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PREPARATION OF *S*-BONDED IRON CARBONYL DERIVATIVES OF MONOTHIOCARBOXYLIC ACIDS

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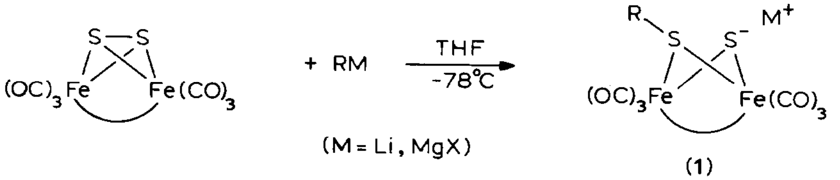
Summary

The reaction of monoanions and the dianion derived from $(\mu\text{-}S_2)Fe_2(CO)_6$ with mono- and di-acid chlorides gave $S_2Fe_2(CO)_6$ clusters containing acyl groups attached to the sulfur atoms. The diacyl groups derived from diacid chlorides bridged two monoanions or bridged the two sulfur atoms of the dianion intramolecularly.

Introduction

We have shown that organolithium and Grignard reagents cleave the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ to give intermediates of type **1** (eq.1) [2]. Addition of alkyl halides, R′X, to such solutions of **1** gave complexes of type $(\mu\text{-}RS)(\mu\text{-}R'S)Fe_2(CO)_6$. Protonation resulted in formation of $(\mu\text{-}RS)(\mu\text{-}HS)Fe_2(CO)_6$.



(1)

In view of the extensive, broad reactivity of organic mercaptides, $RS^- M^+$ [3], it may be anticipated that such bridging thiolate complexes, **1**, will show other reactions in addition to those already described. Cleavage of the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ with two molar equivalents of a complex metal hydride such as $LiBEt_3H$ produces the dianionic intermediate **2**, whose reactions with organic and

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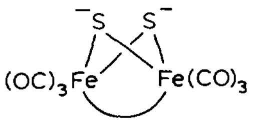


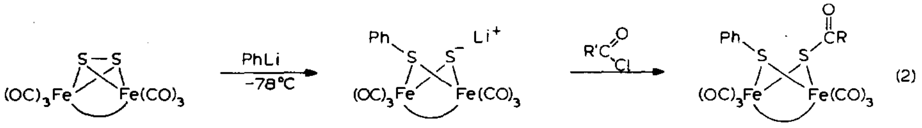
(2)

organometallic halides we have described previously [4]. In the case of **2** also, further studies of its reactivity are in order.

Our current interest in iron carbonyl complexes containing ligands derived from mono- and di-thiocarboxylic acid esters [5], has led us to examine the acylation of anions of type **1** and **2**.

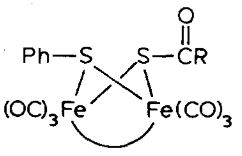
Results and discussion

The reaction of phenyllithium with $(\mu\text{-}S_2)Fe_2(CO)_6$ gave **3**. This anionic reagent could be acylated readily and in high yield to give complexes of type **4** (eq. 2). In the case of the acetyl and pivaloyl chloride reaction products the observation of two CH_3 and two Me_3C signals, respectively, in their proton NMR spectra indicated the presence of two isomers. The possible isomers are **4x**, **4y**, and **4z**, but the available data do not allow us to say which are present in the respective products.

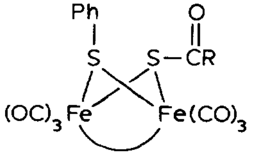


(3)

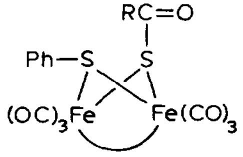
(4a, R = CH_3; 4b, R = Me_3C; 4c, R = Ph)



(4x)

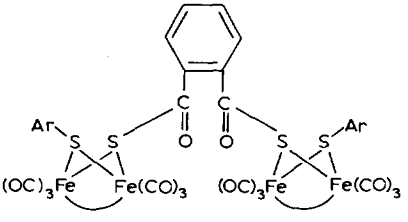


(4y)

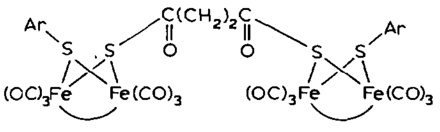


(4z)

Reactions of the *p*-tolylmagnesium bromide/$(\mu\text{-}S_2)Fe_2(CO)_6$, derived anion with *o*-phthaloyl chloride and with succinoyl chloride gave products in which two $(\mu\text{-}p\text{-}CH_3C_6H_4S)(\mu\text{-}S)Fe_2(CO)_6$ units were linked via the difunctional organic moiety, **5** and **6**, respectively, in high yield.

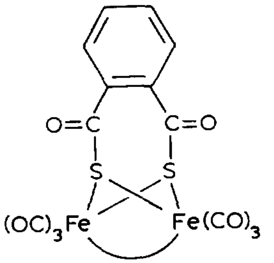


(5, Ar = $p\text{-}CH_3C_6H_4$)



(6, Ar = $p\text{-}CH_3C_6H_4$)

Similar reactions of these diacid halides with the dianion derived from (μ-S_2)$Fe_2(CO)_6$ [4], on the other hand, resulted in formation of bridged complexes, **7** and **8a**, respectively, in good yield, while reaction of the dianion with glutaroyl chloride gave **8b**.



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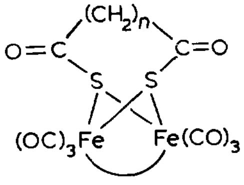

(8a, n = 2;
8b, n = 3)

The compounds reported here represent a new type of metal derivative of monothiocarboxylic acids, RC(O)SH. It may be of interest to explore their chemical reactivity but this is beyond the scope of our present interests.

Experimental

General comments

All reactions were carried out in flame-dried flasks under an atmosphere of prepurified nitrogen unless indicated otherwise. Air- and/or moisture-sensitive materials were handled either in a Vacuum Atmospheres HE-43 Dri-Lab glovebox or by using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl. Reagent-grade dichloromethane (Mallinckrodt) was deoxygenated by purging it with nitrogen for 15 min. Hexane was distilled under nitrogen from sodium metal. All other solvents were dried by the appropriate method and distilled under nitrogen. All solvents were stored under a positive pressure of nitrogen. Thin-layer chromatography (TLC) was used to monitor the progress of the reaction being studied (Eastman or J.T. Baker silica gel plates). The intense colors of the compounds involved made further treatment of the TLC plate unnecessary. Mixtures of reaction products were, in general, separated by column chromatography or filtration chromatography using hexane, pentane or a pentane/dichloromethane (95/5) mixture as eluents.

Reactions of the phenyl-monoanion, 3, with acid chlorides

A 200 ml three-necked flask equipped with a magnetic stir-bar, a nitrogen inlet tube and a rubber septum was charged with 1.0 g (2.91 mmol) of (μ-S_2)$Fe_2(CO)_6$ [4] and 60 ml of THF. The resulting solution was cooled to −78°C and 2.4 ml of 1.23 *M* phenyllithium (2.95 mmol) in diethyl ether was added slowly by syringe. To the green solution which had been formed was added, by syringe, at −78°C, 0.92 ml (~ 12.9 mmol) of acetyl chloride. Examination of the resulting red reaction mixture by TLC (silicic acid, 10% CH_2Cl_2/pentane) showed a single product to be present. The reaction mixture was filtered under nitrogen and the filtrate was evaporated at reduced pressure. The residue was purified by column chromatography (silicic acid, 20% CH_2Cl_2/pentane). Red crystals, m.p. 83–84°C, of **4a** were obtained in 77%

yield. Anal. Found: C, 35.93; H, 1.80. $C_{14}H_8O_7S_2Fe_2$ calcd.: C, 36.23; H, 1.74%. IR (CH_2Cl_2): ester C=O, 1745; terminal C≡O, 2082(vs), 2045(vs), 2005(vs) cm^{-1}. NMR ($CDCl_3$): δ 2.40 and 2.45 (s, 3H total, CH_3 of two isomers present in 1/4.75 ratio), 7.26 (m, 5H, Ph) ppm.

A reaction carried out similarly and on the same scale in which pivaloyl chloride was added to the monoanion solution gave, after similar work-up, **4b**, a dark red oil, in 80% yield. Anal. Found: C, 40.86; H. 2.90. $C_{17}H_{14}O_7S_2Fe_2$ calcd.: C, 40.34; H, 2.79%. IR (CH_2Cl_2): ester C=O, 1733, 1706; terminal C≡O, 2080(s), 2040(vs), 2005(vs) cm^{-1}. NMR ($CDCl_3$): δ 1.20, 1.27 (s, 9H total, 1/1.24 ratio, Me_3C of two isomers), 7.24 (m, 5H, Ph) ppm.

A similar reaction in which benzoyl chloride was added to the monoanion solution gave **4c**, a dark red oil, in 87% yield. Anal. Found: C, 43.14; H, 2.11. $C_{19}H_{10}O_7S_2Fe_2$ calcd.: C, 43.37; H. 1.92%. IR (CH_2Cl_2): ester C=O, 1680; terminal C≡O, 2080(s), 2045(vs), 2002(vs) cm^{-1}. NMR ($CDCl_3$): δ 7.45, 7.90 (m, Ph) ppm.

Reactions of the p-tolyl-monoanion with o-phthaloyl and succinoyl chlorides

To a solution of 0.7 g (~ 2.0 mmol) of (μ-S_2)$Fe_2(CO)_6$ in 60 ml of THF at −78°C was added with stirring 2.5 ml of a 1 *M* solution of *p*-tolylmagnesium bromide in THF. To the resulting dark green solution was added at −78°C 0.14 ml (1.0 mmol) of *o*-phthaloyl chloride. The resulting red reaction mixture was allowed to warm to room temperature. TLC (20% CH_2Cl_2/pentane, silicic acid) showed the presence of only one product. Column chromatography of the residue after removal of volatiles gave a red, glassy solid, m.p. 88–89°C, which was identified as **5**, in 97% yield. Anal. Found: C, 41.59; H, 2.05%. $C_{34}H_{18}O_{14}S_4Fe_4$ calcd.: C, 40.75; H, 1.81. IR (CH_2Cl_2): ester C=O, 1700; terminal C≡O, 2078(s), 2042(vs), 2002(vs) cm^{-1}. NMR (CD_2Cl_2): δ 2.28 (s, 6H, CH_3), 7.0–7.5 (m, 12H, Ph) ppm.

A similar reaction in which one-half molar equivalent of succinoyl chloride was added to the monoanion solution gave **6**, a glassy red solid, in 98% yield. Anal. Found: C, 37.63; H, 2.17. $C_{28}H_{18}O_{14}S_4Fe_4$ calcd.: C, 37.76; H, 1.90%. IR (CH_2Cl_2): ester C=O, 1710; terminal C≡O, 2078(s), 2042(vs), 2002(vs) cm^{-1}. NMR (CD_2Cl_2): δ 2.28 (s, 6H, CH_3), 2.85–3.10 (m, 4H, CH_2), 7.0–7.5 (m, 8H, Ph) ppm.

Reactions of dianion 2 with diacid chlorides

By the usual procedure [4], 2.91 mmol of (μ_2-S)$Fe_2(CO)_6$ in 60 ml of THF at −78°C was treated with a solution of 6 mmol of $LiBEt_3H$ in THF. Subsequently, 2.95 mmol of *o*-phthaloyl chloride was added to the green dianion solution at −78°C. TLC (silicic acid, 10% CH_2Cl_2/pentane) showed that a single product was present. This was isolated by column chromatography (silicic acid, 20% CH_2Cl_2/pentane) and recrystallized from CH_2Cl_2/pentane to give **7** as red-orange crystals, m.p. 150–151°C, in 74% yield. Anal. Found: C, 35.04; H, 0.97. $C_{14}H_4O_8S_2Fe_2$ calcd.: C, 35.33; H. 0.83%. IR (CH_2Cl_2): ester C=O, 1794; terminal C≡O, 2076(s), 2036(vs), 2004(vs) cm^{-1}. NMR ($CDCl_3$): δ 7.26–8.48 (complex m).

A similar 1/1 reaction between dianion **2** and succinoyl chloride gave **8a**, red-bronze needles, m.p. 120–122°C, in 79% yield. Anal. Found: C, 28.13; H, 1.00. $C_{10}H_4O_8S_2Fe_2$ calcd.: C, 28.07; H, 0.94%. IR (CH_2Cl_2): ester C=O, 1820; terminal C≡O, 2079(s), 2039(vs), 2000(vs) cm^{-1}. NMR ($CDCl_3$): δ 2.55 (s, CH_2CH_2).

The 1/1 reaction between dianion **2** and glutaroyl chloride at −78°C in THF gave as product **8b**, a red solid, m.p. 132–133°C, in 80% yield. Anal. Found: C, 30.07; H, 1.51. $C_{11}H_6O_8S_2Fe_2$ calcd.: C, 29.89; H. 1.37%. IR (CH_2Cl_2): ester C=O, 1770; terminal C≡O, 2080(s), 2042(vs), 2004(vs) cm^{-1}. NMR (CD_2Cl_2): δ 1.80 (m, 2H, central CH_2), 2.23 (t, *J* 6.3 Hz, CH_2), 2.52 (t, *J* 7.0 Hz, CH_2) ppm.

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