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Thiocarbonyl complexes of iron
V *. New thiocarbonyl complexes derived by substitution from $Fe(CO)_4CS$

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Abstract

Reaction of $Fe(CO)_4CS$ (**1**) with PR_3 ($PR_3 = PPh_3$, PPh_2Me) in the presence of $ONMe_3$ gives the substituted derivatives $Fe(CO)_3(CS)PR_3$ (**2**) and $Fe(CO)_2(CS)(PR_3)_2$ (**3**) in moderate yields. The compounds have been characterized by infrared, ^{13}C, and ^{31}P NMR spectroscopy. At least two isomers of **2** were identified by IR spectroscopy, the CS ligand is probably in the equatorial position of the trigonal-bipyramidal environment of the iron atom in one of these isomers and in the axial position in the other.

Introduction

Thiocarbonyl derivatives of iron(0) have been restricted until recently to $Fe(CO)_4CS$, which was obtained from the reaction of $Na_2[Fe(CO)_4]$ with thiophosgene [1], and $Fe(CO)_2(CS)[P(OPh)_3]_2$, which was synthesized in low yields by conversion of the readily accessible, corresponding η^2-CS_2 complex into the thiocarbonyl complex by treatment with PBu_3/CCl_4 [2]. Such a desulfurization reaction, which normally provides the most convenient route to transition-metal thiocarbonyl complexes [3], was found not to give $Fe(CO)_2(CS)L_2$ complexes when L was other than $P(OPh)_3$. Recently, however, Dixneuf et al. have described a new and more general route to this type of compound, involving reductive elimination of SMe^- from a cationic $[Fe(CO)_2(\eta^2\text{-}CS_2Me)L_2]^+$ species by treatment with Na/Hg in THF [4], or, in the case of $L = PPh_3$, with PBu_3/CH_3CN [5].

We now report another route to $Fe(CO)_2(CS)L_2$ complexes and to the new monosubstituted species $Fe(CO)_3(CS)L$ involving reactions of $Fe(CO)_4CS$ (**1**) with the phosphines PPh_3 and PPh_2Me in the presence of $ONMe_3$.

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* For Part IV see ref. 15.

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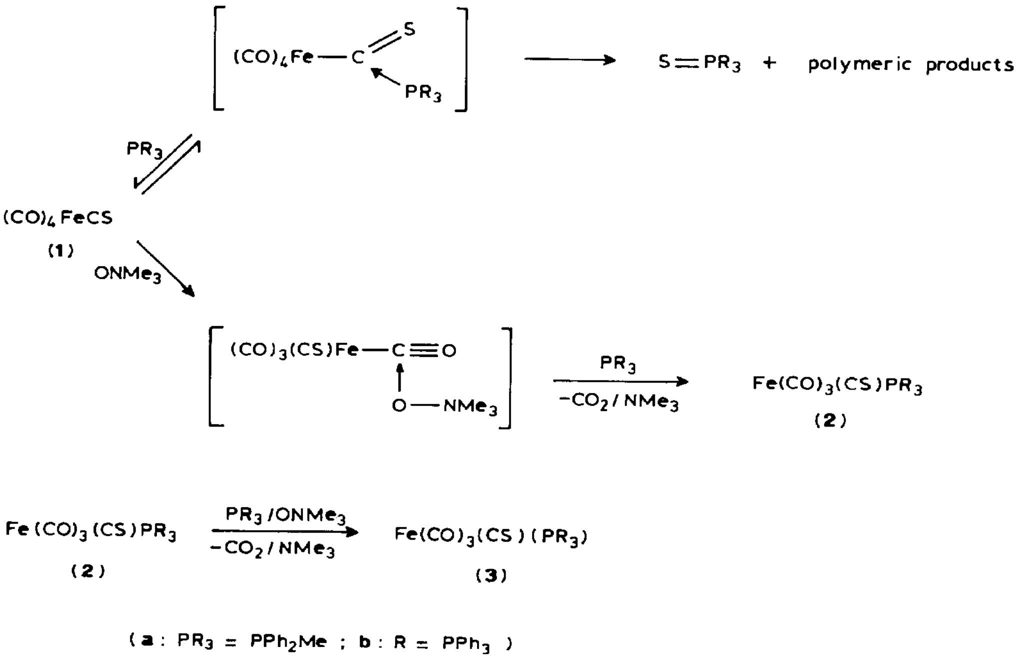
Results and discussion

Attempts to prepare other derivatives by treatment of $Fe(CO)_4CS$ directly with phosphines as in the well-known procedures outlined for $Fe(CO)_5$ [6] failed, although the presence of the more electron withdrawing CS ligand in the molecule should favor CO replacement. The reactions in aromatic solvents gave exclusively brown oily materials, whose IR spectra showed no absorptions in the ν(CS) region. The ^{31}P NMR spectra showed that the corresponding phosphine sulfides, $S{=}PR_3$, had been formed. Addition of trimethylamine-*N*-oxide to a mixture of $Fe(CO)_4CS$ and PR_3 ($PR_3 = PPh_3$, PPh_2Me), however, suppressed the desulfurization reaction and allowed formation of mono- and di-substituted complexes in moderate yields (Scheme 1).

The reaction in the presence of the amine oxide also gives dark brown solutions, from which the thiocarbonyl derivatives can be isolated by extraction of the dried reaction mixture first with pentane (**2**) and then with toluene (**3**).

Trimethylamine-*N*-oxide has been shown to be a valuable reagent for reactions involving displacement of CO ligands, often greatly increasing the reaction rate and allowing use of mild conditions [7,8]. On the basis of kinetic data it was suggested that a coordinatively-unsaturated active intermediate was formed that allowed a suitable base to enter the free coordination site on the transition metal [9].

The desulfurization of **1** in the absence of $ONMe_3$ proceeds slowly with PPh_3 and other trialkylphosphines, whereas phosphites react rapidly at room temperature and $P(NMe_2)_3$ almost explosively, resulting in the corresponding phosphine sulfides [10]. Desulfurization reactions involving phosphines are common in organosulfur

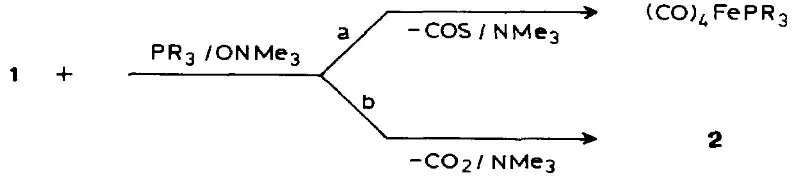


Scheme 1

chemistry but have not been previously observed for a terminal thiocarbonyl group bonded to a transition metal.

We assume that the first step of this desulfurization reaction involves nucleophilic attack of the phosphine molecule at the thiocarbonyl carbon to give an unstable addition compound that finally undergoes elimination of the phosphine sulfide. This mechanism is supported by the observation that a voluminous, bright yellow, cloudy material forms upon addition of PPh_2Me to a solution of **1** in pentane. Attempts to isolate the precipitate by evaporation of the solvent, however, yielded the starting materials. The subsequent phosphine sulfide elimination reaction probably generates highly reactive and unsaturated species such as "$(CO)_4FeC$" that can undergo a variety of subsequent reactions. The results of a study of the reactions of **1** with phosphites and $P(NMe_2)_3$ will be described in a later paper.

As depicted in Scheme 2, competition between two sites is possible in the reaction of the amine oxide with **1**. Nucleophilic attack at the CS carbon atom following pathway a would give the well-known $Fe(CO)_4L$ complexes, whereas attack at one of the CO carbon atoms should give the compounds **2**. The results show that reaction b is favored. In contrast with other "hard" nucleophiles, such as $C(NMe_2)_4$ [11] or $(PPN)NO_2$ [10], attack at the thiocarbonyl carbon atom of **1** was clearly favored (pathway a). However, the presence of trace amounts of the corresponding $Fe(CO)_4L$ complexes, identified by ^{31}P and ^{13}C NMR spectroscopically, show that attack at the thiocarbonyl ligand also ocurred to some extent.



Scheme 2

The formation of **2** and **3** during the reaction of **1** with the system $PR_3/ONMe_3$ demonstrates that the displacement of more than one CO ligand can take place, and oxidation occurs at a second CO carbon atom and is followed by loss of CO_2 and bonding of a futher phosphine ligand. For $L = PPh_3$, the rate of both steps in the presence of $ONMe_3$ must be comparable because **2b** and **3b** are formed in about equal amounts, whereas for $L = PPh_2Me$ the monosubstituted product predominates. Conversion of **2a** into **3a** is readily achieved by treatment with 1 equivalent of $PPh_2Me/ONMe_3$ in CH_2Cl_2 for 12 h.

The IR spectra of the compounds **3** are similar to those reported previously for other $Fe(CO)_2(CS)L_2$ compounds, and exhibit two $\nu(CO)$ bands in the region expected for terminal CO groups and one sharp, strong $\nu(CS)$ band at about 1240 cm^{-1}. Upon going from **1** to **3**, the stepwise introduction of more electron donating phosphines causes a large shift of the $\nu(CO)$ and $\nu(CS)$ bonds to lower frequencies. The $\nu(CO)$ bands for complexes **3** are shifted to higher frequencies relative to those for the corresponding $Fe(CO)_3L_2$ complexes, reflecting the better π-acceptor ability of the CS than of CO ligand. The IR spectra of **2** are more complex than expected for a single species with a rigid array of the ligands and suggest the presence of at least two isomers in solution. In view of the stereochemical non-rigidity of **1**, in

Table 1

Spectroscopic data for the complexes **2a**, **2b** and **3a**, **3b**

Compound	IR [a]		NMR [b]	
	ν(CO)	ν(CS)	^{31}P	^{13}C
$Fe(CO)_3(CS)PPh_2Me$ (**2a**)	2028sh 2020s 1982s 1950vs	1292m 1265s	51.86	18.71 (d,CH_3,J(P,C) 34,56 Hz), 124 to 134 (m′s,C_6H_5), 212.51 (d,CO,J(P,C) 13,37 Hz), 325.89 (d,Cs,J(P,C) 32.73 Hz)
$Fe(CO)_3(CS)PPh_3$ (**2b**)	2048s 2030s 1980s 1945vs 1915sh	1299s 1272s	68.90	124 to 137 (m′s,C_6H_5), 212.75 (d,CO,J(P,C) 14.35 Hz), 326.53 (d,CS,J(P,C) 27.70 Hz)
$Fe(CO)_2(CS)(PPh_2Me)_2$ (**3a**)	1948s 1883s	1228s	60.26	18.96 (m,CH_3), 128 to 133 (m′s, C_6H_5), 212.56 (t,CO,J(P,C) 23.45 Hz), 322.82 (t,CS,J(P,C) 37.8 Hz)
$Fe(CO)_2(CS)(PPh_3)_2$ (**3b**) [c]	1955s 1890s	1240s	77.73 [d]	214.45 (t,CO,J(P,C) 24 Hz), 324.28 (t,CS,J(P,C) 39 Hz)

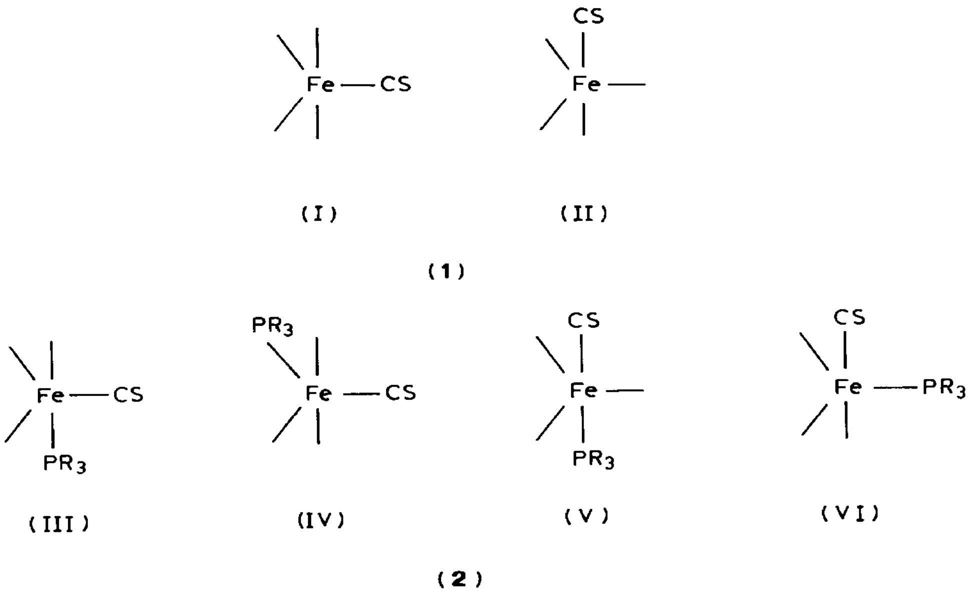
[a] In cm^{-1}, Nujol mull. [b] In ppm, toluene-d_8. [c] ^{13}C NMR data from ref. 5. [d] 77.91 in ref. 5.

which the CS ligand is probably statistically distributed over all five positions, like the PF_3 group in $Fe(CO)_4PF_3$ [12,13], the replacement of one CO by PR_3 can generate four isomers of **2**, as outlined in Scheme 3.

If we assume that the more weakly π-bonding PR_3 group prefers an axial site, and the isomers III and V should predominate, a total of five bands is expected in the ν(CO) region. The spectrum of **2b** shows four strong bands, of which the relatively broad band at 1945 cm^{-1} has a shoulder on the lower frequency side. In contrast, the spectrum of **2a** exhibits only three strong bands, but a shoulder on the highest frequency band indicates that the second isomer is present in small concentrations. The three strong bands observed in **2a** are consistent with the predominance of isomer III. The different isomer distributions for **2a** and **2b** are also reflected in the ν(CS) frequencies. The presence of two equally intense ν(CS) bands in **2b** is consistent with the presence of approximately equal amounts of isomer III and V in equilibrium. In contrast, complex **2a** exhibits two ν(CS) bands with different intensities, indicating that one of the two isomers is preferred. In line with the arguments based on the pattern ν(CO) bands for **2a**, the stronger band at 1265 cm^{-1} must be assigned to isomer III and the less intense band at 1295 cm^{-1} to isomer V. Likewise for **2b**, the ν(CS) bands at 1272 and 1299 cm^{-1} arise from the corresponding isomer III and V, respectively.

The ^{31}P NMR spectra of the PPh_3-substituted derivatives **2b** and **3b** show singlets in the region observed for the corresponding carbonyl congeners, $(CO)_4FePPh_3$ (71.2 ppm) and $(CO)_3Fe(PPh_3)_2$ (81.7 ppm) [14], but the signals are shifted by about 4 to 5 ppm to higher field. On going from **2** to **3**, the introduction of a second phosphine ligand causes a shift of the signals to lower field by about 8.5 ppm.

The ^{13}C NMR spectrum of **2** again reflects the non-rigidity of the ligand array, showing only one signal each for the carbonyl and thiocarbonyl carbon atoms. With one phosphine ligand present, the signals from the CO and CS carbon atoms appear



Scheme 3

as doublets arising from coupling to the phosphorus atom, and no axial-equatorial signal separation can be detected. For **3** the signals from the CS and CO carbon atoms appear as triplets owing to the presence of two phosphorus atoms. The coupling constants ^2J(P, C) are smaller for the monophosphine derivatives **2** than for the disubstituted species **3**, and in all cases larger coupling constants are obtained for the CS than for the CO carbon atoms.

Experimental

Reactions were carried out under dry nitrogen in dried and degassed solvents. The IR spectra were recorded on a Perkin-Elmer 457 spectrometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 300 instrument. Microanalyses were performed by the analytical service of the Fachbereich Chemie der Universität Marburg (Germany).

Preparation of Fe(CO)$_3$(CS)PPh$_2$Me (2a)

A CH_2Cl_2 solution (40 ml) of 270 mg (3.60 mmol) of $ONMe_3$ at −50 °C was added dropwise to a solution of 760 mg (3.58 mmol) of $Fe(CO)_4CS$ (**1**) and 760 mg (3.80 mmol) of PPh_2Me in 50 ml of CH_2Cl_2. The yellow solution turned brown as gas was evolved. The mixture was allowed to warm to room temperature, then stirred for 30 min, and the solvent was removed in vacuo to leave a dark brown oil, which was extracted twice with pentane. The extract was concentrated and the resulting oily residue chromatographed on Al_2O_3. Elution with pentane gave first unchanged **1**, then a second, yellow, band was eluted with CH_2Cl_2/pentane (1/3).

Removal of the solvent gave **2a** as a yellow oil, which could not be crystallized; yield 680 mg (1.77 mmol, 50%). Found: C, 54.46; H, 3.67. $C_{17}H_{13}FeO_3PS$ calc.: C, 53.15; H, 3.41%.

*Preparation of $Fe(CO)_2(CS)(PPh_2Me)_2$ (**3a**)*

A mixture of 520 mg (1.35 mmol) of **2a**, 270 mg (1.35 mmol) of PPh_2Me, and 101 mg of $ONMe_3$ in CH_2Cl_2 solution (50 ml) was stirred for 12 h at room temperature. After evaporation of the solvent the residue was chromatographed on neutral alumina (activity grade III). Some **2a** was first eluted with pentane; a second, yellow, band was eluted with toluene, and concentration of the solution followed by cooling to −78 °C gave pure **3a** as yellow crystals; 80% yield. Found: C, 62.17; H, 4.92. $C_{29}H_{26}FeO_2P_2S$ calc.: 62.60; H, 4.71%.

*Preparation of $Fe(CO)_3(CS)PPh_3$ (**2b**) and $Fe(CO)_2(CS)(PPh_3)_2$ (**3b**)*

A CH_2Cl_2 solution (10 ml) of $ONMe_3$ was added dropwise to a mixture of 490 mg (2.31 mmol) of **1** and 607 mg (2.31 mmol) of PPh_3 in CH_2Cl_2 (50 ml). The dark brown solution was stirred for 40 min and evaporated to dryness. A yellow condensation product was identified as unchanged **1**. The residue was extracted with pentane, and the extract was filtered and then kept to −78 °C for several days, to give yellow crystals of pure **2b**. Additional product was obtained by concentrating the mother liquor and chromatographing the precipitate on neutral alumina (activity grade III); yield 250 mg (0.56 mmol, 20%). Found: C, 59.58; H, 3.56. $C_{22}H_{15}FeO_3PS$ calc.: C, 59.27, H, 3.39%. The brown residue from the pentane extraction was dissolved in toluene and the solution was filtered, then kept for several days at 0 °C, during which a toluene solvate of **3b** separated as red crystals. Attempts to dry the crystals resulted in loss of the toluene to give pure **3b** as yellow microcrystals. Additional **3b** was obtained by concentration of the mother liquor and addition of pentane. Found: C, 68.85; H, 4.55. $C_{39}H_{30}FeO_2P_2S$ calc.: C, 68.83; H, 4.44%.

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