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A NEW ROUTE TO IRON(0) THIOCARBONYL COMPLEX INVOLVING DESULPHURIZATION OF THE Fe(η^2-CS_2R)$^+$ CATION WITH P-n-Bu_3. CRYSTAL STRUCTURE OF Fe(CS)$(CO)_2(PPh_3)_2$

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Summary

Reaction of [Fe(η^2-CS_2R)$(CO)_2(PPh_3)_2$][X] (R = CH_3, CH_2Ph; X^- = PF_6^-, I^-) with P-n-Bu_3 or PEt_3 gives Fe(CS)$(CO)_2(PPh_3)_2$ (**3a**); (ν(CS) 1235 cm^{-1}; $\delta(^{13}C)$ 324.28 ppm). The structure of **3a** has been determined by X-ray diffraction. Crystal data are: *a* 18.821(5), *b* 12.113(3), *c* 18.149(5) Å, β 117.76(6)°, monoclinic, space group $P2_1$, $Z = 4$. The structure is a trigonal-bypyramid with equatorial CS group, *trans* PPh_3 ligands, a Fe–C(S) bond distance of 1.768(8) and a C–S bond distance of 1.563(8) Å.

Introduction

The thiocarbonyl ligand has attracted interest as a small electron-withdrawing ligand capable of distinguishing between two carbonyl ligand sites and providing stabilisation of low valent transition metal complexes [1]. Several routes to low-valent MCS complexes have been described. The most general of these involves the desulphurization of the readily available (η^2-CS_2)metal complexes by phosphines [1,2]. Other routes have been used in more specific situations, such as the reaction of thiophosgene with metal carbonyl anion [3,4], the addition of NaSH to dihalogenocarbene-metal complexes [5] or from (η^2-CS_2R)metal cation, either by addition of borohydride and via M(H)(CS_2R) intermediates [6,7] or by reduction with sodium amalgam [8], depending on the nature of the metal and/or that of the ancillary ligands.

Whereas cationic thiocarbonyliron(II) complexes have been known for some time [9], only a few thiocarbonyliron(0) complexes have so far been made, owing to the

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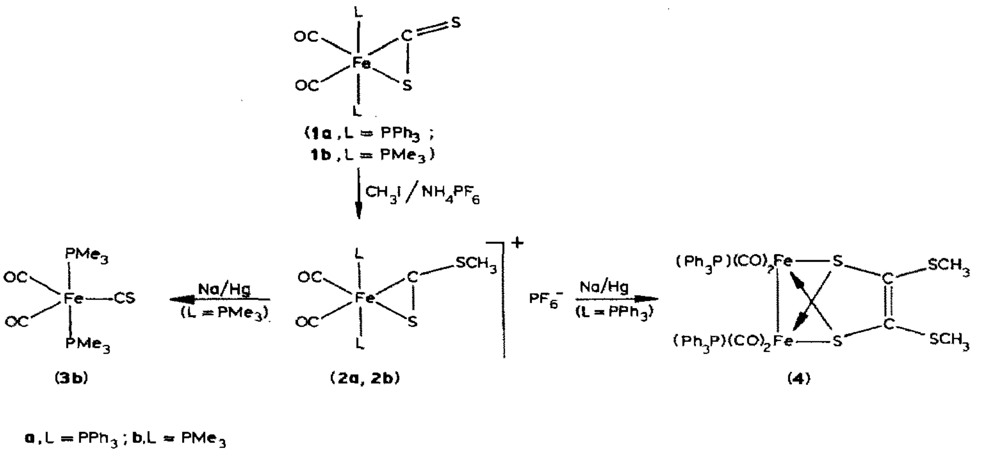


SCHEME 1

inertness of the easily accessible Fe(η^2-CS_2)$(CO)_2(PR_3)_2$ towards desulphurization by phosphines [10]. $FeCS(CO)_4$ [4] was obtained from the reaction of the anion $Fe(CO)_4{}^{2-}$ with thiophosgene. $Fe(CS)(CO)_2(P(OPh)_3)_2$ [11] was produced, in variable yield, on treatment of Fe(η^2-CS_2)$(CO)_2(P(OPh)_3)_2$ with PBu_3/CCl_4. More recently we found that reduction of the Fe(η^2-CS_2R)$(CO)_2(L)_2]^+$ cations (**2**) with sodium amalgam in THF afforded $Fe(CS)(CO)_2(L)_2$ complexes (**3**) (Scheme 1) [8]. However, the reaction appeared to require the presence of very basic phosphines such as L = PMe_3 or L = PMe_2Ph; Thus when **2a**, containing the weaker basic phosphine L = PPh_3, was treated with Na/Hg in THF, the bimetallic complex **4** [12] was formed rather than the corresponding $Fe(CS)(CO)_2(PPh_3)_2$ complex **3a**. Thus none of the known methods could be used to give $Fe(CS)(CO)_2(PPh_3)_2$ (**3a**). We now report a novel and efficient route to this thiocarbonylmetal(0) complex and the results of an X-ray diffraction study on it.

Experimental

Synthesis

General methods

All reactions were performed under nitrogen. All solvents were reagent grade and used without further purification. Infrared spectra were recorded on a Pye-Unicam SP 1100 spectrophotometer with Nujol mulls between KBr plates. ^1H and ^{31}P NMR spectra were recorded on a Bruker WP-80FT spectrometer and ^{13}C NMR spectra were obtained on a Bruker AM 300 WB spectrometer (Centre de Mesures Physiques, Université de Rennes). Microanalyses were carried out by CNRS Microanalyses (Villeurbanne, France).

Synthesis of $Fe(CS)(CO)_2(PPh_3)_2$ (3a)

Method A. A mixture of Fe(η^2-CS_2Me)$(CO)_2(PPh_3)_2{}^+I^-$ [13] (**2a**) (855 mg, 1 mmol) and P-n-Bu_3(0.75 ml, 3 mmol) in acetonitrile (20 ml) was stirred at room temperature. A yellow precipitate formed progressively. After 24 h of stirring, the starting complex **2a** had disappeared as shown by the infrared spectrum. The precipitate was then filtered off on a sintered-glass disc and washed successively with acetonitrile and hexane then dried under vacuum. This product was crystallized from ether, and obtained in 60% yield (460 mg). Anal. Found: C, 68.54; H, 4.42; S, 4.58; P, 9.25. $C_{39}H_{30}FeO_2P_2S$ calc: C, 68.84; H, 4.44; S, 4.71; P, 9.10%.

A white salt separated when hexane was added to the filtrate obtained after the removal of **3a**. After anion exchange with $NaPF_6$, it gave $n\text{-}Bu_3PMe^+$ PF_6^-, as shown by its IR and NMR spectra. The formation of Bu_3PS was also demonstrated by observation of its mass spectrum.

Spectroscopic data for 3a

IR (Nujol) (cm^{-1}): ν(C=O): 1945, 1880; ν(C=S): 1235. ^1H NMR ($CDCl_3$, 80 MHz, 298 K) δ(ppm): 7.7 (m,C_6H_5); ^{31}P NMR (C_6D_6, 32.38 MHz, 305 K) δ (ppm): 77.91 (s, PPh_3); ^{13}C NMR (C_6D_6, 75.469 MHz, 305 K) δ(ppm): 214.45 (t, CO, ^2J(PC) 24 Hz); 324.28 (t, CS,^2J(PC) 39 Hz).

Variations on the synthesis of 3

Influence of the added phosphine

An attempt was made to convert **2a** into **3a** by the action of 3 mmol of various phosphines (PEt_3, PMe_3, PPh_3) on 1 mmol of **2a** as in method A. With PEt_3 a 30% yield of **3a** was obtained, and with PMe_3 a 10% yield. In the latter case, $Fe^I(\eta^2\text{-}CS_2Me)(CO)(PMe_3)_2$ was also formed, in 40% yield. With PPh_3, even after a stirring of 72 h no formation of **3a** was observed.

Influence of the solvent

Method B. When the reaction was performed in dichloromethane (20 ml) the starting complex **2a** (1 mmol with 3 mmol of $P\text{-}n\text{-}Bu_3$) disappeared after 72 h of stirring at room temperature. Evaporation of the solvent, washing of the solid with hexane, and recrystallisation from ether gave **3a** in 45% yield.

Method C. When the reaction was carried out in dimethylsulfoxide (15 ml) the disappearance of **2a** (1 mmol with 3 mmol of $P\text{-}n\text{-}Bu_3$) was completed after only 12 h at room temperature. Addition of hexane, followed by filtration and washing of the precipitate with hexane gave **3a** in 80% yield.

X-Ray data collection and refinement of the structure

A prismatic crystal of dimensions $0.25 \times 0.25 \times 0.25$ mm was used. Crystallographic data: $C_{39}H_{30}FeO_2P_2S \cdot 0.5C_4H_{10}O$; $M_r = 1433.8$, monoclinic, $P2_1$, a 18.821(5), b 12.113(3), c 18.149(5) Å, β 117,76(6)°, V 3661(2) Å3, $Z = 4$, D_x 1.30 mg m^{-3}, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 1.18 mm^{-1}, T 293 K. 7003 reflections were collected of which 4591 had $I > \nu(I)$ (automatic diffractometer CAD-4-Enraf–Nonius). The structure was solved with a Patterson map and several successive scale factor refinements and Fourier differences. Many hydrogen atoms were found from one Fourier difference map: the remaining ones were placed in calculated positions; the best full-matrix least-squares refinement gave $R = 0.055$ and $R_w = 0.050$ with $1/w = \nu^2(F) = 1/4 \{ |\nu^2(I) + (0.06I)^2| / I \}$.

All the calculations were performed on a PDP 11/60 computer.

Results and discussion

The $Fe(\eta^2\text{-}CS_2)(CO)_2(PR_3)_2$ complexes (**1**) are quite inert towards desulphurization by phosphines to produce iron thiocarbonyl complexes. Thus when complex **1a** was treated with an excess of a basic phosphine L (L = PMe_3, PMe_2Ph or $P\text{-}n\text{-}Bu_3$) only substitution of the two PPh_3 groups took place to give the derivatives $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ in 70 to 95% yield [10]. We reported recently a route to $Fe(CS)(CO)_2L_2$ complexes involving reduction of the alkylated products $[Fe(\eta^2\text{-}CS_2R)(CO)_2L_2]^+$ with Na/Hg. However, this method was not suitable for synthesis of $Fe(CS)(CO)_2(Ph_3P)_2$ (**3a**), the tetrathiooxalato diiron complex **4** being formed instead [12] (Scheme 1).

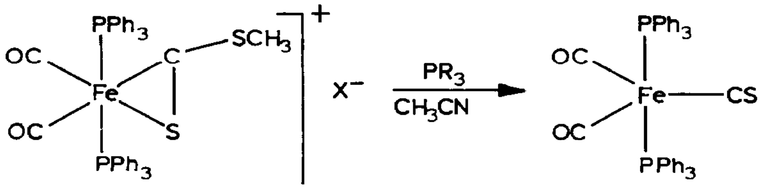
It was observed that in some circumstances $P\text{-}n\text{-}Bu_3$ desulphurized $Fe(\eta^2\text{-}CS_2)(CO)_2[P(OPh)_3]_2$ to give $Fe(CS)(CO)_2[P(OPh)_3]_2$ in variable yields [11]. We decided to attempt to desulphurize the $[Fe(\eta^2\text{-}CS_2R)]^+$ cations **2** with $P\text{-}n\text{-}Bu_3$, and found that this provided an excellent route to the thiocarbonyl iron complex **3a**.

Synthesis

Complex **2a** was stirred for 24 h at room temperature with 3 equivalents of $P\text{-}n\text{-}Bu_3$ in acetonitrile. The yellow precipitate which formed progressively was isolated in 60% yield and identified as complex **3a** (Scheme 2). In addition to **3a**, a white salt was formed and after anion exchange with $NaPF_6$, and precipitation on addition of hexane the salt $Bu_3PCH_3{}^+PF_6{}^-$ was isolated.

An important feature of this desulphurization reaction with $P\text{-}n\text{-}Bu_3$ is that it was always carried out in the presence of a large excess of added phosphine (more than 2 equivalents are necessary). Under such conditions, the starting product is entirely used up.

With other added phosphines, such as PEt_3 or PMe_3, complex **3a** was obtained in lower yields (respectively 30 and 10%). On the other hand, when we used PMe_3 we observed the replacement of both triphenylphosphine ligands of **2a**, and formation of $Fe(\eta^2\text{-}CS_2CH_3)(I)(CO)(PMe_3)_2$ [10] in 40% yield. Furthermore, with PPh_3 as the added phosphine we were unable to convert $(Ph_3P)_2(CO)_2Fe(\eta^2\text{-}CS_2Me^+)$ (**2a**) into the corresponding thiocarbonyl complex **3a**. It thus seems that there is a correlation between the basicity of the added phosphine and the ease of formation of complex **3a**.



(2a) **(3a)**

($X^- = I^-$ or PF_6^- ;
R = n–Bu , Et or Me)

SCHEME 2

Another feature of the desulphurization is the important role of the solvent. When the reaction was performed in dimethylsulfoxide the starting compound **2a** had completely disappeared after 12 h, and the expected thiocarbonyl complex **3a** was obtained in 80% yield. In acetonitrile the reaction was complete in 24 h and 60% yields of **3a** were obtained. In methylene chloride or chloroform, even after a stirring of 72 h, **3a** was isolated in only 45% yield. Finally, when the reaction was carried out in THF there was no detectable reaction. It seemed that the yield of complex **3a** also increased with the polarity of the solvent; thus the best yields are obtained in dimethylsulfoxide, but the procedure and the extraction of the final product are easier when acetonitrile is used.

It has been shown that the nature of the counteranion X^- (PF_6^- or I^-) or that of the substituent R (Me or CH_2Ph) of the Fe(η^2-$CS_2R)^+$] X^- salts does not significantly affect the transformation **2a** → **3a**.

The formation of **3a** clearly involves cleavage of C–SR bond and a formal reduction of the starting complex. However the reaction does not correspond to the reduction of **2a** by P-n-Bu_3. Thus cyclic voltammetry of **2a** in CH_3CN shows that its reduction is irreversible and occurs at -0.74 V_{SCE}, whereas oxidation of Bu_3P in the same condition takes place at a potential of $+0.25$ V_{SCE}. Moreover we have

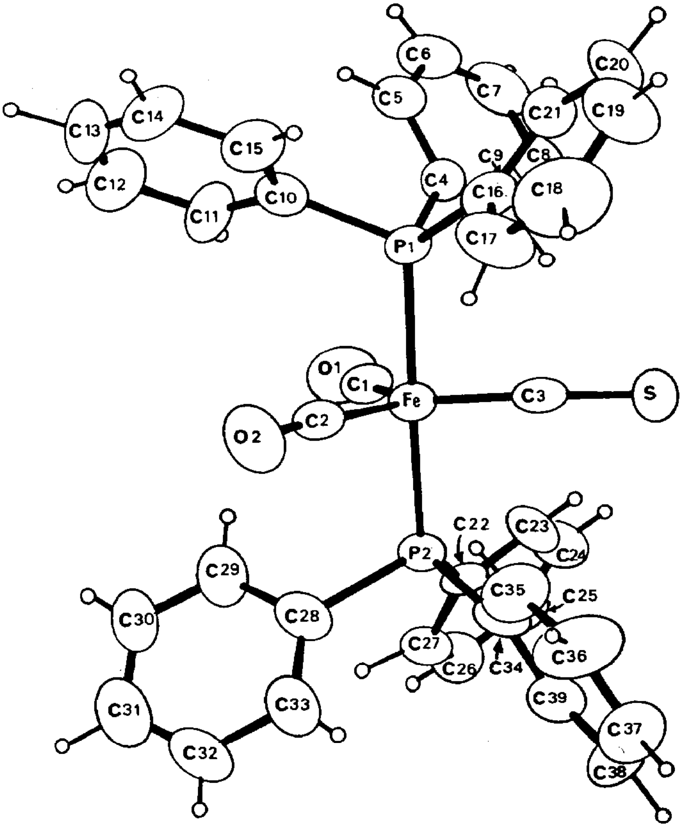


Fig. 1. ORTEP view of one molecule A or B of $Fe(CS)(CO)_2(PPh_3)_2$.

observed that the reduction of cation **2a** leads to the formation of the tetrathiooxalato diiron derivative **4** [12]. Since n-Bu_3P-CH_3^+ and Bu_3PS were formed during the reaction we suggest that the reaction involves addition of the PBu_3 group to the (η^2-CS_2CH_3) cationic ligand followed by loss of $Bu_3PSCH_3^+$. The cation $Bu_3PSCH_3^+$ would be expected to be transformed by an excess of the nucleophile PBu_3 into Bu_3PS and $Bu_3PCH_3^+$.

It is noteworthy that this one-step transformation of **2a** into **3a** allows the preparation of $Fe(CS)(CO)_2(PPh_3)_2$ (**3a**) in only three steps from $Fe(CO)_5$ via complex **1a**, with an overall yield of 65%.

Spectroscopic studies

The IR spectrum of the complex **3a** shows one ν(CS) (1235 cm^{-1}) and two ν(CO) bands (1945 and 1880 cm^{-1}), as expected. The values of the CS frequencies agree with those found in related complexes $L_2(CO)_2FeCS$ [8] (see also Table 3). The CO frequencies can been compared with those of the corresponding derivatives $Fe(CO)_3(PPh_3)_2$ (1973, 1886 cm^{-1}) [14] and $Fe(\eta^2$-$CS_2)(CO)_2(PPh_3)_2$ (1999, 1937 cm^{-1}) [10]. This suggests that the thiocarbonyl ligand bonded to a Fe^0 behaves as a much weaker electron-withdrawing group than the η^2-CS_2 ligand, and also indicates that it is a better π-acceptor group than a corresponding coordinated carbon monoxide.

TABLE 1

BOND DISTANCES (Å) IN $(PPh_3)_2(CO)_2FeCS$

	Molecule A	Molecule B		Molecule A	Molecule B
Fe–P(1)	2.232(2)	2.185(2)	C(14)–C(15)	1.364(13)	1.409(13)
Fe–P(2)	2.178(2)	2.233(2)	C(16)–C(17)	1.370(11)	1.396(10)
Fe–C(1)	1.766(9)	1.778(8)	C(16)–C(21)	1.367(10)	1.418(9)
Fe–C(2)	1.746(8)	1.732(8)	C(17)–C(18)	1.376(15)	1.382(11)
Fe–C(3)	1.550(7)	1.563(8)	C(18)–C(19)	1.33(2)	1.380(11)
S(1)–C(3)	1.550(7)	1.563(8)	C(19)–C(20)	1.299(12)	1.368(11)
P(1)–C(4)	1.821(7)	1.826(7)	C(20)–C(21)	1.370(11)	1.384(10)
P(1)–C(10)	1.843(7)	1.817(6)	C(22)–C(23)	1.375(10)	1.365(9)
P(1)–C(16)	1.845(7)	1.805(6)	C(22)–C(27)	1.409(9)	1.356(9)
P(2)–C(22)	1.791(7)	1.838(7)	C(23)–C(24)	1.352(11)	1.398(10)
P(2)–C(28)	1.840(7)	1.800(7)	C(24)–C(25)	1.378(11)	1.368(14)
P(2)–C(34)	1.801(7)	1.829(7)	C(25)–C(26)	1.362(11)	1.349(14)
O(1)–C(1)	1.164(9)	1.158(8)	C(26)–C(27)	1.394(10)	1.381(11)
O(2)–C(2)	1.171(8)	1.166(8)	C(28)–C(29)	1.361(11)	1.380(10)
C(4)–C(5)	1.393(10)	1.389(9)	C(28)–C(33)	1.357(12)	1.431(10)
C(4)–C(9)	1.375(11)	1.396(10)	C(29)–C(30)	1.369(13)	1.396(11)
C(5)–C(6)	1.395(11)	1.403(10)	C(30)–C(31)	1.385(15)	1.365(13)
C(6)–C(7)	1.329(13)	1.363(11)	C(31)–C(32)	1.318(15)	1.372(14)
C(7)–C(8)	1.353(13)	1.357(11)	C(32)–C(33)	1.393(13)	1.367(11)
C(8)–C(9)	1.368(11)	1.371(11)	C(34)–C(35)	1.375(11)	1.391(11)
C(10)–C(11)	1.381(11)	1.357(11)	C(34)–C(39)	1.400(10)	1.397(9)
C(10)–C(15)	1.368(12)	1.396(10)	C(35)–C(36)	1.347(12)	1.389(11)
C(11)–C(12)	1.352(13)	1.365(14)	C(36)–C(37)	1.381(13)	1.387(11)
C(12)–C(13)	1.37(2)	1.30(2)	C(37)–C(38)	1.373(13)	1.377(11)
C(13)–C(14)	1.35(2)	1.358(15)	C(38)–C(39)	1.399(11)	1.343(10)

The ^{13}C FT NMR spectrum is consistent with the proposed structure for a symmetrically substituted complex. Indeed, the ^{13}C NMR resonances corresponding to the equivalent CO and CS groups occur as a triplet, indicating coupling to two equivalent *trans* phosphines. The chemical shift at low field at 324.28 ppm (^2J(PC) 39 Hz) is consistent with that of a thiocarbonyl ^{13}C nucleus [15].

The only reported crystal structure of a Fe^{0}CS complex is that of Fe(CS)-$(CO)_2[P(OPh)_3]_2$, but the resolution was not sufficient to distinguish between one of the CO groups and the CS ligands. Moreover only one accurate structure for a trigonal bipyramidal thiocarbonyl metal complex, the ionic species [Ir(CS)$(CO)_2$-$(PPh_3)_2$] [PF_6] had previously been reported. The structure of **3a** was therefore been determined.

Crystal and molecular structure of Fe(CS)$(CO)_2(PPh_3)_2$

The crystal of the compound **3a** consists of two crystallographically independent units A and B, and one molecule of diethyl ether separated by normal Van der

TABLE 2

BOND ANGLES(°) IN $(PPh_3)(CO)_2$FeCS

	Molecule A	Molecule B		Molecule A	Molecule B
P(1)–Fe–P(2)	176.08(8)	175.02(8)	P(1)–C(10)–C(15)	123.5(6)	121.3(6)
P(1)–Fe–C(1)	90.7(2)	89.5(2)	C(10)–C(11)–C(12)	122.(1)	122.(1)
P(1)–Fe–C(2)	90.5(2)	88.9(2)	C(11)–C(12)–C(13)	117.(1)	122.(1)
P(1)–Fe–C(3)	86.6(2)	95.3(2)	C(12)–C(13)–C(14)	123.(1)	117.3(9)
P(2)–Fe–C(1)	93.1(2)	88.4(2)	C(13)–C(14)–C(15)	118.(1)	124.(1)
P(2)–Fe–C(2)	88.8(2)	89.0(2)	C(14)–C(15)–C(10)	121.9(9)	115.8(9)
P(2)–Fe–C(3)	90.6(2)	89.7(2)	P(1)–C(16)–C(17)	119.6(6)	122.6(5)
C(1)–Fe–C(2)	113.0(4)	129.4(4)	P(1)–C(16)–C(21)	123.3(6)	119.9(5)
C(1)–Fe–C(3)	121.4(4)	110.3(4)	C(16)–C(17)–C(18)	119.4(9)	122.6(7)
C(2)–Fe–C(3)	124.7(4)	120.2(3)	C(17)–C(18)–C(19)	120.5(9)	118.4(8)
Fe–P(1)–C(4)	115.5(2)	114.5(2)	C(18)–C(19)–C(20)	121.9(9)	120.9(7)
Fe–P(1)–C(10)	114.7(2)	113.9(2)	C(19)–C(20)–C(21)	119.1(8)	121.2(7)
Fe–P(1)–C(16)	116.0(2)	115.1(2)	C(28)–C(21)–C(16)	121.8(8)	119.5(7)
C(4)–P(1)–C(10)	102.0(3)	103.6(3)	P(2)–C(22)–C(23)	121.2(5)	118.7(3)
C(4)–P(1)–C(16)	103.7(3)	103.2(3)	P(2)–C(22)–C(27)	122.2(5)	122.1(6)
C(10)–P(1)–C(16)	103.2(3)	105.2(3)	C(22)–C(23)–C(24)	123.5(8)	119.2(7)
Fe–P(2)–C(22)	114.0(2)	113.1(2)	C(23)–C(24)–C(25)	119.6(7)	118.7(8)
Fe–P(2)–C(28)	115.0(3)	117.0(3)	C(24)–C(25)–C(26)	119.3(7)	121.1(8)
Fe–P(2)–C(34)	115.2(2)	116.1(2)	C(25)–C(26)–C(27)	121.1(7)	117.0(8)
C(22)–P(2)–C(28)	103.7(3)	103.7(3)	C(26)–C(27)–C(22)	128.0(7)	122.2(8)
C(22)–P(2)–C(34)	104.7(3)	103.3(3)	P(2)–C(28)–C(29)	119.9(6)	122.4(6)
C(38)–P(2)–C(34)	102.8(3)	101.7(3)	P(2)–C(28)–C(33)	122.4(6)	122.1(5)
Fe–C(1)–O(1)	175.6(7)	179.2(7)	C(28)–C(29)–C(30)	121.(1)	121.7(9)
Fe–C(2)–O(2)	176.8(7)	177.4(6)	C(29)–C(30)–C(31)	121.(1)	121.7(8)
Fe–C(3)–S	176.9(5)	176.3(5)	C(30)–C(31)–C(32)	119.(1)	117.9(8)
P(1)–C(4)–C(5)	122.4(6)	122.3(5)	C(31)–C(32)–C(33)	120.(1)	121.6(8)
P(1)–C(4)–C(9)	119.9(6)	119.9(6)	C(32)–C(33)–C(29)	121.1(9)	121.7(8)
C(5)–C(4)–C(9)	117.7(7)	117.8(7)	P(2)–C(34)–C(35)	120.7(6)	119.8(5)
C(4)–C(5)–C(6)	119.1(8)	119.7(7)	P(2)–C(34)–C(39)	121.7(6)	123.2(5)
C(5)–C(6)–C(7)	121.1(9)	121.4(7)	C(34)–C(35)–C(36)	123.4(9)	122.1(8)
C(6)–C(7)–C(8)	120.6(8)	118.5(7)	C(35)–C(36)–C(37)	118.8(9)	117.5(8)
C(7)–C(8)–C(9)	119.8(9)	122.1(8)	C(36)–C(37)–C(39)	119.4(9)	119.3(7)
P(1)–C(10)–C(11)	118.7(6)	120.5(6)	C(38)–C(39)–C(34)	119.9(8)	122.5(7)

Waals contacts. An ORTEP plot of the structure of molecules A and B is shown in Fig. 1. Values of bond lengths for both independent molecules A and B are listed in Table 1, and values of bond angles in Table 2. The two independent molecules in the asymmetric unit are essentially identical in stereochemistry. Some of the differences in bond distances between the molecules A and B may be due to the presence of a molecule of ether of solvation in the unit cell. Both units exhibit trigonal bipyramidal coordination around the iron atoms with apical *trans* phosphines, two equatorial carbonyls, and the thiocarbonyl group occupying the third equatorial position. This description is supported by the values of the P(1)–Fe–P(2) (176.08(8) and 175.02(8)°), P(1)–Fe–C(1) (90.7(2) and 89.5(2)°), P(1)–Fe–C(2) (90.5(2) and 88.9(2)°), P(1)–Fe–C(3) (86.6(2) and 95.3(2)°) angles. In both molecules the Fe–P(1) and Fe–P(2) bond lengths are slightly different (molecule A: Fe–P(1) 2.232(2) and Fe–P(2) 2.178(2) Å), but they are in the range found for other iron complexes [10]. The Fe–C(O) bond lengths listed in Table 1 also fall within the range (1.89–1.73) observed for the Fe–C(O) distances in $(PR_3)_2(CO)_2FeL$ complexes [10,11]. In $Fe(CS)(CO)_2[P(OPh)_3]_2$ [11], the structure of the thiocarbonyl ligand was not satisfactorily defined because of the disorder in the structure and of the coordinated thiocarbonyl ligand in **3a** is thus of special interest. The C–S bond lengths (1.550(7) and 1.563(8) Å) are slightly longer than that in the cationic IrCS complex [18]. This observation is consistent with a greater back-donation from the iron to the CS ligand and the lower ν(CS) frequency. The FeCS arrangement is almost linear, with FeC(3)S angles of 176.9(5) and 176.3(5)°. The average Fe–C(3) bond length in the two molecules is 1.768 Å. A significant shortening of this bond, compared with the Fe–C(1) and Fe–C(2) bond lengths is expected since CS is a better π-acceptor than CO [16]. Such shortening has been observed in most of other transition metal complexes containing terminal thiocarbonyl groups [18,25,28]: surprisingly, the value of 1.768 Å for Fe–C(3) is between the averages for Fe–C(1) (1.772(6) Å) and Fe–C(2) (1.739(7) Å); in the CS ligand the C–S bond length is significantly different from the C–O bond lengths.

Tables of thermal parameters and structure factors are available from the authors.

TABLE 3

C–S BOND DISTANCES AND ν(CS) FREQUENCIES FOR MCS COMPLEXES

Compound	ν(C–S) (cm^{-1})	C–S (Å)
$Ir(PPh_3)_2(CO)_2CS^+ PF_6^-$	1321($CHCl_3$) [17]	1.512(3), 1.509(2) [18]
trans-$RhCl(PPh_3)_2CS$	1299(C_6H_6) [2]	1.54(1) [19]
$Rh(3,5\text{-}Me_2Pz)(CS)(PPh_3)_2$	1288/1302(Nujol) [20]	1.56(3) [20]
$Ru_2(Cl)_4(PPh_3)_4CS$	1284(Nujol) [21]	1.14(10) [22]
CS	1274 [23]	1.5349(2) [24]
trans-$W(CO)_4(CNC_6H_{11})(CS)$	1240(CS_2) [25]	1.564(2) [25]
$(PPh_3)_2(CO)_2FeCS$	1235	1.550(7), 1.563(8)
$(C_6H_5CO_2CH_3)Cr(CO)_2CS$	1225(CCl_4) [26]	1.570(2) [27]
$(P(OPh)_3)_2(CO)_2FeCS$	1222 [11]	1.42(1), 1.36(1) [11]
np_3CoCS	–	1.66(8), 1.76(7) [28]
$Mn(C_6H_7)(CS)I(NO)$	–	1.513(6) [29]

Conclusion

The method of forming thiocarbonyl metal complexes described here may be restricted to metal complexes possessing weakly electron-donating ancillary ligands, for it is not successful for the transformation into **3b** of **2b**, which contains the basic phosphine PMe_3. On the other hand, the new simple method can be used in other systems for which the direct desulphurization of the $M(\eta^2\text{-}CS_2)$ precursor appeared to be difficult. The simple transformation of **2** into **3a** represents a novel desulphurization-reduction for the formation of a new Fe^0CS complex.

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