Reactions of Metal Carbonyl Derivatives. Part XIX.[1] Halogenation Studies of Di-μ-alkylthio- and Di-μ-arylthio-bis(tricarbonyliron) and Their Substituted Derivatives

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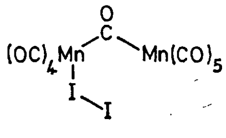
Treatment of $[\{Fe(CO)_3(SR)\}_2]$ (R = Me, Et, Pr^i, or Ph) and $[\{Fe(CO)_2(SR')\}_2(Ph_2PCH_2PPh_2)]$ (R' = Me, Et, or Ph) with iodine produces neutral products of the type $[\{Fe(CO)_3I(SR)\}_2]$ and $[\{Fe(CO)_2I(SR')\}_2(Ph_2PCH_2PPh_2)]$ respectively. In contrast reaction of $[Fe_2(CO)_5L(SMe)_2]$ (L = PPh$_3$, AsPh$_3$, or SbPh$_3$), $[\{Fe(CO)_2L'(SR)\}_2]$ [R = Me or Ph; L' = PEt$_3$, PPh$_3$, P(OMe)$_3$, or P(OPh)$_3$], $[Fe(CO)_3(SR')_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]$ (R' = Me or Bu^t), and $[Fe_2(CO)_3\{P(OPh)_3\}_3(SR'')_2]$ (R'' = Me or Ph) with this reagent under the appropriate conditions affords the ionic species $[Fe_2(CO)_5IL(SMe)_2]^+$, $[\{Fe(CO)_2L'(SR)\}_2I]^+$, $[Fe(CO)_3I(SR')_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]^+$, and $[Fe_2(CO)_3I\{P(OPh)_3\}_3(SR'')_2]^+$ respectively, each containing a bridging iodo-group. The reaction of $[Fe_2(CO)_6\{(SCH_2)_2\}]$ with iodine also gives an ionic compound, shown to have the stoicheiometry $[Fe_3(CO)_6I_5\{(SCH_2)_2\}]$. The non-formation of the neutral product $[Fe_2(CO)_6I_2\{(SCH_2)_2\}]$ in this reaction is attributed to steric effects. The reactivity of the various ionic species towards iodide ions is discussed and a mechanism for the formation of the neutral iodo-compounds *via* bridging halogeno-intermediates is described. The i.r., n.m.r., and Mössbauer spectroscopic data are discussed in terms of possible structures.

It is well established that metal–metal bonds in di- and tri-nuclear metal carbonyl derivatives are cleaved by halogens leading to the formation of the corresponding halogeno-compounds.[2] Examples of this type of reaction include those involving $[\{Cr(CO)_5\}_2]^{2-}$,[3] $[\{M(CO)_5\}_2]$ (M = Mn, Tc, or Re),[4-6] $[\{Fe(CO)_3(PMe_2)\}_2]$,[7,8] $[\{Mo(\eta\text{-}C_5H_5)(CO)_3\}_2]$,[9] $[\{M'(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (M' = Fe, Ru, or Os),[10-15] $[\{M''(\eta\text{-}C_5H_5)(CO)\}_2]$ (M'' = Ni or Pt),[16,17] and $[Os_3(CO)_{12}]$ [18] which give $[Cr(CO)_5I]^-$, $[M(CO)_5X]$, $[\{Fe(CO)_3X(PMe_2)\}_2]$, $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$, $[M'(\eta\text{-}C_5H_5)(CO)_2X]$, $[M''(\eta\text{-}C_5H_5)(CO)I]$, and $[Os_3(CO)_{12}Cl_2]$ (X = Cl, Br, or I) respectively.

The mechanistic aspects of this type of reaction have received little attention. Exceptions are the reactions of decacarbonyl-dimanganese and -dirhenium with iodine.[19,20] The former was proposed to proceed *via* one of two possible mechanisms.[19] One mechanism involved the homolytic fission of the parent $[\{Mn(CO)_5\}_2]$ molecule to $[Mn(CO)_5]$ radical pairs which react further with the iodine to afford $[Mn(CO)_5I]$. The alternative mechanism involved a bridging carbonyl derivative (1) as an intermediate. A subsequent study[20] revealed that iodination of $[\{Re(CO)_5\}_2]$ was best explained in terms of the latter mechanism and in view of this it was concluded that the reaction of $[\{Mn(CO)_5\}_2]$ with iodine also follows this mechanism.



(1)

A different reaction path was observed for the halogenation of $[\{M(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (M = Fe or Ru).[21-24] The

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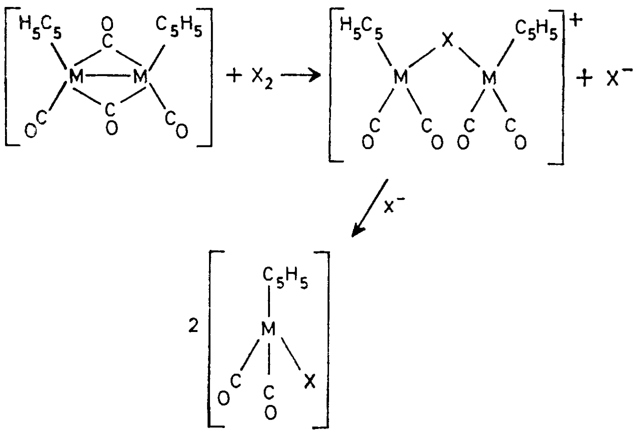
formation of $[M(\eta\text{-}C_5H_5)(CO)_2X]$ was found to proceed *via* the bridging halogeno-species $[\{M(\eta\text{-}C_5H_5)(CO)_2\}_2X]^+$, as shown in Scheme 1. The precursor to this reaction[23,24] contains, unlike $[\{Mn(CO)_5\}_2]$,[25] bridging carbonyl groups as well as a metal–metal bond, with the two iron atoms and the two carbonyls adopting a planar configuration.[26–28]



Scheme 1 M = Fe or Ru

A study of the halogenation of $[\{Fe(CO)_3(SR)\}_2]$ (R = alkyl or aryl) and its substituted derivatives, each containing a non-planar Fe_2S_2 ring,[29] was initiated with the object of establishing whether cleavage of the metal–metal bond in these compounds proceeds *via* a mechanism analogous to that for the 'planar' $[\{M(\eta\text{-}C_5H_5)(CO)_2\}_2]$ compounds.

RESULTS AND DISCUSSION

Synthetic Aspects.—A previous study[30] has revealed that reaction of $[\{Fe(CO)_2(PPh_3)S\}_2]$ and $[\{Fe(CO)_2(PPh_3)(SR)\}_2]$ (R = Et or Ph) with iodine affords the ionic derivatives $[\{Fe(CO)_2(PPh_3)S\}_2I]I_3$ and $[\{Fe(CO)_2(PPh_3)(SR)\}_2I]I_3$ respectively. In contrast the corresponding reactions involving bromine and chlorine gave the trinuclear derivatives $[Fe_3(CO)_4(PPh_3)_2(S)_2X_4]X$ or $[Fe_3(CO)_4(PPh_3)_2(SR)_2X_4]X$ (X = Br or Cl), although hydrolysis of the latter in the presence of a large counter ion such as $[PF_6]^-$ led to the formation of the binuclear species $[\{Fe(CO)_2(PPh_3)S\}_2X]^+$ or $[\{Fe(CO)_2(PPh_3)(SR)\}_2X]^+$.

In this study it has been established that treatment of $[\{Fe(CO)_2L(SR)\}_2]$ [R = Me, L = PPh_3, $P(OMe)_3$, or $P(OPh)_3$; R = Ph, L = PEt_3, PPh_3, $P(OMe)_3$, or $P(OPh)_3$] with iodine affords solely $[\{Fe(CO)_2L(SR)\}_2I]^+$, isolated as the tetraphenylborate or hexafluorophosphate salts, irrespective of the solvent or the I : Fe molar ratio employed; monitoring of the reaction by means of i.r. spectroscopy revealed no new C–O stretching peaks apart from those associated with $[\{Fe(CO)_2L(SR)\}_2I]^+$. The bridged bromo- and chloro-species, $[\{Fe(CO)_2(PPh_3)(SMe)\}_2X][PF_6]$ (X = Br or Cl), were obtained similarly except that water was added at an appropriate stage of the reaction to ensure hydrolysis of any $[Fe_3(CO)_4(PPh_3)_2(SMe)_2X_4]X$ that might have formed, to the binuclear compound.

In contrast, two products are formed in the iodination reactions of the monosubstituted derivatives $[Fe_2(CO)_5L(SMe)_2]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$) in dichloromethane, as revealed by monitoring with i.r., with one product being an intermediate in the formation of the other. Performing the iodinations in ethanol at 0 °C in the presence of $Na[BPh_4]$ led to the separation of the intermediates as tetraphenylborate salts, characterised as $[Fe_2(CO)_5IL(SMe)_2][BPh_4]$. These compounds decompose fairly rapidly in solution and could not be recrystallised or, in the case of $[Fe_2(CO)_5I(SMe)_2(SbPh_3)][BPh_4]$, isolated pure. The latter was thus identified by means of i.r. only. The final product in the iodination reactions could not be isolated because of its instability in solution, but it is proposed to be neutral $[Fe_2(CO)_5I_2L(SMe)_2]$ on the basis of i.r. evidence as discussed later in the text. The tris-substituted derivatives $[Fe_2(CO)_3\{P(OPh)_3\}_3(SR)_2]$ (R = Me or Ph), like the bis-substituted compounds, give solely ionic species as iodination products. These were isolated as their tetraphenylborate salts and were characterised as $[Fe_2(CO)_3I\{P(OPh)_3\}_3(SR)_2][BPh_4]$.

Treatment of the unsubstituted compounds $[\{Fe(CO)_3(SR)\}_2]$ (R = Me, Et, Pr^i, Bu^t, or Ph) with iodine in dichloromethane leads to the formation of neutral $[\{Fe(CO)_3I(SR)\}_2]$ best obtained, however, apart from $[\{Fe(CO)_3I(SBu^t)\}_2]$, by reaction of the parent compound with iodine in methanol in the presence of $[NH_4][Cr(NH_3)_2(SCN)_4]$ followed by precipitation of the product with water as described previously for the preparation of $[\{Fe(CO)_3I(SEt)\}_2]$ and $[\{Fe(CO)_3I(SPh)\}_2]$.[30] Monitoring of these reactions by means of i.r. revealed an intermediate in the formation of $[\{Fe(CO)_3I(SR)\}_2]$. This species was observed to convert rapidly into the final product in the case of R = Me and Et, but for R = Pr^i and Bu^t it was found to be much longer lived, being particularly so for the latter.

TABLE 1

Infrared spectroscopic data

	$\bar{\nu}(C{-}O)/cm^{-1}$	
Parent compound	Intermediate [a]	Final product [a,b]
$[\{Fe(CO)_3(SMe)\}_2]$	2 111, 2 081, 2 070	2 089, 2 048
$[\{Fe(CO)_3(SEt)\}_2]$	2 109, 2 082, 2 068	2 089, 2 046
$[\{Fe(CO)_3(SPr)\}_2]$	2 108, 2 077, 2 061	2 085, 2 044
$[\{Fe(CO)_3(SBu^t)\}_2]$	2 107, 2 077, 2 061	2 092, 2 046

[a] Measured in CH_2Cl_2. [b] Final product is $[\{Fe(CO)_3I(SR)\}_2]$.

The rate of conversion was also shown to be dependent on the iodine : $[\{Fe(CO)_3(SR)\}_2]$ molar ratio, addition of excess of iodine curtailing the conversion. None of the intermediates could be readily isolated but their C–O stretching frequencies (see Table 1) correspond with

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those previously reported for $[Fe_3(CO)_6I_4(SR)_2]I$ (R = Et or Ph).[30]

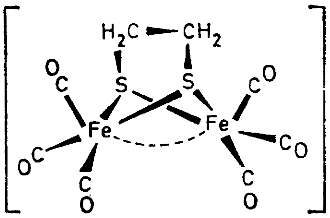
TABLE 2

Conductivity, analytical, and molecular-weight data

Compound	Λ [a] S cm² mol⁻¹	Analyses (%) Found C	H	Halogen	Others	Calc. C	H	Halogen	Others
$[Fe_3(CO)_6I_4\{(SCH_2)_2\}]I$	128	10.8	0.6	60.1		11.1	0.4	58.4	
$[\{Fe(CO)_3I(SEt)\}_2]$	3	18.3	1.5			18.3	1.5		
$[Fe_2(CO)_5I(PPh_3)(SMe)_2][BPh_4]$	96	55.5	3.9	12.3		55.8	3.9	12.0	
$[Fe_2(AsPh_3)(CO)_5I(SMe)_2][BPh_4]$	76	53.1	4.2	13.6		53.6	3.8	11.6	
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][BPh_4]$	83	61.2	4.3	10.2		61.5	4.4	9.9	
$[\{Fe(CO)_2(PPh_3)(SPh)\}_2I][BPh_4]$	70	64.7	4.0	8.9		64.6	4.3	9.0	
$[\{Fe(CO)_2[P(OMe)_3](SMe)\}_2I][BPh_4]$	90	43.0	4.0			42.7	3.4		
$[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2I][BPh_4]$	71	48.7	4.1	11.1	6.0 (S) 5.6 (P)	48.6	4.3	11.2	5.6 (S) 5.5 (P)
$[\{Fe(CO)_2[P(OPh)_3](SPh)\}_2I][BPh_4]$	69	60.6	4.1	8.3	3.9 (P)	60.5	4.0	8.4	4.1 (P)
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][PF_6]$	123	44.2	3.5			45.2	3.3		
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2Br][PF_6]$	101	47.6	3.6			47.3	3.4		
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2Cl][PF_6]$	116	49.3	3.7	3.0		49.3	3.6	3.5	
$[\{Fe(CO)_2I(SMe)\}_2(Ph_2PCH_2PPh_2)]$ [b,c]	1	39.2	3.0	27.2	7.2 (S) 6.6 (P)	38.9	3.0	26.6	6.7 (S) 6.5 (P)
$[\{Fe(CO)_2I(SEt)\}_2(Ph_2PCH_2PPh_2)]$ [d,c]	4	39.7	3.3	27.6		40.3	3.3	25.8	
$[\{Fe(CO)_2I(SPh)\}_2(Ph_2PCH_2PPh_2)]$ [e,c]	10	44.7	2.9	23.6	6.1 (S) 5.8 (P)	45.6	3.0	23.5	5.9 (S) 5.7 (P)
$[Fe_2(CO)_3I\{P(OPh)_3\}_3(SMe)_2][BPh_4]$	72	59.5	4.2			59.8	4.3		
$[Fe_2(CO)_3I\{P(OPh)_3\}_3(SPh)_2][BPh_4]$	104	62.4	4.3	7.3	3.7 (S) 5.4 (P)	62.4	4.2	7.1	3.6 (S) 5.2 (P)

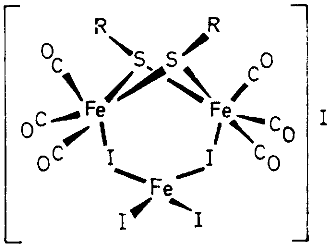
[a] 1×10^{-4} mol dm^{-3} in acetone. [b] *M* 960, calc. 956. [c] Measured osmometrically in chloroform. [d] *M* 991, calc. 984. [e] *M* 810, calc. 1 080.

The products, $[\{Fe(CO)_3I(SR)\}_2]$, are assumed to contain a planar Fe_2S_2 ring on the basis of the structure established by *X*-ray crystallography for $[\{Fe(CO)_3I(PMe_2)\}_2]$.[8] It is thus expected that iodination of the sterically constrained ethylenedithio-derivative, (2), would not proceed beyond the formation of the 'intermediate' and this was indeed observed, reaction of (2) with iodine in dichloromethane affording a product characterised as $[Fe_3(CO)_6I_5\{(SCH_2)_2\}]$ and shown to be a 1 : 1 electrolyte in acetone. The previously isolated species $[Fe_3(CO)_6I_4(SR)_2]I$ (R = Et or Ph) have been proposed to have structure (3), but (4) and (5) are also consistent with the reported[30] spectroscopic and magnetic-susceptibility data. Attempts to establish the structure unequivocally by replacing the anion in $[Fe_3(CO)_6I_5\{(SCH_2)_2\}]$ and its bromo-analogue with other counter ions were however unsuccessful. For instance, treatment of $[Fe_3(CO)_6\{(SCH_2)_2\}X_5]$ (X = Br or I) with $K[SbF_6]$ or $Ag[SbF_6]$ in dichloromethane afforded the parent compound $[Fe_2(CO)_6\{(SCH_2)_2\}]$. Significantly, the tris thio-cation $[Fe_3(CO)_6(SR)_3]^+$ has a structure analogous to (5).[31,32]



(2)

Iodination of $[\{Fe(CO)_2(SR)\}_2(Ph_2PCH_2PPh_2)]$ (R = Me, Et, or Ph), in which the two iron atoms are bridged by a ditertiary phosphine ligand as well as by the two thio-groups,[33,34] also leads to the formation of neutral products, irrespective of the solvent employed. These are shown by elemental analysis and molecular-weight measurements to be $[\{Fe(CO)_2I(SR)\}_2(Ph_2PCH_2PPh_2)]$.



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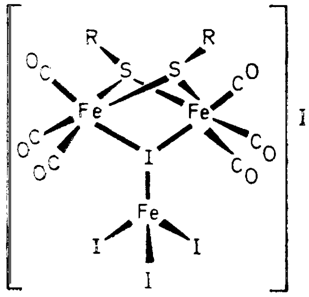

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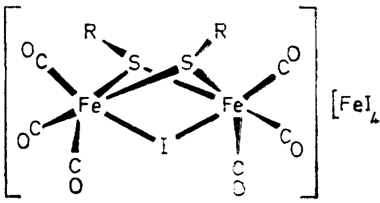

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TABLE 3

Infrared spectroscopic data (cm^{-1})

Compound	C–O Stretching frequencies *
$[Fe_3(CO)_6Br_4\{(SCH_2)_2\}]Br$	2 117s, 2 076s
$[Fe_3(CO)_6I_4\{(SCH_2)_2\}]I$	2 111s, 2 064s
$[\{Fe(CO)_3I(SMe)\}_2]$	2 089s, 2 048m
$[\{Fe(CO)_3I(SEt)\}_2]$	2 089s, 2 046m
$[\{Fe(CO)_3I(SPr^i)\}_2]$	2 085s, 2 044m
$[\{Fe(CO)_3I(SBu^t)\}_2]$	2 092s, 2 046m
$[\{Fe(CO)_3I(SPh)\}_2]$	2 093s, 2 042m
$[Fe_2(CO)_5I(PPh_3)(SMe)_2][BPh_4]$	2 108s, 2 057ms, 2 048ms, 2 007m
$[Fe_2(AsPh_3)(CO)_5I(SMe)_2][BPh_4]$	2 108s, 2 058ms, 2 048ms, 2 007m
$[Fe_2(CO)_5I(SMe)_2(SbPh_3)][BPh_4]$	2 108s, 2 057ms, 2 048ms, 2 006m
$[\{Fe(CO)_2(PEt_3)(SPh)\}_2I][BPh_4]$	2 049ms, 2 038s, 2 002s
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][BPh_4]$	2 046ms, 2 035s, 1 998s
$[\{Fe(CO)_2(PPh_3)(SPh)\}_2I][BPh_4]$	2 048ms, 2 039s, 2 002s
$[\{Fe(CO)_2[P(OMe)_3](SMe)\}_2I][BPh_4]$	2 065ms, 2 054s, 2 018s
$[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2I][BPh_4]$	2 069ms, 2 057s, 2 022s
$[\{Fe(CO)_2[P(OPh)_3](SMe)\}_2I][BPh_4]$	2 070ms, 2 061s, 2 028s
$[\{Fe(CO)_2[P(OPh)_3](SPh)\}_2I][BPh_4]$	2 072ms, 2 063s, 2 030s
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][PF_6]$	2 048ms, 2 038s, 1 998s
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2Br][PF_6]$	2 052s, 2 041s, 2 002s
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2Cl][PF_6]$	2 054s, 2 043s, 2 004s
$[\{Fe(CO)_2I(SMe)\}_2(Ph_2PCH_2PPh_2)]$	2 029s, 1 985s
$[\{Fe(CO)_2I(SEt)\}_2(Ph_2PCH_2PPh_2)]$	2 031s, 1 985s
$[\{Fe(CO)_2I(SPh)\}_2(Ph_2PCH_2PPh_2)]$	2 033s, 1 992s
$[Fe(CO)_3I(SMe)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}][BPh_4]$	2 101s, 2 054ms, 2 044ms, 1 979ms
$[Fe(CO)_3I(SBu^t)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}][BPh_4]$	2 094s, 2 047ms, 2 036ms, 1 974ms
$[Fe_2(CO)_3I\{P(OMe)_3\}_3(SMe)_2][BPh_4]$	2 051s, 1 977ms
$[Fe_2(CO)_3I\{P(OPh)_3\}_3(SMe)_2][BPh_4]$	2 058s, 2 015ms
$[Fe_2(CO)_3I\{P(OPh)_3\}_3(SPh)_2][BPh_4]$	2 062s, 2 020ms

* s = Strong, ms = medium strong, m = medium; measured in CH_2Cl_2.

Intermediates in their formation could not be detected however.

In contrast to the symmetrically bridged derivatives above, the asymmetrically bis-substituted compounds $[Fe(CO)_3(SR)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]$ gave only ionic products on reaction with iodine both in the absence as well as in the presence of a counter ion such as $[BPh_4]^-$. These compounds are highly reactive and thus could not be isolated pure but are considered to be $[Fe(CO)_3I(SR)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]A$ (A = anion) as discussed later.

The conductivity, analytical, and molecular-weight data for all the compounds studied are given in Table 2.

Spectroscopic Studies and Structural Conclusions.—The i.r. and n.m.r. spectroscopic data are recorded in Tables 3 and 4 and the Mössbauer data in Table 5. These results are now discussed in terms of possible structures for the various types of product. The specific compounds represented by the general heading of each sub-section are listed in the Tables.

$[\{Fe(CO)_2L(SR)\}_2X]A$.—The presence of a single methylthio-resonance in the ^1H n.m.r. spectra of $[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][PF_6]$ and $[\{Fe(CO)_2[P(OMe)_3](SMe)\}_2I][BPh_4]$ is interpreted in terms of a structure based on that of $[\{Fe(CO)_3(SEt)\}_2]$ [29] in which the iodine bridges the two iron atoms, the two phosphorus ligands are bonded *trans* to this bridging group, and the two methyl groups are *syn* disposed, as shown in (6). The structure is analogous to that previously proposed [33,34] for $[\{Fe(CO)_2(PPh_3)(SMe)\}_2]$ and a number of analogous compounds.

TABLE 4

Nuclear magnetic resonance spectroscopic data [a]

Compound	Proton resonances [b]	Assignments
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][BPh_4]$	8.04 (s)	CH_3
	2.60 (s,b), 2.94 [c] (mt)	C_6H_5
$[\{Fe(CO)_2[P(OMe)_3](SMe)\}_2I][BPh_4]$	7.49 (s)	$CH_3(SCH_3)$
	6.37 (d) (J_{PH} 11 Hz)	$CH_3(OCH_3)$
	2.51 (s,b), 2.90 (s,b)	C_6H_5
$[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2I][BPh_4]$	6.31 (d) (J_{PH} 10.3 Hz)	CH_3
	2.40 (s,b), 2.89 [c] (mt)	C_6H_5
$[\{Fe(CO)_2I(SEt)\}_2(Ph_2PCH_2PPh_2)]$	8.79 (t) (J_{HH} 7 Hz)	CH_3
	6.68 (q) (J_{HH} 7 Hz)	$CH_2(SC_2H_5)$
	8.44 (b)	$CH_2(PCH_2P)$
	2.45 (s,b), 2.70 (s,b)	C_6H_5

[a] τ Scale ($SiMe_4$ reference); measured in $CDCl_3$ at 38 °C. [b] s = Singlet, d = doublet, t = triplet, q = quartet, mt = multiplet, and b = broad. [c] Centre of broad multiplet.

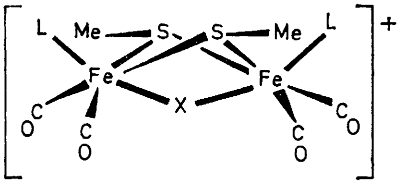
TABLE 5

Mössbauer spectroscopic data ($mm\ s^{-1}$) at 85 K

Compound	Chemical isomer shift,[a] δ	Quadrupole splitting, Δ	Width at half-height, τ	Chi squared (degrees of freedom)
$[Fe_2(AsPh_3)(CO)_5I(SMe)_2][BPh_4]$	Fe_A 0.06 ± 0.02	0.72 ± 0.02	0.34, 0.34	1 070 (484) [b]
	Fe_B 0.21 ± 0.02	1.02 ± 0.02	0.34, 0.30	
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][BPh_4]$	0.117 ± 0.005	0.77 ± 0.01	0.32, 0.35	401 (192)
$[\{Fe(CO)_2(PPh_3)(SPh)\}_2I][BPh_4]$	0.153 ± 0.005	1.00 ± 0.01	0.27, 0.29	581 (488)
$[\{Fe(CO)_2[P(OMe)_3](SMe)\}_2I][BPh_4]$	0.092 ± 0.005	0.71 ± 0.01	0.29, 0.30	298 (192)
$[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2I][BPh_4]$	0.107 ± 0.005	0.64 ± 0.01	0.24, 0.25	458 (488)
$[\{Fe(CO)_2[P(OPh)_3](SPh)\}_2I][BPh_4]$	0.111 ± 0.005	0.78 ± 0.01	0.25, 0.26	579 (488)
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][PF_6]$	0.126 ± 0.005	0.96 ± 0.01	0.26, 0.26	144 (158)
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2Br][PF_6]$	0.128 ± 0.005	1.07 ± 0.01	0.30, 0.30	235 (192)
$[\{Fe(CO)_2(PPh_3)(SMe)\}_2Cl][PF_6]$	0.127 ± 0.005	1.05 ± 0.01	0.27, 0.28	319 (192)
$[\{Fe(CO)_2I(SMe)\}_2(Ph_2PCH_2PPh_2)]$	0.138 ± 0.005	0.48 ± 0.01	0.38, 0.34	299 (192)
$[\{Fe(CO)_2I(SPh)\}_2(Ph_2PCH_2PPh_2)]$	0.144 ± 0.005	0.14 ± 0.01	0.31, 0.31	492 (490)
$[Fe_2(CO)_3I\{P(OPh)_3\}_3(SPh)_2][BPh_4]$	0.15 ± 0.01	0.70 ± 0.01	0.39, 0.48	660 (488)

[a] Relative to metallic iron at 295 K. The $^{57}Co/Rh$ source was also at 295 K throughout. [b] The high chi-squared value reflects the presence of a small impurity contribution to the spectrum, which was not taken into account in the curve fitting.

The solution i.r. spectra of the bis-substituted bridging halogeno-derivatives showed similar band patterns in the C–O stretching region, consisting of three peaks of relative intensity medium strong, strong, and strong. This number of i.r.-active carbonyl-stretching modes ($A_1 + B_1 + B_2$) is predicted for structure (6) which belongs to the point group C_{2v}. Significantly, [{Fe(CO)$_2$(PEt$_3$)(SPh)}$_2$], which in contrast to [{Fe(CO)$_2$(PPh$_3$)(SMe)}$_2$] has a structure in which the triethylphosphine ligands are bonded *trans* to the bridging sulphur groups,[34] gives rise to a bridging iodo-derivative with a structure analogous to [{Fe(CO)$_2$(PPh$_3$)(SMe)}$_2$I]$^+$. The change in the disposition of the phosphine ligands is readily explained in terms of steric factors.



(6)

Iron-57 Mössbauer spectra were obtained at 85 K for eight compounds of this type (see Table 5) and in each case only a single quadrupole doublet was present. A typical spectrum is that for [{Fe(CO)$_2$[P(OMe)$_3$](SPh)}$_2$I][BPh$_4$] (Figure 1). The results are consistent with the proposed structure, in which the iron environments are equivalent both structurally and electronically. The unpaired electron density is therefore distributed evenly between the two iron centres and in this respect these species resemble the binuclear cationic derivatives [{Fe(η-C$_5$H$_5$)(CO)(SR)}$_2$][SbF$_6$].[35] In contrast the cationic diphosphine-bridged derivatives [{Fe(η-C$_5$H$_5$)(CO)}$_2$(Ph$_2$PRPPh$_2$)][SbF$_6$] (R = C$_2$H$_4$ or NEt) contain iron centres which can be distinguished by Mössbauer spectroscopy, the non-equivalence being particularly pronounced at 4.2 K.[36]

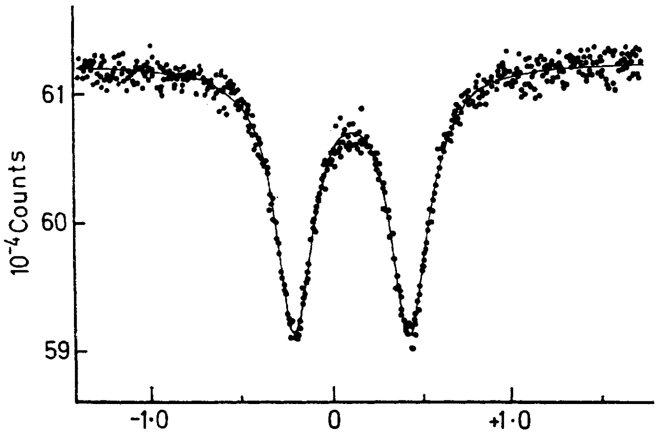


FIGURE 1 Mössbauer spectrum at 85 K of [{Fe(CO)$_2$[P(OMe)$_3$](SPh)}$_2$I][BPh$_4$]. The velocity scale is relative to metallic iron at 295 K

As well as yielding structural information, the spectra of these eight compounds also provide a convenient opportunity to monitor the effect on the Mössbauer parameters of making changes successively at various points within the molecule, the variable groups in question being the bridging unit SR, the ligand L, the halogen X, and the anion. The effect of changing the group R is demonstrated by reference to the data for the two pairs of compounds [{Fe(CO)$_2$(PPh$_3$)(SR)}$_2$I][BPh$_4$] and [{Fe(CO)$_2$[P(OMe)$_3$](SR)}$_2$I][BPh$_4$] (R = Me or Ph). For each pair there was an increase in chemical isomer shift on going from the methyl to the phenyl compound. The increase was larger for the triphenylphosphine than for the trimethyl phosphite derivatives (0.036 compared with 0.017 mm s^{-1}), but in both cases a slight decrease in the *s*-electron density at the iron nucleus is indicated. Small increases in chemical isomer shift occurred also when the ligand L was changed from a tertiary phosphite to a tertiary phosphine, as illustrated by the data for the two series of compounds [{Fe(CO)$_2$L(SPh)}$_2$I][BPh$_4$] [L = P(OMe)$_3$, P(OPh)$_3$, or PPh$_3$] and [{Fe(CO)$_2$L(SMe)}$_2$I][BPh$_4$] [L = P(OMe)$_3$ or PPh$_3$]. The trends discussed above are similar to those observed in previous studies on substituted carbonyl systems [33] and can be rationalised in terms of the differing σ- and π-bonding properties of the various ligands. There were also substantial changes in the quadrupole splitting from compound to compound, indicating that the electric field gradient (e.f.g.) at the iron nucleus is quite sensitive to small alterations in the bonding. However, these effects are less systematic than those which occur in the chemical isomer shift and are not easily rationalised. It is noteworthy, however, that as the ligand L is varied there is an approximate correlation between the chemical isomer shift and quadrupole splitting, an increase in the one parameter being accompanied by an increase in the other. This behaviour is to be compared with that found in a previous study of the neutral compounds [{Fe(CO)$_2$L(SMe)}$_2$] (L = CO, PPh$_3$, AsPh$_3$, or SbPh$_3$ *trans* to the Fe–Fe bond) and [{Fe(CO)$_2$(SMe)}$_2$(L–L)] (L–L = Ph$_2$PCH$_2$PPh$_2$ or Ph$_2$AsCH$_2$AsPh$_2$ *cis* to the Fe–Fe bond).[33] In the first series of compounds an increase in chemical isomer shift was accompanied by a decrease in quadrupole splitting, whereas in the second series an increase in chemical isomer shift was accompanied by an increase in quadrupole splitting. The two types of behaviour were therefore associated respectively with substitution *trans* and *cis* to the iron–iron bond. In the present series of ionic compounds substitution *trans* to the Fe–I bond is preferred on the basis of the i.r. and n.m.r. data, and the observation that there is nevertheless a simultaneous increase in the chemical isomer shift and quadrupole splitting may indicate that the signs of the quadrupole coupling constants are different for the neutral and ionic species.

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[35] J. A. de Beer, R. J. Haines, R. Greatrex, and J. A. van Wyk, *J.C.S. Dalton*, 1973, 2341.

[36] R. Greatrex, R. J. Haines, and A. L. du Preez, unpublished work.

In contrast to the trends noted above, the results for the series of compounds $[\{Fe(CO)_2(PPh_3)(SMe)\}_2X][PF_6]$ (X = Cl, Br, or I) indicate that changing the halogen has no nett influence on the chemical isomer shift and only a minor effect on the quadrupole splitting. This observation confirms previous observations [37] on related systems and is thought to reflect a fortuitous compensation of the effects of σ and π bonding on the electronic environment of the iron nucleus. Finally, it is worth noting, from a comparison of the data for the compounds $[\{Fe(CO)_2(PPh_3)(SMe)\}_2I]A$ ($A = BPh_4$ or PF_6), that both Mössbauer parameters are sensitive to the nature of the anion A, despite the fact that it lies beyond the immediate co-ordination sphere of the resonant atom. This fact should be borne in mind whenever data for a series of ionic species are being compared, if the counter ion is not held constant.

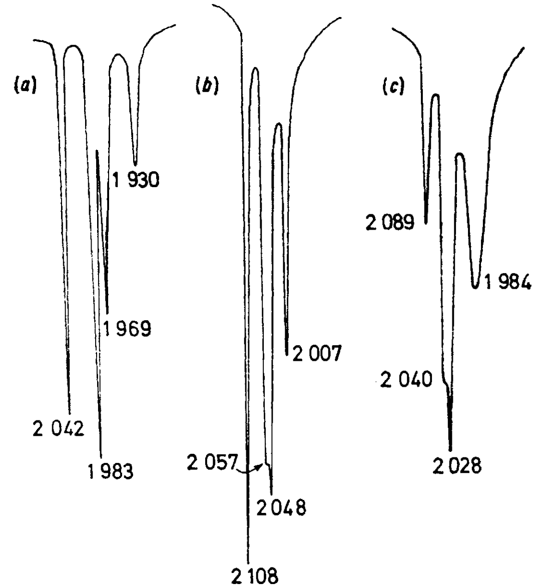


FIGURE 2 Solution i.r. spectra in the C–O stretching region of (a) $[Fe_2(CO)_5(PPh_3)(SMe)_2]$ in cyclohexane, (b) $[Fe_2(CO)_5I(PPh_3)(SMe)_2][BPh_4]$ in dichloromethane, and (c) the product of the reaction of $[Fe_2(CO)_5I(PPh_3)(SMe)_2][BPh_4]$ with I^- in dichloromethane

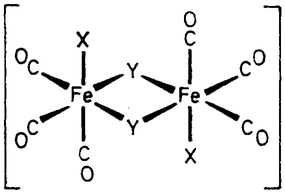
$[Fe_2(CO)_5IL(SR)_2]A$.—The band patterns observed in the C–O stretching region of the solution i.r. spectra of these monosubstituted bridging iodo-derivatives are very similar to those found in the corresponding region of the parent compounds [33] but with the component peaks shifted to higher frequency (see Figure 2). This i.r. evidence suggests a structure analogous to that proposed for the parent species, *viz.* one based on (6) but with a carbonyl group replacing one of the ligands L.

The non-equivalent iron environments are clearly distinguished in the Mössbauer spectrum of $[Fe_2(AsPh_3)(CO)_5I(SMe)_2][BPh_4]$ which consisted of two doublets with coincident lower-velocity components. By comparison with previous data [33] the doublet with the more positive chemical shift is assigned to the substituted iron atom.

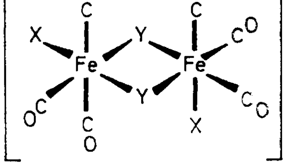
$[Fe_2(CO)_3IL_3(SR)_2]A$.—These compounds are again assumed to have a structure based on their parent compounds with the iodine bridging the two iron atoms. The Mössbauer spectrum of $[Fe_2(CO)_3I\{P(OPh)_3\}_3(SPh)_2][BPh_4]$ consisted of two very broad lines. The expected non-equivalence of the iron environments is therefore indicated but the carbonyl and triphenyl phosphite ligands do not differ sufficiently in their bonding to enable the individual resonances to become clearly resolved. The parameters listed for this compound are based on a two-line fit to the spectrum.

$[\{Fe(CO)_3I(SR)\}_2]$ *and* $[\{Fe(CO)_2I(SR)\}_2(Ph_2PCH_2PPh_2)]$.—The crystal structure of $[\{Fe(CO)_3I(PMe_2)\}_2]$ has been determined [8] and the iodine atoms shown to occupy positions *cis* with respect to the bridging phosphido-groups and *trans* to each other with respect to the Fe_2P_2 ring, (7). In contrast the n.m.r. data for $[\{Fe(CO)_3Cl(PMe_2)\}_2]$ have been interpreted [8] in terms of *cis* disposition for the chlorine groups with respect to the Fe_2P_2 ring as shown in (9). The available spectroscopic data for compounds of the type $[\{Fe(CO)_3I(SR)\}_2]$ synthesised in this study are insufficient to differentiate between any of the five possible structures (7)—(11) however.

The i.r. spectra of the bis-substituted compounds $[\{Fe(CO)_2I(SR)\}_2(Ph_2PCH_2PPh_2)]$ (R = Me, Et, or Ph) contained two C–O stretching peaks of separation *ca.* 45 cm^{-1}. This indicates a symmetric structure for these compounds with the ditertiary phosphine bridging the two iron atoms as found in the parent derivatives



(7)



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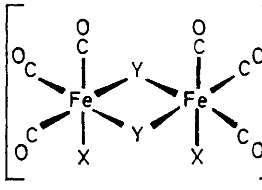

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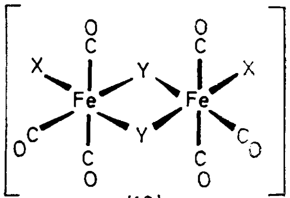

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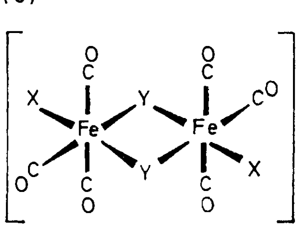

(11)

(X = Cl, Br, or I; Y = SR or PR_2)

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[37] R. H. Herber, R. B. King, and G. K. Wertheim, *Inorg. Chem.*, 1964, **3**, 101.

$[\{Fe(CO)_2(SR)\}_2(Ph_2PCH_2PPh_2)]$.[33,34] Co-ordination of the ligand is expected to occur at ' axial ' positions and thus a *trans* structure analogous to (7) is eliminated. Also *cis* disposition of the iodine groups as in (9) is highly unlikely in view of their bulkiness. A structure with the iodine atoms *trans* to the bridging groups thus seems more plausible [(8), (10), or (11)]. A similar type of structure has been proposed for one of the isomers of $[\{Fe(CO)_3Cl[P(CF_3)_2]\}_2]$.[38] A single methyl triplet was observed in the n.m.r. spectrum of $[\{Fe(CO)_2I(SEt)\}_2(Ph_2PCH_2PPh_2)]$, establishing the equivalence of the ethyl groups. A structure analogous to (11) and with the R groups *syn* disposed is thus proposed for $[\{Fe(CO)_2I(SEt)\}_2(Ph_2PCH_2PPh_2)]$ and its methyl and phenyl analogues.

The Mössbauer spectra for $[\{Fe(CO)_2I(SR)\}_2(Ph_2PCH_2PPh_2)]$ (R = Me or Ph) are consistent with the proposed structure in so far as only one type of iron atom is indicated, a possible structure in which the diphosphine is chelated to a single iron atom being ruled out. A surprising feature of the spectra, considering the grossly asymmetrical nature of the iron environment, is that in each case the quadrupole splitting was very small. This is illustrated in Figure 3 for the phenyl compound, which gave essentially a single line. An upper limit for the quadrupole splitting of 0.14 ± 0.01 mm s^{-1} can be obtained, however, by fitting the spectrum with two Lorentzian lines.

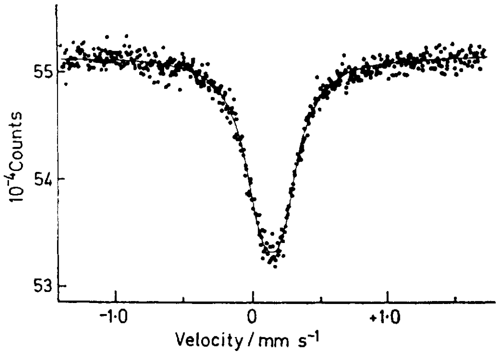


FIGURE 3 Mössbauer spectrum at 85 K of $[\{Fe(CO)_2I(SPh)\}_2(Ph_2PCH_2PPh_2)]$. The velocity scale is relative to metallic iron at 295 K

$[Fe(CO)_3I(SR)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]A$.—As stated earlier these highly reactive compounds could not be isolated pure. They are suggested as being bridging iodo-derivatives of the parent neutral compounds on the basis of their i.r. spectra, showing similar band patterns in the C–O stretching region to the spectra of the latter but with the peaks shifted to higher frequency.

Mechanistic Conclusions.—As discussed earlier in the text, the bridging halogeno-species $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2X]^+$ (X = Cl, Br, or I) have been shown to be intermediates in the reactions of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$ with halogens to give $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$.[21-23] The formation of the latter occurs by halide attack on the bridged intermediate. The bridged halogeno-species $[\{Fe(CO)_2L(SR)\}_2X]^+$ (L = ligand, R = alkyl or aryl group, X = halogen) were thus allowed to react with halide ions in order to establish whether they could be converted into neutral compounds of formula $[\{Fe(CO)_2LX(SR)\}_2]$ and thus that they are intermediates in the formation of the latter. No reaction was observed between $[\{Fe(CO)_2(PPh_3)(SR)\}_2I]^+$ (R = Me or Ph) and iodide ions but this can be readily explained in terms of steric effects; in the absence of any isomerism the expected neutral product, $[\{Fe(CO)_2I(PPh_3)(SR)\}_2]$, would contain the triphenylphosphine ligands and/or the iodine groups in adjacent positions *cis* to the bridging thio-groups. In contrast a reaction was found to occur between $[\{Fe(CO)_2[P(OMe)]_3(SPh)\}_2I]^+$ and iodide ions and significantly $[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2]$ has been shown to isomerise readily in solution. The product could not be isolated because of its instability in solution, but its i.r. spectrum in the C–O stretching region is not inconsistent with it being $[\{Fe(CO)_2I[P(OMe)_3](SPh)\}_2]$ [ν(C–O) at 2 041s and 1 995s cm^{-1}, in CH_2Cl_2]. Further it reacted readily with an equimolar amount of $Ag[SbF_6]$ in solution to give $[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2I]^+$.

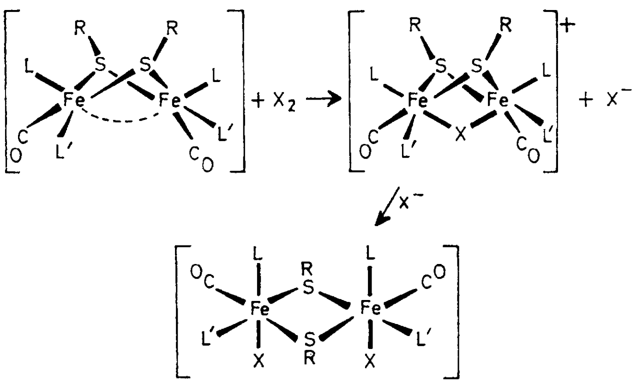
Treatment of the monosubstituted bridged iodo-compounds $[Fe_2(CO)_5IL(SMe)_2][BPh_4]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$) with iodide ions led to rapid formation of the second product produced in the reactions of $[Fe_2(CO)_5L(SMe)_2]$ with iodine. The band patterns of the C–O stretching modes observed in the i.r. spectra of these species are very similar to those found in the spectra of $[Fe_2(CO)_5IL(SMe)_2]^+$ and $[Fe_2(CO)_5L(SMe)_2]$ but with the component peaks shifted to lower frequency with respect to those for $[Fe_2(CO)_5IL(SMe)_2]^+$ [ν(C–O) for the product from the reaction of $[Fe_2(CO)_5I(PPh_3)(SMe)_2][BPh_4]$ with I^- at 2 089m, 2 040ms, 2 028s, and 1 984m cm^{-1}] as illustrated in Figure 2. These compounds could not be isolated but are proposed to be $[Fe_2(CO)_5I_2L(SMe)_2]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$) on the basis of the i.r. evidence. Not unexpectedly the tris-substituted bridged iodo-compounds $[Fe_2(CO)_3I\{P(OPh)_3\}_3(SR)_2][BPh_4]$ (R = Me or Ph), like the bis-substituted derivatives $[\{Fe(CO)_2(PPh_3)(SR)\}_2I][BPh_4]$, also failed to react with halide ions.

As described earlier, monitoring of the reaction of $[\{Fe(CO)_3(SR)\}_2]$ with iodine by means of i.r. spectroscopy revealed an apparent intermediate in the formation of $[\{Fe(CO)_3I(SR)\}_2]$. Addition of iodide ions to a solution containing this intermediate led to formation of the latter. This could be interpreted as indicating that the intermediate is of the type $[\{Fe(CO)_3(SR)\}_2I]^+$. However, the frequencies of its C–O stretching modes are very similar to those reported for $[Fe_3(CO)_6I_4(SR)_2]I$ (R = Et or Ph) of proposed structure (3).[30] The reformulation of this compound as $[\{Fe(CO)_3(SR)\}_2I][FeI_4]$, (5), would be consistent with the cation predicted and thus attempts were made to establish the exact nature of the cation in $[Fe_3(CO)_6I_5\{(SCH_2)_2\}]$ but these were unsuccessful. Significantly, reaction of the latter

[38] J. Grobe, *Z. anorg. Chem.*, 1968, **361**, 47.

with iodide ions gives the parent neutral compound $[Fe_2(CO)_6\{(SCH_2)_2\}]$. In contrast to that found for $[\{Fe(CO)_3I(SR)\}_2]$, intermediates in the formation of $[\{Fe(CO)_2I(SR)\}_2(Ph_2PCH_2PPh_2)]$ (R = Me, Et, or Ph) could not be detected but this is not surprising on stereochemical grounds.

Although it was not possible to isolate more than one type of product from any one of the halogenation reactions of $[\{Fe(CO)_3(SR)\}_2]$ or its mono-, bis-, or tris-substituted derivatives, two types were obtained overall. These correspond respectively to the intermediate and final product expected for a mechanism analogous to that for the halogenation of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2]$.[21–23] On this basis it is proposed that halogenation of $[\{Fe(CO)LL'(SR)\}_2]$ [L,L′ = CO, PR'_3, or $P(OR')_3$; R,R′ = alkyl or aryl group] occurs in general by the mechanism outlined in Scheme 2, although it is also apparent that the second stage only occurs where stereochemical restrictions allow.



SCHEME 2

EXPERIMENTAL

The compounds $[\{Fe(CO)_3(SR)\}_2]$ (R = Me, Et, Pr^i, Bu^t, or Ph) and the various mono-, bis-, and tris-substituted derivatives were synthesised by literature methods or slight modifications of them.[33,34,39–42] All the experiments were under nitrogen.

The i.r. and n.m.r. spectra were recorded on a Perkin-Elmer model 621 grating spectrophotometer and a Varian HA 100 instrument respectively. The Mössbauer spectrometer has been described previously.[35] Conductivities were determined with a Philips PW 9501 conductivity meter. The elemental analyses and molecular-weight measurements were by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany.

$[Fe_2(CO)_5IL(SMe)_2][BPh_4]$ (L = PPh_3, $AsPh_3$, *or* $SbPh_3$).—A solution of iodine (0.21 g, 0.83 mmol) in ethanol (*ca.* 20 cm³) was added dropwise to a stirred suspension of $[Fe_2(CO)_5(PPh_3)(SMe)_2]$ (0.50 g, 0.82 mmol) or $[Fe_2(AsPh_3)(CO)_5(SMe)_2]$ (0.53 g, 0.82 mmol) or $[Fe_2(CO)_5(SMe)_2(SbPh_3)]$ (0.57 g, 0.82 mmol) in ethanol (*ca.* 50 cm³) at 0 °C in the presence of $Na[BPh_4]$ (0.43 g, 1.26 mmol) and the solution was stirred for a further hour at this temperature. The crystalline compound which separated from solution was collected, washed with ethanol, benzene, and light petroleum and dried under a high vacuum. In the case of the reaction involving $[Fe_2(CO)_5(SMe)_2(SbPh_3)]$ addition of light petroleum was necessary to precipitate the product from the ethanol solution. Yields: $[Fe_2(CO)_5I(PPh_3)(SMe)_2][BPh_4]$, *ca.* 60; $[Fe_2(AsPh_3)(CO)_5I(SMe)_2][BPh_4]$, *ca.* 40; and $[Fe_2(CO)_5I(SMe)_2(SbPh_3)][BPh_4]$, *ca.* 40% identified only by means of i.r. spectroscopy.

$[\{Fe(CO)_2(PPh_3)(SMe)\}_2X][PF_6]$ (X = Cl *or* Br).—A solution of bromine (0.19 g, 1.19 mmol) in dichloromethane (*ca.* 30 cm³) or a saturated solution of Cl_2 in CCl_4 was added dropwise to a stirred solution of $[\{Fe(CO)_2(PPh_3)(SMe)\}_2]$ (0.50 g, 0.59 mmol) in dichloromethane (*ca.* 50 cm³). The solution was stirred for 30 min and the solvent removed under reduced pressure. The residue was extracted with acetone, a solution of $[NH_4][PF_6]$ (0.30 g, 2.5 mmol) in acetone was added, and the product precipitated with water. Crystallisation was from acetone–light petroleum. Yields: $[\{Fe(CO)_2(PPh_3)(SMe)\}_2Br][PF_6]$, *ca.* 80; and $[\{Fe(CO)_2(PPh_3)(SMe)\}_2Cl][PF_6]$, *ca.* 60%.

$[\{Fe(CO)_2L(SR)\}_2I][BPh_4]$ [R = Me, L = PPh_3, $P(OMe)_3$, *or* $P(OPh)_3$; R = Ph, L = PEt_3, PPh_3, $P(OMe)_3$, *or* $P(OPh)_3$] *and* $[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][PF_6]$.—A solution of iodine (0.15 g, 0.6 mmol) in methanol (*ca.* 30 cm³) was added dropwise to a stirred solution (suspension) of $[\{Fe(CO)_2(PPh_3)(SMe)\}_2]$ (0.50 g, 0.6 mmol), $[\{Fe(CO)_2[P(OMe)_3](SMe)\}_2]$ (0.34 g, 0.6 mmol), $[\{Fe(CO)_2[P(OPh)_3](SMe)\}_2]$ (0.56 g, 0.6 mmol), $[\{Fe(CO)_2(PEt_3)(SPh)\}_2]$ (0.41 g, 0.6 mmol), $[\{Fe(CO)_2(PPh_3)(SPh)\}_2]$ (0.58 g, 0.6 mmol), $[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2]$ (0.41 g, 0.6 mmol), or $[\{Fe(CO)_2[P(OPh)_3](SPh)\}_2]$ (0.64 g, 0.6 mmol) and $Na[BPh_4]$ (0.41 g, 1.2 mmol) or $[NH_4][PF_6]$ (0.15 g, 1.2 mmol) in methanol (*ca.* 50 cm³) at room temperature. Stirring was continued for 20 min to 3 h. The product which separated from solution was isolated and crystallised from dichloromethane–methanol or dichloromethane–light petroleum. Yields: $[\{Fe(CO)_2(PPh_3)(SMe)\}_2I][BPh_4]$, *ca.* 90; $[\{Fe(CO)_2[P(OMe)_3](SMe)\}_2I][BPh_4]$, *ca.* 85; $[\{Fe(CO)_2[P(OPh)_3](SMe)\}_2I][BPh_4]$, isolated as an oil and identified only by means of i.r.; $[\{Fe(CO)_2(PEt_3)(SPh)\}_2I][BPh_4]$, not isolated, identified only by means of i.r.; $[\{Fe(CO)_2(PPh_3)(SPh)\}_2I][BPh_4]$, *ca.* 60; $[\{Fe(CO)_2[P(OMe)_3](SPh)\}_2I][BPh_4]$, *ca.* 90; and $[\{Fe(CO)_2[P(OPh)_3](SPh)\}_2I][BPh_4]$, *ca.* 90%.

$[\{Fe(CO)_2I(SR)\}_2(Ph_2PCH_2PPh_2)]$ (R = Me, Et, or Ph).—A solution of iodine (0.15 g, 0.6 mmol) in methanol (*ca.* 30 cm³) was added dropwise to a stirred solution of $[\{Fe(CO)_2(SMe)\}_2(Ph_2PCH_2PPh_2)]$ (0.43 g, 0.6 mmol) in benzene (*ca.* 50 cm³) and methanol (*ca.* 20 cm³) or $[\{Fe(CO)_2(SEt)\}_2(Ph_2PCH_2PPh_2)]$ (0.45 g, 0.6 mmol) in benzene (*ca.* 50 cm³) and methanol (*ca.* 30 cm³) or $[\{Fe(CO)_2(SPh)\}_2(Ph_2PCH_2PPh_2)]$ (0.50 g, 0.6 mmol) in dichloromethane (*ca.* 20 cm³) and methanol (*ca.* 40 cm³) and the stirring continued for 30 min to 2 h. The product which separated from solution was crystallised from dichloromethane–methanol or –light petroleum. Yields: $[\{Fe(CO)_2I(SMe)\}_2(Ph_2PCH_2PPh_2)]$, *ca.* 60; $[\{Fe(CO)_2I(SEt)\}_2(Ph_2PCH_2PPh_2)]$, *ca.* 60; and $[\{Fe(CO)_2I(SPh)\}_2(Ph_2PCH_2PPh_2)]$, *ca.* 50%.

$[Fe(CO)_3I(SR)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]$ (R = Me *or* Bu^t).—A solution of iodine (0.15 g, 0.6 mmol) in dichloromethane (*ca.* 10 cm³) was added dropwise to a stirred solution of $[Fe(CO)_3(SMe)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]$ (0.43 g, 0.6 mmol) or $[Fe(CO)_3(SBu^t)_2\{Fe(CO)(Ph_2PC_2H_2PPh_2)\}]$

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(0.48 g, 0.6 mmol) and $\mathrm{Na[BPh_4]}$ (0.41 g, 1.2 mmol) in dichloromethane (*ca.* 50 cm^3) and methanol (*ca.* 5 cm^3) and the reaction monitored by i.r. spectroscopy. The products could not be isolated and were characterised only by means of i.r.

$\mathrm{[Fe_2(CO)_3IL_3(SR)_2]}$ [R = Me, L = $\mathrm{P(OMe)_3}$ *or* $\mathrm{P(OPh)_3}$; R = Ph, L = $\mathrm{P(OPh)_3}$].—A solution of iodine (0.13 g, 0.5 mmol) in benzene (*ca.* 20 cm^3) was added dropwise to a stirred solution of $\mathrm{[Fe_2(CO)_3\{P(OMe)_3\}_3(SMe)_2]}$ (0.33 g, 0.5 mmol) or $\mathrm{[Fe_2(CO)_3\{P(OPh)_3\}_3(SPh)_2]}$ (0.62 g, 0.5 mmol) and $\mathrm{Na[BPh_4]}$ (0.34 g, 1.0 mmol) in benzene (*ca.* 40 cm^3) and methanol (*ca.* 5 cm^3) and in the case of the latter reaction the solution was stirred for a further 4 h. The compound $\mathrm{[Fe_2(CO)_3I\{P(OMe)_3\}_3(SMe)_2][BPh_4]}$ which separated from solution as a red oil was washed with methanol–light petroleum and dried *in vacuo.* It was characterised only by means of i.r. The benzene solution from the second reaction was filtered and the solvent removed under reduced pressure. The red oil so obtained was dissolved in a minimum of dichloromethane and the product precipitated by addition of light petroleum. The microcrystalline solid was finally washed with methanol–light petroleum and dried *in vacuo.*

In a similar manner iodine (0.13 g, 0.5 mmol) in methanol (*ca.* 10 cm^3) was added to a solution of $\mathrm{[Fe_2(CO)_3\{P(OPh)_3\}_3(SMe)_2]}$ (0.56 g, 0.5 mmol) and $\mathrm{Na[BPh_4]}$ (0.34 g 1.0 mmol) in dichloromethane (*ca.* 50 cm^3) and methanol (*ca.* 10 cm^3) and the solution stirred for 12 h. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in acetone and the product precipitated with a methanol–water mixture. The precipitate was extracted with dichloromethane and subsequent removal of the solvent under reduced pressure afforded a crystalline solid which was not purified further. Yields: $\mathrm{[Fe_2(CO)_3I\{P(OMe)_3\}_3(SMe)_2][BPh_4]}$ not isolated, identified only by means of i.r.; $\mathrm{[Fe_2(CO)_3I\{P(OPh)_3\}_3(SMe)_2][BPh_4]}$, *ca.* 40; and $\mathrm{[Fe_2(CO)_3I\{P(OPh)_3\}_3(SPh)_2][BPh_4]}$, *ca.* 60%.

$\mathrm{[\{Fe(CO)_3I(SR)\}_2]}$ (R = Me, Et, Pr^i, *or* Ph).—These compounds were obtained by a previously published method [30] whereby iodine (2 mmol) in methanol was added to a solution of $\mathrm{[\{Fe(CO)_3(SR)\}_2]}$ (R = Me, Et, Pr^i, or Ph) (1 mmol) and $\mathrm{[NH_4][Cr(NH_3)_2(SCN)_4]}$ (2 mmol) in methanol (*ca.* 2.5 cm^3) and the solution stirred for 5 min. Water (*ca.* 25 cm^3) was then added dropwise and the precipitate isolated, washed with methanol–water (1 : 1), and dried *in vacuo.* Yields: 40—60%.

$\mathrm{[Fe_3(CO)_6X_5\{(SCH_2)_2\}]}$ (X = Br *or* I).—A solution of bromine (0.25 g, 1.6 mmol) or iodine (0.5 g, 1.9 mmol) in dichloromethane (*ca.* 15 cm^3) was added dropwise to a stirred solution of $\mathrm{[Fe_2(CO)_6\{(SCH_2)_2\}]}$ (0.5 g, 1.3 mmol) in dichloromethane (*ca.* 20 cm^3) and stirring continued for a further 20 min. The solution was concentrated to *ca.* 20 cm^3 and the crystalline product which separated from solution was isolated, washed with light petroleum, and dried *in vacuo.* Yields: 50—60%.

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