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Thiocarbonyl complexes of iron VIII*. Reaction of $Fe(CO)_4CS$ with the halogens Cl_2, Br_2 and I_2

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Abstract

The halogens Br_2 and I_2 convert the thiocarbonyl complex $Fe(CO)_4CS$ (**1**) by oxidative addition into the corresponding complexes $Fe(CO)_3(CS)X_2$ (**3**:X = Br, I). Treatment of **3** at −80 °C with two equivalents of PPh_3 yields the thiocarbonyl complexes $Fe(CO)(CS)(PPh_3)_2X_2$ (**4**). The action of Cl_2 on **1** produces an unidentified black insoluble material containing terminal CO and CS groups. The compounds have been characterized by elemental analysis, IR, ^{31}P NMR and mass spectroscopy. Based on the spectroscopic results, a *cis* arrangement of the halogen atoms is discussed.

Introduction

Oxidation of carbonyl compounds of the general type $M_n(CO)_m$ with elemental halogens produces transition metal carbonyl halides if mild conditions are applied. Thus, with $Mn_2(CO)_{10}$ cleavage of the Mn–Mn bond occurs to give $Mn(CO)_5X$, while $Fe(CO)_5$ is oxidized to $Fe(CO)_4X_2$ (X = Cl, Br, I). Transition metal complexes containing thiocarbonyl ligands may react in a similar manner although a high electron density at the CS ligand could cause electrophilic reagents in some cases to attack the sulfur atom. In an earlier paper, Dombek and Angelici reported about the oxidation of $W(CO)_5(CS)$ with Br_2 in the presence of PPh_3 giving the seven-coordinate species $W(CO)_2(CS)(PPh_3)_2Br_2$ [1]. No attempts have been made to isolate a phosphine-free complex.

In this paper we have examined the reaction of $Fe(CO)_4(CS)$ (**1**) with Cl_2, Br_2 and I_2. In a previous paper we reported about the reaction of **1** with $N(SnMe_3)_3$ to give mainly $(CO)_3(CS)Fe(SnMe_3)_2$ as a result of a formal oxidative addition of $(SnMe_3)_2$ to **1** [2].

Experimental

All reactions were carried out under dry N_2 in dried and degassed solvents. **1** was prepared as described in ref. 3 and used immediately after synthesis. The IR spectra were recorded on a Perkin-Elmer 457 spectrometer. ^{31}P NMR spectra were run on a Varian XL 100 instrument and the shifts were measured relative to 85% H_3PO_4. The mass spectra were obtained with a CH 7 instrument from MAT (Bremen), 70 eV. Micronanalyses were performed by the analytical service of the Fachbereich Chemie of the University of Marburg (Germany).

Reaction of 1 with Cl_2

A slow stream of dry Cl_2 was bubbled through a stirred solution of 650 mg (3 mmol) of **1** in pentane at −78 °C. A bright yellow solid separated. After 10 min stirring at this temperature, the mixture was allowed to warm to room temperature. At about −50 °C the yellow solid turned brown–black with gas evolution to give a black solid at 0 °C which was filtered and dried in vacuum. The material showed IR bands (in Nujol) at 2115, 2095 ν(CO) and 1370 ν(CS) cm^{-1}.

Preparation of $(CO)_3(CS)FeBr_2$ (3b)

To a solution of 790 mg (3.73 mmol) of **1** in pentane was added dropwise a solution of 600 mg (3.30 mmol) Br_2 in the same solvent at −78 °C. Immediately, an orange–yellow precipitate formed. On slow warming the mixture to room temperature, CO evolution occurred. After stirring the mixture for 1 h at room temperature, an orange–brown precipitate was filtered and dried in vacuum. **3b** is sensitive to the influence of light; yield 1.1 g (97%).

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*For Part VII see ref. 11.

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TABLE 1. Color, analytical data and melting points of **3** and **4**

Complex	Color	Analyses (found (calc.)) (%)				Melting point (°C)
		C	H	Hal	Fe	
$(CO)_3(CS)FeBr_2$ (**3b**)	brown	14.07		45.32	16.20	110d
		(13.97)		(46.49)	(16.25)	
$(CO)_3(CS)FeI_2$ (**3c**)	dark-brown	10.94		58.02	12.74	153d
		(10.91)		(57.98)	(12.76)	
$(CO)(CS)(PPh_3)_2FeBr_2$ (**4b**)	orange	56.55	3.73	19.20	6.77	118–120
		(56.18)	(3.72)	(19.68)	(6.88)	
$(CO)(CS)(PPh_3)_2FeI_2$ (**4c**)	brown	50.96	3.29	28.89	5.55	111d
		(50.34)	(3.34)	(28.00)	(6.16)	

$$\underset{\mathbf{1}}{Fe(CO)_4(CS)} + X_2 \xrightarrow{-78\ ^\circ C} \underset{\mathbf{2}}{[(CO)_4(CS)Fe\cdots X{-}X]} \xrightarrow[-CO]{0\ ^\circ C} \underset{\mathbf{3}}{(CO)_3(CS)FeX_2} \qquad (1)$$

$$\underset{\mathbf{3}}{(CO)_3(CS)FeX_2} \xrightarrow[-2CO]{PPh_3/-78\ ^\circ C} \underset{\mathbf{4}}{(CO)(CS)(PPh_3)_2FeX_2} \qquad (2)$$

$$Fe(CO)_3(CS)PPh_3 + I_2 \xrightarrow{PPh_3} \mathbf{4c} \qquad (3)$$

X	Cl	Br	I
	a	**b**	**c**

Scheme 1.

Preparation of $(CO)_3(CS)FeI_2$ (3c)

610 mg (2.9 mmol) of **1** were similarly treated with 730 mg (2.85 mmol) I_2 in pentane at −78 °C; yield 800 mg (64%). Some unreacted I_2 was removed on the high vacuum line.

Preparation of $(CO)(CS)(PPh_3)_2FeBr_2$ (4b)

To a solution of 770 mg (2.24 mmol) of **3b** in CH_2Cl_2 was added in portions 1.30 g (4.94 mmol) of PPh_3 at −78 °C. The solution turned bright orange with evolution of CO. The mixture was warmed to room temperature and concentrated to half its volume. Addition of pentane precipitated 1.73 g of the complex (95% yield).

Preparation of $(CO)(CS)(PPh_3)_2FeI_2$ (4c)

660 mg (1.5 mmol) of **3c** were treated in a similar manner with 2 equiv. of $P(C_6H_5)_3$ as described for **3b**; yield 1.2 g (90%).

Analytical data for **3** and **4** are given in Table 1.

Results and discussion

The reaction of **1** with X_2 takes place at −78 °C without evolution of CO. With Cl_2 a bright yellow precipitate is formed whereas Br_2 and I_2 give a dark orange and dark brown solid, respectively. We suppose that at first, at low temperature, the addition products **2** are formed*. On elevated temperatures, **2** decompose upon CO evolution to give than the fairly stable oxidative addition products **3** as outlined in eqn. (1) (Scheme 1). In contrast to **3b** and **3c**, the oxidation product with Cl_2, **3a**, could not be isolated pure. On slow warming of the yellow solid **2a** to room temperature it turned black with evolution of CO. The resulting material showed IR bands typically for terminal CO groups at 2115 and 2095 cm^{-1} and an intense band at 1370 cm^{-1} in the region of terminal CS groups but the analytical data were inconsistent with the formulation of the product as **3a**; the low solubility in organic solvents indicates a polymeric material. No markedly change in color was observed on conversion of **2b** or **2c** into **3b** or **3c**, respectively. Without affecting the CS ligand, **1** was oxidized by the heavier halogens apparently in a

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*Similar salt-like adducts of the type $[(CO)_5FeX]X$ (X = Cl, Br, I) were obtained by the oxidation of $Fe(CO)_5$ at low temperature; a structure with six-fold coordinated iron atoms was discussed [4].

TABLE 2. IR (in cm^{-1}) and ^{31}P NMR spectroscopic data of **1**, **3**, **4** and related compounds **5** and **6**

Complex	IR[a]		^{31}P NMR[b]	Reference
	ν(CO)	ν(CS)		
$(CO)_4FeCS$ (**1**)	2103sh, 2100s 2035vs, 2000vs	1320s, 1305s		3
$(CO)_3(CS)FeBr_2$ (**3b**)	2155w, 2105s, 2085m	1351s		this work
$(CO)_3(CS)FeI_2$ (**3c**)	2125m, sh, 2120m, 2085vs	1347s		this work
$(CO)_4FeBr_2$ (**5b**)	2155w, 2112s, 2109, 2082s			5a[c]
$(CO)_4FeI_2$ (**5c**)	2135w, 2089vs 2068s			5a[c]
$(CO)(CS)(PPh_3)_2FeBr_2$ (**4b**)	2040s	1294s	29.3	this work
$(CO)(CS)(PPh_3)_2FeI_2$ (**4c**)	2040s	1311s	61.5	this work
$(CO)_2(PPh_3)_2FeBr_2$ (**6b**)	2038, 1989		82.5	5b[b]
$(CO)_2(PPh_3)_2FeI_2$ (**6c**)				5b

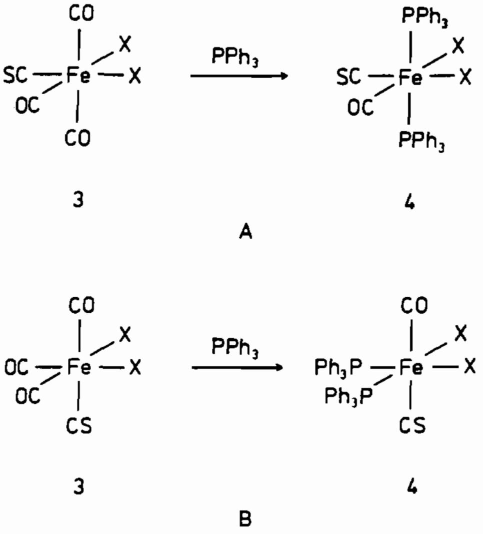
[a] In Nujol mull. [b] In CH_2Cl_2. [c] In $CHCl_3$.

process which appears to be quite similar to that reported for $Fe(CO)_5$ [5].

Reaction of **3** with 2 equiv. of PPh_3 in CH_2Cl_2 at −78 °C quantitatively generates **4** with rapid evolution of CO. Excess PPh_3 did not replace the third CO molecule. The black material, obtained from the oxidation of **1** with Cl_2, did not react with PPh_3. The complex **4c** could also be prepared by the oxidation of $Fe(CO)_3(CS)P(C_6H_5)_3$ with I_2 in the presence of PPh_3 [6].

The presence of the CS ligand in **3** and **4** was clearly established by IR spectroscopy. All compounds exhibit one strong and unsplit band in the region of terminal CS groups, thus indicating the formation of only one stereoisomer. In comparison to **1** the ν(CO) and ν(CS) bands in **3** are shifted to higher frequencies according to the electron release at the central iron atom by the halogen atoms.

If we assume a *cis* arrangement of the halogen atoms in **3** similar to that in $Fe(CO)_4X_2$ (**5**) the CS ligand can be situated *trans* to a halogen atom (equatorial position) or *trans* to a CO group (axial position) as depicted in the arrangements **A** and **B** of Scheme 2. The subsequent replacement of two CO groups leads to compounds with chemically equivalent phosphine groups as evidenced by ^{31}P NMR spectroscopy. For **4** the arrangements **A** and **B** are both consistent with the single resonance signals for the PPh_3 groups but both geometries are difficult to distinguish by the usual spectroscopic methods. However, predictions made for the ν(CO) frequencies (a_1, a_1, b_2) of **3c** from force constant estimations agree better with a *mer*-CO arrangement as shown in **A** [7]. A further argument for structure **A** is the oxidation of $(CO)_2(CS)Fe(PPh_3)_2$ (or a mixture of $(CO)_3(CS)FeP(C_6H_5)_3$ and $P(C_6H_5)_3$) [6, 8], in which the *trans* position of the phosphine ligands was established by an X-ray study [8]; with I_2 a product with identical ν(CO) and ν(CS) bands as in **4c** was obtained. The same arrangement as shown in **A** was also found in the osmium complex $Os(CO)(CS)(PPh_3)_2Cl_2$ [9] and also supposed for the corresponding ruthenium derivative [10].



Scheme 2.

The replacement of two CO groups in **3** by the more electron donating $P(C_6H_5)_3$ ligand causes the ν(CS) and the center of the ν(CO) vibrations in **4** to shift to lower frequencies. Concerning **4**, however, the ν(CO) bands appear at a higher frequence as the center of the ν(CO) bands of the CS-free derivatives **6** as shown in Table 2. This reflects the better π acceptor ability of CS relative to CO. On going from **5** to **3** the introduction of a CS ligand only slightly affects the position of the ν(CO) bands.

The mass spectra (electron impact) of **3b** and **3c** show the molecular ions followed by peaks due to successive loss of CO. Fragments derived from loss of the CS ligand were observed with minor intensities.

The stability of the CS ligand towards oxidation and substitution [11] is probably due to the stronger metal carbon bond of the CS ligand relative to the metal carbon bond of CO. A similar behavior was observed earlier by the reaction of $W(CO)_5CS$ with Br_2 in the presence of PPh_3 [1]. In contrast, the preparation of anionic CS-containing species by treatment of **1** with reducing agents has failed upto the present time [12].

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