Mercaptide Insertion Reactions of an Iron–Iron Bond

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The reaction between $(CF_3)_2C_2S_2$ and $[\{Fe(XR)(CO)_3\}_2]$ (XR = SMe, SEt, SPh, or SePh) affords the salts $[Fe_2(XR)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$. A reaction sequence is proposed involving oxidation of $[\{Fe(XR)(CO)_3\}_2]$ to $[\{Fe(XR)(CO)_3\}_2]^+$ followed by formal insertion of RX· into the iron–iron bond to give $[Fe_2(XR)_3(CO)_6]^+$. Thus the compounds $[Fe_2(XR)_3(CO)_6]^+[PF_6]^-$ (XR = SMe or SPh) were prepared from $[\{Fe(XR)(CO)_3\}_2]$ using $NOPF_6$ as the oxidising agent.

BISPERFLUOROMETHYLDITHIETEN, $(CF_3)_2C_2S_2$, reacts with the iron carbonyls $[Fe(CO)_5]$, $[Fe_2(CO)_9]$, and $[Fe_3(CO)_{12}]$ to give, respectively, $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]$,[1] $[\{Fe\{(CF_3)_2C_2S_2\}(CO)_3\}_2]$,[2,3] and $[Fe_2\{(CF_3)_2C_2S_2\}(CO)_6]$ [4] by displacement of varying numbers of carbon monoxide ligands from the iron carbonyl precursor. The reaction between $(CF_3)_2C_2S_2$ and the dimers $[\{Fe(XR)(CO)_3\}_2]$, (XR = SMe, SEt, SPh, or SePh), also results in the displacement of carbon monoxide to give compounds which were originally formulated [5] as the neutral tetramers $[\{Fe(XR)\{(CF_3)_2C_2S_2\}(CO)\}_4]$ on the basis of solution molecular-weight and i.r. spectral data. However, a single-crystal *X*-ray diffraction study [6] of the complex in which XR = SMe, has shown that these materials are, in fact, the salts $[Fe_2(XR)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$. The formation of such species was quite unexpected and, in formal terms, involves replacement of all ligands by $(CF_3)_2C_2S_2$ in some molecules of $[\{Fe(XR)(CO)_3\}_2]$ and insertion of XR^+ into the iron–iron bond of others. In order to understand more fully the nature of this unusual reaction we have further investigated the chemistry of $[\{Fe(XR)(CO)_3\}_2]$ (XR = SMe or SPh).

DISCUSSION

In refluxing mixtures of benzene and pentane, $(CF_3)_2C_2S_2$ reacted with $[\{Fe(XR)(CO)_3\}_2]$ (XR = SMe, SEt, SPh, or SePh) to give the dark-green crystalline salts $[Fe_2(XR)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ which were soluble in dichloromethane, acetone and, to some extent, in chloroform. The solid-state i.r. spectra (see Table) of these compounds were similar, and contained bands attributable to the CF_3 groups of the dithieten ligand, to the alkyl or aryl groups of the sulphide ligand, and to the presence of the CO ligand. Acetone or chloroform solutions of the salts exhibited only two carbonyl stretching frequencies (Table) consistent with the presence of $\{Fe(CO)_3\}$ fragments of C_{3v} symmetry as shown by the *X*-ray diffraction study.[6] The acetone solutions had specific conductivities in accord with the formulation of the salts as 1 : 1 electrolytes.[7] However, chloroform solutions of the compounds were non-conducting, presumably as a result of extensive ion-pairing which would also account for the misleading molecular-weight data [5] obtained in this solvent. The electronic spectra of the salts were generally similar in appearance. Acetone solutions exhibited two main absorptions at *ca.* 570 and 425 nm, but chloroform solutions exhibited poorly resolved spectra in which well defined maxima were not present.

The formation of $[Fe_2(XR)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ in the reaction between $(CF_3)_2C_2S_2$ and $[\{Fe(XR)(CO)_3\}_2]$ may be rationalized in terms of the following reaction scheme:

$$4(CF_3)_2C_2S_2 + [\{Fe(XR)(CO)_3\}_2] \longrightarrow [\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0 + RXXR + 6CO$$

$$[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0 + [\{Fe(XR)(CO)_3\}_2] \longrightarrow [\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^- + [\{Fe(XR)(CO)_3\}_2]^+$$

$$2[\{Fe(XR)(CO)_3\}_2]^+ + RXXR \longrightarrow 2[Fe_2(XR)_3(CO)_6]^+$$

The first step in this sequence involves the formation of $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ from the reaction between four molecules of $(CF_3)_2C_2S_2$ and one molecule of $[\{Fe(XR)(CO)_3\}_2]$. This reaction also results in the liberation of six molecules of CO and one molecule of the disulphide or diselenide RXXR. The $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$, a strong oxidizing agent,[8] then oxidizes a molecule of $[\{Fe(XR)(CO)_3\}_2]$ to the cation $[\{Fe(XR)(CO)_3\}_2]^+$ with concomitant formation of the anion $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$. Subsequently the cation undergoes an insertion reaction with RXXR to give $[Fe_2(XR)_3(CO)_6]^+$.

In order to test the validity of this scheme the reaction between $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ and $[\{Fe(XR)(CO)_3\}_2]$ in the presence of RXXR was investigated for XR = SMe

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and SPh. In both cases $[Fe_2(XR)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ was formed in yields comparable with those obtained from the reaction between $[\{Fe(XR)(CO)_3\}_2]$ and $(CF_3)_2C_2S_2$.

The possibility that oxidizing agents other than $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ might effect this reaction was also studied. In the presence of PhSSPh, $[\{Fe(XR)(CO)_3\}_2]$ reacted with $AgPF_6$ on two occasions to give a 28% yield of $[Fe_2(SC_6H_5)_3(CO)_6]^+[PF_6]^-$ which was identified by its spectrum. This reaction was, however, irreproducible, and attempts to find an initiator were unsuccessful. Using $NOPF_6$ as the oxidant [9] reproducible results were obtained. Thus, in the presence of PhSSPh, excess of $NOPF_6$ reacted with $[\{Fe(SPh)(CO)_3\}_2]$ to give a 13% yield of $[Fe_2(SPh)_3(CO)_6]^+[PF_6]^-$ along with some $[\{Fe(SPh)(NO)_2\}_2]$ which was identified by mass and i.r. spectrometry. Similarly, the reaction between $NOPF_6$ and $[\{Fe(SMe)(CO)_3\}_2]$ afforded a 13% yield of $[Fe_2(SMe)_3(CO)_6]^+[PF_6]^-$. The specific conductivities of these acetone solutions were in accord with the formulation of the $[PF_6]^-$ salts as 1 : 1 electrolytes.

I.r. spectra of iron sulphide cations

Compound	Solid-state spectrum (KBr disc; in cm^{-1})						ν_{CO}/cm^{-1} (Acetone solution)
$[Fe_2(SPh)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$	2108s	2075s	2060s	1580w			2105
	1480w	1225vs	1170vs	1140vs			2072
	1025w	1000w	895w	850w			
	840w	742m	715m	790m			
	685m	598m	570m	500w			
	480w	360w					
$[Fe_2(SEt)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$	2102s	2065s	1450w	1430w			2100
	1380w	1230vs	1170vs	1140vs			2062
	1045w	1020w	890w	715w			
	690w	600w	570w	495w	360w		
$[Fe_2(SMe)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$	2102s	2065s	1425m	1230vs			2100
	1170vs	1140vs	960w	890w			2062
	840w	722w	715w	690w	600w		
	570m	500w	360w				
$[Fe_2(SePh)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$	2100s	2065s	2055s	2045s	1575w		2098
	1540m	1478m	1440m	1245vs			2060
	1165s	1125s	1020w	1000m			
	895m	840w	735s	718s	690m		
	600s	565m	490w	465w	355w		
$[Fe_2(SPh)_3(CO)_6]^+[PF_6]^-$	3060w	2103s	2078s	2060s			2105
	1575w	1470w	1438m	1382w	998w		2072
	840s	748w	740m	688m			
	565m	553m	490w	478w	415w		
$[Fe_2(SMe)_3(CO)_6]^+[PF_6]^-$	2920w	2110s	2065s	1435m			2100
	1385w	1312w	970m	960m			2062
	840s	595m	562m	550s	490w	420w	

The solid-state i.r. spectra (Table) of $[Fe_2(XR)_3(CO)_6]^+[PF_6]^-$ (XR = SMe or SPh) contained bands attributable to the $[PF_6]^-$ anion, the methyl or phenyl group of the sulphide ligand, and to the CO ligands. Freshly prepared acetone solutions of these two salts exhibited two carbonyl stretching frequencies which were the same as those observed for the $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ salts. It was also noted that, over a period of *ca.* 5 min, the bands at 2105 and 2072 cm^{-1} in the i.r. spectra of acetone solutions of $[Fe_2(SPh)_3(CO)_6]^+[PF_6]^-$ decayed and were replaced by bands at 2080 and 2030 cm^{-1}. Precipitation of the salt from acetone by addition of diethyl ether afforded a material whose i.r. spectrum was identical with that of the original $[Fe_2(SPh)_3(CO)_6]^+[PF_6]^-$. Thus it would seem that a reversible interaction occurs between $[Fe_2(SPh)_3(CO)_6]^+$ and acetone which results in the observed spectral changes. Similar changes were not observed with acetone solutions of $[Fe_2(SMe)_3(CO)_6]^+[PF_6]^-$ or the $[\{Fe\{(CF_3)_3C_2S_2\}_2\}_2]^-$ salts. However, dimethyl sulphoxide solutions of $[Fe_2(XR)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ (XR = SPh or SePh) exhibited similar i.r. spectral changes to those seen with acetone solutions of $[Fe_2(SPh)_3(CO)_6]^+[PF_6]^-$. The electronic spectra of the two compounds were of similar appearance but significant differences were apparent between the spectra of solutions in dichloromethane and acetone.

The reactions of $[\{Fe(XR)(CO)_3\}_2]$ with the oxidizing agents $AgPF_6$, $NOPF_6$, and $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ lend support to the reaction scheme proposed for the formation of $[Fe_2(XR)_3(CO)_6]^+$. While $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ gave the best yields of the cation, this reagent has the disadvantage that the resulting anion $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ obscures some of the spectroscopic properties of the cation. The most suitable oxidant would be $AgPF_6$ were it not for the irreproducible nature of the reaction.

Using a qualitative bonding scheme proposed by Mason and Mingos [10] an iron–iron bond order of one in $[\{Fe(XR)(CO)_3\}_2]$ is indicated while that in $[Fe_2(XR)_3(CO)_6]^+$ is zero. The iron–iron distances of 2·54 Å and 3·06 Å found in $[\{Fe(SEt)(CO)_3\}_2]$ [11] and $[Fe_2(SMe)_3(CO)_6]^+$ respectively are in accord with this difference

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in bond orders. However, the distance found in $[Fe_2(SMe)_3(CO)_6]^+$ is considerably shorter than that of 3·39 Å for the zero-order iron–iron bond in $[\{Fe(\eta^5\text{-}C_5H_5)(SMe)(CO)\}_2]$.[12] This difference may be due to the third mercaptide-bridge ligand ' pulling' the iron atoms closer together about an axis through the other two bridging sulphur atoms. Such an effect would be consistent with Connelly and Dahl's observation [13] that the molybdenum–molybdenum bond length in $[\{Mo(\eta^5\text{-}C_5H_5)(SMe)_2\}_2]^z$ ($z = 0$ or $+1$) is largely determined by the geometric requirements of the four bridging sulphide ligands. In terms of Mason and Mingos' bonding scheme, the formation of $[Fe_2(XR)_3(CO)_6]^+$ involves oxidative removal of an electron from a non-bonding molecular orbital in $[Fe(XR)(CO)_3]_2$, followed by addition of three electrons and two orbitals from a sulphide radical to the overall bonding scheme. The resulting molecule then has a bond order of zero.

In conclusion we note that a wide variety of binuclear transition-metal complexes are known which contain bridging chalcogen or pnicogen atoms. Many of these compounds exhibit electron-transfer reactions and we expect that many other examples of insertion into metal–metal bonds will be found.

EXPERIMENTAL

All reactions were carried out in a nitrogen atmosphere and solvents other than dichloromethane, benzene, and pentane were reagent grade. Dichloromethane was dried over molecular sieves before use, benzene was AnalaR quality, and pentane was dried over sodium and then redistilled from dry magnesium sulphate prior to use. The compounds $(CF_3)_2C_2S_2$, $[\{Fe(XR)(CO)_3\}_2]$, and $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ were prepared by previously described methods; other compounds used were reagent grade.

I.r. and electronic spectra were recorded on Perkin-Elmer model 457 and 402 instruments respectively. Mass spectra were obtained using an A.E.I. MS9 instrument and microanalyses were performed by the Microanalytical Laboratories of the University of Sheffield and Imperial College. Conductivities were measured using a Phillips Conductivity meter at room temperature in acetone (10^{-3}M-solution).

$[Fe_2(SPh)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$.—A mixture of $[\{Fe(SPh)(CO)_3\}_2]$ (2·0 g) and $(CF_3)_2C_2S_2$ (1·8 g) in n-pentane–benzene (2 : 1 v/v; 60 ml) was refluxed for 2·5 h during which time a black solid was precipitated. The mixture was allowed to cool and then filtered to afford the crude product which was purified by recrystallization from dichloromethane–n-hexane–n-octane (yield 1·4 g, 43%) (Found: C, 29·8; H, 1·3; S, 21·6. $C_{40}H_{15}F_{24}Fe_4O_6S_{11}$ requires C, 29·6; H, 0·9; S, 21·7%), $\Lambda = 153$ cm^2 Ω^{-1} mol^{-1}.

$[Fe_2(SMe)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$.—A mixture of $[\{Fe(SMe)(CO)_3\}_2]$ (1·9 g) and $(CF_3)_2C_2S_2$ (2·3 g) in n-pentane–benzene (2 : 1 v/v; 60 ml) was refluxed for 1·5 h. After the mixture had cooled the crude product was isolated by filtration and purified by recrystallization from dichloromethane–n-hexane–n-octane (yield 1·2 g, 33%) (Found: C, 21·1; H, 0·8; S, 24·3. $C_{25}H_9F_{24}Fe_4O_6S_{11}$ requires C, 20·9; H, 0·6; S, 24·6%), $\Lambda = 155$ cm^2 Ω^{-1} mol^{-1}.

$[Fe_2(SEt)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$.—This compound was prepared in the same way as the SMe derivative using $[\{Fe(SEt)(CO)_3\}_2]$ (0·8 g) and $(CF_3)_2C_2S_2$ (0·9 g) in n-pentane–benzene (2 : 1 v/v; 30 ml) (yield 0·3 g, 20%) (Found: C, 23·9; H, 1·4; S, 23·6. $C_{28}H_{15}F_{24}Fe_4O_6S_{11}$ requires C, 22·7; H, 1·0; S, 23·9%), $\Lambda = 154$ cm^2 Ω^{-1} mol^{-1}.

$[Fe(SePh)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$.—A mixture of $[\{Fe(SePh)(CO)_3\}_2]$ (1·5 g) and $(CF_3)_2C_2S_2$ (1·2 g) in benzene (60 ml) was refluxed for 0·5 h and then allowed to cool. The mixture was filtered through Kieselguhr and the residue trapped by the Kieselguhr extracted into dichloromethane. Addition of n-octane, followed by evaporation of the dichloromethane, caused the product to precipitate (yield 1·2 g, 54%). Further recrystallization was effected using dichloromethane–n-octane (Found: C, 27·0; H, 0·9; S, 14·7. $C_{40}H_{15}F_{24}Fe_4O_6S_8Se_3$ requires C, 27·2; H, 0·9; S, 14·6%).

Reaction of $[\{Fe(SPh)(CO)_3\}_2]$ *with* $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$.—A mixture of $[\{Fe(SPh)(CO)_3\}_2]$ (0·5 g), $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ (1·1 g), and PhSSPh (0·2 g) in n-pentane–benzene (2 : 1 v/v; 40 ml) was refluxed for *ca.* 2 h. When cool, the reaction mixture was filtered and the black solid purified by recrystallization from dichloromethane–n-hexane–n-octane (yield 0·7 g, 43%). The product was identified as $[Fe_2(SPh)_3(CO)_6]^+[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ by its i.r. spectrum, and comparison with an authentic sample.

Reaction of $[\{Fe(SMe)(CO)_3\}_2]$ *with* $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$.—This reaction was carried out in the manner described for the SPh derivative using $[\{Fe(SMe)(CO)_3\}_2]$ (0·37 g), MeSSMe (0·1 g), and $[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^0$ (1·0 g) in pentane–benzene (2 : 1 v/v; 40 ml) with a reaction time of 1·0 h (yield 0·56 g, 39%). The product was identified as $[Fe_2(SMe)_3(CO)_6]^+$-$[\{Fe\{(CF_3)_2C_2S_2\}_2\}_2]^-$ by its i.r. spectrum, and comparison with an authentic sample.

$[Fe_2(SPh)_3(CO)_6]^+[PF_6]^-$.—To a stirred solution of $[\{Fe(SPh)(CO)_3\}_2]$ (1·0 g) and PhSSPh (0·3 g) in dichloromethane (100 ml), $NOPF_6$ (1·5 g) was added. After the mixture had been stirred for 0·5 h a slow stream of nitrogen was passed through it for several minutes to purge residual nitric oxide. The mixture was filtered and light petroleum (b.p. 80—100 °C; *ca.* 20 ml) was added to the filtrate which was then evaporated to dryness under reduced pressure. The residual solid was redissolved in dichloromethane, filtered, and more light petroleum was added. Evaporation of the mixture caused brown crystals and an orange powder to precipitate. These were collected by filtration and the mixture washed with acetone (*ca.* 40 ml) which gave an orange solution but left the dark crystals undissolved. The latter were purified by recrystallization from dichloromethane–light petroleum (b.p. 80—100 °C) and were identified as $[\{Fe(SPh)(NO)_2\}_2]$ from i.r. and mass spectral measurements (yield 95 mg, 11%) (Found: C, 31·7; H, 2·2; N, 12·6; S, 14·1. $C_{12}H_{10}Fe_2N_4O_4S_2$ requires C, 32·0; H, 2·2; N, 12·5; S, 14·3%). Addition of ether to the orange acetone solution effected precipitation of the required product which was recrystallized from acetone–ether (yield 0·2 g, 13%) (Found: C, 38·9; H, 2·1; S, 12·2. $C_{24}H_{15}F_6Fe_2O_6PS_3$ requires C, 38·3; H, 2·0; S, 12·8%), $\Lambda = 180$ cm^2 Ω^{-1} mol^{-1}.

$[Fe_2(SMe)_3(CO)_6]^+[PF_6]^-$.—To a stirred solution of $[\{Fe(SMe)(CO)_3\}_2]$ (0·74 g) in dichloromethane (60 ml) was added $NOPF_6$ (1·2 g). After the mixture had been stirred for 14 h a slow stream of nitrogen was passed through the solution for a few minutes to purge residual nitric oxide. The mixture was then filtered, and light petroleum (b.p.

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80—100 °C; *ca.* 15 ml) was added to the filtrate; the resulting solution was evaporated to dryness under reduced pressure. The residual solid or tar was redissolved in dichloromethane, filtered, and light petroleum (b.p. 80—100 °C) was added to it. Evaporation caused the crude product to precipitate as a brown powder which was collected by filtration. I.r. and mass spectra indicated that the light petroleum solution (filtrate) contained a mixture of $[\{Fe(SMe)(CO)_3\}_2]$ and $[\{Fe(SMe)(NO)_2\}_2]$. The crude product was recrystallized from dichloromethane–light petroleum (b.p. 80—100 °C) to give a yellow material which was further recrystallized from acetone–light petroleum (yield 0·15 g, 13%) (Found: C, 19·7; H, 1·8; S, 17·8. $C_9H_9F_6$-$Fe_2OP_6S_3$ requires C, 19·1; H, 1·6; S, 17·0%), $\Lambda = 178$ cm^2 Ω^{-1} mol^{-1}.

Reaction of $[\{Fe(SPh)(CO)_3\}_2]$ *with* $AgPF_6$.—A mixture of $[\{Fe(SPh)(CO)_3\}_2]$ (0·5 g), $AgPF_6$ (1·0 g), and PhSSPh (0·2 g) in dichloromethane (40 ml) was stirred for 1 h. After this time the mixture was filtered and the product precipitated from the filtrate by slow addition of light petroleum (b.p. 60—80 °C). The precipitate was collected by filtration through Kieselguhr then redissolved in dichloromethane and precipitated by addition of ether. Further purification was effected by recrystallization from acetone–ether (yield 0·21 g, 28%). The product was identified as $[Fe_2(SPh)_3(CO)_6]^+$-$[PF_6]^-$ from its i.r. spectrum. The reaction was not reproducible and, although on two occasions yields of *ca.* 28% were obtained, very poor yields were usually obtained.

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