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Preliminary communication

THE OXIDATIVE CLEAVAGE OF $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ BY STRONG ACIDS IN ACETONITRILE SOLUTION

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Summary

In acetonitrile solution and the absence of O_2, strong acids HX cleave $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ instantaneously to $[Fe(\eta\text{-}C_5H_5)(CO)_2(NCMe)]X$, $Fe(\eta\text{-}C_5H_5)(CO)_2X]$ or a mixture of the two. The reaction does not take place in solvents such as dichloromethane, tetrahydrofuran or methanol, or with weaker acids having pK_a (in water) $>$ ca. 1.

We have recently shown that the oxidative cleavage of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ by silver(I) salts proceeds via a two-electron mechanism in most solvents, e.g. tetrahydrofuran, but by a one-electron process in acetonitrile [1]. Here we report another example of the unexpected consequences of using this solvent for reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with electrophiles (or oxidising agents). Thus with strong acids in the absence of O_2 at room temperature it cleaves instantaneously to give high yields of $[Fe(\eta\text{-}C_5H_5)(CO)_2L]^+$ species where L is a solvent molecule, MeCN, or the acid anion. Typically $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ (1 g) reacts with 2.4 mol of $4\text{-}MeC_6H_4SO_3H$ to give the CH_2Cl_2-insoluble $[Fe(4\text{-}MeC_6H_4SO_3)_2 \cdot 4H_2O]$ and the CH_2Cl_2-soluble but C_6H_6-insoluble $[Fe(\eta\text{-}C_5H_5)(CO)_2(NCMe)][4\text{-}MeC_6H_4SO_3]$. The first of these contains 14% of the iron used, whilst the remainder is found in the second although the final yield of this when purified is only 57%. Gaseous HCl, on the other hand, gives a mixture of $[Fe(\eta\text{-}C_5H_5)(CO)_2Cl]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2(NCMe)]Cl$ together with a white crystalline solid which analyses as $HCl \cdot 2MeCN \cdot 2H_2O$.

Other strong acids bring out a similar reaction, e.g. concentrated sulphuric and nitric acids, gaseous HCl, 40% aqueous HBF_4, 65% HPF_6, picric acid, and CCl_3CO_2H which have pK_a (in water) $<$ ca. 1. Weaker acids, with $pK_a >$ ca. 1, are not effective e.g. CH_2ClCO_2H, $MeCO_2H$, $PhCO_2H$ or $\{CO_2H\}_2 \cdot 2H_2O$.

If the reaction between $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ and $4\text{-}MeC_6H_4SO_3H$ in acetonitrile is carried out in the presence of $CHBr_3$ using only one mol of acid, about

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half of the $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ is consumed immediately, but no $[Fe(\eta\text{-}C_5H_5)(CO)_2Br]$ is formed. This implies that the oxidation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ by the acid is a two-electron process. In contrast, the oxidation of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ by silver(I) salts in acetonitrile is a one-electron reaction [1].

The solvent is clearly very important. The reaction of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ with $4\text{-}MeC_6H_4SO_3H$ does not take place or is very slow (≫ 1 week) in dichloromethane, tetrahydrofuran or methanol. It is apparently as fast in $MeNO_2$ as in MeCN but the product has not been identified. Acetone occupies an intermediate position and the reaction is complete after 3 days. When a CH_2Cl_2 (30 ml)/MeCN (30 ml) solvent mixture is used, the reaction is as fast as in pure MeCN, but if this ratio is changed to 60 ml/3 ml, the reaction goes to the extent of ca. 30% within 5 min and then stops.

The reaction may be represented by equation 1.

$$[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4] + 2H^+ + 2MeCN \xrightarrow{MeCN} 2[Fe(\eta\text{-}C_5H_5)(CO)_2(NCMe)]^+ + 2[H] \qquad (1)$$

As the hydrogen does not appear as H_2 gas, it must suffer some other fate. An attractive possibility is that it reduces the acetonitrile solvent, but we have no evidence for this. However, it may be significant that the two other effective solvents, $MeNO_2$ and acetone, are also unsaturated, and could act as hydrogen sinks during the reaction.

In attempting to extend the scope of the reaction, we have used it to prepare $[Ru(\eta\text{-}C_5H_5)(CO)_2(NCMe)][4\text{-}MeC_6H_4SO_3]$ in good yield from $[Ru_2(\eta\text{-}C_5H_5)_2(CO)_4]$. However, $[Co_2\{P(n\text{-}Bu)_3\}_2(CO)_6]$ and $4\text{-}MeC_6H_4SO_3H$ give a carbonyl-free pink solid, whilst $[Mo_2(\eta\text{-}C_5H_5)_2(CO)_6]$ reacts with HPF_6 only. The product is a yellow crystalline solid which has yet to be characterised completely, but which analyses as $[Mo(\eta\text{-}C_5H_5)(NCMe)_3(PF)_2]$.

References

1 B. Callan and A.R. Manning, J. Chem. Soc. Chem. Commun., (1983) 263.