Journal of Organometallic Chemistry, 218 (1981) C34—C36
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

DI-μ-THIOLBIS(TRICARBONYLIRON), $(\mu\text{-HS})_2Fe_2(CO)_6$: AN INORGANIC MIMIC OF ORGANIC THIOLS

DIETMAR SEYFERTH* and RICHARD S. HENDERSON

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received June 9th, 1981)

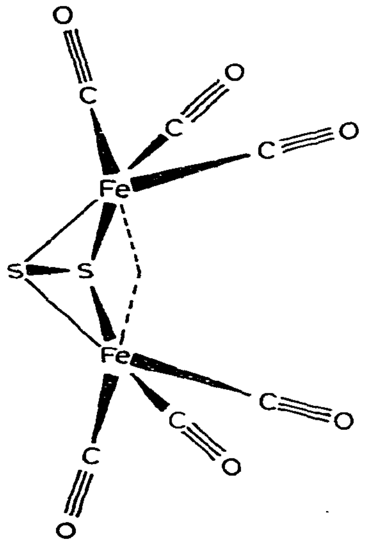
Summary

Di-μ-thiolbis(tricarbonyliron) reacts at room temperature with organic halides in the presence of triethylamine to give high yields of products in which the sulfur ligands have been alkylated and with dimethyltin dichloride to give $(\mu\text{-Me}_2SnS_2)Fe_2(CO)_6$. The SH function of di-$\mu$-thiolbis(tricarbonyliron) adds to activated C=C bonds of functional α,β-unsaturated systems in the presence of piperidine.

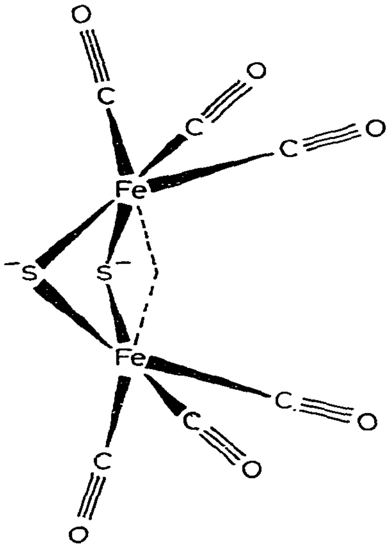
We have reported that potassium hydride and complex metal hydrides convert $(\mu\text{-S}_2)Fe_2(CO)_6$ (I) to the $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$ anion II [1,2]. Brief mention was made of the protonation of this dianion with trifluoroacetic acid to give $(\mu\text{-HS})_2Fe_2(CO)_6$ (III) in 99% yield. This complex was isolated as a red, air-sensitive solid, m.p. 97—99°C (from hexane), whose proton NMR spectrum showed it be a mixture of three isomers: a,e (IIIa, 14 parts), e,e (IIIb, 2 parts) and a,a (IIIc, 1 part) [3,5]. We have investigated the chemistry of III, and we report here our preliminary results. Just as $(\mu\text{-S}_2)Fe_2(CO)_6$ is an inorganic mimic of organic disulfides [1,2,7,8], so $(\mu\text{-HS})_2Fe_2(CO)_6$ mimics the chemistry of organic thiols.

The thiol complex III is a good room temperature source of dianion II, which in most cases has been generated by the action of $LiBEt_3H$ on $(\mu\text{-S}_2)Fe_2(CO)_6$ in THF at —78°C and also used at this temperature [2]. At such low temperatures, reactions with some electrophiles do not proceed well (e.g., CH_2I_2, which gives $(\mu\text{-SCH}_2S)Fe_2(CO)_6$ in only 25% yield). In such cases, slow generation of dianion II at room temperature can be advantageous.

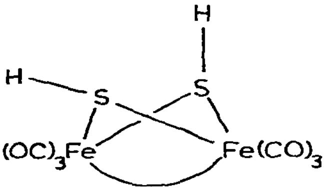
A dark green THF solution of dianion II was prepared under nitrogen by reaction of 2.9 mmol of $(\mu\text{-S}_2)Fe_2(CO)_6$ with 6 mmol of $LiBEt_3H$ at —78°C [2]. Subsequently, 6 mmol of CF_3CO_2H was added, causing an immediate



(I)

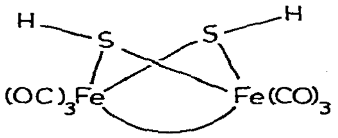


(II)



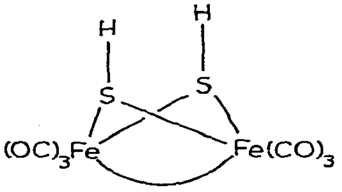
(IIIa)

−2.21, 0.22



(IIIb)

−0.40



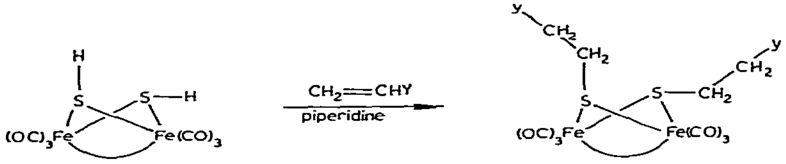
(IIIc)

−2.43

^{1}H NMR
(δ, ppm, in $CDCl_3$)

color change to red, indicating that protonation to give $(\mu\text{-HS})_2Fe_2(CO)_6$ had occurred. At room temperature, 8.1 mmol of CH_2I_2 was added to this solution, followed by 15 mmol of triethylamine, which was added in portions over a 15 min period. After one hour at room temperature, solvent was removed at reduced pressure and the residue was chromatographed to give $(\mu\text{-SCH}_2S)$-$Fe_2(CO)_6$, a dark-red, air-stable solid, m.p. 74—76°C, in 84% yield (for an X-ray diffraction study of this compound (prepared by a different route), see ref. 4). Similarly prepared via the $(\mu\text{-HS})_2Fe_2(CO)_6/Et_3N$ procedure were $(\mu\text{-SCH}_2CH_2S)Fe_2(CO)_6$ (50%, from 1,2-dibromoethane), $(\mu\text{-SCH}_2C_6H_4CH_2S)$-$Fe_2(CO)_6$ (89%, from α,α′-dibromo-o-xylene) and $(\mu\text{-Me}_2SnS_2)Fe_2(CO)_6$ [1,2] (96%, from Me_2SnCl_2).

Another similarity of $(\mu\text{-HS})_2Fe_2(CO)_6$ to organic thiols is found in its addition to α,β-unsaturated organic systems (eq. 1). Addition of 15 mmol of methyl acrylate and 5 mmol of piperidine to a THF solution of 5.8 mmol of $(\mu\text{-HS})_2$-$Fe_2(CO)_6$ at −78°C (reaction period of 30 min at −78°C, then 18 h at room



(1)

(Y = CO_2CH_3, $C(O)CH_3$, CN)

temperature) gave the C=C addition product, $(\mu\text{-}CH_3O_2CCH_2CH_2S)_2Fe_2(CO)_6$, a dark red, slightly air-sensitive oil, in 95% yield [9]. Two isomers were present (by NMR): a,e/e,e = 2.27. A similar piperidine-induced addition of $(\mu\text{-}HS)_2Fe_2(CO)_6$ to methyl vinyl ketone produced $(\mu\text{-}CH_3C(O)CH_2CH_2S)_2Fe_2(CO)_6$, a deep red oil, in 97% yield [9]. The reaction of $(\mu\text{-}HS)_2Fe_2(CO)_6$ with the more reactive acrylonitrile did not require a base catalyst and gave $(\mu\text{-}N{\equiv}CCH_2CH_2S)_2Fe_2(CO)_6$, a red solid, m.p. 90—92°C, in 93% yield [9]. Such additions of $(\mu\text{-}HS)_2Fe_2(CO)_6$ to α,β-unsaturated functional organic compounds thus provide a good route to novel organofunctional di-μ-alkanethiobis(tricarbonyliron) complexes.

We are continuing our studies of the sulfur-functional chemistry of $(\mu\text{-}S_2)Fe_2(CO)_6$ and its derivatives. We note that Beck et al. [10] have prepared the analogous bridging thiol derivative of Roussin's red salt, $(\mu\text{-}HS)_2Fe_2(NO)_4$. It should be of interest to compare the chemistry of these thiol derivatives of the formally similar but structurally different [6,11] dinuclear iron systems.

Acknowledgments. The authors are grateful to the National Science Foundation for support of this work.

References

1 D. Seyferth and R.S. Henderson, J. Am. Chem. Soc., 101 (1979) 508..
2 D. Seyferth, R.S. Henderson and L.C. Song, J. Organometal. Chem., 192 (1980) C1; D. Seyferth, L.-C. Song and R.S. Henderson, J. Am. Chem. Soc., in press.
3 The isomers designation (e = equatorial; a = axial) of Shaver et al. [4] is used.
4 A. Shaver, P.J. Fitzpatrick, K. Steliou and I.S. Butler, J. Am. Chem. Soc., 101 (1979) 1313.
5 Alkylation of dianion II usually gives a mixture of the a,e and e,e isomers, non-bonded interactions between the alkyl substituents making the a,a isomer unfavorable [6].
6 L.F. Dahl and C.-H. Wei, Inorg. Chem., 2 (1963) 328.
7 D. Seyferth and R.S. Henderson, J. Organometal. Chem., 182 (1979) C39.
8 D. Seyferth, R.S. Henderson and M.K. Gallagher, J. Organometal. Chem., 193 (1980) C75.
9 Purified by column chromatography; C,H analysis, IR, NMR and mass spectra were in agreement with the structure indicated.
10 W. Beck, R. Grenz, F. Götzfried and E. Vilsmaier, Chem. Ber., in press.
11 J.T. Thomas, J.H. Robertson and E.G. Cox, Acta Cryst., 11 (1958) 599.