Inorganica Chimica Acta, 77 (1983) L1–L2

Synthesis of μ,μ'-(1,1'-Dithiolatoferrocene)hexacarbonyldiiron

DIETMAR SEYFERTH and BARRY W. HAMES

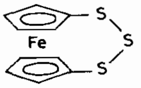
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139, U.S.A.

Received March 2, 1983

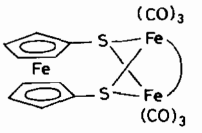
Introduction

A recent report by Nametkin *et al.* [1] described the reaction of a mixture of ferrocene and dodecacarbonyltriiron with elemental sulfur in refluxing benzene. A mixture of sulfur-containing ferrocenes resulted, as well as some $(\mu\text{-}S_2)Fe_2(CO)_6$ and $(\mu_3\text{-}S)_2Fe_3(CO)_9$. No ferrocenyl–sulfur–hexacarbonyl diiron complexes were produced. Heating this reaction mixture with $Fe_3(CO)_{12}$ at 45 °C also failed to yield such products.

We report here that the title complex, *2*, a product of the type sought by the Russian authors, can be prepared by the reaction of 1,2,3-trithia[3]-ferrocenophane, *1*, with $Fe_3(CO)_{12}$.



1



2

Experimental

A 100 ml three-necked flask equipped with a magnetic stir-bar, a no-air stopper and a reflux condenser topped with a nitrogen inlet tube was charged with 0.3580 g (1.28 mmol) of *1* [2], 1.2580 g (2.50 mmol) of $Fe_3(CO)_{12}$ and 50 ml of hexane. The resulting dark green suspension was stirred and heated at reflux under nitrogen for 18 h. The dark brown suspension which was produced was allowed to cool to room temperature and filtered through Celite. The filtrate was evaporated at reduced pressure and the brown residue extracted with three 15 ml portions of pentane. The extracts were transferred onto a silicic acid column. Elution with pentane removed 0.051 g (21% yield) of ferrocene (IR and NMR comparison with an authentic sample).

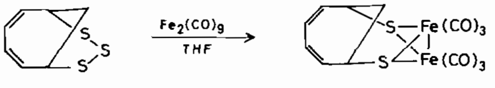
The remainder of the brown reaction residue was slurried in dichloromethane and transferred onto a silicic acid column. Dichloromethane eluted a slow-moving brown-violet band; 1:1 CH_2Cl_2/acetone allowed a more rapid, cleaner separation of this band. The solid obtained by evaporation of the eluate was recrystallized from CH_2Cl_2/hexanes to give 0.160 g of dark-brown, microcrystalline solid, m.p. 205–210 °C (dec), identified as *2* (24% yield, based on *1*). *Anal.* Calcd. for $C_{10}H_8O_6S_2Fe_3$: C, 36.40; H, 1.53. Foind: C, 36.31; H, 1.62. ^1H NMR (in $CDCl_3$): δ 4.36 (m, 2H; H_2, H_5) and 4.00 ppm (m, 2H; H_3, H_4) (assignments based on analogies; *cf.* ref. 3). *IR* (CH_2Cl_2) (cm^{-1}): 2965(m), 2075(m), 2040(s), 2005(vs), 1410(m), 1050(vs), 865(sh,m), 800(vs). ν(CO) 2075, 2040, 2005 cm^{-1}. *Electron impact mass spectrum* (70 eV) (m/Z, relative intensity): 528 (M^+, 12.6), 472 ($M^+ - 2CO$, 11.7), 444 ($M^+ - 3CO$, 9.8), 414 ($M^+ - 4CO$, 14.4), 388 ($M^+ - 5CO$, 22.9), 360 ($M^+ - 6CO$, 100).

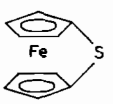
The product, *2*, can be handled in air for brief periods without significant decomposition. However, in solution the complex is mildly air-sensitive.

When the reaction mixture in another experiment was stirred at room temperature for several hours before warming to room temperature, the yield of ferrocene was less than 5%. Another product, $(\mu_3\text{-}S)_2Fe_3(CO)_9$, was obtained in 6% yield. It was identified on the basis of its IR spectrum and its chromatographic properties.

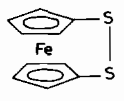
Discussion

The synthesis of complexes of type $(\mu\text{-}RS)_2Fe_2(CO)_6$ can be accomplished readily by the action of a variety of organosulfur compounds on iron carbonyls. Mercaptans, RSH, sulfides, R_2S, and disulfides, RSSR, may be used in reactions with $Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ [4]. One example of the reaction of a trisulfide with $Fe_2(CO)_9$ in THF (eqn. 1) has been reported [5]. For purposes of the present synthesis, trisulfide *1* was available, but the analogous





3



4

0020-1693/83/$3.00

© Elsevier Sequoia/Printed in Switzerland

ferrocenophane mono- and disulfides, *3* and *4*, were not known. The reaction of trisulfide *1* with $Fe_3(CO)_{12}$ proceeded as expected, and the desired complex, *2*, was obtained in modest yield.

Acknowledgement

The authors are grateful to the National Science Foundation for support of this work and to the Natural Sciences and Engineering Research Council of Canada for the award of a postdoctoral fellowship to Barry W. Hames (1981–1983).

References

1 N. S. Nametkin, V. D. Tyurin, S. A. Sleptsova, A. M. Krapivin and A. Ya. Sideridu, *Izv. Akad. Nauk SSSR, Ser. Khim.* (1982) 955 (p. 848, English translation).
2 J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill and J. C. Smart, *J. Organomet. Chem., 27,* 241 (1971).
3 A. Davison and J. C. Smart, *J. Organomet. Chem., 174,* 321 (1979).
4 Gmelin Handbook of Inorganic Chemistry, 8th Edition, 'Eisen-Organische Verbindungen', Part C1, Springer-Verlag, Berlin, 1979, pp. 77–90.
5 A. Shaver, P. J. Fitzpatrick, K. Steliou and I. S. Butler, *J. Organomet. Chem., 172,* C59 (1979).