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The reactions of sulfuryl chloride with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4\text{-}n}(CNMe)_n]$ (n = 0, 1, 2 and 4) and related complexes. The crystal structure of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3][FeCl_4]$

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Abstract

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with SO_2Cl_2 at room temperature is instantaneous. It gives a mixture of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_3]$ $[FeCl_4]$. The product ratio is solvent-dependent with the former product predominating in polar solvents and the latter in non-polar solvents such as benzene. Other $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ (dienyl = MeC_5H_4 or C_9H_7) react similarly. These reactions in benzene provide simple direct routes to the salts. Similar mixtures of covalent chlorides and salts are obtained with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ which gives $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$, $[Fe(\eta\text{-}C_5H_5)(CO)CNMe)Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)][FeCl_4]$, and with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ which gives $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][FeCl_4]$. However $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{P(OPr\text{-}i)_3\}]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(\mu\text{-dppe})]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) give only ionic products $[Fe(\eta\text{-}C_5H_5)(CNMe)_3][FeCl_4]$, $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(OPr\text{-}i)_3\}][FeCl_4]$, and $[Fe(\eta\text{-}C_5H_5)(CO)_2(\eta^1\text{-dppe})][FeCl_4]$ irrespective of the solvent. The mechanisms of the reactions are discussed on the basis of a previously proposed series of reaction pathways starting from adducts in which the electrophile SO_2Cl_2 coordinates to the O or N atom of the μ-CO or μ-CNMe ligand of the dimeric substrates. The crystal and molecular structure of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3][FeCl_4]$ has been determined by an X-ray diffraction study which confirmed the presence of the tetrahedral $[FeCl_4]^-$ anion and the pseudo-octahedral cation with its $Fe(CO)_3$ moiety coordinated to the C_5 ring of a planar indenyl ligand. The structure was solved by direct methods and refined by least squares procedures to R = 0.0631 for 1406 non-zero unique reflec-

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tions. The crystal was monoclinic, space group $P2_1/a$ with a 11.929(3), b 18.612(4), c 7.717(1) Å and β 100.9(1)°, and $Z = 4$.

Introduction

As part of a continuing investigation into the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (n = 0-4) and related compounds including some methylcyclopentadienyl (η-MeC_5H_5) and indenyl (η^5-C_9H_7) derivatives with electrophiles, we decided to look at their reactions with SO_2Cl_2.

Sulfuryl chloride has been utilised in coordination and organometallic chemistry as a mild chlorinating agent [1]. However, our work has shown that under certain circumstances it can act differently to give cationic species.

A preliminary report of this work has been published [1].

Experimental

Previously published methods or variants upon them were used to prepare $[Fe_2(\eta\text{-dienyl})_2(CO)_4]$ (dienyl = C_5H_5 [2] MeC_5H_4 [2] or C_9H_7 [3]) $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (n = 1 [4], 2 [5] or 4 [6]), $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{P(OPr\text{-}i)_3\}]$ [7],$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{Ph_2PCH_2CH_2PPh_2\}]$ [8] and $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [9]. Other chemicals were purchased and used as received except for SO_2Cl_2 which was distilled under nitrogen before use.

Unless otherwise stated, all reactions were carried out at room temperature under nitrogen. Solvents were refluxed over calcium hydride and distilled before use.

IR spectra were recorded with Perkin–Elmer 337 and 283B spectrometers using solid samples dispersed in caesium bromide discs. They were calibrated with polystyrene [10].

Analyses were carried out in the Analytical Laboratory of University College, Dublin.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ *with* SO_2Cl_2

A solution of SO_2Cl_2 in benzene was added dropwise to a stirred solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) in benzene (50 ml) until all of the latter was consumed, as shown by IR spectroscopy. The reaction was immediate. The yellow powder which separated was filtered off, washed with benzene, and dried. It proved to be almost-pure $[Fe(\eta\text{-}C_5H_5)(CO)_3][FeCl_4]$ (60–65% yield), which could be purified by recrystallisation, but at the expense of much loss (final yield ca. 25%). The red filtrate was evaporated to dryness at reduced pressure, and the residue recrystallised from dichloromethane/pentane to give $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ in 30–35% yield.

If Ph_3P was added to the solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (mole ratio 1/1) before the addition of SO_2Cl_2, the precipitate was a tar. This was extracted repeatedly with cold dichloromethane to remove Ph_3PO, and the residue thus obtained was then recrystallised from acetonitrile to give $[Fe(\eta\text{-}C_5H_5)(CO)_3][FeCl_4]$ in 40% yield.

When the same reaction was carried out in dichloromethane solution in the absence of Ph_3P, the most effective work-up involved removal of the solvent from the reaction mixture at reduced pressure. Extraction of the residue with benzene

Table 1

The analyses and IR spectra (2000–2250 cm^{-1}) of the salts described in the text

Compound	M.p. (°C)[a]	Analyses (Found (calcd.) (%))				IR spectra[b]
		C	H	N	Cl	
$[Fe(\eta-C_5H_5)(CO)_3][FeCl_4]$	dec.216	23.7	1.1		34.8	2128(2), 2077(vs)
		(23.8)	(1.2)		(35.2)	
$[Fe(\eta-MeC_5H_4)(CO)_3][FeCl_4]$	dec.205	25.8	1.9		35.0	2130(s), 2077(vs)
		(25.9)	(1.7)		(34.1)	
$[Fe(\eta^5-C_9H_7)(CO)_3][FeCl_4]$	dec.217	31.1	1.6		29.7	2120(s), 2077(vs)
		(31.8)	(1.6)		(31.5)	
$[Fe(\eta-C_5H_5)(CO)_2(CNMe)]$-$[FeCl_4]$	105–107	26.1	2.0	3.3	33.4	2242(vs) [c], 2081(vs), 2090(vs)
		(26.0)	(1.9)	(3.4)	(34.1)	
$[Fe(\eta-C_5H_5)(CO)(CNMe)_2]$-$[FeCl_4]$	115–117	27.4	2.8	5.6	32.3	2212(vs) [c], 2180(vs) [c], 2021(vs)
		(28.0)	(2.6)	(6.5)	(33.1)	
$[Fe(\eta-C_5H_5)(CNMe)_3][FeCl_4]$	dec.116	30.4	3.4	8.8		2216(s) [c], 2180(vs) [c]
		(29.9)	(3.2)	(9.5)		
$[Fe(\eta-C_5H_5)(CO)_2\{P(OPr\text{-}i)_3\}]$-$[FeCl_4]$	103–105	33.1	4.5		23.9	2064(vs), 2019(vs)
		(32.9)	(4.5)		(24.4)	
$[Fe(\eta-C_5H_5)(CO)_2(Ph_2PCH_2$-$CH_2PPh_2)][FeCl_4]$	dec.255	51.6	3.9		18.5	2054(vs), 2012(vs)
		(51.2)	(3.8)		(18.4)	

[a] Determined in sealed tubes. dec. = decomposes with melting. [b] Measured in KBr discs. Peak positions are given in cm^{-1} with relative peak heights in parentheses, s = strong, vs = very strong. [c] Absorption bands due to ν(CN) vibrations. All others due to ν(CO) vibrations.

gave a red benzene-soluble fraction and a yellow insoluble solid. These were then treated as above.

The same procedure, involving reactions in the absence of Ph_3P, was used to prepare $[Fe(\eta^5\text{-dienyl})(CO)_3][FeCl_4]$ from $[Fe_2(\eta^5\text{-dienyl})_2(CO)_4]$ (dienyl = MeC_5H_4 or C_9H_7), $[Fe(\eta-C_5H_5)(CO)_{3-n}(CNMe)_n][FeCl_4]$ from $[Fe_2(\eta-C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 1$ or 2) although the benzene-soluble products were not isolated, $[Fe(\eta-C_5H_5)(CO)_2\{P(OPr\text{-}i)_3\}][FeCl_4]$ from $[Fe_2(\eta-C_5H_5)_2(CO)_3\text{-}\{P(OPr\text{-}i)_3\}]$, $[Fe(\eta-C_5H_5)(CO)_2(dppe)][FeCl_4]$ from $[Fe_2(\eta-C_5H_5)_2(CO)_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$). In the last two cases the salts mentioned were the only products and their yields were virtually quantitative.

With the black isomer of $[Fe_2(\eta-C_5H_5)(CNMe)_4]$ in benzene solution, SO_2Cl_2 gave $[Fe(\eta-C_5H_5)(CNMe)_3][FeCl_4]$ as the final product. However the reaction proceeded with the initial rapid formation of an isolable green solid which precipitated out in high yield. Consistent analyses could not be obtained, as the product decomposed rapidly even in the solid state, but our best experimental values of C, 35.1/28.2; H, 3.98/3.59; N, 10.8/10.0% compare with those calculated (C, 31.95; H, 3.25; N, 8.28) for the 1/2 adduct $[Fe_2(\eta-C_5H_5)_2(CNMe)_4 \cdot 2SO_2Cl_2]$.

The same procedure was used to investigate the reaction of SO_2Cl_2 with $[Ru_2(\eta-C_5H_5)_2(CO)_4]$. The benzene-soluble $[Ru(\eta-C_5H_5(CO)_2Cl]$ was isolated and identified, but the benzene-insoluble reaction products were not identified.

The various $[FeCl_4]^-$ salts which we have isolated are listed in Table 1, together with their melting points, analyses, and IR spectra.

X-Ray-crystal structure determination of $[Fe(\eta-C_9H_7)(CO)_3][FeCl_4]$

$C_{12}H_7Cl_4Fe_2O_3$, $M = 452.7$, monoclinic, a 11.929(3), b 18.612(4), c 7.717(1) Å,

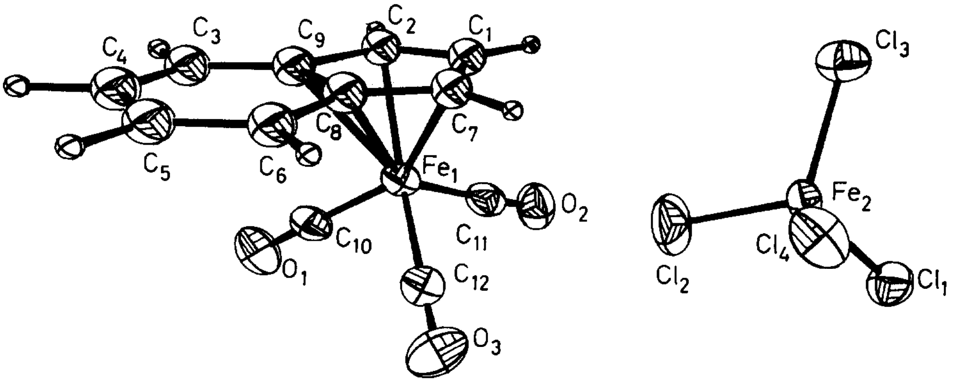


Fig. 1. The structures of the $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$ cation and the $[FeCl_4]^-$ anion.

β 100.9(1)°, V 1682.4 Å^3, $Z = 4$, $D_{\text{calcd.}}$ 1.786 Mg m^{-3}, $F(000)$ 892, $\mu(\text{Mo-}K_\alpha) =$ 22.48 cm^{-1}, space group $P2_1/a$.

All intensity data were obtained as described by Ferguson et al. [12] on a Hilger and Watts Y290 diffractometer using a crystal with dimensions 0.08 × 0.35 × 0.41 mm. Unit cell parameters were determined by a least squares fit of θ values between 12 and 20° measured on the diffractometer. The data were collected by the

Table 2

Final atomic coordinates (fractional, $\times 10^4$) with estimated standard deviations in parentheses for $[Fe(\eta^5\text{-}C_9H_7)(CO)_3][FeCl_4]$

	x/a	y/b	z/c
$[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$			
Fe(1)	2760(1)	1249(1)	3828(2)
C(10)	2121(9)	1382(5)	1538(14)
C(11)	3472(10)	2101(7)	4012(12)
C(12)	4000(10)	727(6)	3413(13)
O(1)	1687(8)	1438(4)	80(10)
O(2)	3909(8)	2643(5)	4235(11)
O(3)	4747(8)	405(5)	3263(12)
C(1)	2368(11)	1470(7)	6274(17)
C(2)	1396(11)	1497(7)	4984(16)
C(3)	306(13)	457(8)	2987(18)
C(4)	395(13)	−219(8)	2686(19)
C(5)	1272(12)	−664(9)	3512(17)
C(6)	2175(10)	−396(6)	4778(14)
C(7)	2831(11)	801(7)	6316(15)
C(8)	2105(8)	357(5)	5142(12)
C(9)	1169(9)	774(13)	4246(13)
$[FeCl_4]^-$			
Fe(2)	6877(1)	1470(1)	9812(2)
Cl(1)	8472(3)	2054(2)	9809(4)
Cl(2)	5758(3)	1651(2)	7258(5)
Cl(3)	6096(3)	1856(2)	11988(4)
Cl(4)	7274(3)	322(2)	10198(4)

θ–2θ method within the range $2 < \theta < 24°$. Intensities were corrected for Lorentz and polarisation effects but not for extinction or absorption. Standard reflections show an intensity variation of less than 2%. A total of 1406 unique reflections with $I > 5\sigma\ I$ were obtained. The observed structure factors were placed on an absolute scale by the K curve method. Neutral atom scattering factors were taken from ref. 12 (hydrogen atoms) and ref. 13 (others) whilst the anomalous dispersion correction factors for non-hydrogen atoms were taken from ref. 14.

All calculations were carried out on a Dec-2060 computer. The structure was solved by direct methods (MULTAN) [15] which located both Fe atoms in the asymmetric unit. The other non-hydrogen atoms were located in difference Fourier maps. Calculated hydrogen atom positions were included in the refinement which was carried out by full-matrix least-squares procedures (SHELX) [16] in which $\Sigma\omega = (|F_0| - |F_c|)^2$ were minimised with the weights ω for each reflection being given by $\omega = 0.4701\ (\sigma^2|F_0| + 0.0064|F_0|^2)^{-1}$. All atoms, except those of the indenyl ligand, were refined anisotropically so that the number of variable parameters was 145. The final R value was 0.0631 and R' $(= \{\Sigma\omega(|F_0| - |F_c|)^2/\Sigma\omega|F_0|^2\}^{\frac{1}{2}})$ 0.0750. The final difference map showed no electron densities > 0.64 eÅ^{-3}.

The structures of the cation and anion are shown in Fig. 1 [17]. Final atom coordinates are listed in Table 2, and selected bond lengths and angles are contained in Table 3.

Tables of anisotropic thermal parameters, hydrogen atom coordinates, and of observed and calculated structure factors may be obtained from the authors.

Table 3

Selected bond lengths and angles for $[Fe(\eta^5\text{-}C_9H_7)(CO)_3][FeCl_4]$ with estimated standard deviations in parentheses

(a) Bond lengths (Å) for $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$		(b) Bond lengths (Å) for $[FeCl_4]^-$	
Fe(1)–C(10)	1.804(11)	Fe(2)–Cl(1)	2.191(4)
Fe(1)–C(11)	1.792(13)	Fe(2)–Cl(2)	2.188(3)
Fe(1)–C(12)	1.843(13)	Fe(2)–Cl(3)	2.190(3)
Fe(1)–C(1)	2.071(13)	Fe(2)–Cl(4)	2.196(3)
Fe(1)–C(2)	2.051(13)		
Fe(1)–C(7)	2.080(12)	(c) Bond angles (°) for $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$	
Fe(1)–C(8)	2.167(10)	C(10)–Fe(1)–C(11)	93.6(4)
Fe(1)–C(9)	2.172(11)	C(10)–Fe(1)–C(12)	96.5(5)
C(1)–C(2)	1.379(18)	C(11)–Fe(1)–C(12)	95.5(5)
C(2)–C(9)	1.467(17)	Fe(1)–C(10)–O(1)	176.9(9)
C(9)–C(3)	1.405(17)	Fe(1)–C(11)–O(2)	175.6(9)
C(3)–C(4)	1.286(19)	Fe(1)–C(12)–O(3)	177.1(10)
C(4)–C(5)	1.391(19)		
C(5)–C(6)	1.401(16)	(d) Bond angles (°) for $[FeCl_4]^-$	
C(6)–C(8)	1.434(15)	Cl(1)–Fe(2)–Cl(2)	107.7(2)
C(8)–C(7)	1.399(15)	Cl(1)–Fe(2)–Cl(3)	109.5(1)
C(8)–C(9)	1.427(14)	Cl(1)–Fe(2)–Cl(4)	108.5(2)
C(7)–C(1)	1.361(18)	Cl(2)–Fe(2)–Cl(3)	111.4(2)
C(10)–O(1)	1.151(12)	Cl(2)–Fe(2)–Cl(4)	110.6(1)
C(11)–O(2)	1.135(14)	Cl(2)–Fe(2)–Cl(4)	109.1(1)
C(12)–O(3)	1.102(13)		

Results and discussion

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with SO_2Cl_2 at room temperature is virtually instantaneous. It gives two products, yellow $[Fe(\eta\text{-}C_5H_5)(CO)_3][FeCl_4]$ (I) and red $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (II). The product ratio is markedly dependent on the solvent with the salt predominating if benzene is used (ca. 65% of added Fe) but being the minor product (ca. 17% of added Fe) in more polar solvents such as dichloromethane, tetrahydrofuran or acetonitrile. The reactions take place in very high yields with virtually all of the Fe from the substrate and Cl from the reagent appearing in the products. CO was evolved.

Because the reaction in benzene solution was a potentially useful synthetic route to $[Fe(\eta\text{-}C_5H_5)(CO)_3]^+$ salts, it was studied in more detail. Using titration techniques, we found that the reaction stoichiometry was as shown in eq. 1.

$$1[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4] + 1.7\ SO_2Cl_2 \xrightarrow{\text{benzene}} 0.65[Fe(\eta\text{-}C_5H_5)(CO)_3][FeCl_4]$$

$$+ 0.7[Fe(\eta\text{-}C_5H_5)(CO)_2Cl] + 1.7\ \text{'}SO_2\text{'} + 0.65\ \text{'}C_5H_5\text{'} + 0.65\ CO \qquad (1)$$

As the salt is insoluble in benzene it separated from the reaction mixture. This slightly-impure powder could be purified by recrystallisation from acetonitrile, but much decomposition took place. However, we had carried out the reaction in the presence of Ph_3P in the hope of preparing $[Fe(\eta\text{-}C_5H_5)(CO)_2PPh_3][FeCl_4]$, this hope was not realised and the course and stoichiometry of the reaction were unchanged, but the product could be purified by recrystallisation from acetonitrile without extensive loss. The role of the Ph_3P is not known but it is converted into Ph_3PO. We tried to determine the fate of the 'SO_2' and 'C_5H_5' fragments in the reaction mixture, but despite many efforts with this and the other reactions we describe, they remain elusive. We can say that SO_2 gas is not evolved during the reaction.

The same comments apply to the reactions of $[Fe_2(\eta\text{-}MeC_5H_4)_2(CO)_4]$ and $[Fe_2(\eta^5\text{-}C_9H_7)_2(CO)_4]$ with SO_2Cl_2, which give $[Fe(\eta\text{-dienyl})(CO)_2Cl]$, $[Fe(\eta\text{-}MeC_5H_4)(CO)_3][FeCl_4]$ and the relatively inaccessible cation of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3][FeCl_4]$.

The reactions between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4\text{-}n}(CNMe)_n]$ ($n = 1$ or 2) and SO_2Cl_2 give $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4\text{-}n}\{CN(Me)H\}_n]^{n+}$ salts [18] unless the reagent is distilled prior to use. Then, the products when $n = 1$ are yellow $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)][FeCl_4]$, green $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$, and red $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$, with the two covalent complexes always being formed in ca. equal amounts. When $n = 2$, only yellow $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2][FeCl_4]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ are formed. Only the two salts were isolated, purified and characterised analytically. However the covalent products could be identified unambiguously by comparing their IR spectra in the $\nu(CO)/\nu(CN)$ region with those of authentic samples. In general the effects of solvent on the proportion of ionic to covalent products formed in these reactions are similar to but less marked than in the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with SO_2Cl_2.

Unlike all the other reactions which we investigated, that of the black crystalline isomer of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ with SO_2Cl_2 in benzene solution does not result in instantaneous dimer cleavage. Instead, an insoluble intermediate precipitates out as a green solid. Unfortunately its rapid decomposition even in the solid state to $[Fe(\eta\text{-}C_5H_5)(CNMe)_3][FeCl_4]$ prevented us from obtaining consistent elemental analysis, but its colour and IR spectrum suggest strongly that it is an adduct $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)SO_2Cl_2\}_2]$. It displays two intense absorption bands at 1590 and 2204 cm^{-1} (KBr disc) due to its $\nu(C{=}N)$ and $\nu(C{\equiv}N)$ vibrations, respectively, which compare with 1595 and 2198 cm^{-1} for the well characterised green 1/2 adduct $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe_2)_2]I_2$ [19]. It also shows relatively strong absorption bands at 1050 and 1220 cm^{-1} which are tentatively assigned to $\nu(S{-}O)$ modes and weaker ones at 278 and 303 cm^{-1} which may be due to $\nu(S{-}Cl)$. These frequencies may be compared with those of 1205 and 1434 cm^{-1} and 403, 408 and 338 cm^{-1} determined for gaseous SO_2Cl_2.

The reaction of SO_2Cl_2 with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{P(OPr\text{-}i)_3\}]$ gives a single product $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(OPr\text{-}i)_3\}][FeCl_4]$ in virtually quantitative yield in benzene, dichloromethane or acetonitrile solution.

A reaction that is of considerable importance from a mechanistic point of view is that of $[Fe_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)_2(\mu\text{-}dppe)]$ with SO_2Cl_2. The sole product formed in very high yield in polar and non-polar solvents is $[Fe(\eta\text{-}C_5H_5)(CO)_2(dppe)][FeCl_4]$ in which the potentially bidentate diphosphine is monodentate.

We also looked at the reaction of $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with SO_2Cl_2. This followed much the same route as did that of its Fe analogue. We were able to isolate $[Ru(\eta\text{-}C_5H_5)(CO)_2Cl]$ and a salt containing the $[Ru(\eta\text{-}C_5H_5)(CO)_3]^+$ cation which could be identified by its IR spectrum. Unfortunately we were not able to characterise the salt unambiguously or to identify the counter-anion.

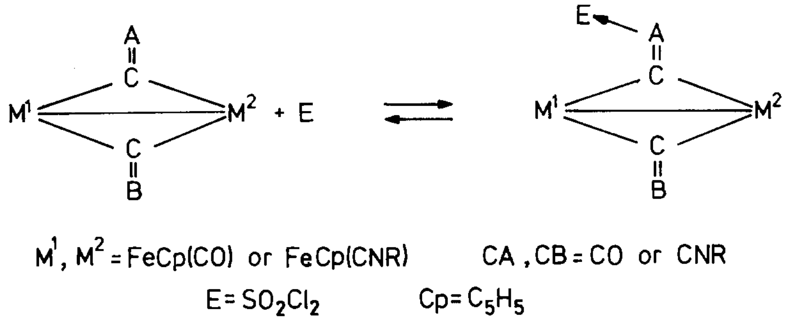
Properties and IR spectra of the salts

The $[FeCl_4]^-$ salts of derivatives of the $[Fe(\eta^5\text{-dienyl})(CO)_3]^+$ cations are yellow solids which are generally soluble in polar solvents such as tetrahydrofuran or acetonitrile, but insoluble or only sparingly soluble in non-polar solvents. Generally, increasing the number of MeNC ligands increases the solubility of the salts. When pure they are indefinitely stable in air.

The IR spectra of the various salts (Table 1) all show an intense absorption band at ca. 375cm^{-1} that we assign to the $\nu(Fe{-}Cl)$ vibration of the $[FeCl_4]^-$ ion [20]. There are also strong absorption bands lying between 2000 and 2240 cm^{-1} due to the $\nu(CO)$ and $\nu(CN)$ vibrations of the cations, which have frequencies and relative intensities consistent with 'piano-stool' structures similar to those found for the cations in $[Fe(\eta\text{-}C_5H_5)(CO)_3][PF_6]$ [21], $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)][BF_4]$ [22], $[Fe(\eta\text{-}C_5H_5)(CO)(\eta^2\text{-}Ph_2PCH_2PPh_2)][BPh_4]$ [23] and $[Fe(\eta^5\text{-}C_9H_7)(CO)_3][FeCl_4]$ (see below).

Structure of $[Fe(\eta^5\text{-}C_9H_7)(CO)_3][FeCl_4]$

An X-ray diffraction study has confirmed that the ionic product from the reaction of $[Fe_2(\eta^5\text{-}C_9H_7)_2(CO)_4]$ with SO_2Cl_2 is $[Fe(\eta^5\text{-}C_9H_7)(CO)_3]^+$ $[FeCl_4]^-$. The solid contains discrete anions and cations with no unusually short anion–cation distances. In the $[FeCl_4]^-$ anion the coordination about Fe is close to tetrahedral with Cl–Fe–Cl bond angles lying in the range 107.7–110.6(2)°. The cation has the 'piano-stool' structure with a *cis*-$Fe(CO)_3$ moiety η^5-bonded to the five-membered ring of a virtually planar indenyl ligand. There appear to be no unusual bond lengths or angles within either the anion or cation (cf. refs. 24 and 25). Figure 1 shows the structures and atom labelling in both the anion and cation, Table 2 gives the positions of the non-hydrogen atoms and Table 3 gives a selection of bond lengths and angles.



Scheme 1

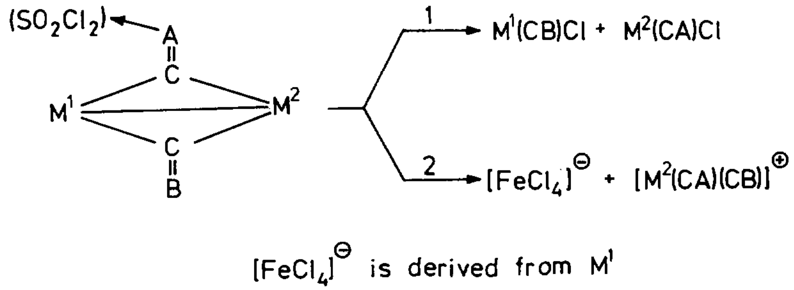
Mechanism of the reaction

The reactions of the various substrates with SO_2Cl_2 are, overall, two-electron oxidative cleavages of their Fe–Fe bonds to give mononuclear products. It is possible to account for these products on the basis of a mechanistic scheme which has been discussed in detail elsewhere. Its first stage is the formation of 1/1 adducts in which the electrophile interacts with the bridging ligand CA of the substrate (Scheme 1).

It is assumed that if the substrates contain MeNC ligands such adducts have CA = CNMe and CB = CO but if they do not contain these ligands then CA = CB = CO (cf. $[Fe_2(\eta\text{-}MeC_5H_4)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CNMe_2\}]I$ [27], $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CO\}\{\mu\text{-}CNMe)_2\}]I$ [27], $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)\{\mu\text{-}CO\}\{\mu\text{-}CN(Me)SnCl_4\}]$ [28], and the relevant arguments in ref. 26.

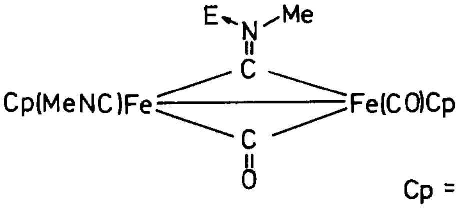
The only adduct detected in the present work is that of SO_2Cl_2 with the black isomer of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$. It is green, and appears to be $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)SO_2Cl_2\}_2]$. It decomposes very rapidly to $[Fe(\eta\text{-}C_5H_5)(CNMe)_3][FeCl_4]$.

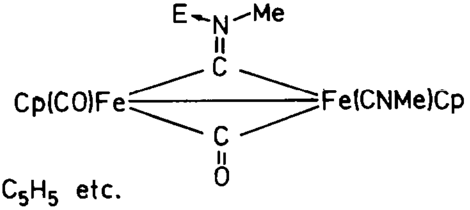
The final products could be formed from the adducts by pathways similar to those suggested for related reactions in ref. 26. Although our inability to account for the SO_2 and C_5H_5 fragments restricts detailed discussion of our results, there are a number of pertinent points which can be made. It is clear that the breakdown of the adducts gives two types of products (Scheme 2); those where there is a symmetrical distribution of the four two-electron ligands (CO, CNMe or phosphines) of the substrate between the two Fe atoms as in pathway 1, and those where the distribution is unsymmetrical, as in 2. In pathway 2 the electrophile or its fragments end up coordinated to M^1 and CA to M^2.



Scheme 2

As the C–A–E system (E = electrophile) is not linear there are two possible isomers of the adduct which differ in the orientation about the C=A bond. This is only important if M^1 and M^2 (together with their attendant ligands) differ as they do for the 1/1 adducts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ which can have the structures **P** and **Q** shown below. On the basis of the proposed mechanism [26], $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ can only be formed from **P** via pathway 1 (Scheme 2) and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]^+$ from Q via 2.





Cp = C_5H_5 etc.

P

Q

The exclusive conversion of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2\{P(OPr\text{-}i)_3\}]$ into $[Fe(\eta\text{-}C_5H_5)(CO)_2\{P(OPr\text{-}i)_3]^+ [FeCl_4]^-$ in high yield implies that in this case only one of the two possible isomers of the 1/1 adduct is formed. In it $M^1 = Fe(CO(\eta\text{-}C_5H_5)$ and $M^2 = Fe\{P(OPr\text{-}i)_3\}(\eta\text{-}C_5H_5)$ whilst CA = CB = CO, i.e. the electrophile E = SO_2Cl_2 coordinates to the μ-CO ligand such that it is adjacent to the metal atom having the least bulky substituent.

There are often close resemblances between the reactions described here and related ones involving halogens as electrophiles. Thus in the reaction of $[Fe(\eta\text{-}C_5H_5)_2(CO)_3PEt_3]$ with I_2, non-polar solvents favour the formation of $[Fe(\eta\text{-}C_5H_5)(CO)_2PEt_3]^+$ salts [29]. i.e. a reaction that proceeds via the equivalent of route 2, (Scheme 2) whilst in polar solvents the equivalent of route 1 becomes more important. It was suggested that this solvent effect could be rationalized by assuming that the initially formed adduct broke down by an intramolecular pathway in which the equivalent of $[\text{electrophile}]^{2-}$ migrates from the bridging CA ligand and oxidatively adds to M^1. As a similar solvent effect is observed for, e.g. the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_9]/SO_2Cl_2$ reaction, it is possible that it proceeds by a similar intramolecular route from the adduct with, effectively, migration of $[SO_2Cl_2]^{2-}$ and its oxidative addition to M^1. This suggestion is consistent with the failure of the reactions to incorporate either a solvent molecule such as MeCN or added Ph_3P into the products. However, although this implies that throughout the reaction sequences the reactants remain intimately associated, this could be due to either intramolecular reaction pathways as above or to strong solvent cage effects.

The formation of $[Fe(\eta\text{-}C_5H_5)(CO)_2(\eta^1\text{-dppe})]^+ [FeCl_4]^-$ from the reaction of SO_2Cl_2 with $[Fe_2(\eta\text{-}C_5H_5)(\mu\text{-}CO)_2(\mu\text{-dppe})]$ is very important. It is to be anticipated on the basis of the suggested mechanism that the two P atoms of the dppe ligand would not be coordinated to the same iron atom in the product whilst the two bridging ligands, CO, would be. The absence of solvent or halide ion incorporation, or of dimerisation to give products such as $(\eta\text{-}C_5H_5)(OC)(X)Fe(dppe)\text{-}Fe(X)(CO)(\eta\text{-}C_5H_5)$ or $[\{(\eta\text{-}C_5H_5)(OC)(X)Fe(dppe)Fe(\mu\text{-}CO)(\eta\text{-}C_5H_5)\}_2]$ (X = Cl or $MeCN^+$; dppe = $Ph_2PCH_2CH_2PPh_2$) tends to rule out intermediate species such as $(\eta\text{-}C_5H_5)(OC)\dot{F}e(dppe)\dot{F}e(CO)(\eta\text{-}C_5H_5)$, $(\eta\text{-}C_5H_5)(OC)\overset{+}{F}e(dppe)\overset{+}{F}e(CO)$-

(ηC_5H_5), or (η-C_5H_5)(OC)(X)Fe(dppe)Fe(CO(η-C_5H_5). Furthermore, if either [Fe(η-C_5H_5)$(CO)_2$(η^1-dppe)] or [Fe(η-C_5H_5)(CO)(η^1-dppe)] were formed, the marked susceptibility of radical species to CO substitution means that both would probably convert to [Fe(η-C_5H_5)(CO)(η^2-dppe)] before undergoing electron transfer to give $[Fe(\eta\text{-}C_5H_5)(CO)(\eta^2\text{-dppe})]^+$.

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