

**The reactions of AgY salts  
 with  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CNMe})_n]$  complexes  
 ( $\text{Y}^- = \text{NO}_3^-$ ,  $\text{BF}_4^-$  or  $\text{PF}_6^-$ ;  $n = 0, 1$  or  $2$ ). The crystal  
 structure of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$**

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**Abstract**

The oxidative cleavage of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CNMe})_n]$  ( $n = 0-2$ ) by  $2\text{AgX}$  gives mononuclear products. It is shown to be a two-electron process in most solvents but a one-electron process in acetonitrile. The two-electron oxidations proceed by way of adducts such as  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{AgPPh}_3\}]\text{BF}_4$  which are isolable when  $n = 2$ , detectable when  $n = 1$  and postulated when  $n = 0$ . The one-electron process gives no adducts, and  $1\text{AgX}$  cleaves all of the substrate to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{L})(\text{NCMe})]^+$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{L})]^-$  ( $\text{L} = \text{CO}$  or  $\text{CNMe}$ ). The latter may combine or react with added  $\text{CHBr}_3$  to give  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{L})\text{Br}]$ . The structure of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$  has been determined by X-ray diffraction.

**Introduction**

Salts of silver(I),  $\text{AgY}$ , have been used to oxidatively cleave the Fe–Fe bond in  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  (I) to give  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]^+$ ,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}]^+$  or  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Y}]$  derivatives depending on the reaction solvent, the anion  $\text{Y}^-$ , and the presence of added ligands L [1,2]. The  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CO})_2(\mu\text{-Diphos})]$  complexes (Diphos =  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$  or  $2$ )) are oxidised by one equivalent of  $\text{AgClO}_4$  or  $\text{AgSbF}_6$  to isolable, paramagnetic  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-CO})_2(\mu\text{-Diphos})]^+$  salts whilst a second cleaves the Fe–Fe bond [3].

In contrast,  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  (III) reacts with  $1\text{AgNO}_3$  in tetrahydrofuran or chloroform to give a relatively stable adduct. On the basis of its IR

spectrum this was thought to have the structure  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{AgNO}_3\}]$  with a direct donor bond to silver from the N atom of the  $\mu\text{-CNMe}$  ligand of III. This adduct decomposes only slowly in solution. However when another equivalent of  $\text{AgNO}_3$  is added, the subsequent reaction is quite fast. Silver metal is precipitated quantitatively and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$  may be isolated in quite high yields [4]. The overall reaction is a 2-electron oxidative cleavage of III.

Herein are reported the results of a systematic study of the reactions of  $\text{AgY}$  salts or their complexes with  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  (I),  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe})]$  (II) and  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  (III). The effects of changing the anion  $\text{X}^-$ , the reaction solvent, the reactant mole ratios, and of adding extra tertiary phosphines or bromoform to the reaction mixtures are recorded and discussed. A preliminary communication has appeared [5].

## Experimental

Literature methods or modifications of them were used to prepare  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  [6],  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe})]$  [7],  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  [8] and related derivatives [7,8],  $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  [9], and  $\text{AgPF}_6 \cdot 2\text{C}_4\text{H}_8\text{O}_2$  ( $\text{C}_4\text{H}_8\text{O}_2 = \text{dioxane}$ ) [9]. Other chemicals were purchased and used as received.

Reactions were carried out at room temperature in the dark and under nitrogen. Solvents were dried and deoxygenated by refluxing over calcium hydride or calcium sulphate (acetonitrile only). They were distilled before use.

Detailed experimental procedures are reported for two typical reactions. They apply with minor modifications to all of the reactions that have been investigated.

### *The reaction of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ with $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$*

Solid  $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (0.31 g) was added to a solution of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  (0.5 g; reactant mole ratio 1/1) in tetrahydrofuran (60 ml). A slow reaction took place with the deposition of grey silver metal. IR spectroscopy showed that the reaction stopped after ca. 2 h. On the addition of more  $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (0.31 g) all of the  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  was oxidised.

The silver metal was filtered off, washed with various organic solvents and dried. Its yield was quantitative. The solvent was removed at reduced pressures from the filtrate. The resultant residue was recrystallized from dichloromethane/pentane mixtures to give a single product, yellow  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4$ .

Similar results were obtained when tetrahydrofuran was replaced by dichloromethane, chloroform, ether or benzene. However, when the reaction was carried out in acetonitrile, it was complete within a few seconds. Silver metal was filtered off and two products separated from the filtrate by chromatography (alumina/dichloromethane). Yellow  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NCMe})]\text{BF}_4$  were purified by recrystallization from dichloromethane/pentane mixtures.

The addition of  $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  (0.62 g) to a solution of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  (0.5 g) and  $\text{Ph}_3\text{P}$  (0.74 g; reactant mole ratio = 2/1/2) in tetrahydrofuran (60 ml) resulted in a slow reaction. After 24 h the precipitated silver metal was filtered off, washed with chloroform and dried. The solvent was removed at reduced pressure from the filtrate. The resultant residue was chromatographed (alumina with dichlo-

romethane) to give yellow  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)]\text{BF}_4$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4$ . These were recrystallized from dichloromethane/pentane mixtures.

In these reactions similar results were obtained if  $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  was replaced by  $\text{AgPF}_6 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ .

*The reaction of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  with  $\text{AgNO}_3$*

Finely-ground solid  $\text{AgNO}_3$  (0.22 g) was added to a solution of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  (0.5 g; mole ratio 1/1) in tetrahydrofuran (60 ml). Over a period of ca. 30 min a red solid precipitated. It was filtered off, washed with pentane, dried, and identified by analysis as the 1:1 adduct  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2 \cdot \text{AgNO}_3 \cdot \text{C}_4\text{H}_8\text{O}]$ . On recrystallization from toluene/dichloromethane mixtures it was converted to  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2 \cdot \text{AgNO}_3]$ . Partial removal of the solvent from the filtered reaction mixture gave a second adduct,  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]_2 \cdot \text{AgNO}_3$ , as a brown-red solid which was filtered off, washed with pentane and dried.

If the reaction was repeated using 0.44 g of  $\text{AgNO}_3$  (reactant mole ratio 2/1) or if  $\text{AgNO}_3$  (0.22 g) was added to the solution of the 1:1 adduct generated as above, all of the  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  was oxidised with the quantitative precipitation of silver metal. This was filtered off as a grey powder, washed with various organic solvents and dried. The filtered reaction mixture contained a single product,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$ , which was isolated by removal of the solvent at reduced pressure, and purified by recrystallization from toluene/pentane. The same result was obtained in the presence of triphenylphosphine (0.69 g).

If the above reaction using equimolar amounts of  $\text{AgNO}_3$  (0.22 g) and  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  (0.5 g) was carried out in acetonitrile, silver metal was precipitated and half of the substrate consumed very quickly. The addition of a second mole of  $\text{AgNO}_3$  resulted in a complete reaction. Silver metal was filtered off, washed with various organic solvents and dried. Removal of the solvent from the filtrate gave a single product, yellow  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{NO}_3$ . It was purified by recrystallization from dichloromethane/hexane mixtures.

The addition of solid  $\text{AgNO}_3$  (0.22 g) to a solution of  $\text{CHBr}_3$  (0.33 g) and  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  (0.5 g; reactant mole ratio 1/1/1) in acetonitrile (60 ml) resulted in an instantaneous, complete reaction. Silver metal precipitated from the reaction mixture. It was filtered off, washed and dried. The two other products  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{Br}]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{NO}_3$  were separated by extracting the first into benzene in which the second is virtually insoluble. They were purified by recrystallization from toluene/pentane and dichloromethane/pentane mixtures respectively.

The various reactions attempted, reaction times and product yields are given in Tables 1–3. The melting points, analyses and IR spectra of the reaction products are summarised in Tables 4 and 5.

Analyses were determined in the Analytical Laboratory of University College, Dublin. IR spectra were run on Perkin–Elmer 283B and 337 spectrometers. They were calibrated with polystyrene, CO, DCl or water vapour.

*Structure of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$*

*Crystal data:*  $\text{C}_9\text{H}_8\text{NO}_2\text{BF}_4\text{Fe}$ ,  $M = 304.8$ , Monoclinic,  $a$  6.913(4),  $b$  15.439(6),  $c$  11.491(5) Å,  $\beta$  95.3 (1)°,  $U$  1221.2 Å<sup>3</sup>,  $Z = 4$ ,  $D_c$  1.658 g cm<sup>-3</sup>,  $F(000) = 608$ ,

$\mu(\text{Mo-K}\alpha)$  13.1 cm<sup>-1</sup>. Systematic absences:  $h0l$  if  $l \neq 2n$  and  $0k0$  if  $k \neq 2n$ . space group  $P2_1/c$  (No. 14).

Cell parameters were determined from precession photographs using Mo-K $\alpha$  radiation. Intensities were estimated visually from precession photographs for the layers 0–2 about [100], 0–3 about [001] and 0–4 about [101]. They were corrected for Lorentz and polarisation effects but not for absorption or extinction. The observed structure factors were placed on a common scale by internal correlation to yield a data set of 1511 non-zero unique reflexions which were used in subsequent calculations.

The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure in which  $\sum w\Delta^2$  was minimised. The weight for each reflexion in the final stages was given by  $w = (1.0 + 0.1|F_o| + 0.002|F_o|^2)^{-1}$ . Approximate hydrogen atom positions for the methyl group were obtained from a difference map with those for the cyclopentadienyl ring being calculated and all positions adjusted to give C–H 1.0 Å. Refinement was terminated when the maximum shift in any parameter was  $< 0.1\sigma$ . The final value for  $R$  was 0.084 and for  $R'$  [ $= (\sum w\Delta^2 / \sum w|F_o|^3)^{1/2}$ ] was 0.117. A final difference map showed no unusual features with a maximum density of  $|0.8| \text{ e}\text{Å}^{-3}$ .

Neutral-atom scattering factors were taken from ref. 10. All calculations were carried out on a UNIVAC 1106 computer with programmes written by F.S.S.

The final atomic coordinates for the non-hydrogen atoms are given in Table 6 and bond lengths and angles in Table 7.

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

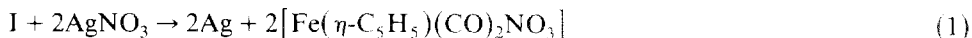
## Results and discussion

The various reactions attempted, their times, and their products and yields are summarised in Tables 1–3. The melting points, analyses, and IR spectra of the reaction products are given in Tables 4 and 5. The quoted yields are based on the proportion of the Fe contained in the substrates I, II or III which is recovered in the isolated and purified products. They are all given to the nearest 5% and are lower than the actual yields in most instances.

The AgY salts are not very soluble in most of the solvents which we have used except for acetonitrile. Consequently many reactions have been carried out using a well-stirred suspension of finely-ground AgY.

### *Reactions of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ (I) in solvents other than acetonitrile (Table 1)*

The reaction of AgNO<sub>3</sub> with I (mole ratio 1/1) in tetrahydrofuran solution results in the cleavage of half of I to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$ . A second equivalent of AgNO<sub>3</sub> completes the oxidation. Spectroscopic and other evidence suggests that the reaction is quantitative (eq. 1). The yields of silver metal and crude  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$  are close to 100% whilst that of pure  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$  is still high.



The course of the reaction is not affected by the presence of CHBr<sub>3</sub> or Ph<sub>3</sub>P or by

Table 1

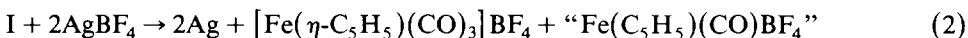
Products and their yields from the reactions of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  (I) with  $\text{Ag}^{\text{I}}$  electrophiles

Reagent <sup>a</sup>	Solvent <sup>b</sup>	Time <sup>c</sup>	Products (Yields (%)) <sup>d</sup>
1 $\text{AgNO}_3$	THF <sup>e</sup>	15	$\text{FeCp}(\text{CO})_2\text{NO}_3 \cdot 0.5 \text{ I consumed}$
2 $\text{AgNO}_3$	THF <sup>e</sup>	15	$\text{FeCp}(\text{CO})_2\text{NO}_3$ (90)
1 $\text{AgNO}_3/1 \text{ CHBr}_3$	THF	15	$\text{FeCp}(\text{CO})_2\text{NO}_3 \cdot 0.5 \text{ I consumed}$ .
2 $\text{AgNO}_3/2 \text{ Ph}_3\text{P}$	THF	24	$\text{FeCp}(\text{CO})_3\text{NO}_3$ (90)
$\text{AgBF}_4$	THF <sup>e</sup>	2	$[\text{FeCp}(\text{CO})_3]\text{BF}_4 \cdot 0.5 \text{ I consumed}$ .
2 $\text{AgBF}_4$	THF <sup>e</sup>	2	$[\text{FeCp}(\text{CO})_3]\text{BF}_4$ (30)
2 $\text{AgBF}_4/2 \text{ Ph}_3\text{P}$	THF	24	$[\text{FeCp}(\text{CO})_2\text{PPh}_3]\text{BF}_4$ (60), $[\text{FeCp}(\text{CO})_3]\text{BF}_4$ (10)
$\text{AgPF}_6$	THF	2	$[\text{FeCp}(\text{CO})_3]\text{PF}_6 \cdot 0.5 \text{ I consumed}$ .
2 $\text{AgPF}_6$	THF	2	$[\text{FeCp}(\text{CO})_3]\text{PF}_6$ (35)
1 $\text{AgNO}_3$	MeCN	Inst.	$\text{FeCp}(\text{CO})_2\text{NO}_3$ , $[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{NO}_3$ , 0.5I
2 $\text{AgNO}_3$	MeCN	Inst.	$\text{FeCp}(\text{CO})_2\text{NO}_3$ (90), $[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{NO}_3$ (10)
1 $\text{AgNO}_3/1 \text{ CHBr}_3$	MeCN	Inst.	$\text{FeCp}(\text{CO})_2\text{Br}$ (45), $\text{FeCp}(\text{CO})_2\text{NO}_3$ (40)
2 $\text{AgNO}_3/\text{O}_2$	MeCN	> 1	$\text{FeCp}(\text{CO})_2\text{NO}_3$ (85), $[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{NO}_3$ (10)
2 $\text{AgNO}_3/2\text{Ph}_3\text{P}$	MeCN	2	$\text{FeCp}(\text{CO})_2\text{NO}_3$ (50), $[\text{FeCp}(\text{CO})_2(\text{PPh}_3)]\text{NO}_3$ (30)
			$[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{NO}_3$ (10)
2 $\text{AgBF}_4$	MeCN	Inst.	$[\text{FeCp}(\text{CO})_3]\text{BF}_4$ (45), $[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{BF}_4$ (10)
2 $\text{AgBF}_4/2 \text{ Ph}_3\text{P}$	MeCN	> 3	$[\text{FeCp}(\text{CO})_2(\text{PPh}_3)]\text{PF}_4$ (55), $[\text{FeCp}(\text{CO})_3]\text{BF}_4$ (20)
			$[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{BF}_4$ (5)
2 $\text{AgPF}_6$	MeCN	Inst.	$[\text{FeCp}(\text{CO})_3]\text{PF}_6$ (40), $[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{PF}_6$ (15)

<sup>a</sup>  $\text{AgBF}_4$  used as  $\text{AgBF}_4 \cdot 0.5 \text{ dioxane}$ ,  $\text{AgPF}_6$  as  $\text{AgPF}_6 \cdot 2 \text{ dioxane}$ . <sup>b</sup> THF = tetrahydrofuran. <sup>c</sup> Time to complete reaction in hours. Inst. < 0.5 min. <sup>d</sup> Cp =  $\eta\text{-C}_5\text{H}_5$ . Yields are those for isolated pure products and are quoted to the nearest 5%. <sup>e</sup> Similar results for other solvents (see text).

the solvent (except acetonitrile). However the reaction times increase in the presence of  $\text{Ph}_3\text{P}$  and along the solvent series dichloromethane (2 h) ~ benzene (2 h) < diethyl ether (5 h) < chloroform (10 h) < tetrahydrofuran (15 h).

$\text{AgBF}_4 \cdot 0.5 \text{C}_4\text{H}_8\text{O}_2$  or  $\text{AgPF}_6 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  ( $\text{C}_4\text{H}_8\text{O}_2 = \text{dioxane}$ ) oxidise I more rapidly than does  $\text{AgNO}_3$  in tetrahydrofuran (THF), chloroform, diethyl ether, benzene or dichloromethane with one equivalent of the electrophile cleaving half and two equivalents cleaving all of I to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4$ . Infrared spectroscopy suggests the reaction stoichiometry shown in eq. 2 but the fate of the “ $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})\text{BF}_4$ ” moiety has not been determined either in this reaction or others where it appears (eqs. 5 or 7). The yield of silver metal is ca. quantitative.



Unless water is rigorously excluded from the reaction mixture, some  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{H}_2\text{O})]\text{BF}_4$  is formed and can be isolated. Two moles of  $\text{PPh}_3$  not only slow the oxidation of I but they change the products to a mixture of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{PPh}_3]\text{BF}_4$  and some  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4$ .

*Reactions of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe})]$  (II) in solvents other than acetonitrile (Table 2)*

Both  $\text{AgNO}_3$  and  $\text{AgBF}_4 \cdot 0.5 \text{C}_4\text{H}_8\text{O}_2$  react with II and other  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNR})]$  substrates (mole ratio 1/1) in tetrahydrofuran. In some reactions red-brown adducts were formed without the precipitation of silver metal. Although they were unstable and could not be isolated from solution, they could be detected by their infrared spectra which, in the  $1550\text{--}2100 \text{ cm}^{-1}$  region, were

Table 2

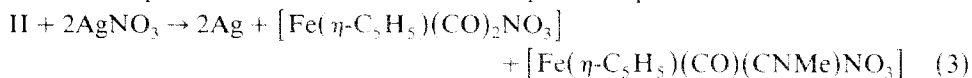
Products and their yields from the reactions of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe})]$  (II) with  $\text{Ag}^+$  electrophiles

Reagent <sup>a</sup>	Solvent <sup>b</sup>	Time <sup>c</sup>	Products (Yields (%)) <sup>d</sup>
1 $\text{AgNO}_3$ <sup>e</sup>	THF <sup>f</sup>	5	$\text{FeCp}(\text{CO})_2\text{NO}_3$ , $\text{FeCp}(\text{CO})(\text{L})\text{NO}_3$ , 0.5II
2 $\text{AgNO}_3$	THF <sup>f</sup>	5	$\text{FeCp}(\text{CO})_2\text{NO}_3$ (40), $\text{FeCp}(\text{CO})(\text{L})\text{NO}_3$ (30)
2 $\text{AgNO}_3/1 \text{ Ph}_3\text{P}^g$	THF	15	$[\text{FeCp}(\text{CO})_2\text{PPh}_3]\text{NO}_3$ (30), $\text{FeCp}(\text{CO})(\text{L})\text{NO}_3$ (50)
$\text{AgBF}_4$ <sup>e</sup>	THF <sup>f</sup>	3	$[\text{FeCp}(\text{CO})_2(\text{L})]\text{BF}_4$ , 0.5II
2 $\text{AgBF}_4$	THF <sup>f</sup>	3	$[\text{FeCp}(\text{CO})_2(\text{L})]\text{BF}_4$ (30)
2 $\text{AgPF}_6$	THF	3	$[\text{FeCp}(\text{CO})_2(\text{L})]\text{PF}_6$ (30)
2 $\text{AgBF}_4/1 \text{ Ph}_3\text{P}^g$	THF	12	$[\text{FeCp}(\text{CO})_2\text{PPh}_3]\text{BF}_4$ (15), $[\text{FeCp}(\text{CO})_2(\text{L})]\text{BF}_4$ (30)
2 $\text{Ag}(\text{PPh}_3)_3\text{Cl}/\text{KPF}_6$	THF	24	$\text{FeCp}(\text{CO})_2\text{Cl}$ (10), $[\text{FeCp}(\text{CO})_2(\text{CNMe})]\text{PF}_6$ (30) $[\text{FeCp}(\text{CO})_2\text{PPh}_3]\text{PF}_6$ (25)
1 $\text{AgNO}_3$	MeCN	Inst.	$[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (40), $[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ (35)
2 $\text{AgNO}_3$	MeCN	Inst.	$\text{FeCp}(\text{CO})_2\text{NO}_3$ (45), $[\text{FeCp}(\text{CO})_2(\text{NCMe})]\text{NO}_3$ (5) $[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ (40)
1 $\text{AgNO}_3/1 \text{ CHBr}_3$	MeCN	Inst.	$[\text{FeCp}(\text{CO})_2\text{Br}]$ (45), $[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ (40)
1 $\text{AgNO}_3/1 \text{ Ph}_3\text{P}^g$ <sup>k</sup>	MeCN	Inst.	ca. 0.5II cleaved, 3 products as for 2 $\text{AgNO}_3/1 \text{ Ph}_3\text{P}$
2 $\text{AgNO}_3/1 \text{ Ph}_3\text{P}^g$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ (45), $\text{Fe}_2\text{Cp}_2(\text{CO})_4$ (5) $[\text{FeCp}(\text{CO})_2\text{PPh}_3]\text{NO}_3$ (20)
1 $\text{AgBF}_4$	MeCN	Inst.	$[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (40), $[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{BF}_4$ (35)
1 $\text{AgPF}_6$	MeCN	Inst.	$[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (40), $[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{PF}_6$ (30)
1 $\text{AgBF}_4/1 \text{ Ph}_3\text{P}^g$	MeCN	Inst.	ca. 0.5II cleaved, 3 products as for 2 $\text{AgBF}_4/1 \text{ Ph}_3\text{P}$
2 $\text{AgBF}_4/1 \text{ Ph}_3\text{P}^g$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{BF}_4$ (45), $[\text{Fe}_2\text{Cp}_2(\text{CO})_4]$ (15), $[\text{FeCp}(\text{CO})_2\text{PPh}_3]\text{BF}_4$ (10)

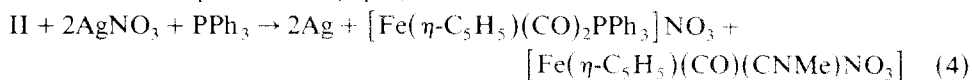
<sup>a</sup>  $\text{AgBF}_4$  used as  $\text{AgBF}_4 \cdot 0.5$ dioxane and  $\text{AgPF}_6$  as  $\text{AgPF}_6 \cdot 2$ dioxane. <sup>b</sup> THF = tetrahydrofuran. <sup>c</sup> Time to complete reaction in hours. Inst. < 0.5 min. <sup>d</sup> Cp =  $\eta^5\text{-C}_5\text{H}_5$  and L = MeCN. Yields are for isolated, pure products, and are quoted to the nearest 5%. <sup>e</sup> 1:1 adducts detected by IR spectroscopy in some reactions (see text). <sup>f</sup> Similar results for other solvents and other  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNR})]$  substrates (see text). <sup>g</sup>  $\text{Ph}_3\text{P}$  may be replaced by other  $\text{R}_3\text{P}$  with slightly different results (see text).

virtually identical with those of  $[\text{cis-Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{E}\}]$  adducts which have been characterised unambiguously by spectroscopy and X-ray diffraction where  $\text{E} = \text{H}^+ \text{BF}_4^-$  [12] and  $\text{Me}^+ \text{I}^-$  [13]. Therefore it is reasonable to suggest that in the present instance  $\text{E} = \text{AgNO}_3$  or solvated  $\text{Ag}^+$  species and that these adducts possess direct  $\text{N} \rightarrow \text{Ag}$  bonds.

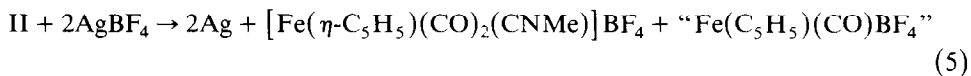
If the adduct obtained from II and 1 $\text{AgNO}_3$  is allowed to stand in solution it decomposes. Half of the II is oxidised to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$ . A second equivalent of  $\text{AgNO}_3$  completes the cleavage of II over a period of ca. 5 h. Silver metal is precipitated, and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$  are formed in equal amounts. The overall reaction is quantitative or close to it with respect to eq. 3.



The presence of one equivalent of  $\text{PPh}_3$  or other tertiary phosphines greatly slows this reaction and a second equivalent has no added effect. II is completely oxidised by two equivalents of  $\text{AgNO}_3$ ; equal amounts of two products are again formed but they are now  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{PPh}_3]\text{NO}_3$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$ . The reaction is quantitative (eq. 4).



$\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  oxidises II more rapidly than does  $\text{AgNO}_3$ . One equivalent cleaves half of II in tetrahydrofuran to the yellow salt  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$  and second completes the oxidation. Two equivalents of  $\text{AgPF}_6 \cdot 2\text{C}_4\text{H}_8\text{O}_2$  behave similarly. Silver metal is precipitated. Spectroscopic studies suggest that the overall reaction is as shown in eq. 5.



If this reaction is carried out in the presence of  $\text{PPh}_3$  or other tertiary phosphines the overall oxidation of II by  $2\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  is slowed. Although silver metal is precipitated quantitatively, there are now two products which are formed in ca. equal amounts according to IR spectroscopy,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{PPh}_3]\text{BF}_4$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$ .

If  $\text{PPh}_3$  and the  $\text{Ag}^{\text{I}}$  electrophile are introduced into the reaction mixture with II in the form of two equivalents of  $[\text{Ag}(\text{PPh}_3)_3\text{Cl}]$ , no reaction takes place in tetrahydrofuran solution until  $\text{KPF}_6$  has been added. Then there is a slow oxidation of all of II with the quantitative precipitation of silver metal and the formation of three products,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}]$ ,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{PPh}_3]\text{PF}_6$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{PF}_6$ .

*Reactions of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  (III) in solvents other than acetonitrile (Table 3)*

Equimolar amounts of III and  $\text{AgNO}_3$  react in tetrahydrofuran solution to give a single product. Some decomposition occurred during work-up and as a consequence two adducts were isolated from the reaction mixture,  $[(\text{III})\text{AgNO}_3]$  and  $[(\text{III})_2\text{AgNO}_3]$ . They have infrared spectra similar to those of other well-characterised  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{E}\}]$  adducts [12,13] and are probably similar complexes with  $\text{E} = \text{AgNO}_3$  or  $0.5\text{AgNO}_3$  and  $\text{N} \rightarrow \text{Ag}$  or  $\text{N} \rightarrow \text{Ag} \leftarrow \text{N}$  bonds respectively (see later).

If the isolated adducts are redissolved in tetrahydrofuran they slowly decompose to a mixture of III and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$  with the deposition of silver metal. The addition of a further equivalent of  $\text{AgNO}_3$  increases the rates of these reactions.  $[(\text{III})_2\text{AgNO}_3]$  gives a 1/2 mixture of III and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$  whilst this last is the sole product from  $[(\text{III})\text{AgNO}_3]$  with a quantitative yield of silver in both instances. Spectroscopic studies suggest that the overall reaction is as shown in eq. 6.



Similar reactions take place in other solvents such as diethyl ether, benzene or dichloromethane, and with related substrates  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNR})_2]$  ( $\text{R} = \text{Et}$ ,  $\text{C}_6\text{H}_{11}$  or  $\text{PhCH}_2$ ).

If  $\text{AgNO}_3$  is replaced by  $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  or  $\text{AgPF}_6 \cdot 2\text{C}_4\text{H}_8\text{O}_2$ , IR spectroscopy shows that adducts are formed which presumably have  $\text{E} = \text{AgBF}_4$  or  $\text{AgPF}_6$ . However, they are much less stable than their  $\text{AgNO}_3$  counterparts and decompose on attempted isolation to a ca. 1/1 mixture of III and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2][\text{Y}]$  ( $\text{Y}^- = \text{BF}_4^-$  or  $\text{PF}_6^-$ ). The addition of a further equivalent of  $\text{AgY}$  to a solution of these adducts hastens this reaction and brings about the

Table 3

Products and their yields from the reactions of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  (III) with  $\text{Ag}^{\text{I}}$  electrophiles

Reagent <sup>a</sup>	Solvent <sup>b</sup>	Time <sup>c</sup>	Products (Yields (%)) <sup>d</sup>
1 $\text{AgNO}_3$ <sup>e</sup>	THF <sup>f</sup>	0.5	Adducts $[(\text{III})\text{AgNO}_3]$ and $[(\text{III})_2\text{AgNO}_3]$
2 $\text{AgNO}_3$ <sup>e</sup>	THF <sup>f</sup>	0.5	$\text{FeCp}(\text{CO})(\text{L})\text{NO}_3$ (65)
2 $\text{AgNO}_3/\text{Ph}_3\text{P}$	THF	1	$\text{FeCp}(\text{CO})(\text{L})\text{NO}_3$ (45)
1 $\text{AgBF}_4$ <sup>g</sup>	THF <sup>f</sup>	1	$[\text{FeCp}(\text{CO})(\text{L})_2]\text{BF}_4$ , 0.5III consumed.
2 $\text{AgBF}_4$	THF <sup>f</sup>	1	$[\text{FeCp}(\text{CO})(\text{L})_2]\text{BF}_4$ (40)
2 $\text{AgPF}_6$	THF	1	$[\text{FeCp}(\text{CO})(\text{L})_2]\text{PF}_6$ (35)
1 $\text{AgBF}_4/2 \text{Ph}_3\text{P}$	THF	2	Adduct $[(\text{III})\text{AgPPh}_3]\text{BF}_4$
1 $\text{AgPF}_6/2 \text{Ph}_3\text{P}$	THF	2	Adduct $[(\text{III})\text{AgPPh}_3]\text{PF}_6$
2 $\text{AgBF}_4/2 \text{Ph}_3\text{P}$	THF	2	$[\text{FeCp}(\text{CO})(\text{L})_2]\text{BF}_4$ (35)
1 $\text{Ag}(\text{PPh}_3)_3\text{Cl}/\text{KPF}_6$	THF	6	Adducts $[(\text{III})\text{AgPPh}_3]\text{PF}_6$ and $[(\text{III})_2\text{AgCl}]$
2 $\text{Ag}(\text{PPh}_3)_3\text{Cl}/\text{KPF}_6$	THF	6	$[\text{FeCp}(\text{CO})(\text{L})_2]\text{PF}_6$ (35) from $[(\text{III})\text{AgPPh}_3]\text{PF}_6$ $\text{FeCp}(\text{CO})(\text{L})\text{Cl}$ (35), (III) (40) from $[(\text{III})_2\text{AgCl}]$
1 $\{\text{Ag}(\text{PPh}_3)\text{Cl}\}_4/\text{KPF}_6$	THF	24	Unstable adduct plus cleavage.
2 $\{\text{Ag}(\text{PPh}_3)\text{Cl}\}_4/\text{KPF}_6$	THF	24	$[\text{FeCp}(\text{CO})(\text{L})_2]\text{PF}_6$ (20)
1 $\text{AgNO}_3$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ , 0.5III cleaved.
2 $\text{AgNO}_3$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ (90)
1 $\text{AgNO}_3/1 \text{CHBr}_3$	MeCN	Inst.	$\text{FeCp}(\text{CO})(\text{L})\text{Br}$ (40), $[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ (45)
2 $\text{AgNO}_3/2 \text{Ph}_3\text{P}$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{NO}_3$ (90)
1 $\text{AgBF}_4$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{BF}_4$ , 0.5III cleaved.
2 $\text{AgBF}_4$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{BF}_4$ (85)
2 $\text{AgPF}_6$	MeCN	Inst.	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{PF}_6$ (80)
2 $\{\text{Ag}(\text{PPh}_3)\text{Cl}\}_4/\text{KPF}_6$	MeCN	1	$[\text{FeCp}(\text{CO})(\text{L})(\text{NCMe})]\text{PF}_6$ (65)

<sup>a</sup>  $\text{AgBF}_4$  used as  $\text{AgBF}_4 \cdot 0.5\text{dioxane}$  and  $\text{AgPF}_6$  as  $\text{AgPF}_6 \cdot 2\text{dioxane}$ . <sup>b</sup> THF = tetrahydrofuran. <sup>c</sup> Time to complete reaction in hours. Inst. < 0.5 min. <sup>d</sup> Cp =  $\eta\text{-C}_5\text{H}_5$  and L = MeNC. Yields are for isolated, pure products and are quoted to the nearest 5%. <sup>e</sup> Similar reactions observed with other  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNR})_2]$  (see text). <sup>f</sup> Similar results obtained in solvents other than MeCN (see text). <sup>g</sup> An unstable adduct formed which decomposed on attempted isolation (see text).

complete oxidation of III to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]\text{Y}$  with the quantitative precipitation of silver (eq. 7).



The reaction of III with  $2\text{AgNO}_3$  is slowed but otherwise unaffected by the presence of tertiary phosphines. However a single equivalent of  $\text{AgBF}_4 \cdot 0.5\text{C}_4\text{H}_8\text{O}_2$  or  $\text{AgPF}_6 \cdot 2\text{C}_4\text{H}_8\text{O}_2$  and two of  $\text{PPh}_3$  convert III to the relatively stable adducts  $[(\text{III})\text{Ag}(\text{PPh}_3)\text{Y}]$ . These have infrared spectra which are consistent with their formulation as  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{AgPPh}_3\}]\text{Y}$ . They decompose slowly in solution in a reaction which is accelerated and goes to completion when a second equivalent of  $\text{AgY}/n\text{PPh}_3$  is added. The products are silver metal and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]\text{Y}$  ( $\text{Y}^- = \text{BF}_4^-$  or  $\text{PF}_6^-$ ). Thus the overall oxidative cleavage of III by  $\text{AgY}$  is slowed but not otherwise changed by the presence of  $\text{PPh}_3$ .

When  $\text{PPh}_3$  and the  $\text{Ag}^+$  electrophile are reacted with III in the form of  $[\text{Ag}(\text{PPh}_3)_3\text{Cl}]$ , nothing happens until  $\text{KPF}_6$  is added. Then two adducts are slowly

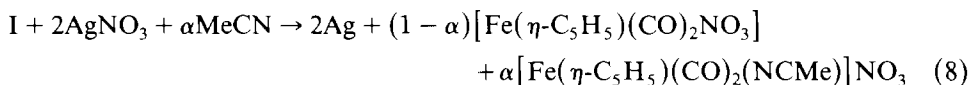


formed and may be isolated. [(III)AgPPh<sub>3</sub>]PF<sub>6</sub> can be recrystallized but [(III)<sub>2</sub>AgCl] is not sufficiently stable. If more [Ag(PPh<sub>3</sub>)<sub>3</sub>Cl]/KPF<sub>6</sub> is added to the reaction mixture the adducts break down with the quantitative precipitation of silver metal. [(III)AgPPh<sub>3</sub>] PF<sub>6</sub> gives [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)(CNMe)<sub>2</sub>]PF<sub>6</sub> whilst [(III)<sub>2</sub>AgCl] gives a mixture of III and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)(CNMe)Cl]. [{Ag(PPh<sub>3</sub>)Cl}<sub>4</sub>] fails to react with III in the absence of KPF<sub>6</sub> but in its presence it forms an adduct with an infrared spectrum similar to that of [(III)AgPPh<sub>3</sub>]PF<sub>6</sub> between 1600 and 2200 cm<sup>-1</sup> but it could not be identified unambiguously as it could not be isolated free of silver metal. Further addition of [{Ag(PPh<sub>3</sub>)Cl}<sub>4</sub>]/KPF<sub>6</sub> cleaved this adduct to give silver metal and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)(CNMe)<sub>2</sub>]PF<sub>6</sub>. In both cases the presence of PPh<sub>3</sub> greatly slows the oxidation of III but it does not change the products.

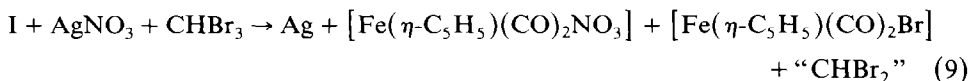
#### Reactions of I, II, and III in acetonitrile

In the absence of PPh<sub>3</sub> the reactions of various AgY with I, II or III in acetonitrile are complete in less than ca. 30 s with the quantitative precipitation of silver metal.

One equivalent of AgNO<sub>3</sub> cleaves half of I to a mixture of [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>NO<sub>3</sub>] and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(NCMe)]NO<sub>3</sub> whilst a second equivalent completes the oxidation according to eq. 8 where α ~ 0.1.

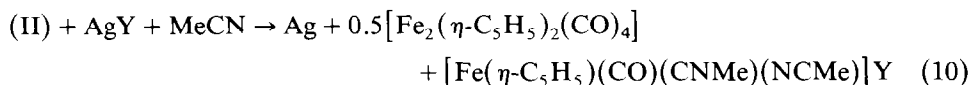


If O<sub>2</sub> is bubbled through the reaction mixture before the addition of AgNO<sub>3</sub>, the reaction is greatly slowed and requires > 5 h before it is complete. It is also slowed by the presence of PPh<sub>3</sub> and then three products are formed, [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>NO<sub>3</sub>], [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)]NO<sub>3</sub> and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(NCMe)]NO<sub>3</sub>. Furthermore, if I, AgNO<sub>3</sub> and CHBr<sub>3</sub> (mole ratio 1/1/1) are reacted, [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>NO<sub>3</sub>] and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Br] are formed quantitatively and in equal amounts as shown in eq. (9) although the fate of "CHBr<sub>2</sub>" has not been determined.



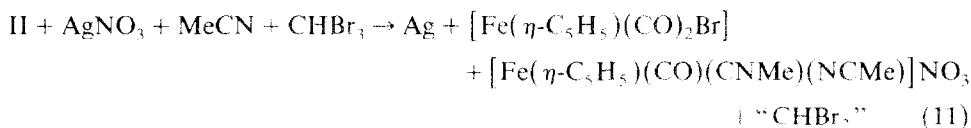
Two equivalents of AgBF<sub>4</sub> · 0.5C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> or AgPF<sub>6</sub> · 2C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> oxidise I completely to a mixture of [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]Y and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(CNMe)]Y with the product ratio depending to some extent on the anion Y<sup>-</sup> (= BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>). This reaction is again slowed by the presence of PPh<sub>3</sub> and the products changed to a mixture of [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)]BF<sub>4</sub>, [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>(NCMe)]BF<sub>4</sub> and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>]BF<sub>4</sub>.

One equivalent of AgY (Y<sup>-</sup> = NO<sub>3</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, or PF<sub>6</sub><sup>-</sup>) instantaneously oxidises all of II to a mixture of [Fe<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>4</sub>] and [Fe(η-C<sub>5</sub>H<sub>5</sub>)(CO)(CNMe)(NCMe)]Y (eq. 10).



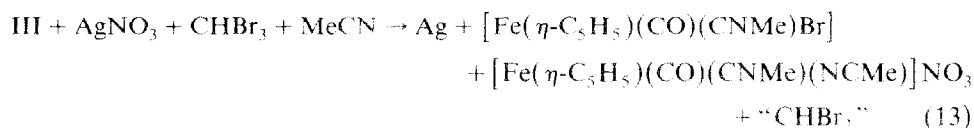
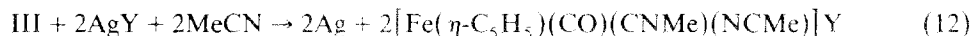
A second equivalent of AgY then oxidises the I as described above. The resulting product distribution is then the same as when the two equivalent are added together to one of II. If CHBr<sub>3</sub> is present in the solution of II prior to the addition of AgNO<sub>3</sub>

(mole ratio 1/1/1),  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Br}]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{NO}_3$  are formed in ca. equal amounts, (eq. 11).



The presence of tertiary phosphines does not noticeably slow these reactions but it does change the products. A single equivalent of  $\text{AgY}/\text{PR}_3$  oxidises only about half of II to give a mixture of the same three products as are obtained when  $2\text{AgY}/1\text{PR}_3$  oxidises all of II viz.  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{Y}$ ,  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)]\text{Y}$ . The yield of the first of these is always ca. 50% but the ratio of the other two depends on both  $\text{Y}^-$  and  $\text{PR}_3$ . Thus for  $\text{PPh}_3$  their yields are 15 and 10% respectively when  $\text{Y}^- = \text{BF}_4^-$  but 5 and 20% when  $\text{Y}^- = \text{NO}_3^-$ , whilst for  $\text{P}(\text{OPh})_3$  they are 5 and 30% when  $\text{Y}^- = \text{BF}_4^-$  but 0 and 30% when  $\text{Y}^- = \text{NO}_3^-$ . Larger amounts of  $\text{PR}_3$  do not appear to have any added effect.

One equivalent of  $\text{AgY}$  ( $\text{Y}^- = \text{NO}_3^-$  or  $\text{BF}_4^-$ ) instantaneously oxidises half of III to a single product,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{Y}$  whilst two equivalents complete the reaction (eq. 12). However in the presence of  $\text{CHBr}_3$ ,  $\text{AgNO}_3$  and III (mole ratio 1/1/1) give equimolar amounts of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{Br}]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{NO}_3$  (eq. 13)



The products of the reaction are not affected by the presence of free  $\text{PPh}_3$  or if  $[\{\text{Ag}(\text{PPh}_3)\text{Cl}\}_4]/\text{KPF}_6$  is the electrophile. However the rate is noticeably slowed in the last case.

In a reaction related to the others in this section,  $\text{AgNO}_3$  and a mixture of I and III (mole ratio 1/1/1) in acetonitrile gives a mixture of products which were identified as  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})][\text{NO}_3]$  (isolated yield 25%),  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3]$  (20%),  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  (12%) and  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{CNMe})]$  (7%).

To determine the lability of the coordinated acetonitrile ligand in the various products, solutions of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{Y}$  ( $\text{Y}^- = \text{NO}_3^-$  or  $\text{BF}_4^-$ ) were refluxed with  $\text{PPh}_3$ ,  $\text{PBu}_3^n$  or  $\text{PPhMe}_2$  in acetonitrile, tetrahydrofuran and dichloromethane. Even after several hours substitution of coordinated MeCN did not take place. This confirms that the products reported in this section are primary ones and are not formed by MeCN displacement from acetonitrile-containing precursors.

#### Mononuclear products

The  $[\text{Fe}^{\text{II}}(\eta\text{-C}_5\text{H}_5)\text{L}_n]$  products are all air-stable and most are crystalline solids. Those of the type  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Y}]$  or  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{Y}]$  are orange to brown in colour,  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NCMe})]\text{Y}$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{Y}$  are yellow to orange, and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)]\text{Y}$ .  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]\text{Y}$

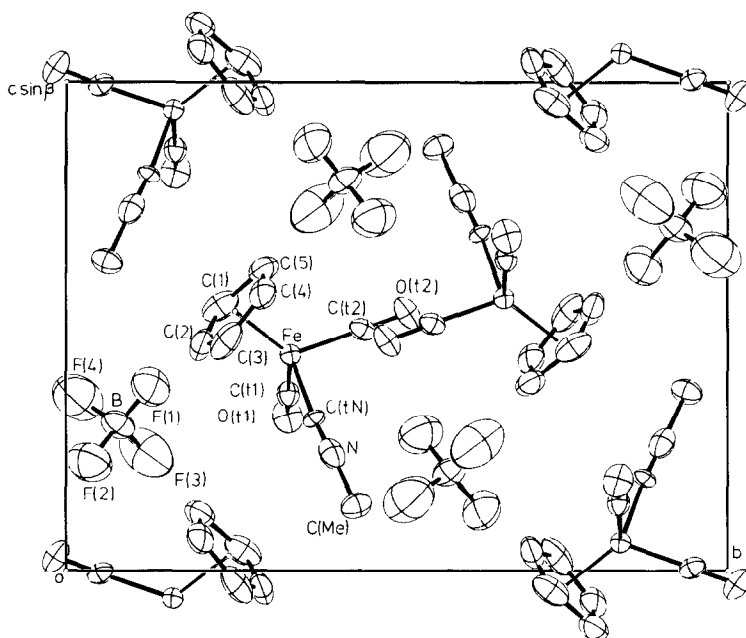


Fig. 1. The packing of the  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]^+$  and  $[\text{BF}_4]^-$  ions in the lattice together with the atom labelling scheme. Hydrogen atoms have been omitted for clarity and the thermal ellipsoids have been drawn to include 35% probability.

$\text{C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})\text{Y}$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]\text{Y}$  are yellow. The IR spectra show the appropriate absorption bands due to free or coordinated  $\text{Y}^-$ , to  $\text{Ph}_3\text{P}$ , and, most importantly, to the stretching vibrations of the CO, CNMe and NCMe ligands. These last are summarised in Table 4. Their frequencies and relative intensities are much as would be expected for these particular compounds and are fully consistent with the anticipated pseudooctahedral coordination about the iron atoms exemplified by  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$ .

*Structure of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$ .* Tan crystals of this compound were grown from dichloromethane solution and a suitable one subjected to an X-ray diffraction study. The structure is as anticipated with discrete tetrahedral  $\text{BF}_4^-$  anions and pseudo-octahedral  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]^+$  cations in which the cyclopentadienyl ring lies parallel to the face opposite that occupied by the three carbonyl/isocyanide carbon atoms. The packing of the ions in the lattice is illustrated in Fig. 1 together with the atom labelling scheme. There are three contacts  $< 3.0 \text{ \AA}$  between the cations and anions;  $\text{N} \cdots \text{F}(4)$  at  $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$  of  $2.92(2)$ ,  $\text{C}(4) \cdots \text{F}(3)$  at  $x - 1, \frac{1}{2} - y, \frac{1}{2} + z$  of  $2.93(2)$  and  $\text{O}(t2) \cdots \text{F}(2)$  at  $x, \frac{1}{2} - y, \frac{1}{2} + z$  of  $2.96 \text{ \AA}$ . The closest cation-cation contacts are from  $\text{O}(t1)$  to  $\text{O}(t2)$  at  $1 - x, 1 - y, 1 - z$  of  $3.13(1)$  and to  $\text{N}$  at  $1 + x, y, z$  of  $3.17(1) \text{ \AA}$ . The structure complements those reported previously for  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6$  [14] and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]\text{BF}_4$  [4] with comparable bond lengths and bond angles within the cation (Table 7).

(Continued on p. 370)

Table 4  
Melting points, analyses and IR spectra of the products from the oxidation of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_{4-n}(\text{CNMe})_n]$  ( $n = 0\text{--}2$ ) by  $\text{Ag}^+$  salts

Compound	M.p. (°C) <sup>a</sup>	Analyses (%) <sup>b</sup>				IR spectra <sup>c</sup>	
		C	H	N			
$\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cl}$	94–96	39.2 (39.6)	2.5 (2.4)	–	2059 (10)	2016 (9.4)	
$\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Br}$	82–83	32.8 (32.7)	2.3 (2.0)	–	2052 (10)	2010 (9.3)	
$\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{NO}_3$	92–93	34.9 (35.2)	2.0 (2.1)	5.8 (5.8)	2069 (10)	2026 (9.8)	
$\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{Cl}^d$	72–73	41.9 (42.6)	3.5 (3.6)	5.7 (6.2)	2193 (9.0) <sup>e</sup>	1995 (10)	
$\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{Br}^d$	102–103	35.6 (35.6)	3.0 (3.0)	5.0 (5.2)	2190 (9.4) <sup>e</sup>	1994 (10)	
$\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3$	102–104	37.4 (38.1)	3.5 (3.2)	11.1 (11.1)	2198 (8.8) <sup>e</sup>	2004 (10)	
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4^d$	dec.230	32.5 (32.9)	1.9 (1.7)	–	2124 (7.8)	2074 (10)	
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]\text{PF}_6^d$	dec.235	27.1 (27.4)	1.5 (1.4)	–	2126 (8.7)	2074 (10)	
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{PPh}_3)]\text{NO}_3$	166–168	60.1 (59.9)	4.0 (4.0)	2.5 (2.8)	2059 (9.9)	2013 (10)	
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{PPh}_3)]\text{BF}_4$	238(dec)	56.5 (57.0)	3.8 (3.8)	–	2057 (9.7)	2014 (10)	
$[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3(\text{PPh}_3)]\text{PF}_6$	227(dec)	51.7	3.5	–	2061 (9.9)	2014 (10)	

[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (NCMe)]NO <sub>3</sub> <sup>d</sup>	94–97	(51.3)	(3.4)	10.5	2015 (10)	2069 (10)	2230 (8.1) <sup>e</sup>
		38.3	3.0	(10.1)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (NCMe)]BF <sub>4</sub> <sup>d</sup>	96–97	(38.6)	(2.9)	4.4	2018 (10)	2069 (10)	
		34.7	2.9	(4.5)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (NCMe)]PF <sub>6</sub> <sup>d</sup>	95	(35.4)	(2.6)	3.7	2018 (10)	2068 (9.2)	
		29.2	2.3	(3.9)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (CNMe)]BF <sub>4</sub> <sup>d</sup>	108–110	(29.7)	(2.2)	4.6	2019 (10)	2064 (9.7)	2207 (7.1) <sup>e</sup>
		34.9	2.5	(4.5)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO) <sub>2</sub> (CNMe)]PF <sub>6</sub>	141–142	(29.4)	(2.6)	3.9	2011 (9.5)	2043 (10)	2203 (8.1) <sup>e</sup>
		29.4	2.1	(3.9)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO)(NCMe)(CNMe)]NO <sub>3</sub>	124–126	(29.7)	(2.2)	14.2	2019 (10)	2069 (1) <sup>f</sup>	2217 (9.3) <sup>e</sup>
		41.1	3.6	(14.3)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO)(NCMe)(CNMe)]BF <sub>4</sub>	184–187	(41.0)	(3.7)	8.5	2010 (10)	2067 (1) <sup>f</sup>	2203 (8.1) <sup>e</sup>
		36.8	3.7	(8.8)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO)(NCMe)(CNMe)]PF <sub>6</sub>	165–168	(37.8)	(3.5)	7.7	2020 (10)	2068 (1) <sup>f</sup>	2210 (9.2) <sup>e</sup>
		32.0	3.1	(7.5)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO)(CNMe) <sub>2</sub> ]BF <sub>4</sub>	dec. 160	(32.0)	(2.9)	8.7	2023 (10)	2207 (9.7) <sup>e</sup>	2228 (9.5) <sup>e</sup>
		37.3	3.6	(8.8)			
[Fe( $\eta$ -C <sub>5</sub> H <sub>5</sub> )(CO)(CNMe) <sub>2</sub> ]PF <sub>6</sub> <sup>d</sup>	dec. 155	(37.8)	(3.5)	7.3	2005 (10)	2205 (9.6) <sup>e</sup>	2224 (9.7) <sup>e</sup>
		31.8	3.0	(7.5)			
		(32.0)	(2.9)				

<sup>a</sup> Determined in sealed tubes. (dec) = melts with decomposition. <sup>b</sup> Calculated values in parentheses. <sup>c</sup> Peak positions (cm<sup>-1</sup>) with relative peak heights in parentheses. Determined in chloroform solution unless it is stated otherwise. <sup>d</sup> IR spectra determined in KBr discs. <sup>e</sup>  $\nu$ (C–NMe) modes. <sup>f</sup>  $\nu$ (N–CMe) modes.

### Adducts of II and III with AgY

Adducts of II with AgY could not be isolated. If they were formed it would be expected that their infrared spectra in the 1600–2100  $\text{cm}^{-1}$  region would show absorption bands with frequencies similar to those observed for related, well-characterised  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{E}\}]$  adducts e.g. for  $\text{E} = \text{Me}^+ \text{I}^-$  in chloroform solution,  $\nu(\text{CO})$  2023 (10) and 1989 (1.7),  $\nu(\mu\text{-CO})$  1827–1840 (2.1) and  $\nu(\mu\text{-C=N})$  1599 (1.7)  $\text{cm}^{-1}$  with relative peak heights in parentheses [13]. When IR spectra are run of the various II/AgY reaction mixtures it is possible to detect in some cases absorption bands at ca. 2000, 1820, and 1600  $\text{cm}^{-1}$ . However the species responsible for them are very unstable and decompose rapidly to the cleavage products (Table 2) and II. Consequently it is very likely that these unstable intermediates are adducts where  $\text{E} = \text{AgY}$ , but we cannot prove it.

A number of adducts of III with AgY have been isolated. All have been characterised by elemental analysis (for C, H and N only) and IR spectra (Table 5), and their slow or very slow decomposition to give metallic silver show that they contain silver. The  $^1\text{H}$  NMR spectra of two have also been obtained. Repeated attempts have been made to grow crystals of them but they have not been successful. However, the data that has been obtained (Table 5) points unambiguously to them being of the type  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{E}\}]$  where  $\text{E} = \text{AgNO}_3$ ,  $\text{AgPPh}_3^+ \text{BF}_4^-$ ,  $0.5\text{AgNO}_3$  or  $0.5\text{AgCl}$  with the  $\mu\text{-CNMe}$  ligand of III acting as a ligand to linearly coordinated  $\text{Ag}^I$  via  $\text{N} \rightarrow \text{Ag}^I$  or  $\text{N} \rightarrow \text{Ag}^I \leftarrow \text{N}$  bonds. The IR spectra of those silver adducts between 1550 and 2200  $\text{cm}^{-1}$  are very similar to those of well-characterised adducts derived from III such as  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})(\mu\text{-CNMe}_2)]$  [13] which is included in Table 5. They show absorption bands at ca. 1570–1600, 1795–1820, 1965–1985 and 2180–2190  $\text{cm}^{-1}$  due to the C–N or C–O stretching vibrations of the  $\mu\text{-}\{\text{C=N}(\text{Me})\text{E}\}$ ,  $\mu\text{-CO}$ .

Table 5

Decomposition points, analysis and IR spectra of some adducts  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2(\text{E})]$  where the electrophile E is a  $\text{Ag}^I$  salt

E	Dec. pt. <sup>a</sup>	Analyses (%) <sup>b</sup>			IR spectra <sup>c</sup>			
		C	H	N				
$\text{AgNO}_3$	125–127	35.1 (35.0)	2.7 (2.9)	7.6 (7.6)	1577 (7.7)	1795 (3.9)	1971 (10)	2185 (9.4)
$\text{Ag}(\text{PPh}_3)\text{BF}_4$	160	48.7 (48.7)	3.6 (3.5)	3.1 (3.2)	1590 (7.5)	1808 (9.0)	1971 (10)	2180 (8.9)
$\text{Ag}(\text{PPh}_3)\text{PF}_6$	155	44.5 (45.4)	3.5 (3.4)	3.0 (3.1)	1594 (7.2)	1813 (9.4)	1982 (10)	2183 (9.3)
$0.5\text{AgNO}_3$	167	41.2 (41.3)	3.5 (3.4)	8.0 (7.5)	1582 (7.8)	1803 (9.8)	1980 (10)	2194 (9.1)
$0.5\text{AgCl}$	131	42.1 (42.5)	3.9 (3.5)	6.0 (6.2)	1511 (8.0)	1537sh	1809 (9.4)	1972 (10) 2181 (8.8)
$\text{MeI}^d$	–	–	–	–	1590 (4.5)	1806 (5.8)	1984 (10)	2173 (8.6) 1821sh 2011sh 2196sh

<sup>a</sup> Decomposition points in  $^\circ\text{C}$ . Determined in sealed tubes. <sup>b</sup> Calculated values in parentheses. <sup>c</sup> Absorption bands between 1500 and 2200  $\text{cm}^{-1}$  only. Peak positions ( $\text{cm}^{-1}$ ) with relative peak heights in parentheses. Determined in KBr discs unless it is stated otherwise. For assignment see text. <sup>d</sup>  $\text{CHCl}_3$  solution. Taken from ref. 13.

Table 6

Final atomic coordinates (fractional  $\times 10^4$ ) for non-hydrogen atoms with estimated standard deviations in parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Fe	2039(2)	3383(1)	4425(1)
C(t1)	4139(13)	3357(6)	3614(9)
O(t1)	5503(11)	3346(5)	3154(8)
C(t2)	2437(14)	4472(7)	4942(8)
O(t2)	2642(11)	5153(5)	5285(7)
C(tN)	373(14)	3745(6)	3107(8)
N	-468(15)	4012(6)	2390(10)
C(Me)	-1782(16)	4386(8)	1331(10)
C(1)	3053(20)	2332(11)	5407(14)
C(2)	1808(28)	2042(8)	4627(14)
C(3)	11(21)	2417(10)	4706(16)
C(4)	187(26)	2973(8)	5660(14)
C(5)	2174(24)	2978(9)	6162(11)
B	6647(25)	785(12)	2979(15)
F(1)	5992(16)	1281(7)	3756(10)
F(2)	5537(18)	357(8)	2217(10)
F(3)	7933(23)	1213(11)	2405(14)
F(4)	7662(25)	182(11)	3537(14)

CO and CNMe ligands respectively. The lowering of the frequency of the  $\nu(\text{C}=\text{N}_\mu)$  vibration on adduct formation and the concomitant rise in the frequencies of the remaining  $\nu(\text{CO}_\mu)$ ,  $\nu(\text{CO})$  or  $\nu(\text{CNMe})$  modes is characteristic [13]. It indicates that

Table 7

Bond lengths (Å) and angles ( $^\circ$ ) with estimated standard deviations in parentheses <sup>a</sup>

Fe–C(t1)	1.796(9)	Fe–C(tN)	1.900(9)
Fe–C(t2)	1.796(10)	Fe··Cp	1.717
C(t1)–O(t1)	1.123(11)	C(1)–C(2)	1.266(20)
C(t2)–O(t2)	1.127(11)	C(2)–C(3)	1.381(20)
C(tN)–N	1.047(13)	C(3)–C(4)	1.389(21)
N–C(Me)	1.560(16)	C(4)–C(5)	1.440(20)
		C(5)–C(1)	1.489(21)
B–F(1)	1.290(17)	B–F(3)	1.331(20)
B–F(2)	1.291(18)	B–F(4)	1.298(21)
C(t1)–Fe–C(t2)	95.0(4)	C(t1)–Fe–Cp	122.6
C(t1)–Fe–C(tN)	93.0(4)	C(t2)–Fe–Cp	122.9
C(t2)–Fe–C(tN)	93.0(4)	C(tN)–Fe–Cp	122.3
Fe–C(t1)–O(t1)	176.9(10)	Fe–C(tN)–N	173.6(10)
Fe–C(t2)–O(t2)	178.0(9)	C(tN)–N–C(Me)	177.9(11)
C(5)–C(1)–C(2)	111.2(13)	F(1)–B–F(2)	123.3(15)
C(1)–C(2)–C(3)	111.2(15)	F(1)–B–F(3)	110.0(15)
C(2)–C(3)–C(4)	107.3(15)	F(1)–B–F(4)	107.0(15)
C(3)–C(4)–C(5)	109.3(13)	F(2)–B–F(3)	107.5(15)
C(4)–C(5)–C(1)	100.9(11)	F(2)–B–F(4)	103.2(16)
		F(3)–B–F(4)	104.2(16)

<sup>a</sup> Cp is the centroid of the cyclopentadienyl ring.

the  $\mu$ -CN(Me)E ligands are more effective  $\pi$ -acceptors than  $\mu$ -CNMe. The spectra, where appropriate, also show absorption bands due to the nitrate group at  $1320\text{ cm}^{-1}$ , the free  $\text{BF}_4^-$  ion at ca.  $1070\text{ cm}^{-1}$ , the  $\text{PF}_6^-$  ion at ca.  $550$  and  $840\text{ cm}^{-1}$ , and the coordinated  $\text{Ph}_3\text{P}$  ligand. It is noticeable that the spectrum of  $(\text{III})_2\text{AgCl}$  does not show an absorption band due to  $\nu(\text{Ag}-\text{Cl})$  which suggests that it is best formulated as  $[(\text{III})_2\text{Ag}]^+\text{Cl}^-$ . Absorption bands due to  $\nu(\text{Ag}-\text{N})$  modes have not been detected. This is not surprising as they would be expected to be weak and to occur in a region of the spectrum at ca.  $400\text{ cm}^{-1}$  which is already crowded.

Satisfactory and reproducible  $^1\text{H}$  NMR spectra of these adducts of III have proved very difficult to obtain due to their low solubility and their slow breakdown with the precipitation of silver metal. One exception is that of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN(Me)AgNO}_3\}]$  in  $(\text{CD}_3)_2\text{SO}$  solution which shows singlets at 5.27 (5), 5.16 (5), 3.97 (3) and 3.18 (3) ppm downfield from  $\text{Me}_4\text{Si}$ , their integrated intensities are given in parentheses. They are assigned respectively to the protons of the two different cyclopentadienyl groups, the  $\mu\text{-}\{\text{CN(Me)AgNO}_3\}$  and the terminal CNMe ligand. The other is that of  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN(Me)AgPPh}_3\}][\text{PF}_6^-]$  in  $\text{CD}_3\text{CN}$  solution where the analogous resonances are found at 5.15 (5), 5.0 (5), 4.15 (3) and 3.21 (3) ppm with a broad resonance due to the  $\text{Ph}_3\text{P}$  protons at 7.61 ppm [15]. These compare with the values of 5.26 (5), 5.20 (5), 4.42 (3) and 4.35 (3), and 3.23 (3) ppm for  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CNMe}_2\}]\text{I}$  with the resonances at 4.42 and 4.35 ppm due to the two different methyl groups of the  $\mu\text{-}\{\text{CNMe}_2\}$  ligand [13].

The spectra of these adducts are consistent in general terms with the proposed structures. However isomers are possible and insufficient data is available to determine which are present. The  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\mu\text{-L})_2(\text{L})_2]$  moiety ( $\text{L} = \text{CO}$  or CNMe) may exist in either *cis* or *trans* forms. Furthermore, the  $\text{Fe}_2\{\mu\text{-CN(Me)AgY}\}$  fragment would be expected to be planar (cf. ref. 13) and so the AgY group could be either *syn* or *anti* with respect to the terminal CNMe ligand. This is illustrated in Fig. 2 where *syn* and *anti* forms of the *cis* isomer are shown.

#### Mechanism of the reactions in solvents other than acetonitrile

In solvents such as tetrahydrofuran, benzene, chloroform, etc., one mole of I, II or III is oxidatively cleaved completely by two moles of AgY salts. One mole of

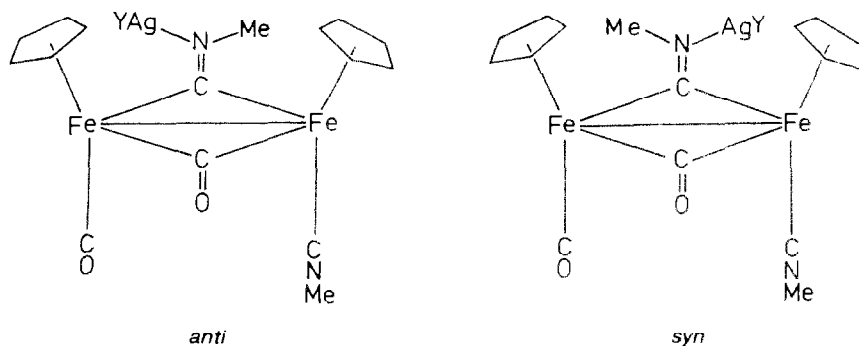
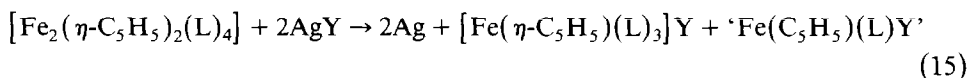
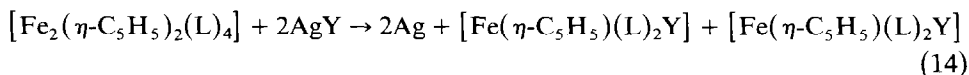


Fig. 2. The *syn* and *anti* forms of the *cis* isomers of the  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN(Me)AgY}\}]$  adducts.



AgY oxidises only half of the dimer. The course or rate of the reactions are not affected greatly by the presence of radical traps such as  $\text{CHBr}_3$ ,  $\text{CHCl}_3$  or  $\text{O}_2$ . These observations tend to rule out a reaction mechanism involving two discrete one-electron steps as is observed in acetonitrile (see below) and suggest that the two  $\text{Ag}^+$  ions act together as a two-electron oxidant.

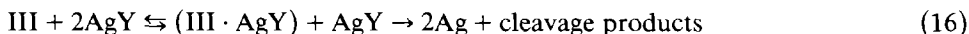
These two-electron processes can take one of two courses as shown in eqs. 14 and 15.



(L = CO or CNMe)

Examples of reactions which take the first route are given in eqs. 1, 3, and 6 whilst those which take the second are given in eqs. 2, 5 or 7. Spectroscopic studies and the weights of silver metal precipitated suggests both types of reaction are quantitative or close to it even though the yields of isolated pure products are often low and the fate of the " $\text{Fe}(\text{C}_5\text{H}_5)(\text{L})\text{Y}$ " fragment has never been determined. In general when  $\text{Y}^-$  is a coordinating anion such as  $\text{NO}_3^-$  the oxidation proceeds as in eq. 14 but when  $\text{Y}^-$  is the non-coordinating  $\text{BF}_4^-$  or  $\text{PF}_6^-$  it follows eq. 15.

It is quite easy to see how two AgY could act together as a two-electron oxidant in their reactions with III. This substrate reversibly forms stable, isolable 1:1 adducts with one AgY. These can then be attacked irreversibly by a second mole of AgY with overall oxidation of III and the precipitation of silver metal (eq. 16).

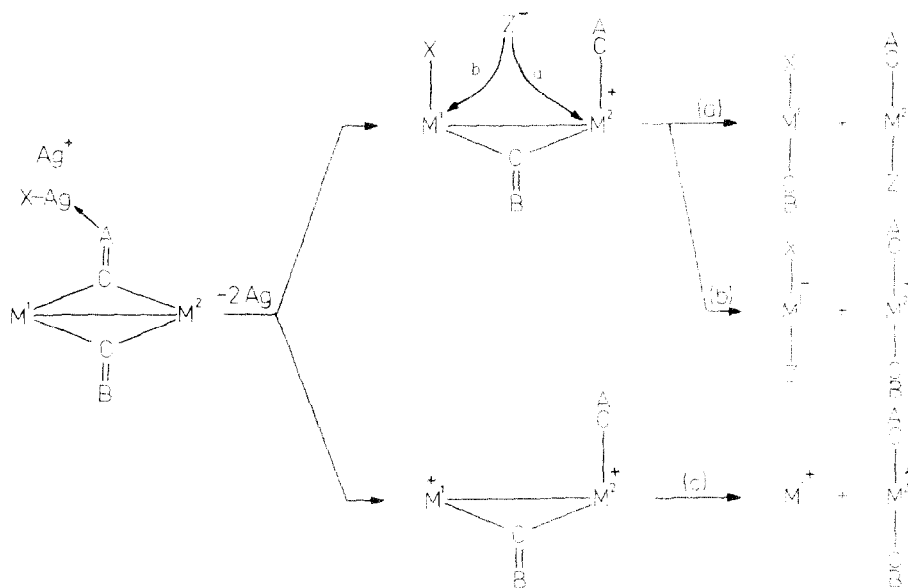


It is reasonable to assume that a similar pair of reactions take place for I and II. Even though the adducts of II with AgY are unstable and those of I have not been observed, both form stable adducts with suitable electrophiles [15].

Previously it has been suggested that the two-electron cleavage of various substrates such as I, II and III proceeds by way of the adducts through various intermediates to the final products [16]. In the present case this would be as shown in Scheme 1 with CA and CB being CO for I, and CNMe and CO, respectively, for II and III.

Furthermore it was argued in ref. 16 that route (a) in Scheme 1 (which gives products corresponding to those in eq. 14) would be favoured if  $\text{X}^-$  and  $\text{Z}^-$  were relatively good nucleophiles, otherwise route (b) and/or (c) (which give products corresponding to those in eq. 15) would be preferred. This is supported by the present work.

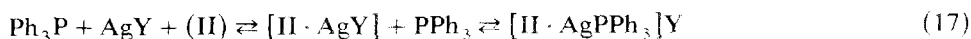
Following the rules laid out in ref. 16 for the further reaction of the adduct ( $\text{III} \cdot \text{AgX}$ ), its breakdown to the neutral product  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{X}]$  must take place through an isomer in which AgX is *syn* to t-CNMe (*syn* form in Fig. 2), but the formation of the salt  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]\text{X}$  can only take place through the *anti* isomer (Fig. 2). We do not know why this should be so, but it is commonly observed [17]. The only significant exception is the reaction of III with  $\text{HgY}_2$  which gives  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{HgY}]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CNMe})_2\text{Y}]$  ( $\text{Y} = \text{Cl}, \text{Br}$



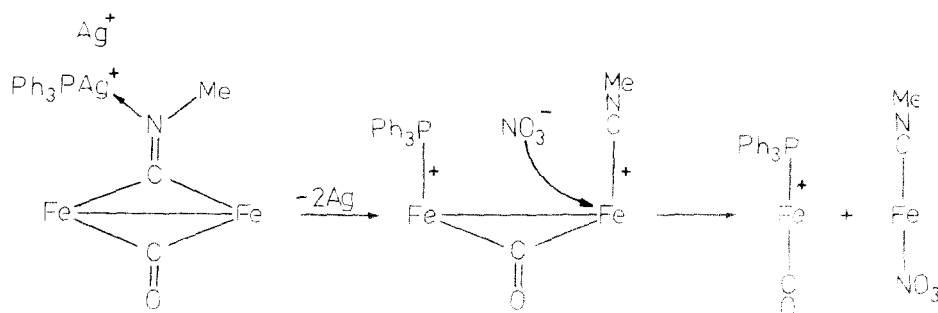
Scheme 1

or I) with the two CNMe ligands coordinated to the same metal atom in a neutral product rather than a cation.

The proposed mechanism also accounts satisfactorily for the effects of  $\text{Ph}_3\text{P}$  on the reactions of II provided it is assumed that there are two adducts present in the solution which are in equilibrium with  $\text{Ph}_3\text{P}/\text{AgY}$  (eq. 17).



For the reaction of II with  $\text{Ph}_3\text{P}/\text{AgNO}_3$  the situation is clear-cut in that it proceeds entirely through  $[\text{II} \cdot \text{AgPPh}_3]\text{NO}_3$ .  $\text{Ph}_3\text{P}$  plays the role of  $\text{X}^-$  (Scheme 1) and ends up coordinated to a different Fe atom than does the CA ligand, CNMe. Furthermore, it is also clear that  $\text{Ph}_3\text{P}$  does not act as the ligand  $\text{Z}^-$  as  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{PPh}_3]\text{NO}_3$  was not formed. Instead  $\text{NO}_3^-$  is preferred (Scheme 2).



Scheme 2

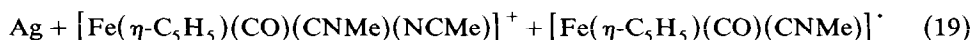
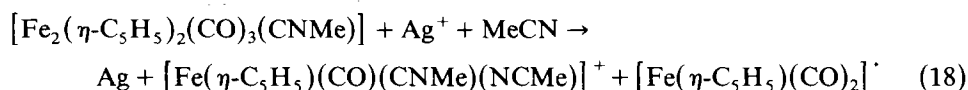
The formation of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)]\text{BF}_4$  but not  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{PPh}_3)]\text{BF}_4$  from the reaction of II with  $\text{Ph}_3\text{P}/\text{AgBF}_4$  shows that here also  $\text{Ph}_3\text{P}$  can act in place of  $\text{X}^-$  but not  $\text{Z}^-$  (Scheme 1). The adduct can break down to either of the observed products (Scheme 1) although  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNMe})]\text{BF}_4$  may arise as shown in Scheme 1.

Similar arguments may be applied to the other reactions carried out in the presence of  $\text{Ph}_3\text{P}$ . However, it should be remembered that the actual products obtained will depend not only on the relative importances of the adducts but also on the rates at which they break down. The presence of  $\text{Ph}_3\text{P}$  slows the rates of oxidation of I–III with  $\text{AgY}$ . This may be correlated with the ability of  $\text{Ph}_3\text{P}$  to stabilize the adducts of III.

#### *Course of the reactions in acetonitrile*

The most obvious consequence of carrying out the reactions of I–III with  $\text{AgY}$  in acetonitrile is that they are much faster than in e.g. tetrahydrofuran, benzene, chloroform etc. Furthermore no adducts can be detected even for III. Similar results were obtained using  $\text{MeNO}_2$  or  $\text{PhCN}$  as solvents, but the reactions were generally slower. This was not pursued.

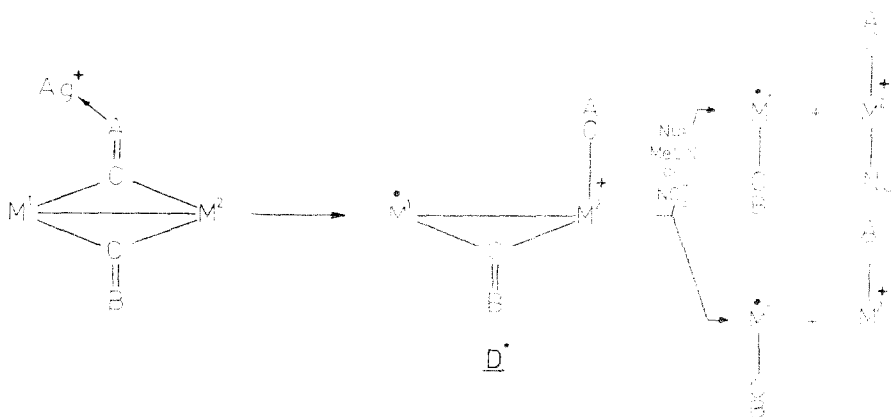
The results are consistent with a reaction mechanism whereby both II and III are oxidatively cleaved in two 1-electron steps. The first of these are shown in eqs. 18 and 19. It is virtually regiospecific for II.



The subsequent fate of the  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2]^\cdot$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})]^\cdot$  radicals depends on circumstances. In the presence of  $\text{CHBr}_3$  they are respectively converted to  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Br}]$  and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{Br}]$ , but in the absence of a suitable radical trap they dimerise to  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$  and  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$  respectively.

We suggested previously that the reactions proceed by way of 1 : 1 adducts which break down by homolysis of the  $\text{Ag-N}$  bond to leave a radical cation  $\mathbf{D}^\cdot$  (Scheme 3) [5]. The subsequent cleavage of  $\mathbf{D}^\cdot$  is either a consequence of attack at the positively charged atom by e.g.  $\text{MeCN}$  or  $\text{NO}_3^-$  to give an 18e mononuclear cation and the 17e radical, or it is spontaneous to give a 16e cation which reacts further. Although we are not completely convinced that this is a realistic description of the reaction mechanism, it has the merit that it explains why the  $\text{MeNC}$  ligand II ends up in the cationic product rather than the radical.

The effects of bromoform and oxygen on the reactions of I with  $\text{AgNO}_3$  in acetonitrile point to a radical process comparable with that for II and III. However, whereas the nucleophile  $\text{Nu}$  which coordinates to the  $\text{Fe}^+$  centre is  $\text{MeCN}$  and not  $\text{NO}_3^-$  for II and III, for I  $\text{NO}_3^-$  is favoured over  $\text{MeCN}$  but not overwhelmingly so. This may be a consequence of the other ligands coordinated to  $\text{Fe}^+$  which are the same for II and III but different for I.



Scheme 3

On the other hand the reactions of I with  $\text{AgBF}_4$  or  $\text{AgPF}_6$  give largely  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3]^+$  salts and only small amounts of  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{NCMe})]^+$ . Although the former may be formed in one-electron processes, they are products typical of a two-electron oxidation whereas the latter could be formed in either of the reaction III with  $\text{AgBF}_4$  which gives  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{NCMe})_2]\text{BF}_4$  by a two-electron process in tetrahydrofuran and  $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{NCMe})(\text{NCMe})]\text{BF}_4$  by a one-electron process in acetonitrile.

The addition of tertiary phosphines slows the reactions of  $\text{AgY}$  with I and II but not III. The products obtained suggest that III continues to react by a one-electron process but for both I and II two-electron process have become more important. This is most clearly seen for II which with one equivalent of  $\text{AgNO}_3/\text{Ph}_3\text{P}$  gives very little  $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_4]$ , the product which is indicative of a one-electron process, whilst only ca. half of II is consumed.

It may be relevant that the importance of the one-electron over the two-electron process in acetonitrile solution should increase along the series  $\text{I} < \text{II} < \text{III}$ . The parallels, the increasing basicity of the  $\mu\text{-CA}$  ligand and the stability of the adducts derived from these substrates.

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