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Reaction of $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OR)_3\}_2$ with phosphines: desulphurization versus substitution. Crystal structures of $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ and $Fe(CO)_3\{P(OPh)_3\}_2$

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Abstract

The reaction of $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OPh)_3\}_2$ **1** with two equivalents of PBu_3 in a minimum volume of a polar solvent such as acetonitrile or dimethylsulfoxide afforded the thiocarbonyl derivative $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ **2** in ca. 80% yield whereas reaction in solvents such as dichloromethane or benzene afforded the substitution products $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OPh)_3\}(PBu_3)$ and $Fe(CO)_2(\eta^2\text{-}CS_2)(PBu_3)_2$. Although desulphurization of $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OR)_3\}_2$ by PBu_3 in polar solvents is not a general route to $Fe(CO)_2(CS)\{P(OR)_3\}_2$ for all R, the new compound $Fe(CO)_2(CS)\{P(OEt)_3\}_2$ has been obtained and characterised spectroscopically. The crystal structures of **2** and $Fe(CO)_3\{P(OPh)_3\}_2$ were determined and are very similar. Both compounds are trigonal bipyramidal about the Fe atom with *trans* apical phosphite ligands and a trigonal planar arrangement of CO/CS groups. The CS ligand in **2** was found to be disordered over two sites with occupancies 0.63 and 0.37.

Keywords: Thiocarbonyl complex; Desulphurization; Carbonyl complexes

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1. Introduction

The desulphurization of co-ordinated carbon disulfide by phosphines (Eq. 1) is a convenient route to thiocarbonyl metal complexes [1].

$$L_nM(CS_2) \xrightarrow{PR_3} L_nM(CS) + SPR_3$$

However, this method has proven to be very sensitive to the nature of both the metal and the ancillary ligands. Thus, the readily accessible complexes $Fe(CO)_2(\eta^2\text{-}CS_2)(L)_2$ $\{L = PR_3$ or $P(OR)_3\}$ [2] are inert towards desulphurization by added phosphine when $L = PR_3$ [3]. Instead, preparation of $Fe(CO)_2(CS)(PR_3)_2$ complexes requires prior formation of the S-alkylated cations $[Fe(CO)_2(\eta^2\text{-}CS_2Me)(PR_3)_2]^+$ and, for $PR_3 = PMe_3$ or $P(Me_2Ph)$, reduction with Na/Hg [4]; for $PR_3 = PPh_3$ treatment of the cation with excess phosphine in polar solvents affords the required thiocarbonyl compound [5]. However, in the case where $L = P(OPh)_3$ the thiocarbonyl complex is directly accessible from $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OPh)_3\}_2$, **1**, and we have previously reported the preparation of $Fe(CO)_2(CS)\{P(OPh)_3\}_2$, **2**, by reaction of **1** with PBu_3 in CCl_4, although in only 10–15% yield [6]. We now report a method for the facile and high yield synthesis of $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ and investigate the generality of the preparative procedure. A redetermination of the crystal structure of **2** is also presented and we further report the crystal and molecular structure of the related iron complex $Fe(CO)_3\{P(OPh)_3\}_2$, **3**.

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2. Experimental

2.1. General methods

All reactions were performed under N_2 using solvents predried by standard procedures. Phosphines and phosphites were purchased from Aldrich and used without further purification. Compound **1** was prepared according to the modified literature procedure [7] given below. Complexes $Fe(CO)_2(CS_2)(L)_2$ where L = $PPh(OMe)_2$, $P(OEt)_3$ or $1/2[(PPh_3)\{P(OMe)_3\}]$ were prepared from **1** by ligand exchange in CH_2Cl_2 solution [7]. $Fe(CO)_3\{P(OPh)_3\}_2$ was prepared according to the literature method [8]. IR spectra were recorded on a Perkin-Elmer 1710FT spectrometer. NMR spectra were obtained in $CDCl_3$ solution on a Jeol JNM-GX270 FT-NMR spectrometer. ^1H (270 MHz) and ^{13}C (67.8 MHz) chemical shifts are reported downfield from tetramethylsilane as internal standard; ^{31}P (109.3 MHz) spectra are referenced to 85% phosphoric acid with downfield shifts reported as positive. All coupling constants are in Hertz. Mass spectra were recorded on a VG Analytical 7070 mass spectrometer. Elemental analyses were performed in the Microanalytical Laboratory, University College Dublin.

2.2. Synthesis of $Fe(CO)_2(CS_2)\{P(OPh)_3\}_2$ 1

A mixture of finely ground $Fe_2(CO)_9$ (1.00 g, 2.75 mmol) and triphenylphosphite (2.87 cm^3, 11.0 mmol) in CS_2 (40 cm^3) was heated at gentle reflux for ca. 30 min and then allowed to stir at room temperature (r.t.) for 1 h. The resulting dark brown solution was filtered to remove unreacted $Fe_2(CO)_9$. EtOH (15 cm^3) was added to the filtrate, the CS_2 was removed under reduced pressure without heating and the resulting precipitate was isolated by filtration and washed with EtOH then diethyl ether to afford analytically pure $Fe(CO)_2(CS_2)\{P(OPh)_3\}_2$ in 50% yield based on reacted $Fe_2(CO)_9$. M.p. 96–100°C dec. Anal. Found: C, 57.5; H, 3.68; S, 8.24%. $C_{39}H_{30}FeO_8P_2S_2$ requires: C, 57.95; H, 3.74; S, 7.93%. IR (cm^{-1}) ν_{CO} 2024, 1963, ν_{CS} 1160 (NCMe). ^1H-NMR δ 7.50 (m, Ph). ^{31}P-NMR δ 141.2 (s).

2.3. Synthesis of $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ 2

2.3.1. Method A

Tri-*n*-butylphosphine (0.46 cm^3, 1.86 mmol) was added to a suspension of $Fe(CO)_2(CS_2)\{P(OPh)_3\}_2$ (0.750 g, 0.93 mmol) in acetonitrile (10 cm^3). The mixture was stirred at r.t. for 1 h to afford an orange–brown solution. The solvent was removed under reduced pressure and the residue was redissolved in a minimum of toluene. Hexane was added to precipitate $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ (0.606 g, 84% yield). M.p. 115°C. Anal. Found: C, 60.0; H, 3.84; S, 4.20%. $C_{39}H_{30}FeO_8P_2S$ requires: C, 60.3; H, 3.89; S, 4.12%. IR (cm^{-1}) ν_{CO} 1995, 1936 (CH_2Cl_2), 1989, 1929, (KBr), ν_{CS} 1266 (KBr). ^1H-NMR δ 7.23 (m, Ph). ^{13}C-NMR δ 315.8 (t, $J_{CP} = 54$, CS), 207.6 (t, $J_{CP} = 34$, CO), 151.0 (d, $J_{CP} = 3.4$, *i*-Ph), 129.6 (s, *o*-Ph), 125.1 (s, *p*-Ph), 122.0 (s, *m*-Ph). ^{31}P-NMR δ 171.8 (s). *m*/*z* (EI) 720 (M–2CO); 410 {–P(OPh)$_3$}; 366 (–CS).

2.3.2. Method B

The above reaction was repeated using one equivalent of PBu_3 to afford a 74% yield of **2** after 90 min reaction time.

2.3.3. Method C

The reaction of Method A was repeated using a suspension of **1** (0.750 g) in 20 cm^3 of acetonitrile. The starting material was consumed after 1 h and a 56% yield of **2** was isolated.

2.3.4. Influence of added phosphine

An attempt was made to convert **1** into **2** by the action of two equivalents of PMe_3 and PPh_3, respectively, on **1** as in Method A. PMe_3 was used as a 1 M solution in THF and afforded a 51% yield of **2** after 90 min reaction time. PPh_3 afforded a mixture of **1**, $Fe(CO)_2(CS_2)\{P(OPh)_3\}(PPh_3)$ and $Fe(CO)_2(CS_2)(PPh_3)_2$ which were identified by their IR spectra [7]. No trace of the thiocarbonyl complex was observed and isolation of the products was not attempted.

2.3.5. Influence of the solvent

The reaction of Method A was performed in DMSO (10 cm^3). After 1 h the mixture was extracted with CH_2Cl_2 and H_2O. Drying and concentration of the organic layer afforded an orange residue which was crystallised from hexane/toluene to afford **2** in 80% yield.

Treatment of **1** with PBu_3 in pyridine gave a solution from which a 65% yield of **2** was isolated after 1 h reaction time. In methanol, **1** gave a suspension and less than 2% yield of **2** after 5 h stirring at r.t. with added PBu_3. A 45% yield of **2** was obtained on reaction of **1** in acetone solution.

Reaction in CH_2Cl_2 afforded a near quantitative yield of $Fe(CO)_2(CS_2)(PBu_3)_2$ and no trace of the thiocarbonyl derivative.

2.4. Synthesis of $Fe(CO)_2(CS)\{P(OEt)_3\}_2$ 4

Tri-*n*-butylphosphine (0.40 cm^3, 1.62 mmol) was added to a solution of $Fe(CO)_2(CS_2)\{P(OEt)_3\}_2$ (0.420 g, 0.81 mmol) in acetonitrile (6 cm^3) and the mixture stirred at room temperature for 4 days. The solvent was removed under reduced pressure and the residue chromatographed on silica TLC plates using CH_2Cl_2/40–60 petroleum ether as eluent. Three bands were developed and identified as the starting material (20% recovered), $Fe(CO)_2(CS)\{P(OEt)_3\}_2$ (ca. 15%) and $Fe(CO)_2(CS_2)(PBu_3)_2$ (ca. 40%). The latter two compounds could only be partially separated.

Spectroscopic data for **4**: IR (cm^{-1}) ν_{CO} 1978, 1915 (CH_2Cl_2), 1973, 1908 (KBr), ν_{CS} 1246 (KBr). ^{1}H-NMR δ 4.17 (m, 2H, CH_2), 1.37 (t, 3H, $J_{HH} = 7$, CH_3). ^{13}C-NMR δ 318.0 (t, $J_{PC} = 50$, CS), 209.9 (t, $J_{PC} = 33$, CO), 61.9 (s, CH_2), 16.2 (s, CH_3).

2.5. X-Ray data collection and structure refinement

X-ray quality single crystals of **2** were grown from a toluene/hexane solution; single crystals of **3** were grown slowly from a $CDCl_3$/hexane mixture. X-ray data were collected on an Enraf Nonius CAD4 diffractometer with graphite monochromatised Mo–K_α radiation ($\lambda = 0.7093$ Å) at 293(2) K. The structures were solved by direct methods, SHELXS-86 [9], and refined by full-matrix least squares using SHELXL-97 [10] for **2** and SHELXL-93 [11] for **3**. 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 atoms to which they were attached. Calculations were performed on a Pentium PC (for **2**) or a Silicon Graphics R4000 (**3**) computer. Details of the X-ray data collection and structure refinement are summarised in Table 1 and selected bond lengths and angles are given in Table 2. Supplementary material comprises a complete list of bond lengths and bond angles, atom positions, thermal parameters, and observed and calculated structure factors.

3. Results and discussion

Two reaction pathways are possible on treatment of $Fe(CO)_2(\eta^2\text{-}CS_2)(L)_2$ $\{L = PR_3$ or $P(OR)_3\}$ with added phosphine PR'_3 viz. ligand substitution (Scheme 1a) or desulphurization of CS_2 to CS (Scheme 1b).

The type of reaction favoured is determined in the first instance by the co-ordinated ligand L. Thus, when $L = PR_3$ substitution products are obtained exclusively and access to the thiocarbonyl compounds is only possible via the S-alkylated cations as described previously by Dixneuf and co-workers [4,5]. However, when $L = P(OR)_3$ both reaction pathways (a) and (b) operate and we find that the ratio of substitution to S-abstraction is then determined by the reaction medium and the concentration of the reactants.

In solvents such as benzene, CH_2Cl_2 and $CHCl_3$, $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OPh)_3\}_2$, **1**, reacts with PBu_3 to substitute first one and then both phosphite ligands for the phosphine [7]. This ligand exchange reaction is maximally suppressed in acetonitrile or dimethylsulfoxide to favour desulphurization and formation of the thiocarbonyl compound $Fe(CO)_2(CS)\{P(OPh)_3\}_2$, **2**. We investigated the reaction in a range of solvents and found that, in general, increasing solvent polarity led to an increase in reaction rate and product yield. The results parallel those described by Dixneuf and co-workers for the desulphurization of $[Fe(CO)_2(PPh_3)_2(CS_2Me)][I]$ by PBu_3: the thiocarbonyl complex $Fe(CO)_2(CS)(PPh_3)_2$, **5**, was obtained in 80% yield after 12 h stirring in DMSO whereas only 45% yield was obtained after 72 h in CH_2Cl_2 or $CHCl_3$ [5].

The extent of ligand substitution versus CS formation in the $Fe(CO)_2(\eta^2\text{-}CS_2)\{P(OPh)_3\}_2$ system was also found to depend on the concentration of the reactants: optimum yields (84%) of **2** were obtained when the

Table 1

Summary of crystal data and details of the data collection and refinement for **2** and **3**

Complex	**2**	**3**
Empirical formula	$C_{39}H_{30}FeO_8P_2S$	$C_{39}H_{30}FeO_9P_2$
Molecular weight (g mol^{-1})	776.48	760.42
Colour, habit	Orange, block	Pale yellow, block
Crystal size (mm)	$0.21 \times 0.32 \times 0.40$	$0.20 \times 0.35 \times 0.40$
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.897(3)	9.832(2)
b (Å)	11.012(2)	10.975(3)
c (Å)	17.218(4)	17.131(3)
α (°)	97.82(2)	96.68(2)
β (°)	92.56(2)	92.99(2)
γ (°)	99.90(2)	99.76(2)
Volume (Å^3)	1826.9(8)	1804.5(7)
Z	2	2
$D_{calc.}$ (g cm^{-3})	1.412	1.399
F(000)	800	784
μ (mm^{-1})	0.61	0.56
θ range for data collection	2 to 25	2 to 25
hkl range	0–11, −13–12, −20–20	0–12, −13–13, −21–21
Reflections collected	7007	7701
Unique reflections	6395	7080
R_{int}	0.028	0.052
Reflections with $I > 2\sigma(I)$	5010	5345
Data/restraints/parameters	6395/9/469	7080/0/460
Goodness-of-fit[b]	0.964	1.091
Final *R* indices $[I > 2\sigma(I)]$	$R_1 = 0.0544$ $wR_2 = 0.1589$	$R_1 = 0.0447$ $wR_2 = 0.1400$
R indices (all data)[a]	$R_1 = 0.0651$ $wR_2 = 0.1698$	$R_1 = 0.0576$ $wR_2 = 0.1503$
Density range in final Δ-map (e Å^{-3})	0.72, −0.45	0.48, −0.46

[a] *R* indices; $R_1 = [\Sigma\|F_o|-|F_c\|]/\Sigma|F_o|$ (based on *F*), $wR_2 = [\Sigma\{w(|F_o^2 - F_c^2|)^2/\Sigma w(F_o^2)^2\}]^{\frac{1}{2}}$ (based on F^2), $w = 1/[(\sigma F_o^2) + (0.1303*P)^2 + 0.42*P]$ for **2**, $w = 1/[(\sigma F_o^2) + (0.1038*P)^2]$ for **3**.

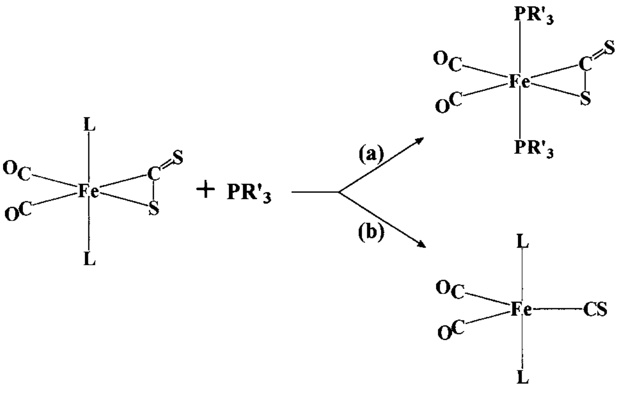
[b] Goodness-of-fit $= [\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{parameters})]^{\frac{1}{2}}$.

Table 2
Selected bond lengths (Å) and angles (°) for **2** and **3**

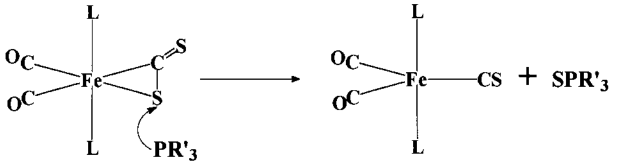
2		**3**	
Bond lengths (Å)			
Fe(1)–P(1)	2.1462(8)	Fe(1)–P(1)	2.1408(8)
Fe(1)–P(2)	2.1528(9)	Fe(1)–P(2)	2.1421(8)
Fe(1)–C(1)	1.793(4)	Fe(1)–C(1)	1.759(3)
Fe(2)–C(2)	1.7803(11)[a]	Fe(1)–C(2)	1.778(3)
Fe(1)–C(3)	1.7724(10)[a]	Fe(1)–C(3)	1.778(3)
P(1)–O(3)	1.597(2)	P(1)–O(4)	1.608(2)
P(1)–O(4)	1.610(2)	P(1)–O(5)	1.595(2)
P(1)–O(5)	1.595(2)	P(1)–O(6)	1.599(2)
P(2)–O(6)	1.607(2)	P(2)–O(7)	1.614(2)
P(2)–O(7)	1.611(2)	P(2)–O(8)	1.604(2)
P(2)–O(8)	1.600(2)	P(2)–O(9)	1.601(2)
S(1)–C(3)	1.5443(10)[a]		
S(11)–C(2)	1.5459(11)[a]		
O(1)–C(1)	1.157(4)	O(1)–C(1)	1.146(3)
O(2)–C(2)	1.1734(11)[a]	O(2)–C(2)	1.150(3)
		O(3)–C(3)	1.148(3)
O(3)–C(4)	1.404(4)	O(4)–C(16)	1.399(3)
O(4)–C(10)	1.399(3)	O(5)–C(10)	1.410(3)
O(5)–C(16)	1.410(3)	O(6)–C(4)	1.413(3)
O(6)–C(22)	1.406(4)	O(7)–C(22)	1.400(3)
O(7)–C(28)	1.389(4)	O(8)–C(28)	1.412(3)
O(8)–C(34)	1.393(5)	O(9)–C(34)	1.394(3)
Bond angles (°)			
P(1)–Fe(1)–P(2)	177.27(3)	P(1)–Fe(1)–P(2)	177.21(3)
Fe(1)–P(1)–O(3)	120.18(8)	Fe(1)–P(1)–O(4)	118.85(7)
Fe(1)–P(1)–O(4)	118.61(8)	Fe(1)–P(1)–O(5)	120.28(6)
Fe(1)–P(1)–O(5)	113.51(8)	Fe(1)–P(1)–O(6)	113.13(6)
Fe(1)–P(2)–O(6)	118.93(9)	Fe(1)–P(2)–O(7)	119.80(7)
Fe(1)–P(2)–O(7)	120.05(9)	Fe(1)–P(2)–O(8)	119.61(8)
Fe(1)–P(2)–O(8)	119.27(10)	Fe(1)–P(2)–O(9)	119.26(7)
Fe(1)–C(1)–O(1)	178.3(3)	Fe(1)–C(1)–O(1)	177.6(2)
		Fe(1)–C(2)–O(2)	179.0(2)
		Fe(1)–C(3)–O(3)	179.0(3)

[a] The thiocarbonyl is disordered with one of the carbonyl groups.

reaction was carried out in a minimum of acetonitrile (nominal concentration ca. 0.1 M) and in the presence of two equivalents of PBu_3. Under these conditions the starting material is consumed within 1 h as evidenced by IR spectroscopy and, after removal of the acetonitrile, the required thiocarbonyl product is easily isolated from the ligand exchange co-products viz. $Fe(CO)_2(CS_2)\{P(OPh)_3\}(PBu_3)$ and $Fe(CO)_2(CS_2)(PBu_3)_2$, by precipitation from hexane in which solvent the latter species are extremely soluble.



Scheme 1. Reaction pathways for $Fe(CO)_2(\eta^2\text{-}CS_2)(L)_2$ and PR'_3.



Scheme 2. Proposed mechanism of reaction of $Fe(CO)_2(CS_2)\{P(OPh)_3\}_2$ with phosphines.

In an experiment in which the volume of acetonitrile was doubled the IR spectra of the reaction mixture showed an increase in ligand substitution products at the expense of thiocarbonyl formation and the isolated yield of **2** was reduced to 56%. In the presence of only one equivalent of PBu_3 the desulphurization reaction was both slower and lower-yielding: a 74% yield of **2** was obtained after 90 min stirring at room temperature.

The above results agree with the postulate that the ligand exchange reaction occurs via a dissociative pathway [7]. The competing desulphurization reaction, however, appears to be bimolecular; this is consistent with the mechanism proposed by Fenster and Butler [12] which involves attack of free phosphine at the co-ordinated sulphur atom of the CS_2 ligand (Scheme 2).

The reaction of **1** with the phosphines PMe_3 and PPh_3 was also investigated. The former reagent was used as a 1 M solution in THF and under these conditions afforded a 51% yield of the thiocarbonyl on stirring with **1** in acetonitrile for 90 min. Reaction with PPh_3, however, afforded an equilibrium mixture of $Fe(CO)_2(CS_2)(L^1)_2$, $Fe(CO)_2(CS_2)(L^1)(L^2)$ and $Fe(CO)_2(CS_2)(L^2)_2$ where $L^1 = PPh_3$ and $L^2 = P(OPh)_3$. The same behaviour is observed on addition of PPh_3 to chloroform solutions of **1** [7]. The results suggest that only the more basic trialkyl phosphines are effective in the desulphurization of **1**.

The synthetic utility of the desulphurization procedure described here appears to be effectively limited to the triphenylphosphite complex **1**. Thus, the bis(phosphonite) compound $Fe(CO)_2(CS_2)\{PPh(OMe)_2\}_2$ failed to react with PBu_3 in acetonitrile even on prolonged stirring (4 days) at room temperature. On heating to 30°C rapid ligand substitution occurred to afford $Fe(CO)_2(CS_2)\{PPh(OMe)_2\}(PBu_3)$ and $Fe(CO)_2(CS_2)(PBu_3)_2$ which were identified spectroscopically [7]. The mixed phosphine/phosphite complex $Fe(CO)_2(CS_2)(PPh_3)\{P(OMe)_3\}$ underwent only slow ligand substitution to afford ca. 40% of the bis-substituted complex $Fe(CO)_2(CS_2)(PBu_3)_2$ after 1 week.

However, the thiocarbonyl complex $Fe(CO)_2(CS)\{P(OEt)_3\}_2$, **4**, was successfully prepared, although in only ca. 15% yield, on extended reaction of $Fe(CO)_2(CS_2)\{P(OEt)_3\}_2$ with PBu_3 in acetonitrile. Compound **4** is difficult to separate from the co-product $Fe(CO)_2(CS_2)(PBu_3)_2$ which has a very similar solubility and R_f value in the solvent mixtures investigated and an analytically pure sample was not obtained. However, **4** was unambiguously identified from the spectroscopic data. The IR spectrum exhibits a strong absorption at 1246 cm^{-1} which may be compared with ν_{CS} frequencies of 1266 and 1235 cm^{-1} in the IR spectra of compounds **2** and **5** [5], respectively. The low-field resonance at δ 318.0 in the ^{13}C-NMR spectrum of **4** is also consistent with a thiocarbonyl ^{13}C nucleus: corresponding chemical shift values are δ 315.8 for **2** and 324.3 for **5**.

3.1. Crystal and molecular structure of $Fe(CO)_2(CS)\{P(OPh)_3\}_2$

An ORTEX [13] diagram of compound **2** is shown in Fig. 1 and selected bond lengths and angles are presented in Table 2. The co-ordination about the iron atom is trigonal bipyramidal with the two phosphite ligands occupying *trans* apical sites [P–Fe–P bond angle 177.27(3)°] and the CO and CS ligands in the equatorial plane of the molecule [C–Fe–C bond angles sum to 359.92(3)°]. We have previously reported the structure of **2** [6] and the CS group was found to be disordered; the present structural determination was undertaken in order to model this disorder properly. Thus, we find the CS ligand to be disordered over two sites involving C(2) and C(3). A model in which the C=S bond length was restrained to be 1.550 Å in both sites was refined to give a refined site occupancy of 0.63 for the major site and 0.37 for the minor site occupancy. The precision of the present structural determination is better by a factor of ca. 3 in the S.D.'s than the structure of **2** reported in the original communication [6].

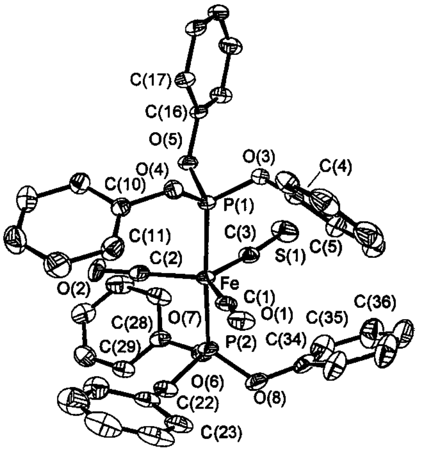


Fig. 1. ORTEX diagram of the molecular structure of $Fe(CO)_2(CS)\{P(OPh)_3\}_2$ **2**.

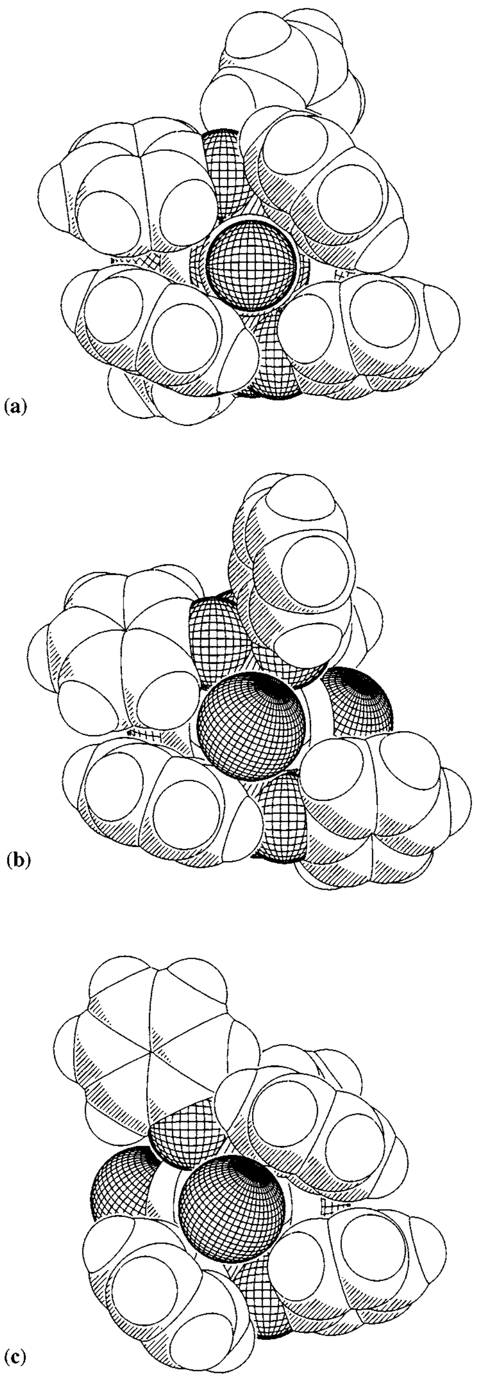


Fig. 2. Three views of **2** with the atoms drawn as their van der Waal's spheres: (a) view down the non-disordered O–C–Fe axis, (b) view down the S–C–Fe minor site and (c) view down the major S–C–Fe site.

Three views down the O/S–C–Fe axes of **2** with the atoms as their van der Waal's spheres are presented in Fig. 2 as PLUTON [14] diagrams. It is evident that four phenyl groups of the phosphite ligands closely surround the non-disordered CO ligand (Fig. 2a) whereas four phenyl groups adopt a more open arrangement around the minor CS site (Fig. 2b). Only three Ph groups are associated with the major CS site (Fig. 2c).

The compound **2** and its phosphine analogue $Fe(CO)_2(CS)(PPh_3)_2$, **5**, reported by Dixneuf and co-workers in 1986 [5] are the only structurally characterised examples of zerovalent iron thiocarbonyl complexes. The latter compound crystallises with two independent molecules, A and B, in the unit cell and there is no disorder of the CS ligand. The C–S bond lengths were determined as 1.550(7) and 1.563(8) Å in molecules A and B, respectively. An average value of 1.768 Å was reported for the corresponding Fe–CS bond lengths.

The thiocarbonyl derivative **2** is closely related to the tricarbonyl iron compound $Fe(CO)_3\{P(OPh)_3\}_2$ **3**. Although this latter complex has been known since 1958 [15] its structure has not been reported; a single crystal X-ray diffraction analysis of **3** was therefore undertaken.

3.2. Crystal and molecular structure of $Fe(CO)_3\{P(OPh)_3\}_2$

An ORTEX [13] diagram of **3** is shown in Fig. 3 and selected bond lengths and angles are given in Table 2. The complex is trigonal bipyramidal about the Fe atom with the phosphite ligands occupying mutually *trans* apical sites [P–Fe–P bond angle 177.21(3)°] and a meridional arrangement of CO groups [C–Fe–C bond angles sum to 359.96(2)°]. Comparison of the structural parameters of molecules **2** and **3** shows that replacement of CO by CS increases the Fe–P bond distances [average Fe–P = 2.141(1) Å in **3**; average Fe–P = 2.150(1) Å in **2**], an effect which may be correlated with the greater π-acidity of the CS ligand versus CO [1] and consequent reduced back-donation into the Fe–P bonds in **2**. The (non-disordered) Fe–CO bond length [1.793(4) Å] in **2** is also slightly longer, and the C–O bond length [1.157(4) Å] slightly shorter, than the corresponding distances in **3** [range of Fe–CO is 1.759(3)–1.778(3) Å; range of C–O is 1.146(3)–1.150(3) Å] although these differences are not statistically significant.

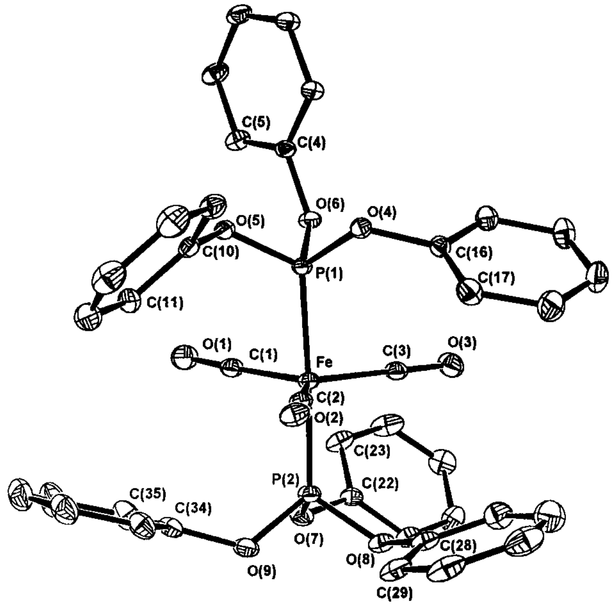


Fig. 3. ORTEX diagram of the molecular structure of $Fe(CO)_3\{P(OPh)_3\}_2$ **3**.

Table 3
Selected bond lengths (Å) and angles (°) for the compounds $Fe(CO)_3(L)_2$ (L = $P(OPh)_3$ **3**, $P(OMe)_3$ **6**, PPh_3 **7**) and **7**·Et_2O

	3	**6**[a]	**7**	**7**·Et_2O
Fe–P	2.1408(8)	2.155(1)	2.2144(9)	2.207(3)
	2.1421(8)		2.2201(9)	2.225(3)
Fe–C	1.759(3)	1.760(5)	1.765(4)	1.755(8)
	1.778(3)	1.764(7)	1.770(4)	1.779(8)
	1.778(3)		1.776(4)	1.783(7)
P–Fe–P	177.21(3)	178.5(1)	172.56(4)	172.54(8)
C–Fe–C	117.07(13)	119.8(2)	118.08(17)	116.9(3)
	120.04(12)	120.6(2)	118.34(17)	117.1(3)
	122.65(12)		123.56(17)	125.9(3)

[a] Molecule lies on a 2-fold axis.

The conformations of the molecules **2** and **3** are essentially identical. In particular we note the presence in both structures of an Fe–P–O bond angle [Fe–P(1)–O(5) = 113.51(8)° in **2** and Fe–P(1)–O(6) = 113.13(6)° in **3**] some 6° smaller than the remaining P(1)–O bond angles (Table 2). A related distortion has previously been described by Ginderow in the structure of $Fe(CO)_3\{P(OMe)_3\}_2$, **6**, in which one of the Fe–P–O bond angles at 113.27(7)° is 5.8° smaller than the average [119.02(7)°] of the remaining two [16]. This asymmetry of the phosphite ligands is manifested in the IR spectra of both compounds **3** and **6** i.e. a splitting of the otherwise degenerate E ν_{CO} band and the appearance of the IR-forbidden A_1 band [17].

The structure of the phosphine analogue of **3** viz. $Fe(CO)_3(PPh_3)_2$, **7**, has recently been reported by two independent groups [18,19] (the latter structure is that of the etherate **7**·Et_2O). A comparison of selected structural data of these molecules is presented in Table 3 together with data for the bis(phosphite) complex **6**.

Two structural features of the phosphine complex **7** and its etherate **7**·Et_2O are notable: the significant deviation from linearity of the P–Fe–P bond angle and the distortion of the $Fe(CO)_3$ unit from trigonal planar geometry as evidenced by the C–Fe–C bond angles, two of which are nearly equivalent [118.08(17) and 118.34(17)° in **7**] while the third [123.56(17)°] is substantially larger. Glaser has recently attributed similar features in the compound $Fe(CO)_3(PPh_2Me)_2$ to packing effects allowing for optimisation of intermolecular phenyl-phenyl interactions [20]. Comparable molecular distortions are not observed in the structures of the

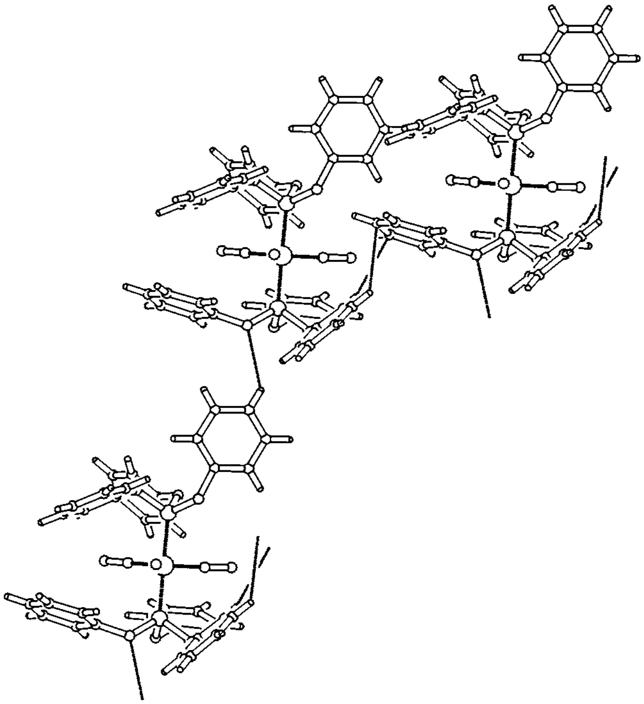


Fig. 4. Hydrogen bonding interactions in $Fe(CO)_3\{P(OPh)_3\}_2$ **3**.

complexes **3** and **6** which contain the less sterically demanding and more flexible phosphite ligands (Tolman cone angles are 128° for $P(OPh)_3$ and 107° for $P(OMe)_3$ versus 145° for PPh_3 [21]).

Analysis of the intra- and intermolecular interactions in **3** using PLATON [22] reveals an intermolecular H...O contact of 2.73 Å involving C(7)–H(7)...O(8)^{i} ($i = x - 1$, $y - 1$, z) and two weaker C–H...π (arene) interactions with H(23)...C(30)^{ii} and H(24)...C(24)^{ii} ($ii = x - 1$, y, z) which are 2.92 Å and 2.91 Å, respectively. These interactions are depicted for **3** in Fig. 4. The related intermolecular interactions in **2** are H(19)...O(6)^{i} 2.72 Å, ($i = 1 + x$, $1 + y$, z), H(32)...C(25)^{ii} 2.92 Å and H(33)...C(24)^{ii} 2.93 Å, ($ii = 1 + x$, y, z).

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