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THE REACTIONS OF $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 0$–4) COMPLEXES WITH HALOGENS AND MERCURY(II) SALTS

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Summary

Halogens, X_2, and HgY_2 ($X = Cl$, Br, I; $Y = X$, F, NO_3, BF_4) cleave the metal–metal bonds in $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ complexes ($n = 0$–4). Typically, e.g., when $n = 2$, X_2 electrophiles give $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)X]$ (**a**) and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]X$ (**b**) in relative yields which depend on X, the reaction solvent and *n*, but HgY_2 give equimolar amounts of $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Y]$ (**c**) and $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ only. $Hg(CN)_2$ reacts more slowly than other HgY_2, and $[Hg(PPh_3)_2I_2]$ does not react at all. It is suggested that the reactions which give rise to products of type (**a**), (**b**) or (**c**) are all two-electron oxidations which proceed by way of adducts containing $\mu\text{-}CA \rightarrow X_2$ or $\mu\text{-}CA \rightarrow HgX_2$ groups (CA = CO or CNMe). One of these adducts has been isolated, namely $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)HgCl_2\}_2]\cdot CHCl_3$.

Introduction

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with halogens (X_2) was originally reported to give $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ [1]. Subsequent work showed that $[Fe(\eta\text{-}C_5H_5)(CO)_3]X$ and $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(\mu\text{-}X)]X$ salts were also formed and that the product ratios depended on both solvent and X_2 [2]. The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with HgY_2 was reported to give $[Fe(\eta\text{-}C_5H_5)(CO)_2Y]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ but has not been investigated further [3]. In contrast HgY_2 and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}L)(\mu\text{-}CS)]$ form $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}L)(\mu\text{-}CS \rightarrow HgY_2)]$ (L = CO [4] and CS [5]; Y = Cl, Br, or I).

Experimental

Previously published methods were used to prepare $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 0$ [6], 1 [7], 2 [8], 3 [8], and 4 [9]), CNMe [10] and $[Hg(PPh_3)_2I_2]$ [11]. $Hg[BF_4]_2\cdot nH_2O$ was prepared from HgO and 40% aqueous HBF_4 solution,

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and isolated as a white crystalline solid by removal of the solvent at reduced pressure. Other chemicals were purchased and used as received.

Unless stated otherwise, reactions were carried out in the dark at room temperature under nitrogen in solvents which had been dried, deoxygenated, and distilled prior to use. The reactions involving HgY_2 salts were carried out in a 3/2 v/v benzene/methanol solution, and those involving halogens in dichloromethane or benzene.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ *(n = 1–4) with* X_2

Chlorine gas was passed through a well-stirred solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (0.5 g) in either benzene or dichloromethane (25 mls) until the reaction was complete. Bromine or iodine was added as a solution in the same solvent (reactant mole ratio 1/1). The reactions were virtually instantaneous. When $n = 1$ or 2 and benzene was used as a solvent, $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]X$ or $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]X$ precipitated out, and was filtered off. The $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]^+$ salts were dissolved in methanol containing NH_4PF_6 and isolated as $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]PF_6$. The $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]X$ were purified by recrystallization from dichloromethane. The other products from the reaction in benzene when $n = 1$ and those from the comparable reaction in dichloromethane were separated by chromatography on alumina and purified by recrystallization from dichloromethane/pentane mixtures. When $n = 2$ removal of the solvent and crystallization of the residue sufficed irrespective of the reaction solvent. When $n = 3$, chromatography followed by crystallization was used to separate and purify the products, but when $n = 4$ removal of the solvent and crystallization of the residue (dichloromethane/pentane) was sufficient.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ *with* HgY_2 *(Y = F, Cl, Br, I,* NO_3 *or* BF_4*) or* $Hg(PPh_3)_2I_2$

To a solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) in benzene/methanol (50 ml) was added HgY_2 (Y = Cl, Br, I or NO_3; mole ratio 1/1). The colour changed almost immediately from purple to orange. The mixture was filtered and the solvent partially removed at reduced pressure. Yellow crystals of $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ separated. They were filtered off, washed with cold ether, and dried. The filtrate, which consisted largely of $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$, was evaporated to dryness and the residue recrystallized from toluene/pentane mixtures.

When X = F, the reaction was carried out as above. The products would not separate on partial removal of the solvent at reduced pressure so all the solvent was removed. The residue was chromatographed (alumina column with benzene/hexane mixtures) to give a low yield of $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2Hg]$ as the only isolable compound.

An instantaneous reaction took place between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) and an excess of $Hg[BF_4]_2 \cdot nH_2O$ (2 g) in acetone (80 ml). CO gas was passed through the mixture for 2 days. Mercury metal separated, and $[Fe(\eta\text{-}C_5H_5)(CO)_3][BF_4]$ was isolated from the mother liquour in 90% yield.

There was no reaction between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) and $[Hg(PPh_3)_2I_2]$ (2.76 g; mole ratio 1/1) in benzene/methanol solution (50 ml). The IR spectrum of the mixture had not changed even after 15 days.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ *(n = 1–4) with* HgY_2 *(Y = Cl, Br or I)*

To a well-stirred solution of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (0.5 g) in benzene/methanol solution (50 ml) was added HgY_2 (reactant mole ratios 1/1). The colour of the mixtures changed almost immediately, generally from purple to brown.

When $n = 1$, the slow removal of the solvent from the filtered reaction mixtures gave yellow crystals of $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$, which were filtered off, washed with ether and dried. Their mother-liquour contained $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Y]$ and some $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$. The former were separated by chromatography (alumina with benzene/hexane mixtures), and purified by recrystallization from toluene/pentane mixtures.

When $n = 2$, the reaction mixtures were filtered and their volumes reduced to ca. 5 ml at reduced pressure. On cooling, crystals of $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ deposited. They were filtered off, washed with ether, and dried. The mother liquours were chromatographed (alumina with benzene/hexane) to give a variety of compounds. Further samples of $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ were isolated, and purified by recrystallization from acetone/ether mixtures. However, the only $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Y]$ complex which could be obtained was that where $Y = I$. It was purified by recrystallization from a toluene/pentane mixture.

When $n = 3$, and $Y = I$, the reaction mixture was filtered and the solvent removed at reduced pressure. The residue was dissolved in ether, and the solution cooled to −78°C to give a low yield of brown $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ from the filtrate. It was subsequently recrystallized from toluene/pentane mixtures.

When $n = 4$, HgY_2 (Y = Cl, Br or I) gave two products, $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Y]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgY]$ identified by infrared spectroscopy. However, only for $Y = I$ could they be separated (chromatography on alumina) and recrystallized from toluene/pentane mixtures in low yields. An identical reaction took place in chloroform solution with both $HgBr_2$ and HgI_2, but $HgCl_2$ gave a very unstable green precipitate which was filtered off and analysed (C, 19.2; H, 1.8; N, 5.0%). On standing in contact with the reaction mixture it redissolved and decomposed, so that only $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgCl]$ were present.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ *(n = 0–4) with* $Hg(CN)_2$

Equimolar amounts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (0.5 g) and $Hg(CN)_2$ were dissolved in a benzene/methanol solution (50 ml). When $n = 0$, no reaction detectable by IR spectroscopy had taken place after 7 days; when $n = 1$ all of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ had been consumed within 2 days and some mercury metal had precipitated out; when $n = 2$ all of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ reacted within one hour; and when $n = 4$ all of the $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ reacted within 30 min. Unfortunately we were not able to separate and purify the products from these reactions. The identities and yields of products from all of the above reactions are summarised in Tables 1 and 2. Their melting points, analyses and IR spectral data between 1900 and 2250 cm^{-1} are given in Table 3.

IR spectra were run on a Perkin–Elmer 337 spectrometer equipped with a Hitachi–Perkin–Elmer readout recorder, and calibrated with CO and DCl [12]. Analyses were carried out in the Analytical Laboratory of University College, Dublin.

Results

Tables 1 and 2 list the products from the various reactions that were carried out, together with their yields. The latter refer to the pure, isolated compounds, and are based on the proportion of iron which appears in the products; it should be remembered that when, e.g., $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]X$ salts were formed this is limited to half of the iron (see below) together with three of the four CO or CNMe ligands.

The reactions were monitored by IR spectroscopy and only the initial products are reported. In some cases limited intermolecular ligand exchange took place on chromatographic separation of these products but the redistributed compounds are not reported. Independent studies show that under the conditions used here (i.e. at room temperature in the dark), the various products appear to be stable towards intermolecular ligand exchange in the absence of alumina.

In all instances a deficiency of the reagent, HgY_2 or X_2, resulted in incomplete reaction, but different products were not formed.

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ with X_2 ($X = Cl$, Br, or I) are all virtually instantaneous at room temperature in the dark. Two types of products are formed, covalent $[Fe(\eta\text{-}C_5H_5)(L)_2X]$ derivatives ($L = CO$ or CNMe) and ionic $[Fe(\eta\text{-}C_5H_5)(L)_3]X$ salts. The former are favoured by the use of dichloromethane as a solvent, low values of n, and $X = I > Br > Cl$. The latter become more important in benzene solution for high n and for $X = Cl > Br \gg I$.

TABLE 1

PRODUCTS AND THEIR YIELDS FROM THE REACTIONS OF HgY_2 WITH $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ COMPLEXES IN METHANOL/BENZENE SOLUTION

Y	Products [a]
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$	
Cl	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgCl]$ (29), $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (15)
Br	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgBr]$ (30), $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ (16)
I	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgI]$ (32), $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (18)
NO_3	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgNO_3]$ (31), $[Fe(\eta\text{-}C_5H_5)(CO)_2NO_3]$ (17)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$	
Cl	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgCl]$ (30), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ (15)
Br	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgBr]$ (29), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$ (16)
I	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgI]$ (31), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ (19)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$	
Cl	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgCl]$ (25), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Cl]$ [b]
Br	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgBr]$ (27), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Br]$ [b]
I	$[Fe(\eta\text{-}C_5H_5)(CO)_2HgI]$ (30), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]]$ (5)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$	
I	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)HgI)]$ (20), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ (3)
$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ (cis isomer)	
Cl	$[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgCl]$ [b], $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Cl]$ [b]
Br	$[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgBr]$ [b], $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Br]$ [b]
I	$[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgI]$ (10), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ (5)

[a] Isolated yield (%) in parentheses based on proportion of original Fe in the reaction mixture. [b] Unstable (see text). Could not be isolated in a pure state.

TABLE 2

PRODUCTS AND THEIR YIELDS FROM THE REACTIONS OF X_2 WITH $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ COMPLEXES

X_2/Solvent	Products [a]
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$	
Cl_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (46), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ (49)
Cl_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ (10), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ (9), $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]Cl$ (20) [b]
Br_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ (47), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$ (48)
Br_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ (7), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$ (7), $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]Br$ (26) [b]
I_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (47), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ (48)
I_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ (37), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ (41), $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]I$ (5) [b]
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$	
Cl_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ (90)
Cl_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl$ (50), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]Cl$ (20)
Br_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$ (92)
Br_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$ (40), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]Br$ (15)
I_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ (98)
I_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ (50), $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]I$ (8)
$[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$	
I_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ (15), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ (15)
I_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ (25), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ [c] $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]I$ (5), $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]I$ (10).
$[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$	
Cl_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CNMe)_3]Cl$ [d]
Cl_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CNMe)_3]Cl$ [d]
Br_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CNMe)_3]Br$ (30)
Br_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CNMe)_3]Br$ (44)
I_2/CH_2Cl_2	$[Fe(\eta\text{-}C_5H_5)(CNMe)_3]I$ (25), $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ (trace) [c]
I_2/C_6H_6	$[Fe(\eta\text{-}C_5H_5)(CNMe)_3]I$ (42)

[a] Isolated yields (%) in parentheses based on the proportion of original Fe in the reaction mixture.
[b] Isolated as PF_6^- salt. [c] Not isolated but identified by IR spectroscopy. [d] Unstable.

The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ with X_2 in dichloromethane gives $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)X]$ only. IR spectroscopy showed that they were formed in ca. equal amounts in a virtually quantitative reaction. In benzene solution these two are again formed in ca. equal amounts together with some $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]X$ salts, which separated from the reaction mixture. There is no evidence for the formation of $[Fe(\eta\text{-}C_5H_5)(CO)_3]X$.

Similarly $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ and X_2 in dichloromethane give covalent products and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)X]$ only are formed in high yields. In benzene $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]X$ salts are also given, but $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]X$ are not. The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$ with I_2 in dichloromethane follows the same pattern and gives, virtually quantitatively, a 1/1 mixture of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)I]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$. However in benzene these plus two ionic products are obtained, $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]I$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]I$.

In contrast, the reactions of X_2 with the black crystalline *cis* isomer of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ give only the $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]X$ salts, except for $X_2 = I_2$ in dichloromethane solution when traces of $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ could be detected by IR spectroscopy. $[Fe(\eta\text{-}C_5H_5)(CNMe)_3]Cl$ was unstable and could not be isolated pure.

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with HgY_2 (Y = halogen, NO_3, or BF_4; mole ratio 1/1) in methanol/benzene solution at room temperature and in the dark were very fast. IR spectroscopic studies show that when X = Cl, Br, I or NO_3 they were virtually quantitative (> 95%) and gave a mixture of ca. equal amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2Y]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$. These were identified unambiguously by the IR absorption bands due to their $\nu(CO)$ vibrations (two in each instance, Table 3) and by their isolation and analyses. The low yields of purified products are a consequence of the practical difficulties encountered in separating them. This problem becomes particularly acute when MeNC-substituted products are obtained (see below).

When a similar reaction was carried out with an excess of $Hg[BF_4]_2 \cdot nH_2O$ in acetone it followed the same pattern as that with, e.g., $HgCl_2$. The IR spectrum of the reaction mixture in the 1700–2200 cm^{-1} region showed the usual pattern of absorption bands due to the $\nu(CO)$ vibrations of equal amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2Y]$ species (Y could be $(H_2O)^+$, $(\text{acetone})^+$ or (BF_4)). Attempts to isolate them failed, but when CO gas was passed through the mixture, mercury metal and $[Fe(\eta\text{-}C_5H_5)(CO)_3]BF_4$ were formed in yields of 100 and 90%, respectively.

The only product to be detected in the reaction mixture from HgF_2 was a $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ species. Attempts to isolate it by crystallization failed, and column chromatography on alumina gave $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2Hg]$.

There was no reaction between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and $[Hg(PPh_3)_2I_2]$ even in 14 days under our standard conditions. Surprisingly, there was no evidence for significant decomposition during this time.

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ with HgY_2 (Y = Cl, Br, or I; mole ratio 1/1) in methanol/benzene solution at room temperature and in the dark were also very fast. IR spectroscopic studies showed that when $n = 1$ they were virtually quantitative and gave ca. equal amounts of two products only, the derivatives $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Y]$, and there was no evidence for the formation of significant amounts of others. The $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ complexes could be isolated in relatively high yields as they precipitated out from the filtered reaction mixtures on partial removal of the solvent at reduced pressure. This left filtrates from which the $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Y]$ derivatives could be obtained by chromatography and crystallization. Unfortunately chromatography resulted in some ligand interchange and the formation of the rearranged products which were not detectable in the initial reaction mixture.

Similarly when $n = 2$ there are two products, $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Y]$ which are formed in equal amounts. All of the first type could be isolated in reasonable yields by fractional crystallization. Of the second type, only $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$ could be isolated by chromatography, albeit in low yields. $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Br]$ decomposed but were identified by comparison of their IR spectra in the $\nu(CN)$ region with those of authentic samples [13] and of $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$.

Reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)_3]$ with HgI_2 in methanol/benzene gives equal amounts of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)HgI]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2I]$. They were isolated only in low yields although the reaction appeared to be virtually quantitative.

All three compounds HgY_2 (Y = Cl, Br or I) cleave the black form of $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_4]$ in methanol/benzene solution to give a 1/1 mixture of $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Y]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgY]$. The products were identified in all cases by IR spectroscopy, but only for Y = I could they be separated and isolated. The same products were observed when the reactions were carried out in chloroform rather than methanol/benzene solution with $HgBr_2$ and HgI_2 as the electrophiles. However, when $HgCl_2$ was used, an unstable green solid separated, which showed two intense absorption bands in its IR spectrum at 2200 and 1599 cm^{-1} (KBr disc). These are due to $\nu(CN)$ and $\nu(C{=}N_\mu)$ vibrations, respectively. Their frequencies and the colour of the compound are similar to those of the well-characterised green 1/2 adduct $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2(\mu\text{-}CNMe_2)_2]I_2$ ($\nu(CN)$ 2198 cm^{-1} and $\nu(C{=}N_\mu)$ 1595 cm^{-1}; CsBr disc) [14]. On this basis, and the analytical data, we formulate it as the 1/2 adduct $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)HgCl_2\}_2]\cdot CHCl_3$. (Analyses: found: C, 19.2; H, 1.8; N, 5.0. $C_{19}H_{23}Cl_7Fe_2Hg_2N_4$ calcd.: C, 19.2; H, 2.0; N, 4.9%.) Its breakdown to $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgCl]$ when left in contact with the reaction mixture is consistent with this formulation.

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ with $Hg(CN)_2$ (mole ratio 1/1) in methanol/benzene solution at room temperature and in the dark followed the same pathway as those of e.g. $HgCl_2$, but have rates which depend markedly on n. Thus when $n = 0$ there was no reaction even after ca. 7 days, and very little decomposition either. When $n = 1$, IR spectroscopic studies showed that all of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ was consumed within two days, and that initially ca. equimolar amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Y]$ complexes were formed, presumably with Y = CN. However, as the reaction proceeded mercury metal was deposited and $[Fe(\eta\text{-}C_5H_5)(CO)_2CN]$ was also formed. When $n = 2$ the reaction was even faster and complete within 1 h. It gave ca. equimolar amounts of $[Fe(\eta\text{-}C_5H_5)(CO)_2HgY]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Y]$ species. When $n = 4$ the reaction was complete within $\frac{1}{2}$ h to give ca. equimolar amounts of $[Fe(\eta\text{-}C_5H_5)(CNMe)_2Y]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2HgY]$ species. These cyano complexes are rather unstable and we were unable to isolate pure samples of any of them and they were identified solely by IR spectroscopy.

Discussion

The results show that the stoichiometries of the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(L)_4]$ (L = CO or CNMe) with the electrophiles HgY_2 (eq. 1) and X_2 (eq. 2 and 3) are as shown below.

$$[Fe_2(\eta\text{-}C_5H_5)_2(L)_4] + HgY_2 \rightarrow [Fe(\eta\text{-}C_5H_5)(L)_2HgY] + [Fe(\eta\text{-}C_5H_5)(L)_2Y] \quad (1)$$

$$[Fe_2(\eta\text{-}C_5H_5)_2(L)_4] + X_2 \rightarrow [Fe(\eta\text{-}C_5H_5)(L)_2X] + [Fe(\eta\text{-}C_5H_5)(L)_2X] \quad (2)$$

$$[Fe_2(\eta\text{-}C_5H_5)_2(L)_4] + X_2 \rightarrow [Fe(\eta\text{-}C_5H_5)(L)_3]X + \text{‘}Fe(\eta\text{-}C_5H_5)LX\text{’} \quad (3)$$

(*Continued on p. 62*)

TABLE 3

MELTING POINTS, ANALYSES AND IR SPECTRA OF THE COMPOUNDS OBTAINED FROM THE REACTIONS OF MERCURY(II) HALIDES AND HALOGENS WITH $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ COMPLEXES ($n = 0$–4)

Compound	M.p. [a] (°C)	Analyses (Found (calcd.)(%))				IR spectra [b]
		C	H	N	X	
$[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$	44–51	39.2 (39.6)	2.5 (2.4)		15.6 (15.8)	2016 (9.1), 2060 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$	81–82	32.8 (32.7)	2.3 (2.0)		31.3 (31.1)	2009 (9.3), 2052 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)_2I]$	101–103	27.3 (27.6)	2.0 (1.6)		42.1 (41.8)	2001 (9.0), 2043 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)_2NO_3]$	92–94	34.9 (35.2)	2.0 (2.1)	5.8 (5.8)		2026 (8.8), 2067 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)_2HgCl]$	102–104	20.1 (20.3)	1.4 (1.2)		8.6 (8.6)	1969 (8.7), 2014 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)_2HgBr]$	120–122	18.4 (18.4)	1.4 (1.1)		16.0 (17.0)	1969 (9.1), 2014 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)_2HgI]$	115–117	16.2 (16.6)	1.1 (0.9)		25.7 (25.2)	1963 (7.7), 2009 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)_2HgNO_3]$	70–71	18.8 (19.1)	0.9 (1.1)	3.1 (3.1)		1968 (9.7), 2025 (10)
$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$	71–73	42.2 (42.6)	3.9 (3.6)	6.0 (6.2)	15.9 (15.7)	1993 (10), 2189 (8.5)
$[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Br]$	102–103	36.0 (35.5)	2.6 (2.9)	5.1 (5.1)	29.8 (29.6)	1992 (10), 2187 (9.4)

[Fe(η-C_5H_5)(CO)(CNMe)I]	127–129	29.9 (30.2)	2.8 (2.5)	4.5 (4.4)	40.0 (40.0)	1985 (10), 2180 (8.5)
[Fe(η-C_5H_5)(CO)(CNMe)HgI]	141–143	18.8 (18.6)	1.9 (1.6)	2.7 (2.7)	24.4 (24.5)	1952 (10), 2153 (8.8)
[Fe(η-C_5H_5)(CNMe)$_2$I]	106–108	33.3 (32.7)	3.3 (3.3)	8.4 (8.4)		2151 (8.8), 2177 (10)
[Fe(η-C_5H_5)(CO)$_3$]BF_4	dec. 226	32.5 (32.9)	1.9 (1.7)		26.9 (26.1)	2074 (10), 2124 (7.8)
[Fe(η-C_5H_5)(CO)$_2$(CNMe)]PF_6	140–141	29.4 (29.8)	2.1 (2.2)	3.4 (3.9)	30.9 (31.4)	2011 (9.5), 2043 (10), 2207 (7.1)
[Fe(η-C_5H_5)(CO)(CNMe)$_2$]Cl	108–109	44.7 (45.0)	4.6 (4.1)	9.9 (10.5)	12.8 (13.3)	2023 (10), 2203 (7.9), 2228 (7.8)
[Fe(η-C_5H_5)(CO)(CNMe)$_2$]Br	102–103	37.8 (38.8)	3.8 (3.5)	9.0 (9.0)	23.7 (25.7)	2022 (10), 2203 (9.1), 2228 (8.3)
[Fe(η-C_5H_5)(CO)(CNMe)$_2$]I	212–214	32.5 (33.5)	3.3 (3.0)	7.8 (7.8)		2023 (10), 2204 (8.0), 2229 (7.4)
[Fe(η-C_5H_5)(CNMe)$_3$]Br [c]						2178 (10), 2213 (8.8)
[Fe(η-C_5H_5)(CNMe)$_3$]I	226–227	34.6 (35.5)	3.8 (3.7)	10.7 (11.3)		2177 (10), 2213 (9.2)
[Fe(η-C_5H_5)(CNMe)$_2$Cl] [c]						2155 2180
[Fe(η-C_5H_5)(CNMe)$_2$Br] [c]						2151 2178
[Fe(η-C_5H_5)(CNMe)$_2$HgCl] [c]						2145 2177
[Fe(η-C_5H_5)(CNMe)$_2$HgBr] [c]						2143 2171
[Fe(η-C_5H_5)(CNMe)$_2$HgI] [c]						2134 2166

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[a] Determined in sealed tubes. dec. = decomposes without melting. [b] Peak positions (cm^{-1}) with relative peak heights in parentheses. $CHCl_3$ solution. [c] Compounds not isolated as all are unstable. IR spectra of reaction mixture with absorption bands having ca. equal intensities.

The '$Fe(\eta\text{-}C_5H_5)LX$' moiety in eq. 3 is included only to balance the equation. Its fate has never been determined. However in a related reaction (eq. 4) [15], the '$Co(CO)_2I$' fragment has been trapped as $[Co(PPh_3)_2(CO)_2I]$ by the addition of Ph_3P to the reaction mixture.

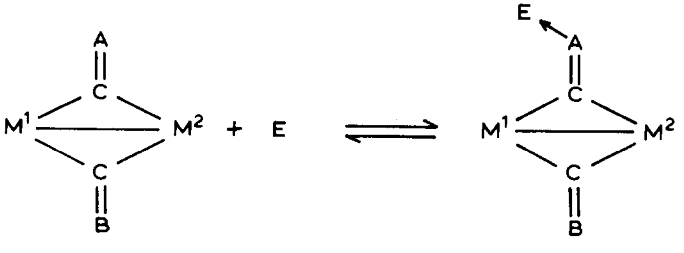
$$[(\eta\text{-}C_5H_5)(OC)Fe(\mu\text{-}CO)\{\mu\text{-}C(SMe)_2\}Co(CO)_2] + I_2 \rightarrow [Fe(\eta\text{-}C_5H_5)(CO)_2\{C(SMe)_2\}]I + \text{'}Co(CO)_2I\text{'} \qquad (4)$$

One of the most striking features of the reactions of HgY_2 ($Y = Cl$, Br, I, or in some instances, NO_3, BF_4 or CN) with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 0$–4) is their regiospecificity. In each case they are virtually quantitative and give ca. equal amounts of two products as outlined in the Results section. There is no evidence that other products are formed in the initial reaction, and in particular the following were not observed: $[Fe(\eta\text{-}C_5H_5)(CO)_2Y]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)\text{-}HgY]$ when $n = 1$ or 2, or $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Y]$ or $[Fe(\eta\text{-}C_5H_5)(CNMe)_2\text{-}HgY]$ when $n = 2$ or 3. If these compounds had been formed in significant amounts, their absorption bands would have been clearly visible in the IR spectra of the reaction mixtures.

The reactions of the substrates with X_2 are also regiospecific, although the presence of two competing reaction pathways may obscure this. The symmetrical cleavage pathway (eq. 2) always gives two products only as outlined in the Results section; when $n = 2$ $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$ and $[Fe(\eta\text{-}C_5H_5)(CNMe)_2X]$ are not formed. A single product arises from unsymmetrical cleavage (eq. 3) when $n = 1$, 2, or 4 and there is no evidence for the formation of $[Fe(\eta\text{-}C_5H_5)(CO)_3]X$ when $n = 1$ or $[Fe(\eta\text{-}C_5H_5)(CO)_2(CNMe)]X$ when $n = 2$. However when $n = 3$ both possible salts are formed but this is easily rationalized (see below).

There is no evidence for one-electron processes in these reactions, and a deficiency of the electrophile has no noticeable effect on the reaction products. Consequently it is assumed that only two-electron pathways are important.

It is possible to rationalize these observations in a consistent way if the reactions are considered within the mechanistic framework proposed elsewhere [16]. It was suggested that the first step of the reactions of polynuclear metal carbonyls derivatives with an electrophile, E, was the formation of adducts containing μ-(CA → E) bonds. In the reactions described here this may be represented by the following (eq. 5) where $M^1(\mu\text{-}CA)(\mu\text{-}CB)M^2 = [Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$.



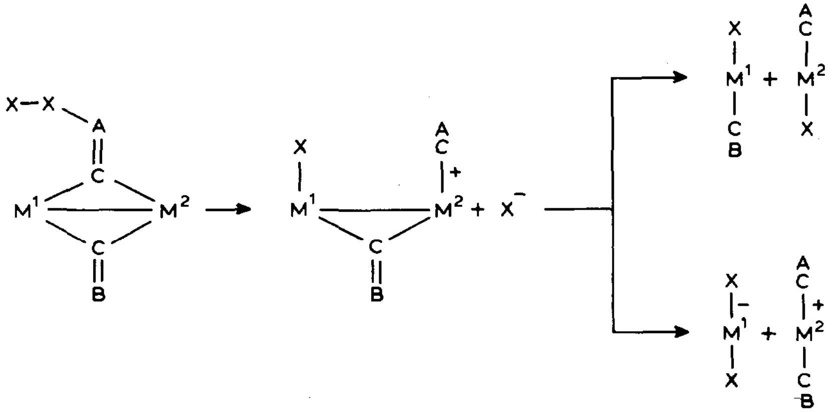
(5)

$(CA \rightarrow E = CA \rightarrow HgY_2$ or $CA \rightarrow X\text{-}X)$

When $n = 0$, μ-CA can only be μ-CO, but when $n = 1$–4, it is more likely to be μ-CNMe with its intrinsically more basic N atom (cf. ref. 16).

Only one adduct, $[Fe_2(\eta\text{-}C_5H_5)_2(CNMe)_2\{\mu\text{-}CN(Me)HgCl_2\}_2]\cdot CHCl_3$, was observed in the present work. It was probably isolated because of its low solubility in the reaction solvent employed. Otherwise adducts were not observed, probably because their subsequent reactions are too fast. However their closely related thiocarbonyl counterparts give isolable $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CS \rightarrow HgY_2)]$ [4] and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CS)(\mu\text{-}CS \rightarrow HgY_2)]$ [5] derivatives (Y = Cl, Br, or I) and related adducts in which two CO ligands have been replaced by CNMe [17]. μ_3-CNMe bonding through N to mercury(II) halides or iodine is known in the stable adducts $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)HgY_2\}]$ and $[Co_3(\eta\text{-}C_5H_5)_3(\mu_3\text{-}S)\{\mu_3\text{-}CN(Me)I\}]I_3$ [18]. There is also circumstantial evidence for the formation of adducts in these reactions. The failure of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ to react with either $[I(py)_2]NO_3$ (py = pyridine) [19] or $[Hg(PPh_3)_2I_2]$ may be attributed to the absence of a vacant coordination site on the iodine or mercury and the inability of the μ-CO ligand of the substrate to displace the strongly bound pyridine or Ph_3P from them. The reactivities of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ towards the relatively weak Lewis acid $Hg(CN)_2$ are also consistent with the formation of adducts as reaction intermediates. Other studies have shown that the basicities and nucleophilicities of these substrates towards acids and alkyl halides are much greater when CA = CNMe rather than CO [20]. They increase as the number of MeNC ligands increase, i.e. along the series $n = 0 \ll 1 < 2$, which is the observed pattern of reactivity towards $Hg(CN)_2$.

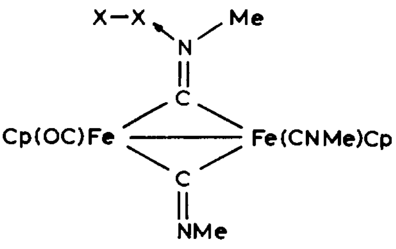
Possible ways in which the adducts of the halogens X_2 with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ may break down to the final products have been discussed in detail in ref. 16. Particular attention was paid to the parallel reactions 2 and 3 and the effect of solvent and X_2 on their relative importances. A similar discussion is applicable to the corresponding reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 1$–4), and similar reaction pathways are utilized as shown in eq. 6 and 7. It should be remembered that in all of these adducts μ-CA = μ-CNMe.



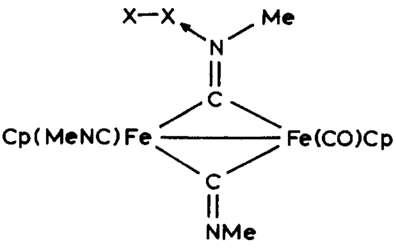
(6)

(7)

Reaction 6 corresponds to that in eq. 2 and reaction 7 to that in eq. 3. The two ionic products obtained when $n = 3$ may arise via eq. 6 from the two different isomers of the same adduct, **A** and **B**.

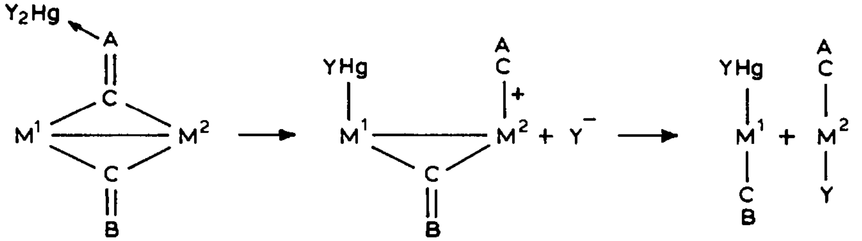


(A)



(B)

A similar reaction pathway for the breakdown of the adducts of HgY_2 (eq. 8) accounts for the product of the reaction given in eq. 1.



(8)

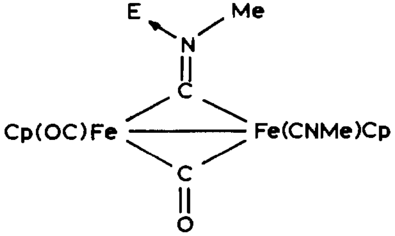
It should be noted that this mechanism predicts that the μ-ligand to which the electrophile E (X_2 or HgY_2) was coordinated in the adduct (MeNC when $n = 1$–4) and the part of E which migrates from CA to M^1 in step (a) of eq. 6, 7 and 8 (the equivalent of HgY^- or X^-) should end up on different metal atoms in the products. This is unambiguously observed when $n = 1$ or 2 for the HgY_2 reactions (eq. 1 and pathway 8) and for the reactions involving X_2 which give ionic products (eq. 3 and pathway 7).

The covalent products from the reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ with HgY_2 and X_2 differ as shown in eq. 9 and 10:

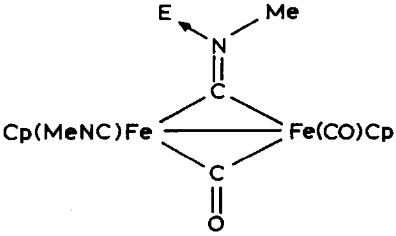
$$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2] + HgY_2 \rightarrow [Fe(\eta\text{-}C_5H_5)(CO)_2HgY] + [Fe(\eta\text{-}C_5H_5)(CNMe)_2Y] \quad (9)$$

$$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2] + X_2 \rightarrow 2[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)X] \quad (10)$$

The second type of reaction is the more common for this substrate, e.g. with $SnCl_4$ it gives $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)SnCl_3]$ [21]. It is possible to rationalize this difference by saying that reaction 9 proceeds via adduct **C** below and 10 via its isomer **D**, but it is not clear why this should be so.



(C)



(D)

($E = HgY_2$ or X_2)

It may be relevant that the formation of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)_2]X$ from $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ by reaction with X_2 proceeds via an adduct of type **C** rather than **D**. This raises the possibility that certain electrophiles give more than one adduct which may break down to different products, i.e. one preferentially breaks down by the route shown in eq. 6 and another by that shown in eq. 7.

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ complexes ($n = 1$–4) with halogens, X_2, parallel those of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ [2]. Changing X_2 and the reaction solvent have similar effects on the product ratios. However there is one important difference, namely that the the MeNC-substituted analogues of the $[\mu\text{-}X\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^+$ salts are not formed.

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