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Formation of Bis(μ-methanethiolato)-μ_4-thioxotetrakis(tricarbonyliron) in the Reaction between Dodecacarbonyltriiron and Dimethyldisulphide

CHRISTOPHER GLIDEWELL* and ANDREW. R. HYDE

Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST, U.K.

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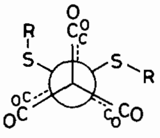
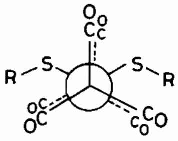
The synthesis of the alkane- and arene-thiolato irontricarbonyl complexes $Fe_2(SR)_2(CO)_6$ has been very intensively investigated in recent years [1–7]. These complexes can be formed by the interaction of thiols RSH, sulphides R_2S, or disulphides R_2S_2 with any of the binary carbonyls of iron, and in an extensive study of the relative reactivity of each type of starting material, the orders of reactivity were deduced as: $Fe(CO)_5 < Fe_2(CO)_9 < Fe_3(CO)_{12}$ and $R_2S < R_2S_2 < RSH$ [6].

For the majority of alkyl substituents, two isomeric forms of $Fe_2(SR)_2(CO)_6$ are identifiable on the basis of their n.m.r. spectra [1, 5, 7, 8]: these two isomers have been assigned the *anti* and *syn* structures, (I) and (II) respectively [9]:



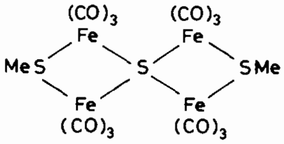
(I)



(II)

but for sterically demanding substituents such as t-butyl or aryl, only the anti isomer can be observed [2, 5]. When R is small, however, the two isomers may be readily separated by chromatography. It has generally been supposed [1, 5, 6] that in the reactions of disulphides R_2S_2 with iron carbonyls, these two isomers are the sole organometallic complexes produced, although it is known [4] that reactions involving thiols are more complex.

We have observed, using the simple expedient of employing silica rather than alumina [1] as the chromatography medium, that from the reaction of $Fe_3(CO)_{12}$ and Me_2S_2 in refluxing benzene not only are the *anti* and *syn* isomers of $Fe_2(SMe)_2(CO)_6$ isolable in yields of around 20% and 5% respectively, but a third component is readily isolated in *ca.* 1% yield, identified by microanalysis, and by m.pt., i.r. and ^1H n.m.r. spectra, as the known [10] compound, $[MeS\{Fe(CO)_3\}_2]_2S$, (**III**):



(III)

This compound has been observed as a low-yield product in a number of other reactions, including those between $Fe_3(CO)_{12}$ and CH_3SCN [10], and $Fe_2(CO)_9$ and cyclo-octatetraenyl methyl sulphide, $C_8H_7SCH_3$ [11]. A similar compound, $[t\text{-}BuS\{Fe(CO)_3\}_2]_2S$ is formed, along with many other products, when t-BuSH reacts over a long period with $Fe_3(CO)_{12}$, but less sterically hindered thiols do not appear to react in this way [4].

The formation of (III) in a wide range of reactions suggests the possibility that it may be an early product in the reactions of iron carbonyls with sulphur-containing ligands: this in turn raises the question of whether $Fe_2(SMe)_2(CO)_6$ and $[MeS\{Fe(CO)_3\}_2]_2S$ are components of a common reaction pathway. We find that neither of these compounds yields any trace of the other upon reflux during 10 h in benzene, either in the presence or in the absence of added Me_2S_2. Hence, since the normal preparative procedure for $Fe_2(SR)_2(CO)_6$ involves a reflux time of only 5 h, we conclude that $Fe_2(SMe)_2(CO)_6$ and $[MeS\{Fe(CO)_3\}_2]_2S$ are on divergent pathways from a common intermediate, which may be either the starting carbonyl $Fe_3(CO)_{12}$ or a subsequent product. It is unlikely that (**III**) is formed by thermolysis of $Fe_2(SMe)_2(CO)_6$, under any conditions, since thermal analysis of $Fe_2(SR)_2(CO)_6$ indicates that the initial decomposition process is loss of four moles of carbon monoxide per mole of $Fe_2(SR)_2(CO)_6$, rapidly followed by loss of the remaining carbonyl ligands [6].

Two attractive possibilities for the identity of the common intermediate are $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$, both of which have been observed as early reaction products in the reaction between $Fe_3(CO)_{12}$ and R_2S_2 [7]: this represents a sulphur abstraction reaction, analogous to that between $Fe_3(CO)_{12}$ and episulphides, which also yields $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ [12, 13]. It has been shown that in the reaction of elemental sulphur with $Fe_3(CO)_{12}$ the formation of the iron–sulphur carbonyls is sequential [6]: the initially formed $Fe_2S_2(CO)_6$ reacts with $Fe_3(CO)_{12}$ to form $Fe_3S_2(CO)_9$, and it is entirely plausible that a similar sequence occurs in sulphur-abstraction processes.

However we find that upon reflux in benzene, under the usual reaction conditions for this system, neither $Fe_2S_2(CO)_6$ nor $Fe_3S_2(CO)_9$ reacts with Me_2S_2 to give any $Fe_2(SMe)_2(CO)_6$: aside from decompo-

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*Author to whom correspondence should be addressed.

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sition products (iron, iron sulphides, and carbon monoxide), the only product identified (other than starting materials) was a small quantity of $Fe_2S_2(CO)_6$ formed from $Fe_3S_2(CO)_9$. Since the initial $Fe_3S_2(CO)_9$ was free of any impurities, this latter observation indicates that under particular conditions, the interconversion of $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ is at least partially reversible. Overall however the observations with $Fe_2S_2(CO)_6$ and $Fe_3S_2(CO)_9$ rule out both of these complexes as the common intermediate preceding $Fe_2(SMe)_2(CO)_6$ and $[MeS\{Fe(CO)_3\}_2]_2S$.

The sole remaining type of iron–sulphur carbonyl species which may plausibly be regarded as the common intermediate is $Fe_3(SR)_2(CO)_9$: such a complex was isolated amongst many other products from the prolonged reaction or t-BuSH with $Fe_3(CO)_{12}$, where the initial product is known to be $Fe_3(Sbu\text{-}t)(H)(CO)_9$ [4]. However we have never detected the formation of such a species in any reaction of Me_2S_2, either with $Fe_3(CO)_{12}$ or with $Fe_3(CO)_9S_2$. It is significant in this content that in an extensive study [4] of the reactions of alkane-thiols, RSH, with $Fe_3(CO)_{12}$, compounds of type $Fe_3(SR)(H)(CO)_9$ were observed only when R was i-Pr, s-Bu, or t-Bu, while $Fe_3(SR)_2(CO)_9$ was observed only in the case of R = t-Bu. No such complexes were observed when R was an unbranched primary alkane, and it was suggested [4] that the stability of both $Fe_3(SR)(H)(CO)_9$ and $Fe_3(SR)_2(CO)_9$ types was strongly dependent on the steric requirements of R. Hence our non-observance of either $Fe_3(SMe)(H)(CO)_9$ or of $Fe_3(SMe)_2(CO)_9$ is not surprising: indeed, so far as we are aware, the existence of neither of these methyl complexes has been recorded in the literature.

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