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REACTIONS OF METAL CARBONYL DERIVATIVES
IV*. BRIDGED SULPHIDO DERIVATIVES OF IRON CARBONYL**

J. A. DE BEER AND R. J. HAINES***
Research and Process Development, South African Iron and Steel Industrial Corporation Limited, P.O. Box 450, Pretoria (Republic of South Africa)

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SUMMARY

The secondary alkanethiols RSH (R=i-C_3H_7 and s-C_4H_9) react with $Fe_3(CO)_{12}$ in refluxing benzene to afford initially $Fe_3(CO)_9(H)(SR)$ which reacts further with the thiol to yield $[Fe(CO)_3SR]_2$. The corresponding reaction involving the tertiary alkanethiol t-C_4H_9SH similarly affords $Fe_3(CO)_9(H)$(S-t-C_4H_9). Prolonged heating of a benzene solution of this thiol and $Fe_3(CO)_{12}$ affords four products, *viz.* $[Fe(CO)_3$S-t-$C_4H_9]_2$, $Fe_3(CO)_9$(S-t-$C_4H_9)_2$, $Fe_4(CO)_{12}$(S)(S-t-$C_4H_9)_2$ and $Fe_3(CO)_9S_2$. It is established that compounds of the type $[Fe(CO)_3SR]_2$ are synthesised in highest yield by reacting $Fe_2(CO)_9$ with the appropriate thiol in benzene at room temperature. Structures for the tri- and tetranuclear compounds containing bridging sulphido and where appropriate bridging hydrido groups are proposed based on the infrared, NMR and mass spectroscopic data. The mass spectra of the compounds $[Fe(CO)_3SR]_2$ (R=i-C_3H_7 and t-C_4H_9), $Fe_3(CO)_9(H)(SR^1)$ (R^1=i-C_3H_7, s-C_4H_9 and t-C_4H_9), $Fe_3(CO)_9$(S-t-$C_4H_9)_2$ and $Fe_4(CO)_{12}$(S)(S-t-$C_4H_9)_2$ are discussed.

INTRODUCTION

It is well established[1] that the action of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ on primary alkyl or aryl mercaptans effects fission of the thiol to afford the dinuclear bridged sulphido derivatives $[Fe(CO)_3SR]_2$. Examples of compounds synthesised by this method include $[Fe(CO)_3SR]_2$ (R=C_2H_5[2,3], t-C_4H_9[4], C_6H_5[2,3], $C_{10}H_7$[5] and C_6F_5[6]), $Fe_2(CO)_6S_2C_6H_3CH_3$[7], $Fe_2(CO)_6S_2C_2H_4$[7] and $Fe_2(CO)_6SC_6H_4NH$[8]. Polynuclear derivatives have been obtained from this type of reaction in only two cases. An early study made before spectroscopic techniques were readily available reported that $[Fe(CO)_3SC_{10}H_7]_{3-4}$ and $Fe_3(CO)_{10}S_2CH_2$ could be isolated from the reactions of $Fe_3(CO)_{12}$ with 2-thionaphthol and 2-mercaptobenzothiazole or parathioformaldehyde, respectively[5], but it was subsequently shown[9] that the product from the reaction of $Fe_3(CO)_{12}$ with 2-mercaptobenzothiazole is in fact $Fe_3(CO)_9S_2$. By contrast, the reactions of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with thiols yield at least three types of products.

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* For Part III, see ref. 25.

** A preliminary communication of this work has been presented[26].

*** To whom correspondence concerning this publication should be addressed.

For instance the reaction of $M_3(CO)_{12}$ (M = Ru and Os) with RSH (R = C_2H_5, n-C_4H_9 and C_6H_5) in refluxing benzene affords[10] initially $M_3(CO)_{10}(H)(SR)$. Further reaction of $M_3(CO)_{10}(H)(SR)$ with the thiol under more rigorous conditions yields[11] $[M(CO)_3SR]_2$, and $[M(CO)_2(SR)_2]_x$.

In order to study the influence of the stereochemistry of the bridging group on the reactivity of bridged sulphido derivatives of iron, we synthesised $[Fe(CO)_3SR]_2$ (R = i-C_3H_7, s-C_4H_9 and t-C_4H_9) by reacting $Fe_3(CO)_{12}$ with the appropriate thiol in refluxing benzene. In addition to $[Fe(CO)_3SR]_2$, some unusual tri- and tetranuclear bridged sulphido derivatives of iron carbonyl have been isolated from these reactions. The characterisation of these compounds is reported here.

RESULTS

The reaction of $Fe_3(CO)_{12}$ with an excess of the secondary alkanethiols RSH (R = i-C_3H_7 and s-C_4H_9) in refluxing benzene afforded the dinuclear derivatives $[Fe(CO)_3SR]_2$ in good yield (> 60 %). Monitoring of the reactions by infrared spectroscopy revealed that intermediates were present in the formation of $[Fe(CO)_3SR]_2$. These were subsequently isolated in high yield by employing equimolar quantities of the two reagents in the above reactions and shown to have the formula $Fe_3(CO)_9(H)(SR)$. The tertiary alkyl sulphido derivative $Fe_3(CO)_9(H)(S\text{-}t\text{-}C_4H_9)$ was obtained similarly. In contrast to the reactions of the secondary alkanethiols discussed above, the reaction of $Fe_3(CO)_{12}$ with t-C_4H_9SH in refluxing benzene yielded three other products as well as $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$. These were characterised as $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$, $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$ and $Fe_3(CO)_9S_2$. The reactions of $Fe_3(CO)_{12}$ with the primary alkanethiols RSH (R = C_2H_5, n-C_3H_7, n-C_4H_9 and i-C_4H_9), HSC_2H_4SH and C_6H_5SH in refluxing benzene were also monitored but products other than those of the type $[Fe(CO)_3SR]_2$ could not be detected.

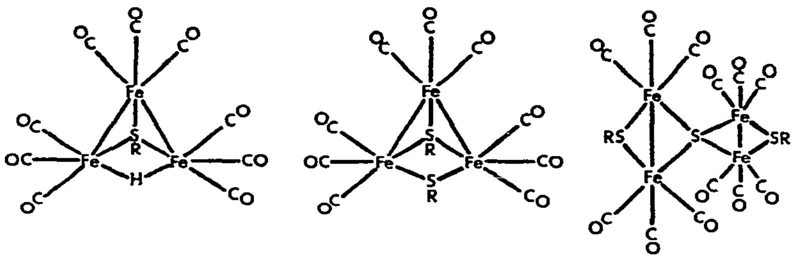

Fig. 1. Proposed structures for the compounds $Fe_3(CO)_9(H)(SR)$, $Fe_3(CO)_9(SR)_2$ and $Fe_4(CO)_{12}(S)(SR)_2$.

The reaction of $Fe_2(CO)_9$ with various thiols in benzene at ambient temperature did not afford the range of products discussed above. Thus a single compound, *viz.* $[Fe(CO)_3SR]_2$, was isolated from the reactions involving the secondary alkanethiols RSH (R = i-C_3H_7 and s-C_4H_9) as well as C_2H_5SH. The yield of $[Fe(CO)_3SR]_2$ in these reactions was excellent (> 90 %). The corresponding reaction of t-C_4H_9SH afforded a low yield of $Fe_3(CO)_9(H)(S\text{-}t\text{-}C_4H_9)$ as well as $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ however.

Attempts were made to obtain compounds of the type $Fe_3(CO)_9(SR)_2$ by other methods. Thus $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ was isolated in low yield from the reaction of

$[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ with $Fe_3(CO)_{12}$ in refluxing benzene. There was no evidence for the formation of $Fe_3(CO)_9(S\text{-}i\text{-}C_3H_7)_2$ in the corresponding reaction involving $[Fe(CO)_3S\text{-}i\text{-}C_3H_7]_2$ however. Trinuclear products could also not be isolated from the reactions of $[Fe(CO)_3S\text{-}i\text{-}C_3H_7]_2$ and $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ with $Fe_2(CO)_9$ in benzene at room temperature.

DISCUSSION

$Fe_3(CO)_9(H)(SR)$

The compounds $Fe_3(CO)_9(H)(SR)$ ($R = i\text{-}C_3H_7$, $s\text{-}C_4H_9$ and $t\text{-}C_4H_9$) sublime readily and are soluble in all common organic solvents apart from petroleum ether. With the exception of $Fe_3(CO)_9(H)(S\text{-}s\text{-}C_4H_9)$ they are stable under nitrogen in the crystalline state but all three decompose in the presence of air. Although the highest ion observed in the mass spectra of these compounds corresponds with $Fe_3(CO)_9(H)(SR)$, it is possible that the parent molecular ion is not observed and thus by analogy with the ruthenium and osmium derivatives the compounds might be formulated as $Fe_3(CO)_{10}(H)(SR)$. For this reason and in view of the close similarity of the analytical data for $Fe_3(CO)_9(H)(SR)$ and $Fe_3(CO)_{10}(H)(SR)$, these compounds were successively crystallised, sublimed and recrystallised and analysed at each stage of the purification. The analytical data were always consistent with the stoichiometry $Fe_3(CO)_9(H)(SR)$.

The infrared spectra of $Fe_3(CO)_9(H)(SR)$ ($R = i\text{-}C_3H_7$, $s\text{-}C_4H_9$ and $t\text{-}C_4H_9$) measured in cyclohexane contain eight peaks in the terminal carbonyl stretching region which is indicative of a structure of low symmetry. Further there are no peaks which can be assigned to bridging carbonyl stretching modes. These spectra are also quite different to those of $Ru_3(CO)_{19}(H)(SR)$ and $Os_3(CO)_{10}(H)(SR)$[10], further indication that the iron derivatives are not analogous to these latter complexes. The NMR spectra of $Fe_3(CO)_9(H)(SR)$ contain a peak in the region τ 33 which is consistent with the presence of a hydride ligand. Other peaks in these spectra are readily assigned to the alkyl protons.

The parent molecular ion $Fe_3(CO)_9(H)(SR)^+$ is observed in high abundance in the mass spectra of these trinuclear derivatives. These spectra are somewhat complex however as a result of competitive fragmentation processes and consequently only the salient features will be discussed. The major fragmentation involves loss of carbonyl groups from the parent ion to give $Fe_3(H)(SR)^+$, followed by elimination of an olefin (C_3H_6 or C_4H_8) to yield $Fe_3(H)(SH)^+$ and finally loss of hydrogen to afford $Fe_3(H)(S)^+$ and Fe_3S^+. Degradation of Fe_3S^+ to Fe_2S^+, Fe_2^+ and Fe^+ then occurs. A secondary fragmentation process involves initial loss of an olefinic group to give $Fe_3(CO)_9(H)(SH)^+$ followed by competitive loss of hydrogens and carbonyls giving ions of the type $Fe_3(CO)_{9-n}(H)(SH)^+$, $Fe_3(CO)_{9-n}(H)S^+$ and $Fe_3(CO)_{9-n}S^+$ ($n = 0\text{–}9$). Interestingly based on the relative intensities of the spectral peaks, carbonyls are more readily lost in the initial stages of this fragmentation but hydrogen is more readily eliminated in the latter stages. This is consistent with the known bonding properties of metal carbonyls. A third minor fragmentation process appears to be the elimination of hydrogen from the alkyl groups to give ions of the type $Fe_3(CO)_{9-n}(H)(SC_3H_5)^+$ ($n = 3\text{–}9$). As the molecular weight of C_4H_8 is double that of a carbonyl group, the above fragmentation patterns were established primarily from the spectrum of $Fe_3(CO)_9(H)(S\text{-}i\text{-}C_3H_7)$. Many fragmentation steps were confirmed by the presence of the appropriate metastable peaks in the spectra. A feature of

TABLE 1

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA

Compound[a]	ν(CO)[b] (cm^{-1})	NMR data	
		Peak[i,j]	Assignment
$[Fe(CO)_3SC_2H_5]_2$	2071 (ms), 2034 (s), 2000 (s), 1987 (s)[c]	8.69 (t; *J* 7.4)[k] 8.65 (t; *J* 7.3) 8.90 (t; *J* 7.3) 7.73 (m)	CH_3 (*syn*-isomer) CH_3 (*anti*-isomer) CH_3 (*anti*-isomer) CH_2 (both isomers)
$[Fe(CO)_3S\text{-n-}C_3H_7]_2$	2070 (ms), 2033 (s), 1999 (s), 1986 (s)[c]		
$[Fe(CO)_3S\text{-i-}C_3H_7]_2$	2070 (ms), 2033 (s), 1999 (s), 1988 (s)[c]	8.68 (d; *J* 6.5)[k] 8.63 (d; *J* 6.5) 8.86 (d; *J* 6.6) 7.42 (m)	CH_3 (*syn*-isomer) CH_3 (*anti*-isomer) CH_3 (*anti*-isomer) CH (both isomers)
$[Fe(CO)_3S\text{-n-}C_4H_9]_2$	2070 (ms), 2033 (s), 1999 (s), 1986 (s)[c]		
$[Fe(CO)_3S\text{-i-}C_4H_9]_2$	2070 (ms), 2033 (s), 1999 (s), 1987 (s)[c]		
$[Fe(CO)_3S\text{-s-}C_4H_9]_2$	2069 (ms), 2031 (s), 1997 (s), 1985 (s)[c]		
$[Fe(CO)_3S\text{-t-}C_4H_9]_2$	2069 (ms), 2033 (s), 1999 (s), 1987 (s)[c]	8.50[k] 8.53 8.62	CH_3 (*syn*-isomer) CH_3 (*anti*-isomer) CH_3 (*anti*-isomer)
$Fe_3(CO)_9(H)(S\text{-i-}C_3H_7)$	2084 (m), 2046 (s), 2023 (s), 2011 (s), 2001 (m), 1995 (m), 1969 (sh), 1965 (w)[c]	9.09 (d; *J* 6.7)[k] 7 (vb) 32.9	CH_3 CH FeHFe
$Fe_3(CO)_9(H)(S\text{-s-}C_4H_9)$	2083 (m), 2042 (s), 2022 (s), 2008 (s), 2000 (m), 1994 (m), 1967 (sh), 1960 (w)[c]	8.27 (d; J 7.3)[k] 8.74 (t; *J* 7.4) 7–9 (vb) 33.1	CH_3 CH_3 CH_2, CH FeHFe
$Fe_3(CO)_9(H)(S\text{-t-}C_4H_9)$	2083 (m), 2045 (s), 2023 (s), 2011 (s), 2000 (m), 1993 (m), 1968 (sh), 1963 (w)[c]	8.94[k] 32.8	CH_3 FeHFe
$Fe_3(CO)_9S_2$	2062 (s), 2044 (s), 2023 (s), 2003 (sh)[c]		
$Fe_3(CO)_9(S\text{-t-}C_4H_9)_2$	2071 (w), 2041 (s), 2011 (s), 2003 (s), 1997 (sh), 1977 (m), 1964 (vw), 1954 (vw)[c]	8.44[k] 8.71	CH_3 CH_3
$Fe_4(CO)_{12}(S)(S\text{-t-}C_4H_9)_2$	2081 (m), 2053 (s), 2038 (vs), 2000 (ms), 1987 (s)[d]	8.53[k]	CH_3
$Fe_3(CO)_9S_2$	2062 (s), 2045 (s), 2024 (s), 1985 (w)[c,e]		
$Ru_3(CO)_{10}(H)(SC_2H_5)$	2105 (m), 2064 (s), 2056 (s), 2026 (vs), 2012 (m), 2008 (s), 1994 (m)[c,f]		
$Os_3(CO)_{10}(OCH_3)_2$	2107 (m), 2071 (ms), 2056 (s), 2016 (vs), 1989 (s), 1978 (m), 1951 (w)[c,g]	5.27[l]	CH_3

(*continued*)

TABLE 1 (*continued*)

Compound[a]	ν(CO)[b] (cm^{-1})	NMR data	
		Peak[i,j]	Assignment
$Fe_4(CO)_{12}(S)(SCH_3)_2$	2082 (m), 2059 (s), 2042 (vs), 2010 (s), 1995 (s)[d,h]	7.67[k]	CH_3

[a] All new compounds are red, diamagnetic and non-electrolytes in acetone. [b] Abbreviations: vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; vw, very weak; sh, shoulder. [c] Measured in C_6H_{12}. [d] Measured in $CHCl_2CHCl_2$. [e] Ref. 12. [f] Ref. 10. [g] Ref. 15. [h] Ref. 16. [i] τ scale; measured at 38° (TMS reference); *J* in Hz. [j] Abbreviations: d, doublet; t, triplet; m, multiplet; vb, very broad. [k] Measured in $CDCl_3$. [l] Measured in CCl_4.

the spectra of the three compounds is the high abundance of trinuclear ions; there are very few peaks which can be assigned to dinuclear ions based on the ratio $(M-2)/M$. This is indicative of a cyclic structure. Further the preferential loss of carbon monoxide to hydrogen suggests that the hydride group is bridging.

Based on the above infrared, NMR and mass spectroscopic data, the structure shown in the figure is proposed for the compounds of the type $Fe_3(CO)_9(H)(SR)$.

$Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$

The compound $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ sublimes readily and has similar solubility and stability properties to the compounds $Fe_3(CO)_9(H)(SR)$ discussed above. The stoichiometry $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ and not $Fe_3(CO)_{10}(S\text{-}t\text{-}C_4H_9)_2$ was confirmed in an analogous manner to that described above for the compounds $Fe_3(CO)_9(H)(SR)$.

The infrared spectrum of this compound shows a complex pattern in the terminal carbonyl stretching region; no peaks can be assigned to bridging carbonyl stretching modes. This complexity is in contrast to the simple pattern observed in the infrared spectrum of $Fe_3(CO)_9S_2$[12] and thus it can be concluded that the structure of $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ is not based on the symmetrical structure of $Fe_3(CO)_9S_2$[13,14]. The spectrum of $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ is also very different to that of $Os_3(CO)_{10}(OCH_3)_2$ in the C–O stretching region[15]. The NMR spectrum of $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ contains two peaks of equal intensity which can be assigned to the methyl protons. This is consistent with the two tert-butyl groups being non-equivalent. However, the NMR spectrum of $Os_3(CO)_{10}(OCH_3)_2$ contains a single resonance assigned to the methyl protons[15].

The metal-containing ions observed in the mass spectrum of this compound are given in Table 2. Compared with that found for $Fe_3(CO)_9(H)(SR)$, the fragmentation pattern is relatively simple. Initial stepwise loss of carbonyl groups from the parent ion $Fe_3(CO)_9(SC_4H_9)_2^+$ occurs to give $Fe_3(SC_4H_9)_2^+$. Elimination of butene to yield $Fe_3(SC_4H_9)(SH)^+$ is then followed by competitive loss of butene and hydrogen to afford the ions $Fe_3(SC_4H_9)S^+$, $Fe_3(SH)_2^+$, $Fe_3(SH)S^+$ and $Fe_3S_2^+$. $Fe_3S_2^+$ is then degraded to $Fe_2S_2^+$, Fe_2S^+, Fe_2^+ and Fe^+. Interestingly the spectrum contains peaks corresponding to $Fe_3(CO)(SC_4H_9)(SH)^+$ and $Fe_3(CO)(SC_4H_9)S^+$ which shows that there is a tendency for the elimination of a butene group and hydrogen before the loss of the final carbonyl. The fragmentation processes above were confirmed by

TABLE 2

MASS SPECTRUM OF $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$
Metal-containing ions only.

Ion	m/e	Relative abundance
$Fe_3(CO)_9(SC_4H_9)_2^+$	598	1.7
$Fe_3(CO)_8(SC_4H_9)_2^+$	570	13.7
$Fe_3(CO)_7(SC_4H_9)_2^+$	542	21.9
$Fe_3(CO)_6(SC_4H_9)_2^+$	514	18.1
$Fe_3(CO)_5(SC_4H_9)_2^+$	486	5.4
$Fe_3(CO)_4(SC_4H_9)_2^+$	458	58.5
$Fe_3(CO)_3(SC_4H_9)_2^+$	430	61.0
$Fe_3(CO)_2(SC_4H_9)_2^+$	402	50.8
$Fe_3(CO)(SC_4H_9)_2^+$	374	41.7
$Fe_3(SC_4H_9)_2^+$	346	20.3
$Fe_3(CO)(SC_4H_9)(SH)^+$	318	6.1
$Fe_3(CO)(SC_4H_9)S^+$	317	5.0
$Fe_3(SC_4H_9)(SH)^+$	290	37.1
$Fe_3(SC_4H_9)S^+$	289	15.8
$Fe_3SC_4H_8S^+$	288	13.7
$Fe_3(SH)_2^+$	234	16.2
$Fe_3(SH)S^+$	233	50.0
$Fe_3S_2^+$	232	100.0
$Fe_2(SH)_2^+$	178	14.5
$Fe_2(SH)S^+$	177	18.0
$Fe_2S_2^+$	176	27.0
Fe_2S^+	144	13.1
Fe_2^+	112	2.5
Fe^+	56	Not measurable

the presence of the appropriate metastable peaks in the spectrum. For instance the peak at 243.1 corresponds to the step $Fe_3(SC_4H_9)_2^+ \rightarrow Fe_3(SC_4H_9)(SH)^+$. As was found for $Fe_3(CO)_9(H)(SR)$, a high abundance of trinuclear ions is observed in the spectrum of $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$. This indicates $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ to be cyclic.

A structure, similar to that proposed for $Fe_3(CO)_9(H)(SR)$, in which a bridging sulphido group has replaced the bridging hydride is proposed for this compound.

$Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$

The compound $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$ is very soluble in all common organic solvents and is stable in air in the crystalline state. As shown in Table 1, the infrared spectrum of this derivative in the C–O stretching region is very similar to that of $Fe_4(CO)_{12}(S)(SCH_3)_2$, previously obtained in very low yield from the reaction of $Fe_3(CO)_{12}$ with CH_3SCN in benzene[16]. The NMR spectrum of $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$ contains a single methyl resonance as was found[16] for $Fe_4(CO)_{12}(S)(SCH_3)_2$. The tertiary butyl groups are thus equivalent. The mass spectrum of this derivative is explained in terms of a primary fragmentation involving stepwise loss of carbonyl groups from the parent ion till $Fe_4(CO)_3(S)(SC_4H_9)_2^+$, followed by competitive loss of butene groups, carbonyls and hydrogens giving finally $Fe_4S_3^+$. Fragmentation of $Fe_4S_3^+$ yields $Fe_4S_2^+$, $Fe_3S_3^+$, $Fe_3S_2^+$, Fe_3S^+, $Fe_2S_2^+$, Fe_2S^+, Fe_2^+, FeS^+ and Fe^+. In view of the similarity of the infrared and NMR spectra of $Fe_4(CO)_{12}(S)(SCH_3)_2$ and

$Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$, a structure corresponding to that previously established for $Fe_4(CO)_{12}(S)(SCH_3)_2$ by an X-ray crystallographic analysis[16] is proposed for $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$.

$Fe_3(CO)_9S_2$

The infrared and mass spectra of the $Fe_3(CO)_9S_2$ isolated in this study are identical with the spectra[12,17] of the compound $Fe_3(CO)_9S_2$ isolated from the reaction of $[Fe(CO)_4]^{2-}$ with sulphurous acid[12]. Furthermore none of its C–O stretching frequencies corresponds with those of $[Fe_3(CO)_9S_2][Fe_2(CO)_6S_2]$[9,18] previously isolated from the reaction of $Fe_3(CO)_{12}$ with cyclohexene sulphide[18]. It would thus appear that the conformer of $Fe_3(CO)_9S_2$ prepared in this study has the same structure as that isolated from the sulphurous acid preparation[13,14] but different to that of the conformer of $Fe_3(CO)_9S_2$ in $[Fe_3(CO)_9S_2][Fe_2(CO)_6S_2]$[13].

$[Fe(CO)_3SR]_2$

The compounds $[Fe(CO)_3SR]_2$ ($R = n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_4H_9$ and $s\text{-}C_4H_9$) could not be isolated in the crystalline state. They were obtained as red oils and identified by means of infrared spectroscopy only. The crystalline compounds $[Fe(CO)_3\text{-}SC_6H_5]_2$ and $Fe_2(CO)_6S_2C_2H_4$, previously synthesised by other workers[2,3,7], were identified similarly. The derivatives $[Fe(CO)_3SR]_2$ ($R = C_2H_5$, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$)

TABLE 3

MASS SPECTRA OF $[Fe(CO)_3SR]_2$ ($R = i\text{-}C_3H_7$, $t\text{-}C_4H_9$)
Metal-containing ions only.

Ion	$R = i\text{-}C_3H_7$		$R = t\text{-}C_4H_9$	
	m/e	Relative abundance	*m/e*	Relative abundance
$Fe_2(CO)_6(SR)_2^+$	430	44.7	458	31.1
$Fe_2(CO)_5(SR)_2^+$	402	8.6	430	3.9
$Fe_2(CO)_4(SR)_2^+$	374	32.3	402	17.9
$Fe_2(CO)_3(SR)_2^+$	346	28.6	374	19.0
$Fe_2(CO)_2(SR)_2^+$	318	59.3	346	41.9
$Fe_2(CO)(SR)_2^+$	290	46.9	318	33.9
$Fe_2(SR)_2^+$	262	100.0	290	82.2
$Fe_2(CO)(SR)(SH)^+$	248	3.1	262	7.5
$Fe_2(CO)(SR)S^+$	247	1.7		
$Fe_2(SR)(SH)^+$	220	74.0	234	80.9
$Fe_2(SR)S^+$	219	13.2	233	8.6
$Fe_2S_2C_4H_8^+$			232	6.0
$Fe_2SC_4H_8^+$			200	4.4
$Fe_2(SH)_2^+$	178	90.8	178	100
$Fe_2(SH)S^+$	177	92.0	177	71.5
$Fe_2S_2^+$	176	36.1	176	33.0
$Fe_2(SH)^+$	145	v.w.[a]	145	2.9
Fe_2S^+	144	17.7	144	20.4
Fe_2^+	112	2.6	112	3.4
Fe^+	56	7.1	56	n.m.[b]

[a] Very weak. [b] Not measurable.

have been previously reported[2-4,19,20] but their spectroscopic properties are not well documented. In view of this the infrared, NMR and mass spectroscopic data of the three compounds are now discussed. The infrared spectra in the C–O stretching region and the NMR spectra are recorded in Table 1. Peak assignments in the NMR spectra to the *syn*- or *anti*-isomer are based on the relative intensities of the resonances.

The mass spectra of $[Fe(CO)_3SR]_2$ ($R = i\text{-}C_3H_7$ and $t\text{-}C_4H_9$) (Table 3) are very similar to the spectra of $[Fe(CO)_3SR]_2$ ($R = CH_3$ and C_2H_5) previously reported[21,22]. The parent ion $[Fe(CO)_3SR]_2^+$ first loses stepwise its carbonyl groups to give $Fe_2(SR)_2^+$. This is followed by loss of alkene (C_3H_6 or C_4H_8) and hydrogen to yield $Fe_2S_2^+$, which degrades to Fe_2S^+, Fe_2^+ and Fe^+. An interesting feature of the spectra of the two compounds is the apparent loss of CH_2 from the parent ions to give ions of *m/e* 416 and 444 and formulated as $Fe_2(CO)_6(SC_3H_7)(SC_2H_5)^+$ and $Fe_2(CO)_6(SC_4H_9)(SC_3H_7)^+$ respectively. Other peaks in the spectra correspond to the stepwise loss of carbonyl groups from these ions. In view of the very weak nature of the peaks corresponding to these ions, they have not been included in Table 3 however.

The NMR data are consistent with all three compounds $[Fe(CO)_3SR]_2$ ($R = C_2H_5$, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$) occurring in two isomeric forms (*syn* and *anti*) in solution. The detection of both isomers of $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ is in contrast to that observed in previous syntheses of $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ where only the *anti*-isomer was formed as established by infrared[4] and NMR spectroscopy[20]. It should be added however that the $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ prepared in this study contains only about 10% of the *syn*-isomer.

From the results above it would appear that the stability of the trinuclear derivatives of the type $Fe_3(CO)_9(H)(SR)$ ($R = i\text{-}C_3H_7$ and $t\text{-}C_4H_9$) and $Fe_3(CO)_9(SR)_2$ ($R = t\text{-}C_4H_9$) is a function of the stereochemistry of the group R. In fact a tertiary butyl group is necessary to stabilise $Fe_3(CO)_9(SR)_2$. For other alkyl groups the results indicate that $Fe_3(CO)_9(SR)_2$ is unstable with respect to $[Fe(CO)_3SR]_2$. The inability to synthesise $Fe_3(CO)_9(S\text{-}i\text{-}C_3H_7)_2$ by reacting $[Fe(CO)_3S\text{-}i\text{-}C_3H_7]_2$ with $Fe_3(CO)_{12}$ whereas $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ may be isolated from the corresponding reaction involving $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$, is consistent with this observation.

Metal–metal bonds are known to be stronger in second and third than in first row transition metal derivatives. This would explain why compounds of the type $Fe_3(CO)_9(H)(SR)$ and not $Fe_3(CO)_{10}(H)(SR)$ ($R = i\text{-}C_3H_7$, $s\text{-}C_4H_9$ and $t\text{-}C_4H_9$) are isolated from the reaction of $Fe_3(CO)_{12}$ with RSH. The structure proposed for the derivatives $M_3(CO)_{10}(H)(SR)$ ($M = Ru$ and Os) contains an $M(CO)_x$ ($x = 4$) unit bonded to an $M_2(CO)_6(H)(SR)$ moiety through two M–M bonds[10]. Although the assumed structure of the trinuclear iron derivatives also contains an $Fe(CO)_x$ group bonded to an $Fe_2(CO)_6(H)(SR)$ moiety through two Fe–Fe bonds, it would appear that a sulphur group bridging *three* iron atoms is required to stabilise these compounds. The value of x must therefore necessarily be three.

EXPERIMENTAL

The compounds $Fe_2(CO)_9$[23] and $Fe_3(CO)_{12}$[24] were synthesised according to literature methods. The thiols were obtained commercially (Koch–Light and Fluka). All experiments were performed under a nitrogen atmosphere. The chromatographic separations were effected on an alumina column (50 × 1.5 cm; Merck acid washed alumina, activity III). The infrared and mass spectra were recorded on a Perkin–Elmer model 621 grating spectrophotometer and an A.E.I. MS9 mass spectrometer respectively. The NMR spectra were obtained using the Varian A60 and 100 MHz instrument. The elemental analyses (C, H, S) were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany, Mr. G. J. Roberts, National Chemical Research Laboratory, C.S.I.R., Pretoria and Mrs. M. Liebenberg, Microanalytical Section, Iscor. The iron analyses were determined by an Atomic Absorption Spectroscopic method using a Techtron AA4.

Reaction of $Fe_3(CO)_{12}$ with approximately equimolar RSH ($R = i\text{-}C_3H_7$, $s\text{-}C_4H_9$ and $t\text{-}C_4H_9$). Preparation of $Fe_3(CO)_9(H)(SR)$

A solution of $Fe_3(CO)_{12}$ (5.0 g, 10 mmole) and i-C_3H_7SH (0.95 g, 12.5 mmole) or s-C_4H_9SH (1.1 g, 12.5 mmole) or t-C_4H_9SH (1.1 g, 12.5 mmole) in benzene (ca. 100 ml) was refluxed for 1 h. The solution was filtered, reduced to a small volume and transferred to an alumina column. The column was eluted with petroleum ether to remove $[Fe(CO)_3SR]_2$. Elution with benzene afforded a deep red band which was collected. The solvent was removed under reduced pressure to afford the title compound as a red residue. Purification was achieved by crystallisation from benzene/petroleum ether, followed by sublimation (55°/0.01 mm) and finally by recrystallisation from benzene/petroleum ether. Yield >60%.

μ-Hydrido-μ-(isopropylsulphido)nonacarbonyltriiron, $Fe_3(CO)_9(H)(S\text{-}i\text{-}C_3H_7)$. (Found after 1st crystallisation: C, 28.92; H, 1.64. Found after sublimation: C, 29.13; H, 1.61. Found after 2nd crystallisation: C, 28.92; H, 1.61; Fe, 33.49; S, 6.34; M^+, 496. $C_{12}H_8Fe_3O_9S$ calcd.: C, 29.07; H, 1.63; Fe, 33.79; S, 6.47%; mol.wt., 496. $C_{13}H_8Fe_3O_{10}S$ calcd.: C, 29.81; H, 1.54; Fe, 30.54; S, 6.12%; mol.wt., 524.)

μ-Hydrido-μ-(sec-butylsulphido)nonacarbonyltriiron, $Fe_3(CO)_9(H)(S\text{-}s\text{-}C_4H_9)$. (Found: C, 30.83; H, 2.01; Fe, 32.96; S, 6.10; M^+, 510. $C_{13}H_{10}Fe_3O_9S$ calcd.: C, 30.63; H, 1.98; Fe, 32.86; S, 6.29%; mol.wt., 510.)

μ-Hydrido-μ-(tert-butylsulphido)nonacarbonyltriiron, $Fe_3(CO)_9(H)(S\text{-}t\text{-}C_4H_9)$. (Found after 1st crystallisation: C, 30.36; H, 1.87; Fe, 33.09. Found after sublimation and 2nd crystallisation: C, 30.54; H, 1.88; Fe, 33.05; S, 6.38; M^+, 510. $C_{13}H_{10}Fe_3O_9S$ calcd.: C, 30.63; H, 1.98; Fe, 32.86; S, 6.29; mol.wt., 510. $C_{14}H_{10}Fe_3O_{10}S$ calcd.: C, 31.27; H, 1.87; Fe, 31.15; S, 5.96%; mol.wt., 538.)

Reaction of $Fe_3(CO)_{12}$ with an excess of RSH ($R = i\text{-}C_3H_7$ and $s\text{-}C_4H_9$). Preparation of $[Fe(CO)_3SR]_2$

A solution of $Fe_3(CO)_{12}$ (5.0 g, 10 mmole) and i-C_3H_7SH (3.8 g, 50 mmole) or s-C_4H_9SH (4.5 g, 50 mmole) in benzene (ca. 100 ml) was refluxed for 8 h. The solvent and excess ligand were removed under reduced pressure. The residue was dissolved in benzene and the solution filtered. The filtrate was reduced to a small volume and transferred to an alumina column. The column was eluted with petroleum ether to afford a red band which was collected.

Bis[μ-(isopropylsulphido)tricarbonyliron], $[Fe(CO)_3S\text{-}i\text{-}C_3H_7]_2$. The solution collected above was evaporated to dryness and the red residue of $[Fe(CO)_3S\text{-}i\text{-}C_3H_7]_2$ crystallised from petroleum ether. Yield >60%. (Found: C, 33.64; H, 3.26; Fe, 25.79; S, 14.58; M^+, 430. $C_{12}H_{14}Fe_2O_6S_2$ calcd.: C, 33.51; H, 3.28; Fe, 25.97; S, 14.91%; mol.wt., 430.)

Bis[μ-(sec-butylsulphido)tricarbonyliron], $[Fe(CO)_3\text{-}s\text{-}C_4H_9]_2$. The solution collected above was evaporated to afford a red oil. This oil was identified as $[Fe(CO)_3\text{-}s\text{-}C_4H_9]_2$ by means of infrared spectroscopy.

Reaction of $Fe_3(CO)_{12}$ with excess $t\text{-}C_4H_9SH$. Preparation of $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$, $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$, $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$ and $Fe_3(CO)_9S_2$

A solution of $Fe_3(CO)_{12}$ (5.0 g, 10 mmole) and $t\text{-}C_4H_9SH$ (4.5 g, 50 mmole) in benzene (ca. 100 ml) was refluxed for 12 h. The solvent and excess ligand were removed under reduced pressure. The residue was dissolved in benzene and the solution filtered. The filtrate was reduced to a small volume and transferred to an alumina column. The column was eluted with petroleum ether to afford a broad red band which was collected in several fractions. Each fraction was in turn rechromatographed using petroleum ether as eluent. The broad band which was obtained in each case was again collected in several fractions. This overall procedure was repeated until $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$, $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$, $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ and $Fe_3(CO)_9S_2$ were separated as determined by monitoring with infrared. The compounds were eluted from the column in the order given.

Bis[μ-(tert-butylsulphido)tricarbonyliron], $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$. The fraction containing $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ was evaporated to afford a red crystalline material which was recrystallised from petroleum ether. Yield 35%. (Found: C, 36.79; H, 3.85; Fe, 24.05; S, 14.18; M^+, 458. $C_{14}H_{18}Fe_2O_6S_2$ calcd.: C, 36.71; H, 3.96; Fe, 24.38; S, 14.00%; mol.wt., 458.)

μ-Sulphidobis-μ-(tert-butylsulphido)dodecacarbonyltetrairon, $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$. The fraction containing $Fe_4(CO)_{12}(S)(S\text{-}t\text{-}C_4H_9)_2$ was evaporated to afford a red crystalline material which was recrystallised from petroleum ether. Yield 5%. (Found: C, 30.94; H, 2.39; Fe, 28.87; S, 12.24; M^+, 770. $C_{20}H_{18}Fe_4O_{12}S_3$ calcd.: C, 31.20; H, 2.36; Fe, 29.01; S, 12.49%; mol.wt., 770.)

Bis-μ-(tert-butylsulphido)nonacarbonyltriiron, $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$. The solvent was removed from the fraction containing $Fe_3(CO)_9(S\text{-}t\text{-}C_4H_9)_2$ to afford a red crystalline material. The pure compound was obtained by crystallising several times from petroleum ether. Yield 5%. (Found after 1st crystallisation: C, 33.92; H, 2.97. Found after 2nd crystallisation: C, 33.99; H, 3.29. Found after 3rd crystallisation: C, 34.09; H, 3.16; Fe, 27.80; S, 10.63; M^+, 598. $C_{17}H_{18}Fe_3O_9S_2$ calcd.: C, 34.15; H, 3.03; Fe, 28.02; S, 10.72%; mol.wt., 598. $C_{18}H_{18}Fe_3O_{10}S_2$ calcd.: C, 34.54; H, 2.90; Fe, 26.76; S, 10.24%; mol.wt., 626.)

Di-μ-sulphidononacarbonyltriiron, $Fe_3(CO)_9S_2$. The solvent was removed from the fraction containing $Fe_3(CO)_9S_2$ to afford a red crystalline material. The pure compound was obtained by recrystallising from petroleum ether. Yield 10%. (Found: C, 22.30; Fe, 34.74; S, 13.34; M^+, 484. $C_9Fe_3O_9S_2$ calcd.: C, 22.35; Fe, 34.63; S, 13.26%; mol.wt., 484.)

Reaction of $Fe_2(CO)_9$ with RSH ($R=C_2H_5$, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$). Preparation of bis-[μ-(ethylsulphido)tricarbonyliron], $[Fe(CO)_3SC_2H_5]_2$

A suspension of $Fe_2(CO)_9$ (1.0 g, 2.7 mmole) and C_2H_5SH (0.6 g, 10 mmole) or $i\text{-}C_3H_7SH$ (0.75 g, 10 mmole) or $t\text{-}C_4H_9SH$ (0.9 g, 10 mmole) in benzene (ca. 60 ml) was stirred for 6 h at room temperature. The solution from the reaction involving C_2H_5SH or $i\text{-}C_3H_7SH$ was filtered and the filtrate evaporated to dryness. The red residue of $[Fe(CO)_3SR]_2$ was crystallised from petroleum ether. Yield >90%. The solution from the t-C_4H_9SH reaction was reduced to a small volume and transferred to an alumina column. The column was eluted with petroleum ether to afford a red band which was collected. The solvent was removed under reduced pressure to afford $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ as a red crystalline material. Purification was achieved by crystallisation from petroleum ether. Yield 70%. (Found: C, 29.91; H, 2.43; Fe, 27.53; S, 16.17; M^+, 402. $C_{10}H_{10}Fe_2O_6S_2$ calcd.: C, 29.88; H, 2.51; Fe, 27.78; S, 15.95%; mol. wt., 402.)

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