

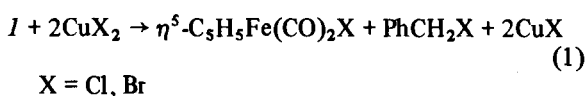
### Mechanisms of the Cleavage Reactions of the Compounds $\eta^5\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2\text{R}$ by Copper(II) Compounds

W. N. ROGERS, J. A. PAGE and M. C. BAIRD

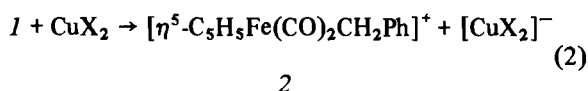
Department of Chemistry, Queen's University, Kingston, Ont., Canada K7L 3N6

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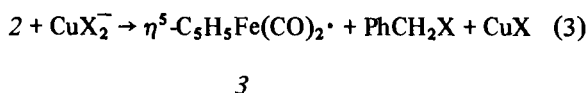
We have recently presented evidence [1] that cleavage of the iron benzyl compound,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{Ph}$  (1), with copper(II) halides proceeds in  $\text{CH}_2\text{Cl}_2$  with the stoichiometry



It was suggested that the reaction involves an  $\text{S}_{\text{E}}$  (oxidative) process [2], as in (2),



followed by nucleophilic attack by halide ion on the benzylic carbon atom of the seventeen-electron cationic intermediate, 2 as in (3).



The presumed seventeen-electron iron radical, 3, would then abstract a halogen atom from a second copper(II) halide in a subsequent fast step, leading to the observed stoichiometry.

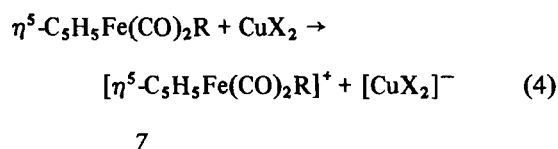
We now present evidence that the iron radical, 3, is indeed formed during the reaction, and that the cleavage involves inversion of configuration at the benzylic carbon atom, as required by (3). We also find that while the analogous methyl, ethyl and n-butyl compounds also undergo cleavage via  $\text{S}_{\text{E}2}$  (oxidative) (2) rather than classical  $\text{S}_{\text{E}2}$  processes, the latter two involve a subsequent step other than as in (3).

The involvement of 3 in the reaction was demonstrated by the observations that cleavage of 1 with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{CuBr}_2$  in  $\text{CH}_2\text{I}_2$  yields up to 65%  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ . This can only form via abstraction of iodine from the solvent by the radical, 3. In contrast, cleavage by  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  in  $\text{CH}_2\text{Br}_2$  yields only the chloroiron product, presumably because of the greater strength of the carbon-bromine bond.

Cleavage of (R)(-)- $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CHDPh}$  [3] with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  or  $\text{CuBr}_2$  in  $\text{CH}_2\text{Cl}_2$  yields the corresponding (S)(+)-benzyl halides. Thus the overall cleavage reactions proceed with inversion of configuration, consistent with  $\text{S}_{\text{N}2}$  displacement of 3 by halide ion, as in (3).

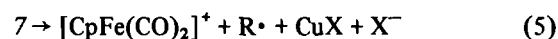
The methyl compound,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Me}$  (4) is cleaved with the same stoichiometry as in (1), and is further similar to 1 in that reactions in  $\text{CH}_2\text{I}_2$  give significant amounts of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ , but no  $\text{MeI}$ . Thus we believe that 1 and 4 are cleaved by essentially the same mechanism.

The ethyl (5) and n-butyl (6) analogues, however, behave rather differently. While both react with anhydrous  $\text{CuCl}_2$  and  $\text{CuBr}_2$  as in (1), reactions with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  give much lower yields of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  (~10%). In addition, reaction of 6 in  $\text{CH}_2\text{I}_2$  gives no  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ , but does give some 10% of n-BuI. These data are consistent with an initial  $\text{S}_{\text{E}}$ (oxidative) step, as in (4).



R = Et, n-Bu

However, a significant route to decomposition of the seventeen-electron species, 7, must involve formation of an alkyl rather than the iron radical, possibly as in (5)



The alkyl radical would be scavenged very efficiently by a second copper(II) halide [5], or could abstract halogen from the solvent. The sixteen-electron cationic iron species would combine with halide ion unless, as is apparently the case with  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , the chloride is heavily solvated and thus rendered less nucleophilic [6] by water.

The proposed mechanisms are reasonable if it is considered that (3) and (5) essentially provide alternative routes for the decomposition of species such as 2 and 7. Those alkyl groups, methyl and benzyl, which relatively easily undergo  $\text{S}_{\text{N}2}$  reactions, do so. This process is less facile for primary alkyl ligands [7], however, and the ethyl and n-butyl compounds react via another route, as in (5).

On this basis, it seemed likely that cleavage of 1 by copper(II) in the absence of a good nucleophile might result in the decomposition of the cation, 2, to give benzyl rather than iron radicals. It was encouraging, therefore, to find that cleavage of 1

with  $\text{Cu}(\text{NO}_3)_2(\text{OPPh}_3)_2$  [8] in  $\text{CH}_2\text{Cl}_2$  gave a 90% yield of bibenzyl, the product expected from the formation of benzyl radicals.

The role of  $\text{S}_{\text{E}}(\text{oxidative})$  rather than  $\text{S}_{\text{E}}2$  processes (*i.e.* involving possibly outer-sphere electron transfer rather than direct attack at the  $\alpha$ -carbon atom) was demonstrated by competition experiments. If the rate-determining step in the cleavage reactions involves electron transfer, the relative rates should reflect the relative oxidation potentials of the substrates [1]. Thus the compounds 4, 5 and 6 (oxidation potentials =  $1.27 \pm 0.04$  volts vs.  $\text{Ag}/\text{AgCl}$ , 0.1 M  $\text{Et}_4\text{NCl}$  in  $\text{CH}_2\text{Cl}_2$ , reference) should react at about the same rate, while 1 (1.28 V) should react at lower rate than  $\eta^5\text{-C}_5\text{H}_5\text{FeCO}(\text{PPh}_3)\text{CH}_2\text{Ph}$  (8) (0.80 V). On the other hand, direct attack of a copper(II) compound at the  $\alpha$ -carbon atom should be hindered sterically both by substituents at the  $\alpha$ -carbon atom [9], and by the bulky triphenylphosphine.

Cleavage of 1:1 mixtures of 4 and 5, 4 and 6, and 1 and 8 with deficiencies of copper(II) salts, followed by recovery of unreacted iron alkyl compounds, showed that while 4, 5 and 6 are indeed cleaved at essentially identical rates, 8 is cleaved at a rate about ten times that of 1.

## Acknowledgments

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