

Preliminary communication

THE REACTION OF $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}]^+$ WITH Ag^{I} SALTS. ANION CONTROL OF THE REACTION PRODUCTS

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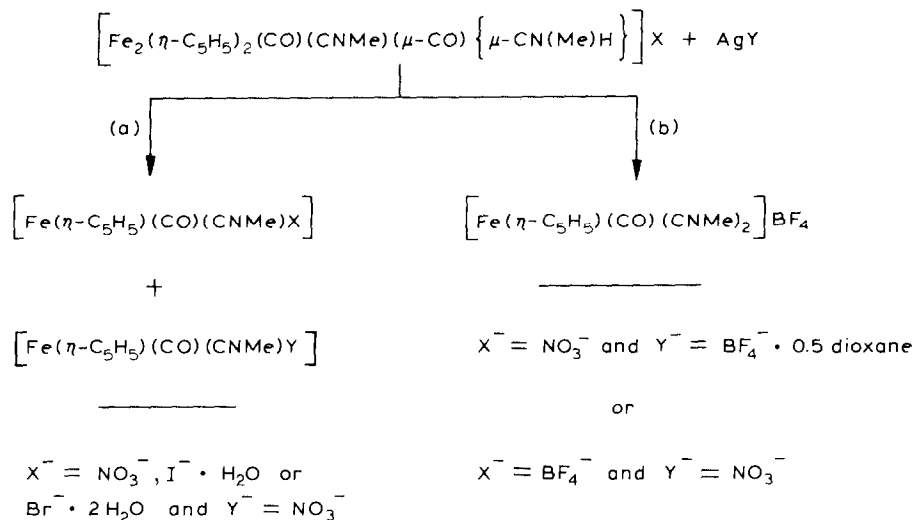
Summary

The reactions of equimolar amounts of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})\{\text{CN}(\text{Me})\text{H}\}]\text{X}$ and AgY in methanol results in a two-electron oxidation of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ to give $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]\text{BF}_4$ when either X^- or Y^- are the non-coordinating anion BF_4^- , but $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{X}]$ and $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{Y}]$ when both X^- and Y^- are potentially coordinating anions such as NO_3^- , Br^- or I^- .

We have reported previously that $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ reacts quantitatively with 2AgNO_3 in tetrahydrofuran. A two-electron oxidation gives $2[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})\text{NO}_3]$ via an isolable 1:1 adduct [1,2]. The IR spectrum of the adduct is consistent with it having a structure such as $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{AgNO}_3\}]$ [1].

To further our studies we have used one electrophile, H^+ , to convert $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ to a 1:1 adduct $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}]^+$ and a second, Ag^+ , to complete the oxidation. The red $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})(\text{CNMe})(\mu\text{-CO})\{\mu\text{-CN}(\text{Me})\text{H}\}]\text{X}$ salts have been prepared from $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ by a number of routes. (i) The direct reaction with one equivalent of $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$ gave the salt where $\text{X}^- = p\text{-MeC}_6\text{H}_4\text{SO}_3\cdot\text{H}_2\text{O}^-$ which was not isolated but used in situ. (ii) The reaction with one mole of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2\{\mu\text{-CN}(\text{Me})\text{H}\}_2][\text{X}]_2$ in methanol followed by partial removal of the solvent at reduced pressure gave those salts where $\text{X}^- = \text{BF}_4^-$ or PF_6^- in 25% yield. (iii) The reaction with one equivalent of $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]\text{PF}_6$ in dichloromethane or ether solutions at 20°C gave the salt where $\text{X}^- = \text{PF}_6^-$ as a bright red precipitate in 60% yield. (iv) $\text{NiX}_2\cdot n\text{H}_2\text{O}$ in ether at -10°C followed by the recrystallization of the initial products from acetone ether mixtures at 20°C gave the salts where $\text{X}^- = \text{Br}^- \cdot 2\text{H}_2\text{O}$, $\text{I}^- \cdot \text{H}_2\text{O}$, and $\text{NO}_3^- \cdot 0.5\text{H}_2\text{O}$. The subsequent reaction

of these salts with one equivalent of AgY in methanol results in the precipitation of silver and, overall, a two-electron oxidative cleavage of the Fe—Fe bond of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ with H^+ and Ag^+ acting together as the oxidant. However, the reaction products depend critically on the nature of the counteranions present (Scheme 1).



N.B. H_2O or dioxane is not incorporated into the final products

SCHEME 1

When both X^- and Y^- are coordinating anions such as NO_3^- , Br^- or I^- , the four CO/CNMe ligands of $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{CNMe})_2]$ are shared equally between the Fe atoms of the two mononuclear products (route a) (Scheme 1). However, if either X^- or Y^- are the non-coordinating anion BF_4^- (or PF_6^-), the only isolated product is the BF_4^- (or PF_6^-) salt of the $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})_2]^+$ cation (route b), but the fate of the ' $\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})^+$ ' fragment is unknown. When $\text{X}^- = p\text{-MeC}_6\text{H}_4\text{SO}_3^-$ and $\text{Y}^- = \text{NO}_3^-$, products from both (a) and (b) are formed.

If methanol is replaced by acetonitrile, which is potentially a good ligand, the only products are $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{CNMe})(\text{NCMe})]^+$ salts irrespective of the nature of X^- and Y^- .

In all of the reactions silver is precipitated virtually quantitatively, but we have obtained no information on the fate of the H^+ electrophile which does not seem to be lost as H_2 .

References

- 1 A.R. Manning, R. Kumar, S. Willis and F.S. Stephens, *Inorg. Chim. Acta*, **61** (1982) 141.
- 2 B. Callan and A.R. Manning, *J. Chem. Soc., Chem. Commun.*, (1983) 263.