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Preliminary communication

THE DITHIOBIS(TRICARBONYLIRON) DIANION: IMPROVED PREPARATION AND NEW CHEMISTRY

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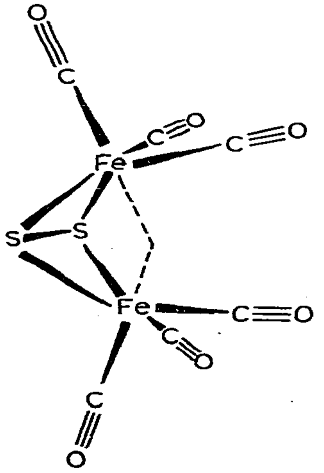
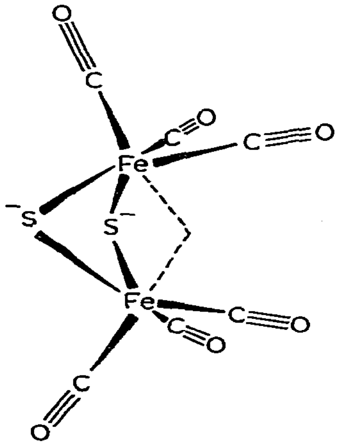
Summary

The reaction of two molar equivalents of lithium triethylborohydride in THF at −78°C with one of $(\mu\text{-}S_2)Fe_2(CO)_6$ results in formation of the $[S_2Fe_2(CO)_6]^{2-}$ dianion in essentially quantitative yield. Reactions of this dianion with organic halides and with halides of tin, germanium, silicon and nickel are reported. Protonation of the dianion produces $(\mu\text{-}HS)_2Fe_2(CO)_6$.

The action of sodium sand or potassium hydride in tetrahydrofuran (THF) on μ-dithiobis(tricarbonyliron) (I) results in formation of a dianion, presumably II, whose reaction with iodomethane gives $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$ (III) [1]. The yields



(I)



(II)

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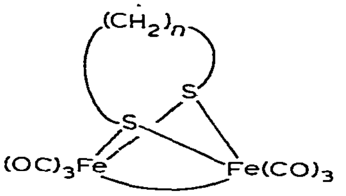
of III ranged from 34% (Na procedure) to 53% (KH procedure). In the expectation that a homogeneous reaction using a soluble reducing agent would give better product yields, we examined the action of lithium triethylborohydride [2], which is THF-soluble, on (μ-S_2)$Fe_2(CO)_6$. This useful complex hydride had been shown to reduce organic disulfides to lithium thiolates [3], as well as various metal—metal bonded transition metal complexes to the metal anions [4]. Under appropriate conditions, $LiBEt_3H$ reacted with (μ-S_2)$Fe_2(CO)_6$ rapidly and cleanly to give dianion II in essentially quantitative yield. Such facile access to $[S_2Fe_2(CO)_6]^{2-}$ has allowed us to develop its chemistry much further than had been possible before and we report here the preliminary results of our studies of its reactions.

Slow addition of 1 *M* $LiBEt_3H$ in THF to a deep red solution of (μ-S_2)$Fe_2(CO)_6$ in THF at −78°C under nitrogen resulted in a color change to deep green when one molar equivalent of the hydride had been added. Addition of a second equivalent of $LiBEt_3H$ formed the dianion in essentially quantitative yield, as evidenced by the isolation of the isomers of (μ-$CH_3S)_2Fe_2(CO)_6$ [1] in 92% yield when iodomethane was added to the reaction mixture. Treatment of such dianion solutions with benzyl chloride and allyl bromide gave (μ-$PhCH_2S)_2Fe_2(CO)_6$ [5], m.p. 91—92.5°C*, and (μ-CH_2=$CHCH_2S)_2Fe_2(CO)_6$, a red oil, b.p. 103—105°C at 0.2 mmHg, in yields of 83 and 86%, respectively, Complexes containing bidentate sulfur ligands could be constructed by reactions of the dianion with 1,3-dibromopropane and 1,4-dibromobutane. Complexes IV (m.p. 80—82°C, 92% yield) and V (red oil, 89% yield) were thus prepared.



(IV, *n* = 3;
V, *n* = 4)

Addition of trifluoroacetic acid to the dianion solution gave the bridging thiol complex (μ-$HS)_2Fe_2(CO)_6$ (VII) a very air-sensitive, ruby-red solid, m.p. 97—99°C, in quantitative yield. The proton NMR spectrum of the product showed the presence of three isomers, VIIa, VIIb and VIIc, in a ratio of 14/2/1. This complex has proven to be a versatile reagent for the further development of the chemistry of sulfur-ligand-bridged $Fe_2(CO)_6$ complexes [6].

The reaction of alkyllithium reagents with (μ-S_2)$Fe_2(CO)_6$ results in cleavage of the S—S bond to alkylate one sulfur atom and form the anion at the other [1]. It is likely that the reaction of (μ-S_2)$Fe_2(CO)_6$ with $LiBEt_3H$ follows a similar course, the first equivalent of the hydride forming the monoanion, the second de-

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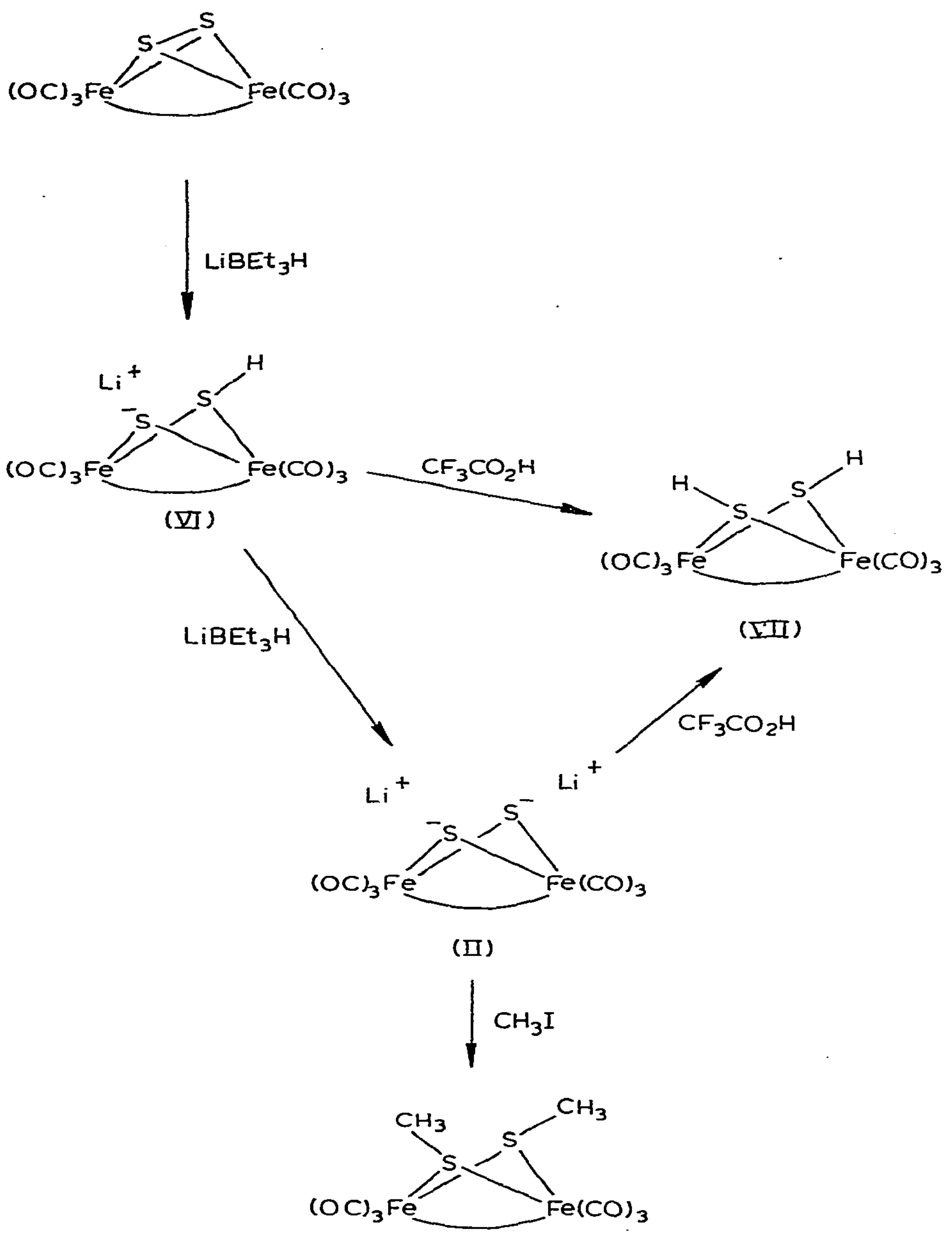
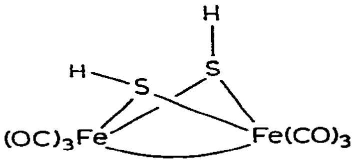
*Melting points of obviously air-sensitive products were taken in sealed capillaries. All new compounds were characterized by analysis and by their IR, proton NMR and mass spectra. The mass spectra of most products derived from (μ-S_2)$Fe_2(CO)_6$ showed the parent ion and fragment ions formed by the successive loss of the six CO ligands. Their infrared spectra are characterized by the presence of three or four medium to strong bands in the region 1950—2090 cm^{-1}. The color of most of the products was some shade of red: from orange-red through deep red to red-black.



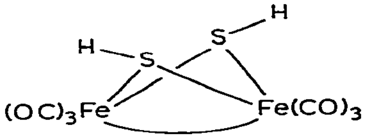
SCHEME 1

protonating the latter, as shown in Scheme 1. In this connection it is noteworthy that one equivalent of $LiBEt_3H$ is sufficient to form the green solution, and that addition of CF_3CO_2H to such a 1/1 reaction mixture gives VII in essentially quantitative yield. No unconverted $(\mu\text{-}S_2)Fe_2(CO)_6$ is left.

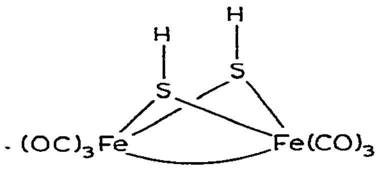
The improved preparation of the $[S_2Fe_2(CO)_6]^{2-}$ dianion has allowed the synthesis of many new $R_nMS_2Fe_2(CO)_6$-type clusters, VIII. A tin compound (VIII, $R_nM = Me_2Sn$) had been prepared earlier [1]; by the $LiBEt_3H$ route it was obtained in 92% yield. Other $(\mu\text{-}R_2SnS_2)Fe_2(CO)_6$ complexes were prepared as well:



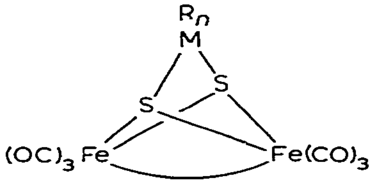
(VIIa)



(VIIb)

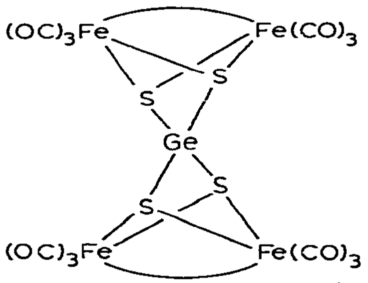


(VIIc)



(VIII)

R = Et, m.p. 118°C (dec.), 71% yield, and R = n-C_4H_9, m.p. 85°C, 77% yield. Similarly prepared were (μ-R_2GeS_2)$Fe_2(CO)_6$ compounds, with R = Me (m.p. ~ 113°C (dec.), 98% yield), R = Ph (m.p. 131—132°C, 84% yield) and R = Cl (m.p. 120—122°C, 78% yield). The latter was prepared in a reaction in which the dianion was allowed to react with an excess of $GeCl_4$. When one-half molar equivalent of $GeCl_4$ was added to the dianion solution, IX, a red solid, m.p. ~140°C (dec.), was obtained in 78% yield* [6]. Reactions of $[S_2Fe_2(CO)_6]^{2-}$ with di-



(IX)

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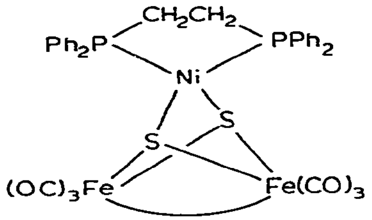
*Compounds VIII ($R_nM = Cl_2Ge$) and IX were identical in all respects with products which Russian workers [7] had obtained by reactions of I with $HGeCl_3 \cdot 2OEt_2$ and $HGeCl_3 \cdot NEt_3$, respectively, i.e., $GeCl_2$ precursors. Structures derived from $GeCl_2$ insertion into the Fe—Fe bond of I were suggested for these products. Our results suggested that insertion into the S—S bond had occurred instead, and this was confirmed by an X-ray diffraction study of IX (obtained by the $HGeCl_3 \cdot NEt_3$ route) by Struchkov and his coworkers [8].

organodichlorosilanes resulted in the formation of very air-sensitive silicon derivatives: (μ-Et_2SiS_2)$Fe_2(CO)_6$, m.p. 78—79°C, 80% yield; (μ-$PhMeSiS_2$)$Fe_2(CO)_6$, m.p. 94—95°C, 93% yield; (μ-Ph_2SiS_2)$Fe_2(CO)_6$, m.p. 80—82°C, 82% yield.

A transition metal halide, ($Ph_2PCH_2CH_2PPh_2$)$NiCl_2$, also reacted with $[S_2Fe_2(CO)_6]^{2-}$ (in a THF/acetone solvent system) to give a $NiFe_2S_2$ cluster complex, X, a brown-black, air-stable solid, m.p. 159—162°C, in 93% yield.



(X)

It is clear that the ready availability of the $[S_2Fe_2(CO)_6]^{2-}$ dianion makes possible the preparation of a great diversity of new heteronuclear poly-metal-sulfur complexes which should have interesting chemistry and applications of their own. This and other aspects of the chemistry of (μ-S_2)$Fe_2(CO)_6$ and its derived anions are receiving further attention in these laboratories.

Acknowledgment

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