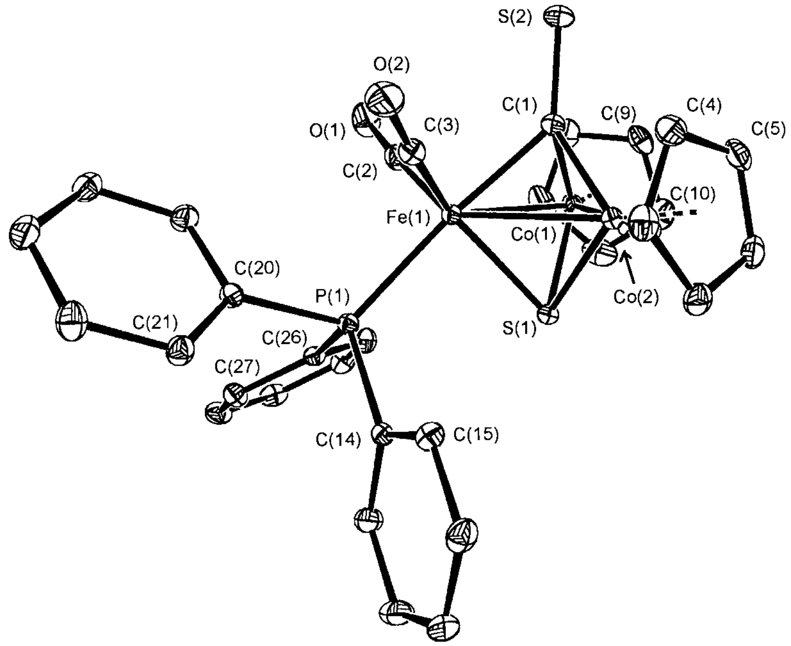

Fig. 2. Molecular structure and atom labelling of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$.

$C_5H_5)\}_2\{Fe(CO)_2(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$, $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(P(OPh)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSEt)]I$, $[\{Co(\eta\text{-}C_5H_5)\}_2(Fe(CO)_2(P(OMe)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$, and $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(P(OMe)_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSEt)]I$ which were further purified by recrystallization from dichloromethane–hexane mixtures. Yields were 70%–80%.

If MeI is replaced by $MeOSO_2CF_3$ or $EtOSO_2CF_3$, the reactions with $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ are virtually instantaneous. The $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSR)][SO_3CF_3]$ complexes were isolated and purified as described above, but when $L = P(OPh)_3$ or $P(OMe)_3$ the products were oils, so they were dissolved in a saturated solution of $Na[BPh_4]$ in ethanol (15 cm^3). After 20 min, the black precipitates were filtered off, washed with ethanol and dried. The $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CSR)][BPh_4]$ (R = Me or Et) thus obtained required no further purification.

$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ (0.3 g, 0.43 mmol) was dissolved in benzene (20 cm^3) and $HgCl_2$ (0.12 g, 1.3 mmol) added. The mixture was stirred for 3 h. The black precipitate was filtered off, washed with benzene then hexane and dried. It analysed as $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS \cdot Hg_2Cl_4)]$ without further purification (yield of 45%).

2.4. The structure of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$

The crystal was grown from a tetrahydrofuran–hexane mixture, and the data collected on a Enraf-Nonius CAD4F diffractometer. The structure was solved by direct methods, SHELXS-86 [9], and refined by full-matrix least squares using SHELXL-93 [10]. Data were corrected for Lorentz and polarisation effects but not for absorption.Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. Nonhydrogen atoms were refined anisotropically. All calculations were performed on a VAX 6610 computer. The ORTEX program [11] was used to obtain the drawings (Figs. 2 and 5). The crystal data is given in Table 3, and selected bond angles and lengths in Table 4. Supplementary material includes a complete list of bond lengths and bond angles, atom positions, thermal parameters, and observed and calculated structure factors.

2.5. The structure of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$

The crystal was grown from dichloromethane–hexane mixtures. It was subjected to an X-ray diffraction study.

Table 3
Crystal data and structure refinement for (a) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ and (b) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$

Complex	a	b
Empirical formula	$C_{31}H_{25}Co_2FeO_2PS_2$	$C_{32}H_{28}Co_2FeIO_2PS_2$
Formula weight	698.31	840.24
Temperature	293(2) K	293(2) K
Wavelength	0.71069 Å	0.71069 Å
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions	$a = 9.4550(10)$ Å	$a = 13.276(2)$ Å, $\alpha = 112.600(10)°$
	$b = 23.161(2)$ Å, $\beta = 95.24(2)°$	$b = 16.881(2)$ Å, $\beta = 104.100(10)°$
	$c = 13.119(2)$ Å	$c = 17.228(2)$ Å, $\delta = 105.800(10)°$
Volume	2860.9(6) $Å^3$	3155.3(7) $Å^3$
Z	4	4
Density (calculated)	1.621 mg m^{-3}	1.769 mg m^{-3}
Absorption coefficient	1.876 mm^{-1}	2.683 mm^{-1}
$F(000)$	1416	1664
Crystal size	0.2 × 0.2 × 0.35 mm	0.28 × 0.32 × 0.35 mm
θ range for data collection	2.33 to 29.96°	2.22 to 27.97°
Index ranges	$0 \le h \le 10$; $0 \le k \le 24$; $-14 \le l \le 14$	$0 \le h \le 16$; $-22 \le k \le 21$; $-22 \le l \le 22$
Reflections collected	6639	18 433
Independent reflections	6229 [R (int) = 0.0081]	14 935 [R (int) = 0.0413]
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	6229/0/352	14 935/0/736
Goodness-of-fit on F^2	0.434	0.671
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0257$, $wR_2 = 0.0731$	$R_1 = 0.1020$, $wR_2 = 0.2692$
R indices (all data)	$R_1 = 0.0393$, $wR_2 = 0.0909$	$R_1 = 0.1119$, $wR_2 = 0.2887$
Largest difference of peak and hole	0.238 and −0.335 $eÅ^{-3}$	2.169 and −2.187 $eÅ^{-3}$

R indices: $R_1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$ (based on F), $wR_2 = [[\Sigma_w(|F_o - F_c|)^2|]/[\Sigma_w(|F_o|)^2]]^{1/2}$ (based on F^2).
$w = q/[(\sigma F_o)^2 + (a \cdot P)^2 + b \cdot P + d + e\sin(\theta)]$.
Goodness-of-fit $= [\Sigma_w(|F_o^2| - |F_c^2|)^2/(\text{Nobs' } N \text{ parameters})]^{1/2}$.

Data was collected and the structure solved as described in Section 2.4. One of the cyclopentadienyl rings is disordered (C(10)–C(14)) over two sites each of which is 50% occupied. The high R_1 value is probably due to the observed disorder which, despite satisfactory relative site occupancy and thermal parameters for the disordered ring, may affect the rest of the structure. Hydrogen atoms were included in calculated positions on all carbon atoms except those of the disordered cyclopentadienyl ring. The ORTEX program [11] was used to obtain the drawings, Figs. 3–6. The crystal data is given in Table 3, and selected bond angles and lengths in Table 4. Supplementary material includes a complete list of bond lengths and bond angles, atom positions, thermal parameters, and observed and calculated structure factors.

3. Results and discussion

The reaction of $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)]$ with two equivalents of $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ in benzene solution at room temperature gave a high yield of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ as the only metal-containing product. This is a green crystalline air-stable solid which is soluble in most organic solvents to give moderately air-sensitive solutions. Its MeC_5H_4 counterpart has been prepared similarly, but it is much less stable and decomposes spontaneously even in the absence of air. A similar difference in thermal stability has been observed between $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)]$ and $[Co_3(\eta\text{-}MeC_5H_4)_3(\mu_3\text{-}S)(\mu_3\text{-}CNPh)]$ [1].

When $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CS_2)]$ is replaced by $[Fe(CO)_2\{P(OPh)_3\}_2(\eta^2\text{-}CS_2)]$ the reaction with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ gives a mixture of two $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2L\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ products, one where L = PPh_3 and the other where L = $P(OPh)_3$. This is attributed to the lability of L = $P(OPh)_3$ and PPh_3 in $[Fe(CO)_2(L)_2(\eta^2\text{-}CS_2)]$ complexes as liberated PPh_3 replaces $P(OPh)_3$ from unreacted $[Fe(CO)_2\{P(OPh)_3\}_2(\eta^2\text{-}CS_2)]$ [7]. In contrast, $[Fe(CO)_2(L)_2(\eta^2\text{-}CS_2)]$ where L = PMe_3 or PBu^n_3 failed to react with $[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ while when L = CNMe a reaction took place but the product could not be identified.

$[Co(\eta\text{-}C_5H_5)(PPh_3)_2]$ also reacts with $[Fe(CO)_2(PPh_3)_2(\eta^2\text{-}CSSMe)][SO_3CF_3]$ with cleavage of the coordinated C–S bond to give the salt $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)][SO_3CF_3]$ in good yield. This may also be prepared by alkylating $[\{Co(\eta\text{-}C_5H_5)\}_2(Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ with $MeOSO_2CF_3$ (see below).

$[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ reacted with $P(OPh)_3$ or $P(OMe)_3$ on UV irradiation but not in the dark to give good yields of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ (L = $P(OPh)_3$ or $P(OMe)_3$). However under the same conditions PMe_3,

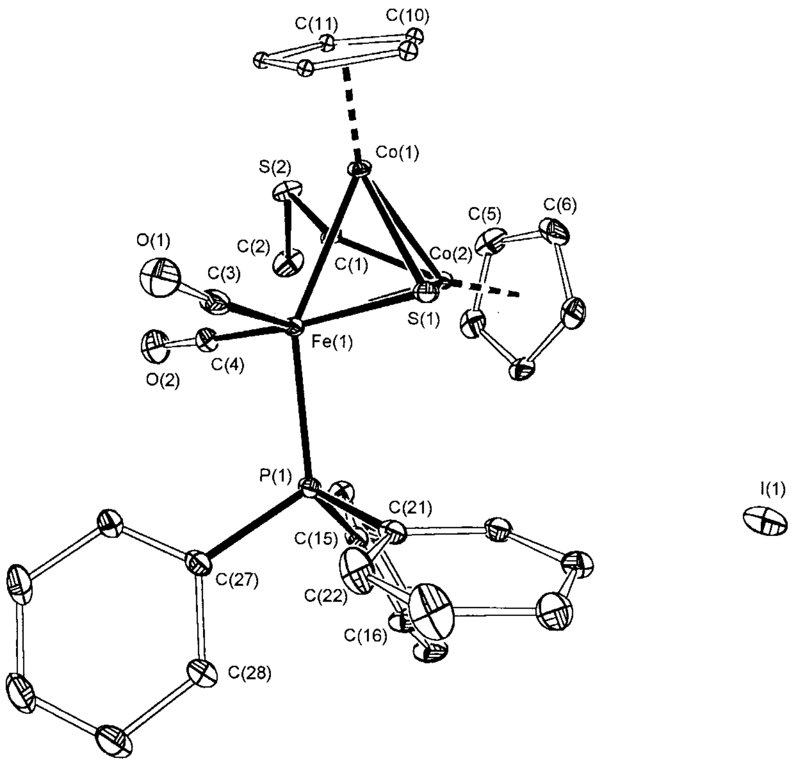

Fig. 3. Molecular structure and atom labelling of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$, cation 1.

PBu^n_3, CO or CNMe gave black decomposition products which contained no CO ligands.

As a consequence of back-bonding into the C–S π^* orbitals, the S atom of a μ_3-CS ligand would be expected to be nucleophilic and to form adducts with electrophiles. Thus, the reactions of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ with RI (R = Me, Et or allyl) or $ROSO_2CF_3$ (R = Me or Et) gave 1:1 adducts. The disappearance of absorption bands due to the ν(CS) vibration of the cluster on formation of these adducts suggests that it is reasonable to formulate them as $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CSR)]X$ salts containing a CS–R bond which are analogous to the known $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CS\text{–}E)]$ adducts where E is an electrophile or electron-deficient moiety such as $Cr(CO)_5$ [2–4]. The counter-anion X^- is I^-, $[SO_3CF_3]^-$ or, after anion exchange, $[BPh_4]^-$. These green-brown solid salts are air-stable solids soluble in polar solvents to give slightly air-sensitive solutions.

If the alkylation of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ is carried out in chloroform solution using a very high concentration of $MeOSO_2CF_3$, there is spectroscopic evidence (see below) for the formation of a 1:2 adduct which is probably best formulated as $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe_2)][SO_3CF_3]_2$

Table 4
Selected bond lengths and angles for (a) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$, (b) cation 1 of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$ and (c) cation 2 of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]I$

Complexes					
a		b		c	
Bond lengths (Å)					
Co(1)–Co(2)	2.4378(5)	Co(1)–Co(2)	2.4273(12)	Co(4)–Co(3)	2.4157(12)
Co(1)–Fe(1)	2.5099(6)	Co(1)–Fe(1)	2.4771(11)	Co(3)–Fe(2)	2.5025(12)
Co(2)–Fe(1)	2.5061(6)	Co(2)–Fe(1)[a]	2.5574(13)	Co(4)–Fe(2)[a]	2.5202(13)
Co(1)–C(1)	1.910(3)	Co(1)–C(1)	1.875(6)	Co(4)–C(101)	1.887(6)
Co(2)–C(1)	1.922(3)	Co(2)–C(1)	1.870(6)	Co(3)–C(101)	1.892(7)
Fe(1)–C(1)	2.085(2)	Fe(1)–C(1)	1.987(6)	Fe(2)–C(101)	1.957(6)
Co(1)–S(1)	2.1266(7)	Co(1)–S(1)	2.136(2)	Co(4)–S(3)	2.119(2)
Co(2)–S(1)	2.1370(7)	Co(2)–S(1)	2.128(2)	Co(3)–S(3)	2.146(2)
Fe(1)–S(1)	2.1925(7)	Fe(1)–S(1)	2.192(2)	Fe(2)–S(3)	2.185(2)
Fe(1)–C(2)	1.764(3)	Fe(1)–C(3)	1.775(8)	Fe(2)–C(103)	1.782(8)
Fe(1)–C(3)	1.764(3)	Fe(1)–C(4)	1.784(9)	Fe(2)–C(104)	1.784(7)
Fe(1)–P(1)	2.353(7)	Fe(1)–P(1)	2.273(2)	Fe(2)–P(2)	2.276(3)
C(2)–O(1)	1.147(3)	C(3)–O(1)	1.137(11)	C(103)–O(101)	1.141(10)
C(3)–O(2)	1.148(4)	C(4)–O(2)	1.149(11)	C(104)–O(102)	1.140(9)
C(1)–S(2)	1.638(3)	C(1)–S(2)	1.728(7)	C(101)–S(4)	1.723(6)
		C(2)–S(2)	1.790(10)	C(102)–S(4)	1.803(10)
Bond angles (degrees)					
Co(2)–Co(1)–Fe(1)	60.84(2)	Co(2)–Co(1)–Fe(1)	64.84(4)	Co(3)–Co(4)–Fe(2)	60.88(4)
Co(1)–Co(2)–Fe(1)	61.001(14)	Co(1)–Co(2)–Fe(1)	59.53(3)	Co(4)–Co(3)–Fe(2)	61.62(4)
Co(1)–Fe(1)–Co(2)	58.15(2)	Co(1)–Fe(1)–Co(2)	57.62(3)	Co(4)–Fe(2)–Co(3)	57.49(3)
S(2)–C(1)–Co(1)	133.3(2)	S(2)–C(1)–Co(1)	122.5(3)	S(4)–C(101)–Co(4)	132.9(4)
S(2)–C(1)–Co(2)	133.0(2)	S(2)–C(1)–Co(2)	133.3(4)	S(4)–C(101)–Co(3)	125.8(3)
S(2)–C(1)–Fe(1)	133.8(2)	S(2)–C(1)–Fe(1)	136.5(4)	S(4)–C(101)–Fe(1)	135.2(4)
Co(1)–S(1)–Co(2)	69.75(2)	Co(1)–S(1)–Co(2)	69.39(6)	Co(4)–S(3)–Co(3)	68.98(5)
Co(1)–S(1)–Fe(1)	71.04(2)	Co(1)–S(1)–Fe(1)	69.82(6)	Co(4)–S(3)–Fe(2)	71.65(6)
Co(2)–S(1)–Fe(1)	70.73(3)	Co(2)–S(1)–Fe(1)	72.59(6)	Co(3)–S(3)–Fe(2)	70.57(5)
C(1)–Co(1)–S(1)	93.98(8)	C(1)–Co(1)–S(1)	90.8(2)	C(101)–Co(4)–S(3)	91.4(2)
C(1)–Co(2)–S(1)	93.29(8)	C(1)–Co(2)–5(1)	91.2(2)	C(101)–Co(3)–S(3)	90.4(2)
C(1)–Fe(1)–S(1)	87.36(8)	C(1)–Fe(1)–S(1)	86.3(2)	C(101)–Fe(2)–S(3)	87.6(2)
C(2)–Fe(1)–C(3)	97.75(14)	C(3)–Fe(1)–C(4)	94.7(5)	C(103)–Fe(2)–C(104)	102.7(4)
C(2)–Fe(1)–P(1)	95.93(9)	C(3)–Fe(1)–P(1)	97.3(3)	C(103)–Fe(2)–P(2)	91.3(2)
C(3)–Fe(1)–P(1)	94.12(9)	C(4)–Fe(1)–P(1)	93.8(3)	C(104)–Fe(2)–P(2)	89.0(2)
C(1)–Fe(1)–P(1)	174.14(7)	C(1)–Fe(1)–P(1)	140.1(2)	C(101)–Fe(2)–P(2)	170.2(2)
C(1)–Fe(1)–C(2)	127.38(11)	C(1)–Fe(1)–C(3)	122.6(3)	C(101)–Fe(2)–C(103)	97.5(3)
C(1)–Fe(1)–C(3)	86.38(12)	C(1)–Fe(1)–C(4)	83.1(4)	C(101)–Fe(2)–C(104)	85.0(3)
C(2)–Fe(1)–S(1)	127.38(11)	C(3)–Fe(1)–5(1)	93.2(3)	C(103)–Fe(2)–S(3)	125.5(3)
C(3)–Fe(1)–S(1)	134.38(10)	C(4)–Fe(1)–S(1)	169.1(3)	C(104)–Fe(2)–S(3)	131.8(3)
P(1)–Fe(1)–S(1)	88.13(3)	P(1)–Fe(1)–S(1)	92.78(7)	P(2)–Fe(2)–S(3)	90.71(6)
		C(1)–S(2)–C(2)	107.7(4)	C(101)–S(4)–C(102)	104.2(3)

[a] Eclipsed Fe–Co bonds in cations (see Section 3.2).

by analogy with the related $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CN(H)(Me)Et)]^{2+}$ salts [1].

The only other Lewis acid which was investigated was $HgCl_2$ which with $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ gave $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSHg_2Cl_4)]$. The frequencies of its ν(CO) vibrations suggest that although it is a 1:2 adduct, it contains only one CS–Hg bond and not two. In a related reaction, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ gave a 1:1 adduct, $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CSHgCl_2)]$ [4].

3.1. Spectroscopic data

The infrared spectra of the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ complexes show a number of absorption bands due to the $\eta\text{-}C_5H_5$ and L ligands, and two due to the ν(CO) vibrations of their $Fe(CO)_2(L)$ moieties (Table 1). These lie at 1934 and 1986 cm^{-1} ($CHCl_3$ solution) when $L = PPh_3$. As expected, when $L = P(OPh)_3$ or $P(OMe)_3$ they lie at higher frequencies, i.e., ca. 1948 and 1996 cm^{-1}. In the KBr disc spectra of the clusters where $L = PPh_3$ and $P(OPh)_3$ there are respectively one (1020 cm^{-1}) and two (1040 and 1072 cm^{-1}) absorption bands of moderate intensities in the 1000–1100 cm^{-1} region which disappears on alkylation with RI. Their frequencies compare with those of two bands 1039 and 1075 cm^{-1} in the spectrum of $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ [2–4] and they are attributed to the ν(CS) vibration of the μ_3-CS ligands of the various clusters, but it is not clear why there should be two absorption bands for some compounds when only one would be expected. When $L = P(OMe)_3$ the ν(CS) band could not be identified.

The ν(CO) vibrations of the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CSR)]^+$ salts have frequencies which are ca. 25–35 cm^{-1} higher than those of their $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ precursors. This is because the $\mu_3\text{-}CSR^+$ ligand would be expected to be a better π-acceptor than μ_3-CS and, consequently, reduce the back-bonding to the CO ligands in the molecule. The IR spectra of these salts do not contain absorption bands in the 1000–1100 cm^{-1} region due to the ν(CS) mode of the μ_3-CS ligand, but it has not proved possible to identify any bands due to the two ν(CS) modes of the μ_3-CSR ligand.

The ν(CO) bands of the second species formed on reaction of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ with excess $MeOSO_2CF_3$ have frequencies of 1979 and 2031 cm^{-1}, 20 cm^{-1} greater than those of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)][SO_3CF_3]$. This implies strongly that it is a dication, probably containing a $\mu_3\text{-}CSMe_2^{2+}$ ligand (see above).

On the other hand, the ν(CO) vibrations of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)] \cdot 2HgCl_2$ have frequencies close to those of the $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$ cation. Therefore, it probably contains one μ_3-CS–Hg bond and not two (see Section 3).

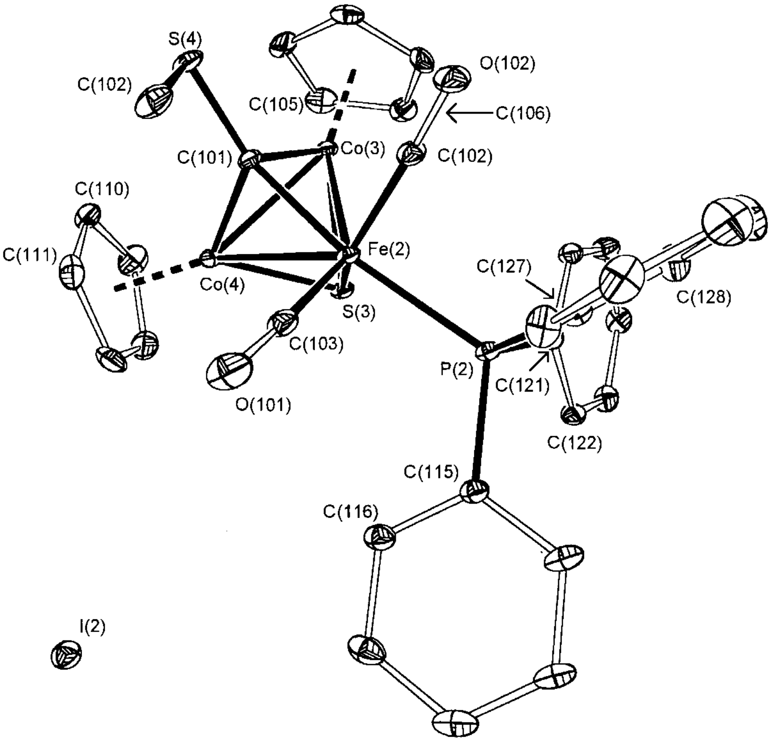

Fig. 4. Molecular structure and atom labelling of $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$, cation 2.

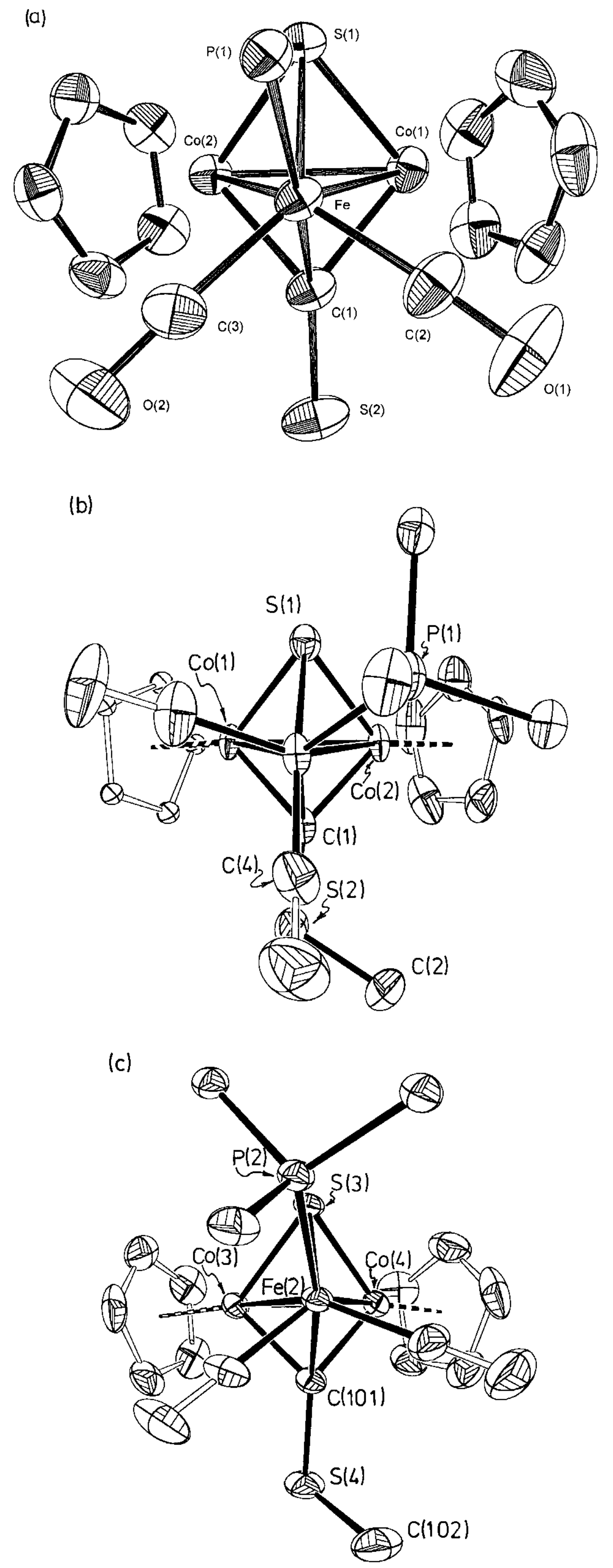

Fig. 5. The structures of: (a) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CS)]$; (b) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$, cation 1; (c) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$, cation 2, when viewed along an axis from Fe to the midpoint of the Co–Co bond perpendicular to the $FeCo_2$ plane.

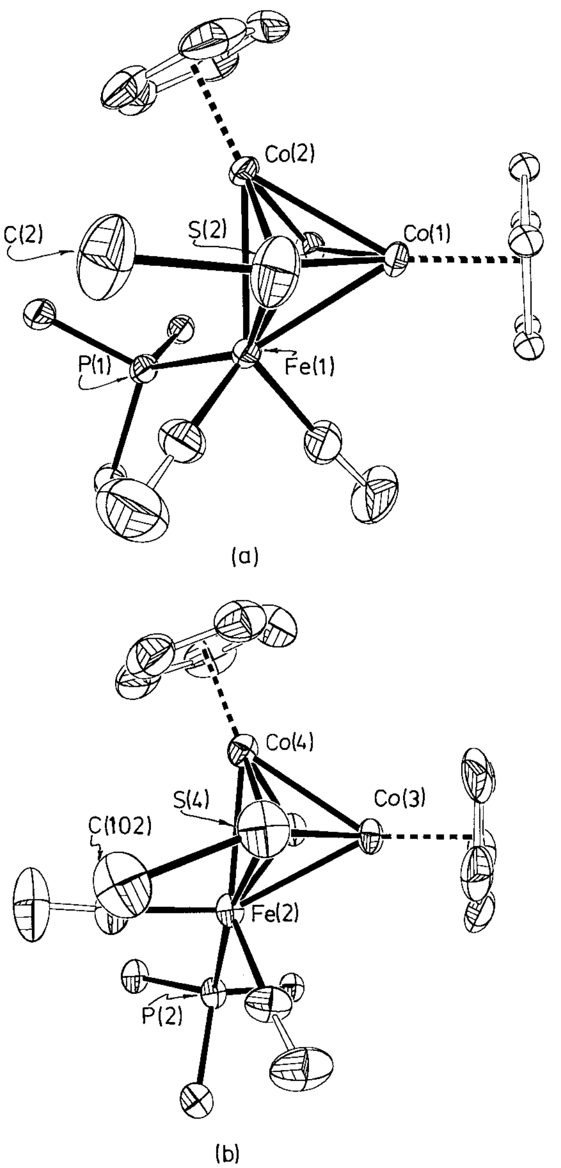

Fig. 6. The structures of (a) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$, cation 1; (b) $[\{Co(\eta\text{-}C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3\text{-}S)(\mu_3\text{-}CSMe)]^+$, cation 2, when viewed along an axis perpendicular to the $FeCo_2$ plane.

The ^1H NMR spectra of the neutral clusters and the salts are unremarkable and show resonances appropriate to the $\eta\text{-}C_5H_5$ and L ligands of all compounds, the R group of the cations, and the $[BPh_4]^-$ anion where it is present (Table 2). The ^{13}C NMR spectra were much more difficult to obtain due to the relative instability of the neutral compounds and the relatively low solubilities of the salts. The singlets due to the C_5H_5 ligands were always observed as, in many cases, were the resonances due to the CO and PPh_3, $P(OPh)_3$ or $P(OMe)_3$ ligands, and the group R. Where they were observed, the first were invariably doublets due to $^{31}P–^{13}C$ coupling. However, the ^{13}C resonances due to the μ_3-CS and μ_3-CSR^+ ligands have not been detected. This is not surprising as they are quaternary carbon atoms which would be expected to have long relaxation times and, therefore, weak resonances.

The ^1H NMR spectrum of $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CS)]$ is independent of temperature between −30 and +60°C. The single $\eta-C_5H_5$ resonance in the spectra of all $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3-S)(\mu_3-CS)]$ indicates that in solution the clusters retain the mirror-plane of symmetry found in the solid state or that rotation of the $Fe(CO)_2(L)$ moiety is fast on the NMR time scale even at −30°C. The spectra of the $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3-S)(\mu_3-CSR)]^+$ also show a single $\eta-C_5H_5$ resonance, and when R = Me, a single CH_3 resonance or, when R = Et, a conventional triplet/quartet for CH_3 and CH_2 protons. As the C–S–R moiety is nonlinear (see Section 3.2), this implies that the rotation of the $Fe(CO)_2(L)$ moiety and inversion at S of μ_3-CSR are fast on the NMR time scale. The presence of two structurally distinct cations in the unit cell of solid matter $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(L)\}(\mu_3-S)(\mu_3-CSMe)]I$ (see Section 3.2) is consistent with this suggestion.

3.2. The structures of [{Co(η-C₅H₅)}₂{Fe(CO)₂(PPh₃)}(μ₃-S)(μ₃-CS)] and [{Co(η-C₅H₅)}₂{Fe(CO)₂(PPh₃)}(μ₃-S)(μ₃-CSMe)]I

The molecular structure and atom labelling of $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CS)]$ are illustrated in Figs. 2 and 5. Selected bond lengths and bond angles are listed in Table 4. The crystal of the salt contains well-separated I^- anions and two different $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CSMe)]^+$ cations. The structures of the latter and their atom labelling are illustrated in Figs. 3–6. Selected bond lengths and bond angles are listed in Table 4.

The three clusters have structures which are similar but different in detail. They are based on a $FeCo_2$ triangle capped on one face by a μ_3-S and on the other by the C atom of a μ_3-CS or μ_3-$CSMe^+$ ligand, bonding more or less equally to all three metal atoms. Each Co atom is also η^5-bonded to a C_5H_5 ligand which has its centroid lying more or less in the $FeCo_2$ plane. The coordination polyhedron about Fe is completed by three terminal ligands, one PPh_3 and two CO, in a *cis*-$Fe(CO)_2(PPh_3)$ arrangement. In both cations the triply-bridging C–S–Me ligand is bent at S. When the cations are viewed along the perpendicular to the Co_2Fe plane (Fig. 6), it can be seen that the S–Me bond lies over a Fe–Co bond; more or less centrally so in cation 1 but oriented towards the Fe atom in cation 2.

In $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CS)]$ the $Fe(CO)_2(PPh_3)$ moiety is oriented such that P–Fe–Cμ is almost linear with an angle of 174°. The molecule almost possesses a plane of symmetry which bisects the Co–Co bond and includes Fe, P, C(1), S(1) and S(2) (Fig. 5). The two Co–Fe bonds are almost equal, 2.5099(6) and 2.5061(6) Å, and longer than the Co–Co bond, 2.4378(5) Å. It is noticeable that the bonds from C(1) and S(1) to Fe are also longer than those to the two Co atoms which are similar. Furthermore, the Fe–C bond to μ_3-CS is ca. 0.3 Å longer than those to *t*-CO. As $Fe(CO)_2(L)$ is isolobal with $Co(\eta-C_5H_5)$, this structure and those of the two cations may be compared with those of related 48-electron clusters of the general type $[Co_3(\eta-C_5H_5)_3(\mu_3-X)(\mu_3-CY)]$ (X or Y = O, NR, or S [12–14]) where the Co–Co bond lengths are dependent on the size of the μ_3-X ligand. In $[Co_3(\eta-C_5H_5)_3(\mu_3-S)(\mu_3-CS)]$ where X = S, they are 2.43–2.44(1) Å [2,3].

The $Fe(CO)_2(PPh_3)$ moiety is oriented differently in the two cations. Cation 2 has a conformation which is very similar to that of $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CS)]$ with P(2) almost lying on the plane which includes S(4), C(101), Fe(2) and S(3) and an almost linear P(2)–Fe(2)–C(101) (170.2(2)°) (Fig. 5). In cation 1 the $Fe(CO)_2(PPh_3)$ moiety has been rotated through 60° (Fig. 5) so that one Fe–Co bond differs from the other, i.e., Fe(1)–Co(1) is *trans* and Fe(1)–Co(2) is *cis* to PPh_3 (Fig. 3).

The bent μ_3-C–S–R^+ ligands in the cations might be expected to distort the $FeCo_2$ triangle in the same way that the bent μ_3-CNR ligand distorts the Co_3 triangle in the related complex $[Co_3(\eta-C_5H_5)_3(\mu_3-S)(\mu_3-CNTy)]$ (Ty = *p*-MeC_6H_4) with an increase in the length of the M–M bond which is eclipsed by R [15]. In cation 2 it does because the eclipsed Fe(2)–Co(4) is the longer by 0.0177 Å, but the effect is small compared to that observed in $[Co_3(\eta-C_5H_5)_3(\mu_3-S)(\mu_3-CNTy)]$, 0.088 Å. However, a much larger difference is found in cation 1 (0.0803 Å), but this may be due to the differing environments of the two Fe–Co bonds (see above).

Replacing μ_3-CS by the stronger π-acceptor μ_3-$CSMe^+$ ligand does not greatly change the bonding within the Co_2FeS part of the cluster. The sums of the metal–metal bond lengths and metal–sulphur bond lengths are respectively 7.4564 Å and 6.4561 Å in $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CS)]$, 7.4618 Å and 6.456 Å in cation 1, and 7.4384 Å and 6.450 Å in cation 2. However, the metal–carbon distances appear to be significantly shortened, perhaps due to increased metal–carbon π-bonding. Their sum is reduced from 5.917 Å in $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CS)]$ to 5.732 Å in cation 1 and 5.736 Å in cation 2.

In going from $[\{Co(\eta-C_5H_5)\}_2\{Fe(CO)_2(PPh_3)\}(\mu_3-S)(\mu_3-CS)]$ to the cations 1/2, the Cμ–S bond length increases from 1.638(3) Å to 1.728(7)/1.723(6) Å. They are shorter than the S–Me distances of 1.790(10)/1.803(10) Å. These bond lengths should be compared with the terminal thiocarbonyl ligand C–S bond length of 1.512 Å in $[Ir(PPh_3)_2(CO)_2(CS)]^+$ [16], 1.55 Å in CS_2, the C=S bond lengths of 1.611(5) Å in the thioketone $C_6H_5C_6H_4(Ph)C{=}S$, 1.712 Å in thiophene and 1.819 Å in thioalkanes [17]. They imply that the order of the μ_3-C–S bond is close to 2 in [{Co(η-C_5H_5)}$_2${Fe(CO)$_2$(PPh$_3$)}(μ_3-S)(μ_3-CS)] and that it declines markedly on formation of the S–Me$^+$ bond though it is still greater than in a normal C–S single bond involving a sp^3 hybridised carbon atom as is found in the CS–Me$^+$ ligand. These arguments are consistent with the observed μ-C–S–Me bond angle of 107.7(4)/104.2(3)° which lies between the values of ca. 100° in thioalkanes or cycloalkanes and 136.8(2)° for the μ-C–NC(O)Ph angle in the closely related [{Co(η-C_5H_5)}$_2$(Fe(CO)$_2$(PPh$_3$)}(μ_3-S)(μ_3-CNC(O)Ph] [18]. They point to a sulphur atom at which the orbital hybridisation is closer to sp^3 than sp^2.

3.3. Pathway and limitations of the reaction

When the reactions of [Co(η-C_5H_5)(PPh$_3$)$_2$] with RNCS were investigated, it was proposed that they proceeded via an undetected and reactive [Co(η-C_5H_5)(PPh$_3$)(η^2-SCNR)] complex which with excess RNCS gave [Co(η-C_5H_5)(PPh$_3$)($S_2C_2N_2R_2$)] and with excess [Co(η-C_5H_5)(PPh$_3$)$_2$] gave [Co$_3$(η-C_5H_5)$_3$(μ_3-S)(μ_3-CNR)] [1]. The second, with its S–C bond cleavage and cluster formation is a specific example of the general reaction summarised in Eq. (1), and the present work describes two others.

$$\begin{aligned}&(\mathrm{L})\mathrm{M}(\eta^2\text{-SCX}) + \mathrm{M}'(\mathrm{L}')_2\\&\quad\rightarrow \mathrm{MM}'_2(\mu_3\text{-S})(\mu_3\text{-CX}) + \mathrm{L} + 2\mathrm{L}'\end{aligned}\tag{1}$$

M and M′ are 14e transition metal-based fragments, L and L′ are 2e donor ligands, and X = O, S, SR$^+$, NR or a related isolobal moiety. In principle this reaction is capable of wide application with variations of the transition metals, their ancillary ligands and X. However, the present work has revealed that it has limitations independent of the stability of the final product. Thus the reagent incorporating M′ must be capable of providing a 14e fragment with ease, and the substrate (L)M(η^2-SCX) must have one labile ligand and be able to provide a 16e fragment. Thus, although [Co(η-C_5H_5)(PPh$_3$)$_2$] is capable of performing its role, the same is not true for all [Fe(CO)$_2$(L)$_2$(η^2-CS$_2$)]. Those which do not have labile L capable of undergoing facile exchange, i.e., when L = CNMe or trialkylphosphines [5] do not react with [Co(η-C_5H_5)(PPh$_3$)$_2$].

The actual course of the reactions is more problematical. [Fe(CO)$_2$(PPhMe$_2$)$_2$(η^2-CS$_2$)] reacts with [Mn(η-C_5H_5)(CO)$_2$(THF)] to give [Fe(CO)$_2$(PPhMe$_2$)$_2$(η^2-SCSMn(η-C_5H_5)(CO)$_2$] [19] so it would be reasonable to assume that the first step of the reactions with [Co(η-C_5H_5)(PPh$_3$)$_2$] are the formation of [Fe(CO)$_2$L$_2$(η^2-SCSCo(η-C_5H_5)(PPh$_3$)]. However such a proposal is not reasonable for the [Fe(CO)$_2$(PPh$_3$)$_2$(η^2-SCSMe)]$^+$/[Co(η-C_5H_5)(PPh$_3$)$_2$] reaction.

Consequently we suggest that the reaction proceeds with the coordination of Co(η-C_5H_5) moieties to the two faces of a (L)(CO)$_2$FeSC(X) triangle to give a trigonal bipyramidal intermediate with apical Co atoms. This is a *closo* deltahedron as defined by the Wade–Mingos skeletal electron pair rules. This can rearrange to the observed trigonal bipyramidal complex with apical CX and S groups. Perhaps it does so by way of a *closo–nido–closo* process similar to that proposed for alkyne cleavage in a similar situation [20], and may be driven by the well known tendency of more electronegative fragments (i.e., those based on main group elements) to occupy cluster apices of lower connectivity whereas those fragments of lower electronegativities (i.e., those based on transition metals) occupy cluster apices of higher connectivities.

References

[1] E.P. Cullen, J. Fortune, A.R. Manning, P. McArdle, D. Cunningham, F.S. Stephens, Organometallics 9 (1990) 1443.
[2] H. Werner, K. Leonard, Angew. Chem., Int. Ed. Engl. 18 (1979) 627.
[3] H. Werner, K. Leonard, O. Kolb, E. Rottiger, H. Vahrenkamp, Chem. Ber. 113 (1980) 1654.
[4] J. Fortune, A.R. Manning, Organometallics 2 (1983) 1719.
[5] P.V. Broadhurst, B.F.G. Johnson, J. Lewis, P.R. Raithby, J. Chem. Soc., Chem. Commun. (1980) 812.
[6] A.R. Manning, L. O'Dwyer, P.A. McArdle, D. Cunningham, J. Chem. Soc., Chem. Commun. (1992) 897.
[7] P. Conway, S.M. Grant, A.R. Manning, J. Chem. Soc., Dalton Trans. (1979) 1920.
[8] H. Yamazaki, Y. Wakatsuki, J. Organomet. Chem. 139 (1977) 157.
[9] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.
[10] G.M. Sheldrick, SHELXL-93, A computer program for crystal structure determination, University of Göttingen, Germany, 1993.
[11] P.A. McArdle, J. Appl. Crystallogr. 27 (1994) 438.
[12] V.A. Uchtman, L.F. Dahl, J. Am. Chem. Soc. 91 (1969) 3763.
[13] P.D. Frisch, L.F. Dahl, J. Am. Chem. Soc. 94 (1972) 5082.
[14] R.L. Bedard, A.D. Rae, L.F. Dahl, J. Am. Chem. Soc. 108 (1986) 5924.
[15] A.R. Manning, L. O'Dwyer, P.A. McArdle, D. Cunningham, J. Organomet. Chem. 474 (1994) 173.
[16] J.S. Field, P. Wheatley, J. Chem. Soc., Dalton Trans. (1972) 2269.
[17] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1.
[18] A.R. Manning, L. O'Dwyer, P.A. McArdle, D. Cunningham, J. Organomet. Chem. 503 (1995) C46.
[19] T.G. Southern, U. Oehmichen, J.Y. Le Marouille, H. Le Bozec, D. Grandjean, P.H. Dixneuf, Inorg. Chem. 9 (1980) 2976.
[20] J.-H. Halet, Coord. Chem. Rev. 635 (1995) 637.