

**THE REACTIONS OF Ag^I ELECTROPHILES WITH
 [Fe₂(η-C₅H₅)₂(CO)₂(L){CN(Me)H}]⁺ AND [Fe₂(η-C₅H₅)₂(CO)₂{CN(Me)H}₂]²⁺
 SALTS (L = CO or CNMe)**

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Summary

The protonated species [Fe₂(η-C₅H₅)₂(CO)₂(μ-CO){μ-CN(Me)H}]X, [Fe₂(η-C₅H₅)₂(CO)(CNMe)(μ-CO){μ-CN(Me)H}][X], and [Fe₂(η-C₅H₅)₂(CO)₂{μ-CN(Me)H}₂][X]₂ react with one equivalent of AgY. The Ag⁺ and one H⁺ act together as a two-electron oxidant. Silver metal is precipitated quantitatively and the substrates cleaved to give mono-nuclear products of the type (a) [Fe(η-C₅H₅)(CO)(L)X] and [Fe(η-C₅H₅)(CO)(L)Y] or (b) Fe(η-C₅H₅)(CO)(L)(CNMe)[X] (L = CO, CNMe). If X⁻ and Y⁻ are both coordinating anions such as NO₃⁻, I⁻, or Br⁻ or the solvent is MeCN products of type (a) are usually obtained with X = Y = MeCN⁺ if acetonitrile is used as the solvent. However, if either X⁻ or Y⁻ is a non-coordinating anion such as BF₄⁻ or PF₆⁻ and methanol is the solvent, the products are usually those of type (b). When X⁻ = [*p*-MeC₆H₄SO₃]⁻, both types of products are obtained in significant amounts. If two equivalents of Ph₃P are added to the methanol solution of [Fe₂(η-C₅H₅)₂(CO)₂{μ-CN(Me)H}₂][BF₆]₂, no reaction takes place until the third equivalent of AgNO₃ has been added. The products have been isolated and characterised by analysis and infrared spectroscopy. The previously unreported [Fe₂(η-C₅H₅)₂(CO)(CNMe)(μ-CO){μ-CN(Me)H}] X salts are described for X⁻ = BF₄⁻, PF₆⁻, Br⁻·2H₂O, I⁻·H₂O, NO₃⁻·0.5H₂O, and *p*-MeC₆H₄SO₃⁻.

Elsewhere we have shown that [Fe₂(η-C₅H₅)₂(CO)₂(CNMe)₂] (II), reacts with one equivalent of AgNO₃ to give a 1:1 adduct formulated as [Fe₂(η-C₅H₅)₂(CO)(CNMe)(μ-CO){μ-CN(Me)AgNO₃}] [1,2]. It is quite stable in methanol or chloroform solutions, but it reacts very rapidly with a second equivalent of AgNO₃ to give virtually quantitative yields of silver metal and [Fe(η-C₅H₅)(CO)(CNMe)(NO₃)]. The overall reaction is a two-electron oxidative cleavage of II.

Herein are described reactions which are related to the above. However, instead of using the same electrophile both to form the 1:1 adduct and to oxidise it, we have used one electrophile, H^+ , to form the adduct, and the second, a salt of Ag^I , to attack it.

Experimental

Published procedures or modifications thereof were used to prepare $[Fe_2(\eta-C_5H_5)_2(CO)_3\{CN(Me)H\}][X]$, and $[Fe_2(\eta-C_5H_5)_2(CO)_2\{CN(Me)H\}]_2[X]_2$ salts ($X^- = BF_4^-$ or PF_6^-) [3], $[Fe_2(\eta-C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ ($n = 1$ [4] or 2 [5]), $[Ag(PPh_3)_3Cl]$ [6], $[AgPF_6 \cdot 2dioxane]$ [7], and $[AgBF_4 \cdot 0.5dioxane]$ [7]. Other chemicals were purchased.

Unless it is stated otherwise the reactions were carried out in the dark at room temperature under nitrogen and in purified solvents. These were dried over calcium hydride (tetrahydrofuran or dichloromethane), magnesium (methanol) or calcium sulphate (acetonitrile) under nitrogen, and distilled prior to use.

Infrared spectra were run on PE 337 and 283 B spectrometers and calibrated with polystyrene.

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

TABLE I
THE PRODUCTS AND THEIR YIELDS FROM THE REACTIONS DESCRIBED IN THE TEXT ^a

Electrophile	X	Products (Yield (%)) ^a
<i>[Fe₂Cp₂(CO)₃{CN(Me)H}]X + electrophile</i>		
AgNO ₃	BF ₄	[FeCp(CO) ₃ NO ₃] (8); [FeCp(CO) ₃ (L)]BF ₄ (28)
AgNO ₃ ^b	BF ₄	[FeCp(CO) ₃ NO ₃] (9); [FeCp(CO)(L)NCMe]BF ₄ (50)
<i>[Fe₂Cp₂(CO)₂(L){CN(Me)H}]X + electrophile</i>		
AgNO ₃	I · H ₂ O	[FeCp(CO)(L)I] (40); [FeCp(CO)(L)NO ₃] (23)
AgNO ₃	Br · 2H ₂ O	[FeCp(CO)(L)Br] (42); [FeCp(CO)(L)NO ₃] (27)
AgBF ₄ · 0.5dioxane	NO ₃ · 0.5H ₂ O	[FeCp(CO)L ₂]BF ₄ (31)
2AgNO ₃	<i>p</i> -MeC ₆ H ₄ SO ₃ · 2H ₂ O	[FeCp(CO)(L)NO ₃] (25); [FeCp(CO)L ₂] [MeC ₆ H ₄ SO ₃] (20); [FeCp(CO) ₃ L][MeC ₆ H ₄ SO ₃] (25)
AgNO ₃	PF ₆ or BF ₄	[FeCp(CO)(L) ₂]X (25); [FeCp(CO) ₃ L]X (5)
AgNO ₃ ^b	PF ₆ or BF ₄	[FeCp(CO)(L)(NCMe)NO ₃] (43); [FeCp(CO)(L)NCMe]BF ₄ (37)
<i>[FeCp₂(CO)₂{CN(Me)H}]₂X₂ + electrophile</i>		
AgNO ₃	BF ₄ or PF ₆	[FeCp(CO)L ₂]X (30)
AgNO ₃ ^b	BF ₄ or PF ₆	[FeCp(CO)(L)(NCMe)]X (80)
Cu(NO ₃) ₂ · 3H ₂ O	PF ₆	[FeCp(CO)(L) ₂]PF ₆ (28)
CuCl ₂ · 2H ₂ O	PF ₆	[FeCp(CO)(L) ₂]PF ₆ (16)
(Ph ₃ P) ₃ AgCl	PF ₆ ^d	No reaction
2AgNO ₃ /2Ph ₃ P	PF ₆	No reaction
3AgNO ₃ /2Ph ₃ P	PF ₆	[FeCp(CO)L ₂]X (28)

^a All in MeOH solution unless it is otherwise stated. L = MeNC. Cp = $\eta-C_5H_5$. ^b MeCN solution.
^c Yields of isolated, purified solids except where stated. ^d Reaction carried out in both MeCN and MeOH solution with and without added KPF₆.

Preparation of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}][\text{X}]$ salts

(a) A methanol solution (50 ml) containing equimolar amounts of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ (1 g) and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\text{CN}(\text{Me})\text{H}\}_2][\text{X}]_2$ ($\text{X}^- = \text{PF}_6^-$ (1.77 g) or BF_4^- (1.4 g)) was stirred for 30 min. Slow removal of the solvent gave single products $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}][\text{X}]$ as analytically pure red solids in ca. 25% yield.

(b) The addition of $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ (0.5 g) to a solution of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ (1 g, mole ratio 1/1) in dichloromethane or methanol (50 ml) gave a single product. It was identified spectroscopically as containing the $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}]^+$ cation, presumably as its $[p\text{-MeC}_6\text{H}_4\text{SO}_3]^-$ salt. It was generally used in situ, but it could be isolated as a red oil.

(c) Various $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNR})\{\text{CN}(\text{R})\text{H}\}][\text{X}]$ have been obtained from a wide variety of reactions [2]. These are mentioned in the Results and Discussion Section.

Reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\text{CN}(\text{Me})\text{H}\}_2][\text{PF}_6]_2$ with AgNO_3

A solution of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\text{CN}(\text{Me})\text{H}\}_2][\text{PF}_6]_2$ (0.8 g) in methanol (50 ml) was stirred for 3 h without change or decomposition. The addition of one equivalent of AgNO_3 (0.2 g, mole ratio 1/1) brought about an immediate reaction and the complete disappearance of the substrate. Silver metal precipitated as a grey powder and was filtered off. The solvent was removed at reduced pressure from the filtrate and the resultant residue chromatographed on alumina. The various products were recrystallised from suitable solvents. In this particular case $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2][\text{PF}_6]$ was the sole product and it was recrystallised from dichloromethane/hexane mixtures. Infrared spectroscopy was used to monitor the reaction and the subsequent work-up to ascertain that the initial and the isolated products were the same. There was no evidence that they were not in any of the reactions that we investigated.

The above procedure was used for all of the reactions which are mentioned in the Results and Discussion Section or are listed in Table 1. This Table lists the reaction products; the yields quoted are for purified complexes and are based on the proportion of the initial Fe which they contain. Table 2 gives the melting points, analyses and infrared spectra of the various reaction products. Table 3 gives the melting points, analyses and some infrared spectral data of some $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}][\text{X}]$ salts.

Results and discussion

Reactions of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3\{\text{CN}(\text{Me})\text{H}\}][\text{X}]$ salts

As for most of the reactions described herein, that of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CN}(\text{Me})\text{H})][\text{X}]$ ($[(\text{I})\text{H}]^+[\text{X}]^-$) ($\text{X}^- = \text{BF}_4^-$ or PF_6^-) with one equivalent of AgNO_3 proceeds with the complete and virtually instantaneous cleavage of the Fe-Fe bond to give mononuclear complexes which do not contain $\mu\text{-CO}$, $\mu\text{-CNMe}$ or $\mu\text{-CN}(\text{Me})\text{H}$ ligands. In the process $\mu\text{-CN}(\text{Me})\text{H}$ ligands have been converted to terminal CNMe. If the reaction is carried out in methanol two products were obtained, the benzene-soluble $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$ and the benzene-insoluble $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})][\text{X}]$ in yields of 8 and 28%, respectively. Similar results

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TABLE 2. MELTING POINTS, ANALYSES AND INFRARED SPECTRA (1700-2200 cm⁻¹) OF THE REACTION PRODUCTS

	M.p. ^a (°C)	Analyses (Found (calcd.) (%))				Infrared spectra ^b		Medium
		C	H	N	Halogen			
<i>[Fe(η-C₅H₅)(CO)₂NO₂]/X</i>	92-93	34.9 (35.2)	2.0 (2.1)	5.8 (5.8)		2026 (9.8)	2069 (10)	CHCl ₃
<i>[Fe(η-C₅H₅)(CO)₂(CNMe)₂]/X</i>	102-104	37.4 (38.1)	3.5 (3.2)	11.1 (11.1)		2004 (10)	2198 (8.8)	CHCl ₃
X = Br	102-103	35.6 (35.6)	3.0 (3.0)	5.0 (5.2)	29.6 (29.6)	1994 (10)	2190 (9.4)	KBr
X = I	123-125	29.5 (30.3)	2.5 (2.5)	4.3 (4.3)	40.3 (40.1)	1986 (10)	2184 (9.2)	KBr
<i>[Fe(η-C₅H₅)(CO)₂(CNMe)₂]/X</i>	109-111	34.9 (35.4)	2.5 (2.5)	4.6 (4.6)	25.3 (24.9)	2019 (10)	2064 (9.7)	KBr
X = PF ₆	141-142	29.4 (29.8)	2.1 (2.2)	3.9 (3.9)	30.9 (31.4)	2011 (9.5)	2043 (10)	CHCl ₃
X = <i>p</i> -CH ₃ C ₆ H ₄ SO ₃	128-130	49.8 (49.4)	3.8 (3.9)	3.5 (3.6)		2016 (9.6)	2057 (10)	CH ₂ Cl ₂
<i>[Fe(η-C₅H₅)(CO)₂(CNMe)₂]/X</i>	160 (dec.)	37.3 (37.8)	3.6 (3.5)	8.7 (8.8)		2023 (10)	2207 (9.7) ^c	CHCl ₃
X = PF ₆	155 (dec.)	31.9 (31.8)	3.0 (2.9)	7.3 (7.4)		2005 (10)	2205 (9.6) ^c	KBr
<i>[Fe(η-C₅H₅)(CO)₂(CNMe)(NCMe)]/X</i>	122-124	41.1 (41.0)	3.6 (3.7)	14.2 (14.3)		2010 (10)	2067 (1) ^d	CHCl ₃
X = NO ₂	182-184	36.8 (37.8)	3.7 (3.5)	8.5 (8.8)		2010 (10)	2067 (1) ^d	CHCl ₃
X = PF ₆	165-168	32.0 (32.0)	3.1 (2.9)	7.7 (7.5)		2020 (10)	2081 (1) ^d	CH ₂ Cl ₂

^a (dec.) decomposed on heating. ^b Peak positions (cm⁻¹) with relative peak heights in parentheses. Due to *ν*(CO) vibrations, unless stated otherwise. ^c Due to *ν*(C-NMe) modes. ^d Due to *ν*(N-CMe) vibrations.

TABLE 3
 DECOMPOSITION POINTS, ANALYSES AND INFRARED SPECTRA OF SOME $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}]_x$ COMPLEXES

X	Dec. pt (°C) ^a	Analyses (Found (calcd.)) (%)			IR spectra ^b					
		C	H	N	$\nu\{\text{C-N}(\text{Me})\text{H}\}_\mu$	$\nu(\text{C-O})_\mu$	$\nu(\text{C-O})$	$\nu(\text{C-NMe})$	$\nu(\text{N-H})$	
BF_4	145	41.0 (41.0)	4.0 (3.6)	5.4 (5.4)	1574 (7.2)	1804 (9.0)	1982 (10)	2189 (9.1)	3271 (2.8)	
PF_6	137	31.1 (31.9)	3.1 (2.9)	7.3 (7.4)	1582 (7.5)	1808 (8.7)	1978 (10)	2181 (8.9)	3318 (3.2)	
$\text{Br}\cdot 2\text{H}_2\text{O}$	98	38.7 (38.4)	4.0 (3.2)	5.6 (5.6)	1571 (6.7)	1796 (9.0)	1979 (10)	2184 (8.1)		
$\text{I}\cdot\text{H}_2\text{O}$	110	36.7 (36.5)	3.1 (3.6)	5.1 (5.3)	1572 (7.9)	1799 (9.9)	1979 (10)	2184 (8.1)		
$\text{NO}_3\cdot 0.5\text{H}_2\text{O}$	110	42.4 (42.5)	3.9 (3.9)	9.3 (9.3)	1580 (7.9)	1799 (9.8)	1974 (10)	2181 (8.5)		
$p\text{-MeC}_6\text{H}_4\text{SO}_3^c$	Oil		not isolated		1587 (6.8)	1810 (7.2)	1985 (10)	2180 (7.9)	3310 (2.5)	

^a Decomposition point determined in sealed tubes. ^b Peak positions (cm^{-1}) with relative peak heights in parentheses. Determined in KBr discs except for $p\text{-MeC}_6\text{H}_4\text{SO}_3^-$ salt. ^c Infrared spectrum run in CHCl_3 solution.

were obtained using dichloromethane solutions, but in acetonitrile two products were formed in ca. equal amounts, the benzene-soluble $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$ and the benzene-insoluble $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})][\text{X}]$ (isolated yields of 8 and 50%, respectively). In all cases, monitoring the infrared spectra of the reaction mixture suggests that the reactions are quantitative.

Under the same conditions $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe}_2)]$ [8] is not cleaved by AgNO_3 or $[\text{AgPF}_6 \cdot 2\text{dioxane}]$. Anion exchange takes place.

Reactions of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}]^+ \text{ salts}$

The products from the reactions of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}][\text{X}]$, $([(\text{II})\text{H}]^+ [\text{X}]^-)$ with AgY is markedly dependent on X^- and Y^- as well as the reaction solvent. Thus in methanol solution when $\text{X}^- = \text{Br}^-$ or I^- , one equivalent of AgNO_3 cleaves them completely. Infrared spectroscopy shows that two products are formed in ca. equal amounts, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{X}]$ and $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$ (Table 1).

In contrast, when either X^- or Y^- are the poorly coordinating anions $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$ but methanol is still the solvent, ionic products are obtained. Thus with $[(\text{II})\text{H}][\text{NO}_3] \cdot 0.5 \text{H}_2\text{O}$ one equivalent of $\text{AgBF}_4 \cdot 0.5 \text{C}_4\text{H}_8\text{O}_2$ ($\text{C}_4\text{H}_8\text{O}_2 = \text{dioxane}$) gives $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2][\text{BF}_4]$ as the sole product. Similarly AgNO_3 cleaves $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNR})(\mu\text{-CO})\{\mu\text{-CN}(\text{R})\text{H}\}][\text{PF}_6]$ ($\text{R} = \text{Et}$ and C_6H_{11}) to give $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNR})_2][\text{PF}_6]$ only in isolated yields of 25–30%, but when $\text{R} = \text{Me}$ two products are obtained, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2][\text{PF}_6]$ in 25% yield and much smaller amounts of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})][\text{PF}_6]$. Similar results are obtained when $[\text{PF}_6]^-$ is replaced by $[\text{BF}_4]^-$.

An apparently similar reaction of $[(\text{II})\text{H}][p\text{-MeC}_6\text{H}_4\text{SO}_3] \cdot \text{H}_2\text{O}$ is anomalous. Two equivalents of AgNO_3 are necessary to bring about a complete reaction rather than one, and three products are obtained, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})][p\text{-MeC}_6\text{H}_4\text{SO}_3]$ and $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2][p\text{-MeC}_6\text{H}_4\text{SO}_3]$. It is likely that the presence of the $[p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3]^-$ ion is responsible for this behaviour.

If the solvent is changed to the strongly-coordinating acetonitrile, the course of the reaction of $[(\text{II})\text{H}][\text{X}]$ with AgNO_3 is independent of the anions. Two products are obtained, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})][\text{NO}_3]$ and $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})][\text{X}]$ in yields of 37 and 43% respectively when $\text{X}^- = \text{PF}_6^-$. Similar results are obtained when $\text{X}^- = \text{BF}_4^-$ or $p\text{-MeC}_6\text{H}_4\text{SO}_3^-$.

Reactions of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\text{CN}(\text{Me})\text{H}\}_2]^{2+} \text{ salts}$

In methanol solution, $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\mu\text{-CN}(\text{Me})\text{H}\}_2]^{2+} [\text{X}]_2$, $([(\text{II})\text{H}_2][\text{X}]_2)$ ($\text{X}^- = \text{PF}_6^-$ or BF_4^-) react immediately with one equivalent of AgNO_3 to give a single product, $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]\text{X}$ in 30% yield. If one equivalent of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe})]$ is added to the reaction mixture after all of the $[(\text{II})\text{H}_2][\text{X}]_2$ has been consumed, it is converted to $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}]^+$ but a second equivalent is not. This suggests that the cleavage of $[(\text{II})\text{H}_2]^{2+}$ by Ag^+ requires one H^+ but not the other which remains in the reaction mixture.

AgNO_3 may be replaced by $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. In both instances $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2][\text{X}]$ is obtained. However, whereas only 1 mol of

the former is required to consume all of the $[(\text{II})\text{H}_2]^{2+}$, 4 mol of the latter were necessary.

In the presence of two equivalents of Ph_3P , $[(\text{II})\text{H}_2][\text{PF}_6]_2$ fails to react with two equivalents of AgNO_3 in methanol solution but a third converts it to $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]^+$ salts. In a related reaction, $[(\text{II})\text{H}_2][\text{PF}_6]_2$ did not react with $[\text{Ag}(\text{PPh}_3)_3\text{Cl}]$ in either methanol or acetonitrile solution even in the presence of excess KPF_6 . It was consumed completely on the subsequent addition of one equivalent of AgNO_3 .

If acetonitrile is used as the solvent for the reaction of $[(\text{II})\text{H}_2][\text{X}_2]$ with AgNO_3 , there is a single product. $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})][\text{X}]$ is obtained in ca. 80% yield ($\text{X}^- = \text{BF}_4^-$ or PF_6^-).

Preparation and some properties of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}][\text{X}]$ salts

There are two obvious routes to these previously unreported complexes: (a) the reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ (II) with one equivalent of a protic acid and (b) proton exchange between $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ (II) and the readily obtained $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\text{CN}(\text{Me})\text{H}\}_2][\text{X}]_2$ salts ($[(\text{II})\text{H}_2][\text{X}]_2$). Route (a) has been used to prepare $[(\text{II})\text{H}][p\text{-MeC}_6\text{H}_4\text{SO}_3]$ in high yields and (b) to prepare its PF_6^- or BF_4^- counterparts in lower yields (25%).

However, these salts have turned up as unexpected products from other reactions (c) one equivalent of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2][\text{PF}_6]$ reacts with II in dichloromethane or ether solutions at 20°C to give high yields of $[(\text{II})\text{H}][\text{PF}_6]$. (d) II reacts with 1 mol of NiI_2 , $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ or $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in wet tetrahydrofuran solutions to give $[(\text{II})\text{H}][\text{X}]$ where $\text{X}^- = [\text{I} \cdot \text{H}_2\text{O}]$, $[\text{Br}^- \cdot 2\text{H}_2\text{O}]$ or $[\text{NO}_3^- \cdot 0.5 \text{H}_2\text{O}]$, respectively. (e) Dilute solutions of $[(\text{II})\text{H}_2]^{2+}$ salts in acetonitrile rapidly lose H^+ to give $[(\text{II})\text{H}]^+$. A similar but slower reaction takes place in methanol. The dissociation is reversible. It is not observed in more concentrated solutions and attempts to isolate $[(\text{II})\text{H}]^+$ salts by removal of the solvent at reduced pressures results in the reformation of $[(\text{II})\text{H}_2]^{2+}$.

Infrared spectra of $[(\text{II})\text{H}]^+$ salts show absorption bands due to the anion where appropriate, together with those due to the cation. In particular (Table 3) there are intense bands at ca. 1578, 1810, 1984 and 2193 cm^{-1} due to the C–N or C–O stretching vibrations of the $\mu\text{-CN}(\text{Me})\text{H}$, $\mu\text{-CO}$, CO or CNMe ligands respectively. These have frequencies and relative intensities (Table 3) which are similar to those of the related $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\mu\text{-CN}(\text{Me})\text{Me}\}]\text{I}$ [8].

It is therefore reasonable to suggest that like them $[(\text{II})\text{H}]^+$ has the structure $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}]^+$ (Fig. 1) with a ca. planar $\text{Fe}_2(\mu\text{-C})_2$ moiety. Both *cis* and *trans* isomers are possible and the H may be *syn* to the MeNC or *anti* to it. The *cis*, *anti* isomer is shown in Fig. 1. The spectra of the $[(\text{II})\text{H}]^+$ salts also show an absorption band at ca. 3300 cm^{-1} due to their $\nu(\text{N-H})$ vibrations. Its frequency is a function of the anion and it cannot be detected at all when water of crystallization is present. This behaviour is probably due to hydrogen bonding involving the N–H group. It has been observed previously for $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CNMe})_2(\mu\text{-CNMe})\{\mu\text{-CN}(\text{Me})\text{H}\}][\text{X}]$ salts derived from weak acids HX such as acetic acid [9].

The $[(\text{II})\text{H}]\text{X}$ are red solids or oils which are soluble only in polar solvents such as chloroform, ethers, or alcohols. They are markedly less stable in solution

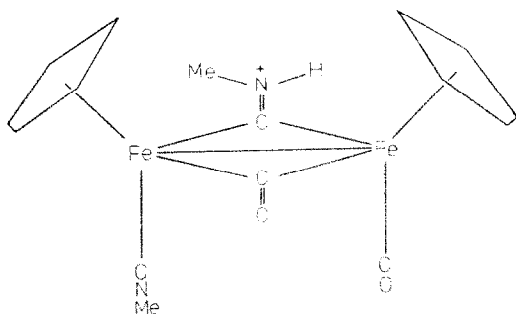


Fig. 1. The structure of $[(\text{II})\text{H}]^+$. The *cis, anti*-isomer is shown.

than are those of $[(\text{II})\text{H}_2]^{2+}$ and attempts to recrystallize them are often not successful. Unless air is excluded they are oxidised to $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]^+$ salts.

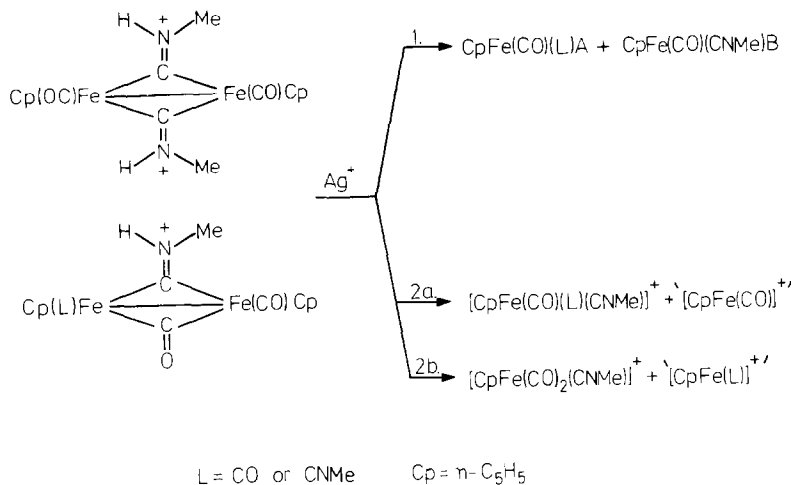
Comments and conclusions

Acids HX protonate the $\mu\text{-CNMe}$ ligands of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe})]$ (I) and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ (II) to give salts of the cations $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}]^+$ ($[(\text{I})\text{H}]^+$), $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}]^+$ ($[(\text{II})\text{H}]^+$) and $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\mu\text{-CN}(\text{Me})\text{H}\}_2]^{2+}$ ($[(\text{II})\text{H}_2]^{2+}$). Reactions of these salts with one equivalent of Ag^+ results in their oxidative cleavage to mono-metallic products with the conversion of $\mu\text{-CN}(\text{Me})\text{H}$ ligands to terminal CNMe. In all reactions silver metal is precipitated as a grey powder. Analysis shows that it normally contains a relatively high proportion of organic matter which presumably arises from the solvent, but when this is allowed for the yields of silver are close to 100%. In the reactions of both $[(\text{I})\text{H}]^+$ and $[(\text{II})\text{H}]^+$, all of their H^+ are consumed, but only half the H^+ of $[(\text{II})\text{H}_2]^{2+}$ is utilized.

The oxidative cleavage of both I and II in the reactions described herein are two-electron processes. The H^+ coordinated to the $\mu\text{-CNMe}$ ligand and Ag^+ together act as a two-electron oxidant. This is consistent with other work which shows that if H^+ is replaced by Ag^+ , the $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{L})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{AgL}\}]^+$ adducts ($\text{L} = \text{CO}$ or CNMe ; $\text{L}^1 = \text{e.g. Ph}_3\text{P}$ or NO_3^-) react with another equivalent of Ag^+ in methanol so that the two Ag^+ together act as a two-electron oxidant giving, overall, reaction products similar to those reported here [2,10]. However whereas the Ag^+/Ag^+ system acts as two one-electron oxidants in acetonitrile without the detectable formation of the 1:1 adducts [10], different behaviour is observed for H^+/Ag^+ (Table 3). There are two ways in which cleavage of $[(\text{I})\text{H}]^+$, $[(\text{II})\text{H}]^+$ or $[(\text{II})\text{H}_2]^{2+}$ can take place. These are illustrated in Scheme 1.

Route 1 is followed when both X^- and Y^- are coordinating ions such as Cl^- , Br^- , I^- or $[\text{NO}_3]^-$, or the strongly coordinating MeCN is used as the reaction solvent. The counteranions or MeCN are incorporated into the products as the ligands A or B.

If either of the counteranions X^- or Y^- is the non-coordinating $[\text{BF}_4]^-$ or $[\text{PF}_6]^-$ and MeCN is not used as the solvent, the reaction proceeds largely by route 2 for



SCHEME 1

[(I)H]⁺ and exclusively by it for [(II)H]⁺ and [(II)H₂]²⁺. The fate of the '[Fe($\eta\text{-C}_5\text{H}_5$)(CO)]⁺' and '[Fe($\eta\text{-C}_5\text{H}_5$)(L)]⁺' fragments is unknown.

These results show that the anions X⁻ and Y⁻ are not innocent bystanders; they actually participate in the reaction. Different products are obtained when both X⁻ and Y⁻ are coordinating anions * (route 1) and when one is not (route 2). This suggests that there are two stages in the reaction in which the coordinating abilities of X⁻/Y⁻ are called into play.

Ph₃P prevents AgNO₃ from oxidising [(II)H₂]²⁺. This suggests that the 'Ph₃PAgNO₃' which is probably formed cannot attack the substrate. Preformed [Ag(PPh₃)₃Cl] is similarly inactive. However three equivalents of Ph₃P do not prevent Ag⁺ salts from attacking [(II)Ag]⁺ adducts [2]. Therefore it is probable that the Ph₃P complexes of Ag^I fail to attack [(II)H₂]²⁺ because they are weak oxidants and not because steric factors prevent them from doing so.

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* In this context acetonitrile may take the place of a coordinating anion but methanol, tetrahydrofuran, dichloromethane etc. may not.