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Further reactions of $[(\eta\text{-}C_5H_5)(CO)_2FeC(S)SMLn]$ ($MLn = Fe(\eta\text{-}C_5H_5)(CO)_2$, $Re(CO)_5$) with organic electrophiles

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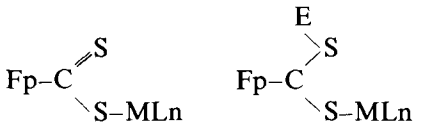
Abstract

Reaction of FpC(S)SMLn (Fp = $Fe(\eta\text{-}C_5H_5)(CO)_2$; MLn = Fp (**1a**), $Re(CO)_5$ (**1b**)) with MeC(O)Cl affords [FpCS]Cl and LnMSC(O)Me (**3**); **1a** reacts with $(CF_3CO)_2O$ to yield $[Fp(CO)]CF_3CO_2$ and $FpSC(O)CF_3$ (**5**). In both cases the reactions have been shown to occur via the unstable *S*-acylated intermediates $[FpC[SC(O)R]SMLn]^+$ (R = CF_3, Me). Alkylation of **1a** with RBr (R = Me, Et, CH_2Ph, CH_2CHCH_2) or CF_3SO_2OR (R = Me, Et) followed by treatment of the stable *S*-alkylated derivatives $[FpC(SR)SFp]^+$ with I^- provides a useful alternative method for the synthesis of a variety of FpC(S)SR.

The reaction of the $\mu_2:\eta$ (C, S) carbon disulfide complexes FpC(S)SMLn (**1**) with Lewis acid-metal species or alkylating reagents (E) has provided a series of tri- and di-nuclear complexes with CS_2 bridges of the type **2** [1–4].



(**1**) (**2**)

Moreover the low basicity of the thione-sulfur function in **1** has been shown to allow its nucleophilic addition at the thiocarbonyl carbon rather than CO or CS replacement in the $[Fe(\eta\text{-}C_5H_5)(CO)_2(CS)]^+$. These reactions have given the new metallacycles $[(CO)(\eta\text{-}C_5H_5)\overline{FeC(SMLn)SC(Fp)S}]$ [5]. It was therefore expected that the C=S group in **1** might, under suitable conditions, form *S*-acyl adducts by use of carboxylic acid anhydrides or acetyl chloride.

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We describe here the results of these reactions, which unexpectedly result in desulfurization of the CS_2 bridging molecule, as shown by the formation of $FpSC(O)R$ (R = CF_3, Me). It is also shown that the type **1** complexes are convenient starting materials for the synthesis of a variety of iron dithiocarboxylate complexes FpC(S)SR.

1. Acylation reactions

The reaction of FpC(S)SFp (**1a**) and an excess of MeC(O)Cl in Et_2O did not produce the expected [FpC[SC(O)Me]SFp]Cl, but gave two other products in approximately equimolar amounts namely [Fp(CS)]Cl [6], which precipitates during the reaction, and $FpSC(O)CH_3$ (**3a**) isolated by chromatography on alumina of the reaction solution. Similarly $FpC(S)SRe(CO)_5$ (**1b**) was shown to react with MeC(O)Cl to form [Fp(CS)]Cl and $(CO)_5ReSC(O)Me$ (**3b**).

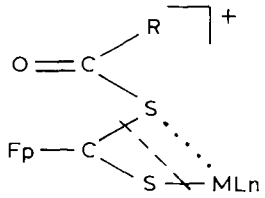
$$FpC(S)SMLn + ClC(O)Me \rightarrow [Fp(CS)]Cl + LnMSC(O)Me \quad (1)$$

(**1a**: MLn = Fp; **1b**: MLn = $(CO)_5Re$) (**3a–3b**)

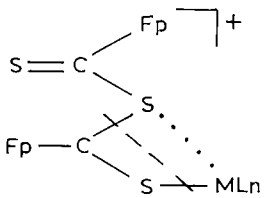
When reaction 1 was carried out in CH_2Cl_2 **3a** was obtained as main product. In this case infrared analysis of the reaction solution showed the presence of FpCl and $Fe(\eta\text{-}C_5H_5)(CO)(CS)Cl$ (ν(CS) 1318 cm^{-1}), which are produced from [Fp(CS)]Cl by substitution of the chloride counter ion for CO or CS [7]. Nevertheless alumina chromatography of the reaction mixture allowed separation of only two products, namely **3a** and variable amounts of FpCl. The analytical and spectroscopic data for type **3** complexes (Table 1) are as expected and, in the case of **3a**, identical with those of the same compound prepared from FpCl and KSC(O)Me in the presence of $AgNO_3$.

The products of eq. 1 not only indicate that acetyl chloride acts as desulfurizing reagent of the bridging CS_2, but also provide clues to the reaction mechanism.

The desulfurization reactions of both organic molecules [8] and CS_2-containing complexes [9] by organometallic reagents have been suggested to occur through carbenes. The initial step of the acylation reaction 1 may likewise involve formation of the carbene intermediate $[FpC(SC(O)Me)SMLn]^+$. Decomposition of this thioanhydride-like complex via C–S and S–M cleavage (**Ia**) would yield $[Fp(CS)]^+$ and **3**.



(Ia)



(Ib)

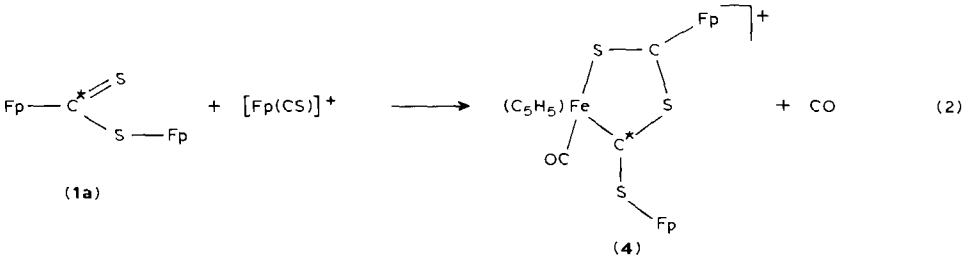
The depicted mechanism is consistent both with the demonstrated *Z*-electrophilic addition at the thione group of **1** and the ease of S–M cleavage of type **2** cationic complexes [4,5]. Direct evidence for the proposed mechanism is given by the closely related reaction between $[Fp(CS)]^+$ and **1a** containing 10% ^{13}C enriched bridging CS_2, which gives the cyclic species **4** (eq. 2).

Table 1

Properties and selected IR (cm^{-1}) and ^1H NMR data

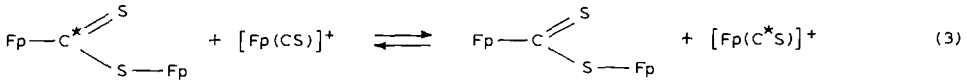
Compound	M.p. (°C)	Yield (%) [a]	ν(CO) [b]	Chemical shift δ (ppm) [c]
FpSC(O)Me (**3a**)	59–60	58	2040s, 1994s, 1626m	5.07(s, C_5H_5), 2.43(s, Me)
$(CO)_5$ReSC(O)Me (**3b**)	82–83	50	2135w, 2037w, 2041vs, 1997s, 1644m	–
FpSC(O)CF_3 (**5a**)	61–63	73	2051s, 2006s, 1673m	5.15(s, C_5H_5)
$(CO)_5$ReSC(O)CF_3 (**5b**)	75–76	61	2143w, 2080w, 2041vs, 1996s, 1645m	–
[FpC(SMe)SFp]I (**7a**)	118 (dec)	85	2042s, 1999s	5.58, 5.49(s, C_5H_5), 3.38(s, Me)
[FpC(SEt)SFp]SO_3CF_3 [d] (**7b**)	137 (dec)	92	2047sh, 2041s, 2003s	5.58, 5.51(s, C_5H_5), 4.00(q, CH_2), 1.58(t, CH_3)
[FpC(SCH_2Ph)SFp]Br (**7c**)	–	81	2040s, 1995s	7.40(m, Ph), 5.40, 5.33(s, C_5H_5), 5.08(s, CH_2)
[FpC($SCH_2CH{=}CH_2$)SFp]Br (**7d**)	–	78	2041s, 1997s	5.42, 5.25(s, C_5H_5)
FpC(S)SMe [e] (**6a**)	70–71	72	2033s, 1981s	4.94(s, C_5H_5), 2.64(s, Me)
FpC(S)SEt (**6b**)	55–58	70	2032s, 1983s	4.87(s, C_5H_5), 3.23(q, CH_2), 1.21(t, CH_3)
FpC(S)SCH_2Ph [e] (**6c**)	71–73	65	2032s, 1982s	7.13(m, Ph), 4.91(s, C_5H_5), 4.54(s, CH_2)
FpC(S)$SCH_2CH{=}CH_2$ (**6d**)	45–48	48	2030s, 1984s	5.86(m, CH), 5.18(m, CH_2), 4.88(s, C_5H_5), 3.96(d, SCH_2)
FpOC(O)CF_3 [f]	73–74	65	2054s, 2016s, 1680m	5.17(s, C_5H_5)

[a] Calculated from FpC(S)SMLn. [b] In CH_2Cl_2. [c] Neutral compounds in $CDCl_3$, cationic in acetone-d_6. [d] See ref. 3. [e] See ref. 13. [f] See ref. 10.



(2)

We expected to find ^{13}C enrichment only at the carbon bonded to the endocyclic iron, but surprisingly the ^{13}C NMR spectrum of **4** showed that the signals previously assigned [5] to the endocyclic carbons (329.23, 284.23 ppm) were equally enriched. This observation is consistent with the existence of the equilibrium 3 involving the CS_2/CS exchange via intermediate Ib prior to form the metallacycle by reaction between the CS- and CS_2-containing species (eq. 2).



(3)

By analogy with acetyl chloride, $(CF_3CO)_2O$ reacts with **1a** to form $FpSC(O)CF_3$ (**5a**), a yellow precipitate of $[Fp(CO)]CO_2CF_3$, and some unidentified organic sulfur-containing compounds (eq. 4).

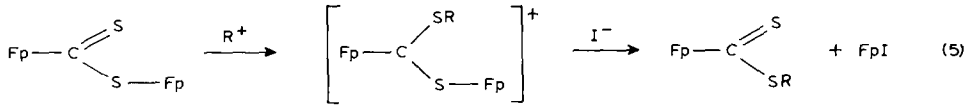
$$FpC(S)SFp + (CF_3CO)_2O \rightarrow [Fp(CO)]CO_2CF_3 + FpSC(O)CF_3 + \ldots \quad (4)$$
(**1a**) (**5a**)

The isolated iron carbonyl salt dissolves in CH_2Cl_2 to form the red $FpOC(O)CF_3$ [10]. The formation of **5a** suggests that the desulfurization reaction 4 proceeds as described above. If this is the case, the $[Fp(CO)]CO_2CF_3$ product of eq. 4 should be a side-product of the reaction between $[Fp(CS)]CO_2CF_3$ and the excess of $(CF_3CO)_2O$. It can thus be assumed that under the experimental conditions we use, trifuoroacetic anhydride behaves like NH_2R, NCO^- or NCS^-, which are known to desulfurize $[Fp(CS)]^+$ to form $[Fp(CNR)]^+$ [11] and FpCN [12], respectively.

Although the acetic anhydride does not react with **1a** nor **1b**, the latter was found to react with $(CF_3CO)_2O$ to give $(CO)_5ReSC(O)CF_3$ (**5b**) as the only isolated organometallic species.

2. Synthesis of FpC(S)SR via alkylation of FpC(S)SFp

Successive use of Fp^-, CS_2, and alkylating reagents has been shown to yield the dithiocarboxylate derivative FpC(S)SR (**6**) [13]. Alkylation of **1a** with a suitable alkyl halide (MeI, $PhCH_2Br$, CH_2CHCH_2Br) or CF_3SO_2OR (R = Me, Et), followed by treatment of the resulting stable cationic dithiocarbene intermediate $[FpC(SR)SFp]^+$ (**7**) [1,3], has now provided an alternative method for obtaining FpC(S)SR (**6**).



(1a) (7) (6)

The best way of carrying out the sequence 5 is to isolate **7** in order to avoid competitive *S*-alkylation of **6**, and then treat the crude cationic species with an excess of tetrabutylammonium iodide. Chromatographic separation then gives **6** in yields of 40–70%, together with FpI. This new route implies that FpC(S)SFp is a storable equivalent of $[FpCS_2]^-$ for synthesis of dithiocarboxylate complexes which are known to be precursors for all the mononuclear Fp-containing CS_2 [14] and CS [15] compounds. Thus the Fp moiety can be regarded as a protective group for one of the two sulfur atoms of the unstable $[Fp(CS_2)]^-$ ion. The facile nucleophilic

cleavage of the S–Fp bond in cationic dithiocarbenes $[MC(SR)SFp]^+$ regenerates the thionic sulphur. When iodide ion is used as the nucleophile, the FpI product can be reused for synthesizing **1a** [16].

It is also noteworthy that even $FpC(S)SRe(CO)_5$ (**1b**) gives $FpC(S)SCH_3$ under the same conditions [2], but the use of **1b** for this purpose is less satisfactory in view of its observed instability of and the lower yield of the synthesis starting from $[Fp(CS_2)]^-$ and $(CO)_5ReBr$ [2].

Experimental

All manipulations were carried out by standard Schlenk techniques under pure dinitrogen. Solvents were dried by standard methods, and degassed and distilled before use. The MeC(O)Cl, $(CF_3CO)_2O$, and alkyl halides were distilled prior to use. The 99% ^{13}C enriched carbon disulfide was purchased from Stohler/KOR. All the other reagent-grade chemicals were used as received. The compounds $(\eta\text{-}C_5H_5)(CO)_2FeCl$ [17], FpC(S)SFp [2,16]. $FpC(S)SRe(CO)_5$ [2] and $[(\eta\text{-}C_5H_5)(CO)FeC(SFp)SC(Fp)S]SO_3CF_3$ [5] were prepared by published procedures; $KSC(O)CH_3$ was prepared from thioacetic acid [18] and KOH in anhydrous Et_2O and dried under vacuum. For recording of spectra the following instruments were used. IR: Perkin–Elmer 257 spectrophotometer, ^1H NMR and ^{13}C NMR: JEOL-60, Varian XL 100, MS: JEOL JMS-D (75 eV). Melting points were determined with a Buchi instrument and are uncorrected. Spectroscopic properties, melting points, and yields of the complexes are reported in Table 1.

Reaction of FpC(S)SMLn with ClC(O)Me

The complex FpC(S)SMLn (**1**) (0.6 mmol) and acetyl chloride (0.2 cm^3, 3 mmol) were allowed to react in 50 cm^3 of Et_2O at room temperature for 24 h. The precipitate of [Fp(CS)]Cl (0.08 g, 0.3 mmol) was filtered off and characterized by IR spectroscopy (ν(CO) (KBr): 2095, 2065; ν(CS) 1348 cm^{-1}). The filtrate was evaporated under vacuum and the residue chromatographed on an alumina column. Elution with light petroleum/CH_2Cl_2 (4/1) yielded LnMSC(O)Me (**3**), which was crystallized from CH_2Cl_2/hexane at −20 °C. In the case of FpC(S)SFp small amounts of FpCl were recovered from a second fraction from the chromatographic separation.

The reaction of FpC(S)SFp (**1a**) and an excess of ClC(O)Me in CH_2Cl_2 gave **3a** (60%) and FpCl (32%) after chromatography on alumina.

FpSC(O)Me (**3a**): orange yellow. Found: C, 41.90; H, 3.05. $C_9H_8O_3FeS$ (calcd.: C, 42.88; H, 3.20%. MS: $m/e = 252$ $[M]^+$, 224 $[M-(CO)]^+$, 196 $[M-(CO)_2]^+$.

$(CO)_5ReSC(O)Me$ (**3b**): pale yellow. Found: C, 21.21; H, 1.09. $C_7H_3O_6ReS$ calcd.: C, 20.95; H, = 0.75%.

Preparation of FpSC(O)Me (3a)

To an acetone solution (70 cm^3) of FpCl (0.26 g, 1.25 mmol) was added $AgNO_3$ (0.25 g, 1.50 mmol). After 2 h of stirring the solution was filtered and an excess of KSC(O)Me (1.70 mmol) was added. The mixture was refluxed for 2 h, then filtered and evaporated under vacuum. The residue was dissolved in $CHCl_3$ and the solution dried over $CaCl_2$. Evaporation of the solvent left a residue which was recrystallized from CH_2Cl_2/n-hexane at −20 °C to give yellow crystals of FpSC(O)Me (**3a**) in 63% yield.

Reaction of FpC(S)SMLn with $(CF_3CO)_2O$

A solution of FpC(S)SMLn (0.6 mmol) and trifuoroacetic anhydride in 70 cm^3 of Et_2O was stirred for 1 h at room temperature, and the yellow $[Fp(CO)]CF_3CO_2$ (IR (KBR) ν(CO) 2124, 2071; $\nu(CF_3CO_2)$ 1681, 1434, 1197, 1142 cm^{-2}) was then filtered off. The filtrate was evaporated under vacuum and the residue extracted with light petroleum (ca. 100 cm^3). Concentration of the extract to 20 cm^3 followed by crystallization at $-20\,°C$ gave $FpSC(O)CF_3$ (**5**).

The $[Fp(CO)]CF_3CO_2$ was dissolved in CH_2Cl_2, and then stirred at room temperature for 24 h, filtered and evaporated to dryness. The residue, which was then dissolved in CH_2Cl_2/hexane, upon recrystallization gave red crystals of $FpOC(O)CF_3$ [10].

$FpSC(O)CF_3$ (**5a**): yellow. Found: C, 34.62; H, 1.91. $C_9H_5O_3F_3FeS$, calcd.: C, 35.32; H, 1.65%. MS: $m/e = 306\ [M]^+$, 278 $[M-(CO)]^+$, 250 $[M-(CO)_2]^+$, 140 $[(C_5H_5)FeF]^+$.

$(CO)_5ReSC(O)CF_3$ (**5b**): pale yellow. Found: C, 19.26. C_7O_6ReS, calcd.: C, 18.46%. MS: $m/e\ ^{187}Re = 456\ [M]^+$, 428 $[M-(CO)]^+$, 400 $[M-(CO)_2]^+$, 372 $[M-(CO)_3]^+$, 344 $[M-(CO)_4]^+$, 316 $[M-(CO)_5]^+$, 219 $[ReS]^+$.

Preparation of FpC(S)SR (6)

The title complexes were prepared in a two step sequence involving: (i) *S*-alkylation of **1a**, and (ii) treatment of the resulting dithiocarbene complexes $[FpC(SR)SFp]^+$ (**7**) with tetrabutylammonium iodide. The first step was carried out in CH_2Cl_2 (50 cm^3) starting from FpC(S)SFp (0.5 mmol) and the stoichiometric amount of CF_3SO_2OEt or a two fold excess of RX (RX = MeI, $PhCH_2Br$, CH_2CHCH_2Br). In the case of CF_3SO_2OEt only few minutes were required for formation of $[FpC(SEt)SFp]SO_3CF_3$ (**7b**), but with the alkyl halides MeI or RBr longer reaction times were needed (24 h). In all the cases the **7a–7d** complexes were isolated from the reaction mixture by precipitation with Et_2O, and characterized by IR and NMR spectroscopy (Table 1). In the second step a solution of the crude cationic complex $[FpC(SR)SFp]^+$ (**7**) in acetone was treated with tetrabutylammonium iodide (30 mmol) under reflux for 4 h. The solution was then evaporated and the residue chromatographed on an alumina column with light petroleum/CH_2Cl_2 (3/1) as eluent. The FpC(S)SR complexes obtained from the first fraction were recrystallized from n-pentane at $-20\,°C$; FpCl was recovered from the second fraction (50%).

$FpC(S)SC_2H_5$ (**6b**): yellow-orange. Found: C, 42.55; H, 3.62. $C_{10}H_{10}FeO_2S_2$ calcd.: 42.57; H, 3.57%.

$FpC(S)SCH_2CHCH_2$ (**6d**) orange-yellow. Found: C, 46.20; H, 3.10. $C_{11}H_{10}FeO_2S_2$ calcd.: C, 44.91; H. 3.43%. ^1H NMR (C_6D_6): 5.79 (ddt, *J* 17.0, 6.9, 6.7 Hz, =CH, 1H), 5.02 (d, *J* 17.0 Hz, $=CH_2$, 1H), 4.88 (d, *J* 9.8 Hz, $=CH_2$, 1H), 4.03 (s, C_5H_5, 5H), 3.96 (d, *J* 6.9 Hz, CH_2, 2H).

Acknowledgments

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