Journal of Organometallic Chemistry, 339 (1988) 125–131
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

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

L. Busetto *, S. Bordoni and V. Zanotti

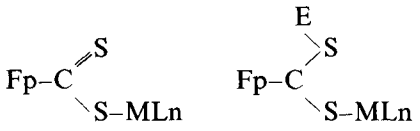
Dipartimento di Chimica Fisica ed Inorganica, Università di Bologna, viale Risorgimento 4, 40136 Bologna (Italy)

(Received June 29th, 1987)

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.

0022-328X/88/$03.50

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**).

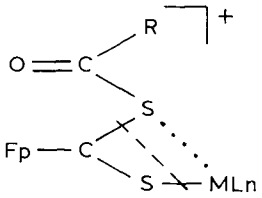
$$FpC(S)SMLn + ClC(O)Me \rightarrow [Fp(CS)]Cl + LnMSC(O)Me \quad (1)$$

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

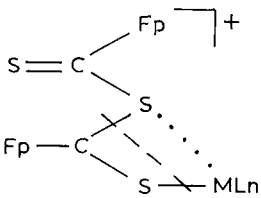
When reaction 1 was carried out in CH_2Cl_2 **3a** was obtained as main product. In this case infrared analysis of the reaction solution showed the presence of FpCl and $Fe(\eta\text{-}C_5H_5)(CO)(CS)Cl$ (ν(CS) 1318 cm^{-1}), which are produced from [Fp(CS)]Cl by substitution of the chloride counter 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)

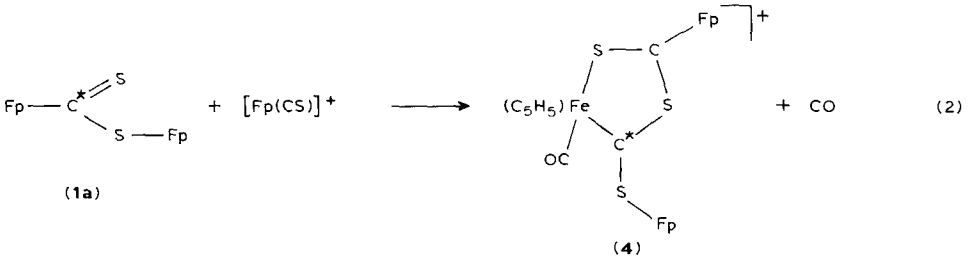
The depicted mechanism is consistent both with the demonstrated *Z*-electrophilic addition at the thione group of **1** and the ease of S–M cleavage of type **2** cationic complexes [4,5]. Direct evidence for the proposed mechanism is given by the closely related reaction between $[Fp(CS)]^+$ and **1a** 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

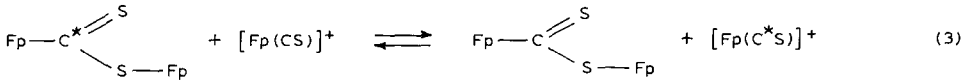
Compound	M.p. (°C)	Yield (%) [a]	ν(CO) [b]	Chemical shift δ (ppm) [c]
FpSC(O)Me (**3a**)	59–60	58	2040s, 1994s, 1626m	5.07(s, C_5H_5), 2.43(s, Me)
$(CO)_5$ReSC(O)Me (**3b**)	82–83	50	2135w, 2037w, 2041vs, 1997s, 1644m	–
FpSC(O)CF_3 (**5a**)	61–63	73	2051s, 2006s, 1673m	5.15(s, C_5H_5)
$(CO)_5$ReSC(O)CF_3 (**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).

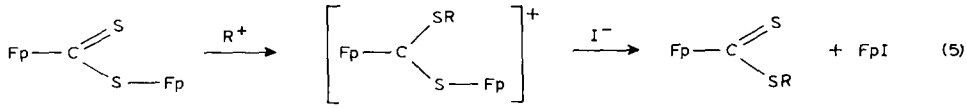
$$\underset{(\mathbf{1a})}{FpC(S)SFp} + (CF_3CO)_2O \rightarrow [Fp(CO)]CO_2CF_3 + \underset{(\mathbf{5a})}{FpSC(O)CF_3} + \ldots \quad (4)$$

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

We thank the CNR and the Ministero della Pubblica Istruzione for financial support.

References

1 L. Busetto, A. Palazzi and M. Monari, J. Organomet. Chem., 228 (1982) C19.
2 L. Busetto, A. Palazzi and M. Monari, J. Chem. Soc., Dalton Trans., (1982) 1631.
3 M. Stolzenberg, W.P. Fehlhammer, M. Monari, V. Zanotti and L. Busetto, J. Organomet. Chem., 272 (1984) 73.
4 L. Busetto, M. Monari, A. Palazzi, V.G. Albano, and F. Demartin, J. Chem. Soc., Dalton Trans., (1983) 1849.
5 L. Busetto, V. Zanotti, V.G. Albano, D. Braga and M. Monari, J. Chem. Soc., Dalton Trans., (1987) 1133.
6 L. Busetto and R.J. Angelici, J. Am. Chem. Soc., 90 (1968) 3283.
7 R.J. Angelici and J.W. Dunker, Inorg. Chem., 24 (1985) 2209.
8 H. Alper and H.N. Paik, J. Org. Chem., 42 (1977) 3520.
9 L. Busetto, V. Zanotti, V.G. Albano, D. Braga and M. Monari, J. Chem. Soc., Dalton Trans., (1986) 1791.
10 R.B. King and R.N. Kapoor, J. Organomet. Chem., 15 (1968) 457.
11 L. Busetto and A. Palazzi, Inorg. Chim. Acta, 19 (1976) 233.
12 L. Busetto, M. Graziani, and U. Belluco, Inorg. Chem., 10 (1971) 78.
13 F.B. McCormick and R.J. Angelici, Inorg. Chem., 18 (1979) 1231.
14 C. Bianchini, C. Mealli, A. Meli, M. Sabat, Stereochemistry of Organometallic and Inorganic Compounds, Elsevier, Amsterdam, 1986.
15 P.V. Broadhurst, Polyhedron, 4 (1985) 1801.
16 J.E. Ellis, R.W. Fennel and E.A. Flom, Inorg. Chem., 15 (1976) 2031.
17 J.S. Piper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1915) 165.
18 B. Sjoberg, Svensk. Kem. Tid., 63 (1951) 90.