Silver(I) Salts as One-electron or Two-electron Oxidants in their Reactions with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ Derivatives (n = 0—2). The Effect of Varying the Reaction Solvent

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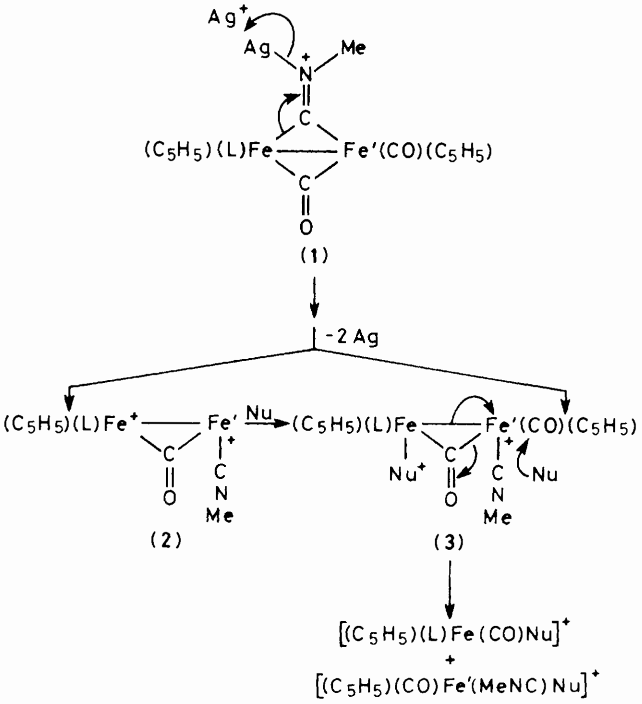
In tetrahydrofuran $AgNO_3$ acts as a two-electron oxidant and cleaves $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ to give a mixture of $[Fe(\eta\text{-}C_5H_5)(CO)_2NO_3]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$ *via* a detectable adduct, but in acetonitrile it acts as a one-electron oxidant to give $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)(NCMe)]NO_3$ and the $[Fe(\eta\text{-}C_5H_5)(CO)_2]^{\cdot}$ radical which then dimerises or reacts with added radical traps.

Silver(I) salts are widely employed as oxidants in organometallic chemistry. For example two moles of them will cleave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ to mononuclear species containing the $[Fe(\eta\text{-}C_5H_5)(CO)_2]^+$ moiety, although it is not clear whether they act as one- or two-electron oxidants.[1] It is of relevance to this particular problem that, in tetrahydrofuran, $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ and $AgNO_3$ (mole ratio 1:1) give an adduct which is formulated as $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}CO)\{\mu\text{-}CN(Me)Ag\}]^+$,[2] and which decomposes slowly on standing to a mixture of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$ but reacts rapidly with a further equivalent of $AgNO_3$ to give a quantitative yield of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$. Silver metal is deposited in both instances. This suggests that the cleavage of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$ is a two-electron process, and may be rationalized in the same way as other reactions of these dimers with electrophiles.[3] This is shown in Scheme 1 (L = CNMe).

The structure illustrated for the adduct (**1**) is one of a number of reasonable possibilities which may have been chosen. It is similar to that found in the related adduct (Me^+ replacing Ag^+)† $[Fe_2(\eta\text{-}MeC_5H_4)_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)]I$ where the ligand dimensions are consistent with the presence of a μ-iminium ion, $\mu\text{-}C{=}^{+}NMe_2$.[4] Nu is a nucleophile and we have used the same one to bring about both the (**2**) → (**3**) and the (**3**) → products reactions, but this need not necessarily be the case. In the present instance they may be $[NO_3]^-$ or tetrahydrofuran which is replaced subsequently by $[NO_3]^-$. The conversion of the adduct (**1**) into the intermediate (**3**) may not proceed *via* another intermediate (**2**), but may be direct and induced by attack of Nu on Fe in (**1**).



Scheme 1. L = CO or CNMe.

A similar reaction is observed for $AgNO_3$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ in tetrahydrofuran (mole ratio 2:1) which gives two products, $[Fe(\eta\text{-}C_5H_5)(CO)_2NO_3]$ and $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)NO_3]$. A mechanism identical to that shown in Scheme 1 is proposed except that now L = CO.

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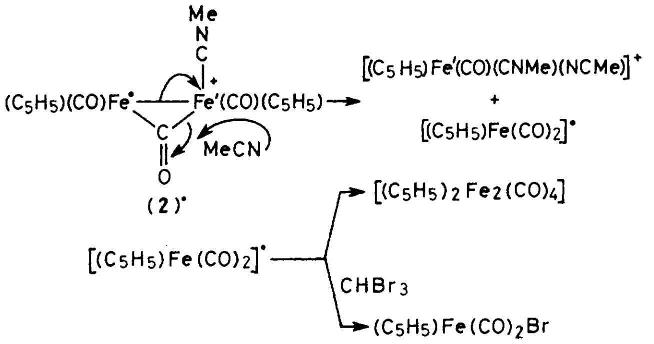
† The ν(C=N) frequencies in the Ag^+ and Me^+ adducts are very similar (refs. 2,4).



Scheme 2

In both of these reactions if only 1 equiv. of $AgNO_3$ is used the adducts slowly break down to the unchanged substrates and the usual cleavage products, *i.e.* the two-electron mechanism is retained.

On the other hand if the reaction between $AgNO_3$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ is carried out in acetonitrile solution (reactant mole ratio 1 : 1), it is virtually instantaneous. No adduct is observed, silver metal is precipitated in quantitative yield, and comparable amounts of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)(NCMe)]NO_3$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ are formed. We suspected that a one-electron oxidation was taking place with the formation of a cation and a radical, and so we repeated the reaction in the presence of $CHBr_3$ (reactant mole ratio 1 : 1 : 1). The formation of equal amounts of $[Fe(\eta\text{-}C_5H_5)(CO)(CNMe)(NCMe)]NO_3$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ but no $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ appears to confirm our suspicions. It is possible to explain these observations as is illustrated in Scheme 2. It is assumed that an adduct (**1**) has been formed but not detected, and that it breaks down by homolytic scission of the Ag–N bond. The subsequent nucleophilic attack on the radical–cation intermediate (**2**)• will be at the positive centre Fe.

Comparable results were obtained with $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(CNMe)_2]$.

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNMe)]$ with $AgNO_3$ in tetrahydrofuran or dichloromethane do not result in the formation of significant amounts of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$. They are not affected by the presence of $CHBr_3$.

These observations highlight the extreme importance of the solvent in the reactions of transition metal carbonyl, isocyanide, or related complexes with electrophiles. However it also indicates that acetonitrile is an unusual solvent which can bring about a quite fundamental change in the mechanism of these reactions.

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References

1 W. E. Williams and F. J. Lalor, *J. Chem. Soc., Dalton Trans.*, 1973, 1329.
2 A. R. Manning, R. Kumar, S. Willis, and F. S. Stephens, *Inorg. Chim. Acta*, 1968, **61**, 141.
3 A. R. Manning, unpublished work.
4 S. Willis, A. R. Manning, and F. S. Stephens, *J. Chem. Soc., Dalton Trans.*, 1980, 186.