# Some Unusual Bridged Sulphido-derivatives of Iron Carbonyl

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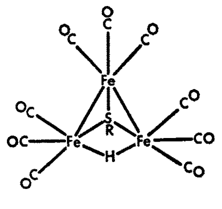
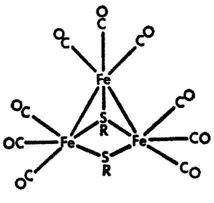
*Summary* The reactions of $Fe_3(CO)_{12}$ with the secondary and tertiary alkyl thiols RSH (R = $Pr^i$, $Bu^s$, and $Bu^t$) in refluxing benzene afford the novel bridged sulphido-derivatives $Fe_3(CO)_9(H)(SR)$, $Fe_3(CO)_9(SBu^t)_2$, and $Fe_4(CO)_{12}(SBu^t)_2(S)$.

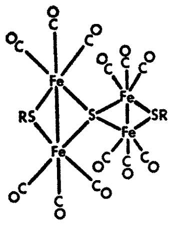
A PREVIOUS study has shown that triruthenium and triosmium dodecacarbonyl react with thiols RSH to produce trinuclear $M_3(CO)_{10}(H)(SR)$ as well as dinuclear $[M(CO)_3SR]_2$ (M = Ru and Os; R = Et, $Bu^n$, and Ph) derivatives.[1] In contrast, the corresponding reactions involving $Fe_3(CO)_{12}$ have been reported to yield $[Fe(CO)_3SR]_2$ as the sole product.[2] These observations have been interpreted in terms of the relative strengths of metal–metal bonds in first and second and third row transition metal derivatives. We report the isolation of compounds other than $[Fe(CO)_3SR]_2$ from the reactions of $Fe_3(CO)_{12}$ with certain thiols.



(I)



(II)



(III)

As has been previously found for primary alkyl thiols, the reactions of $Fe_3(CO)_{12}$ with an excess of the secondary alkyl thiols RSH (R = $Pr^i$ and $Bu^s$) in refluxing benzene were observed to afford $[Fe(CO)_3SR]_2$† in good yield. However, by monitoring these reactions by means of i.r. spectroscopy intermediates in the formation of the dinuclear products were detected. These intermediates were subsequently isolated in good yield by using only a slight excess of the thiol in the above reactions and were formulated as $Fe_3(CO)_9(H)(SR)$ [and not $Fe_3(CO)_{10}(H)(SR)$] on the basis of the analytical and mass spectrometric data (R = $Pr^i$, $M^+ = 496$; R = $Bu^s$, $M^+ = 510$). In view of the close similarity of the analytical data for $Fe_3(CO)_{10}(H)(SR)$ and $Fe_3(CO)_9(H)(SR)$, the above compounds were purified by successive crystallisation, sublimation, and recrystallisation and analysed at each stage of the purification. The formula $Fe_3(CO)_{10}(H)(SR)$ was further eliminated on the basis of the large difference in the i.r. spectra in the 2200—1900 cm$^{-1}$ region of $Fe_3(CO)_9(H)(SR)$ and $Ru_3(CO)_{10}(H)(SR)$. $Fe_3(CO)_9(H)(SBu^t)$ was similarly isolated from the reaction of $Fe_3(CO)_{12}$ with an equimolar amount of the tertiary alkyl thiol $Bu^tSH$. In contrast to the result with the secondary alkyl mercaptans, prolonged heating of a benzene solution of $Fe_3(CO)_{12}$ and an excess of $Bu^tSH$ was observed to afford three other compounds in low yield as well as the major product $[Fe(CO)_3SBu^t]_2$. These were characterised as $Fe_3(CO)_9(SBu^t)_2$ ($M^+ = 598$), $Fe_4(CO)_{12}(SBu^t)_2(S)$ ($M^+ = 770$), and $Fe_3(CO)_9S_2$ ($M^+ = 484$).

The i.r. spectra of $Fe_3(CO)_9(H)(SR)$ (R = $Pr^i$, $Bu^s$, and $Bu^t$) and $Fe_3(CO)_9(SBu^t)_2$ contain no peaks in the bridging carbonyl stretching region while the n.m.r. spectra of $Fe_3(CO)_9(H)(SR)$ show resonance peaks readily assigned to metal hydride protons [*e.g.* $Fe_3(CO)_9(H)(SBu^t)$, $\tau$ 32·8 p.p.m.]. The very high abundance of peaks in the mass spectra of $Fe_3(CO)_9(H)(SR)$ and $Fe_3(CO)_9(SBu^t)_2$ corresponding to trinuclear ions indicates a cyclic structure, while successive loss of carbon monoxide in preference to hydrogen in the fragmentation process suggests that the hydride group is bridging. The above spectroscopic data is consistent with the structures (I) and (II) for $Fe_3(CO)_9(H)(SR)$ and $Fe_3(CO)_9(SBu^t)_2$ respectively. These derivatives provide rare examples of sulphur bridging three metal atoms by formal use of five valence electrons. The i.r. spectrum of $Fe_4(CO)_{12}(SBu^t)_2(S)$ in the C–O stretching region corresponds with that of the known $Fe_4(CO)_{12}(SMe)_2(S)$ [previously isolated in low yield from the reaction of $Fe_3(CO)_{12}$ with MeSCN[3]]. Structure (III) corresponding to that previously established for $Fe_4(CO)_{12}(SMe)_2(S)$[3] is thus suggested for $Fe_4(CO)_{12}(SBu^t)_2(S)$. The i.r. spectrum of the $Fe_3(CO)_9S_2$ synthesised in this study is identical with that of the compound $Fe_3(CO)_9S_2$ synthesised by treating $[Fe(CO)_4]^{2-}$ with sulphurous acid[4] and for which a structure has been established.[5]

The reactions of $Fe_3(CO)_{12}$ with the primary alkyl thiols RSH (R = Et, $Pr^n$, $Bu^n$, $Bu^i$, and $PhCH_2$), $HSC_2H_4SH$ and PhSH have also been closely studied. Products other than $[Fe(CO)_3SR]_2$ could not be detected in these reactions. It thus appears that the stability of the trinuclear derivatives discussed above is a function of the stereochemistry of the group R and furthermore that a tertiary alkyl sulphido-group is necessary to stabilise $Fe_3(CO)_9(SR)_2$. Consistent with this latter finding is the observation that whereas $Fe_3(CO)_9(SBu^t)_2$ is formed in the reaction of $[Fe(CO)_3SBu^t]_2$ with $Fe_3(CO)_{12}$, $Fe_3(CO)_9(SPr^i)_2$ could not be detected in the reaction of $[Fe(CO)_3SPr^i]_2$ with $Fe_3(CO)_{12}$.

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† Satisfactory elemental analyses were obtained for all new compounds.

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