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Preliminary communication

REGIOSPECIFICITY IN THE REACTIONS OF $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_{4-n}(CNMe)_n]$ (n = 0—2) WITH MERCURY(II) HALIDES

RAJESH KUMAR and A.R. MANNING*
Department of Chemistry, University College, Belfield, Dublin 4 (Ireland)

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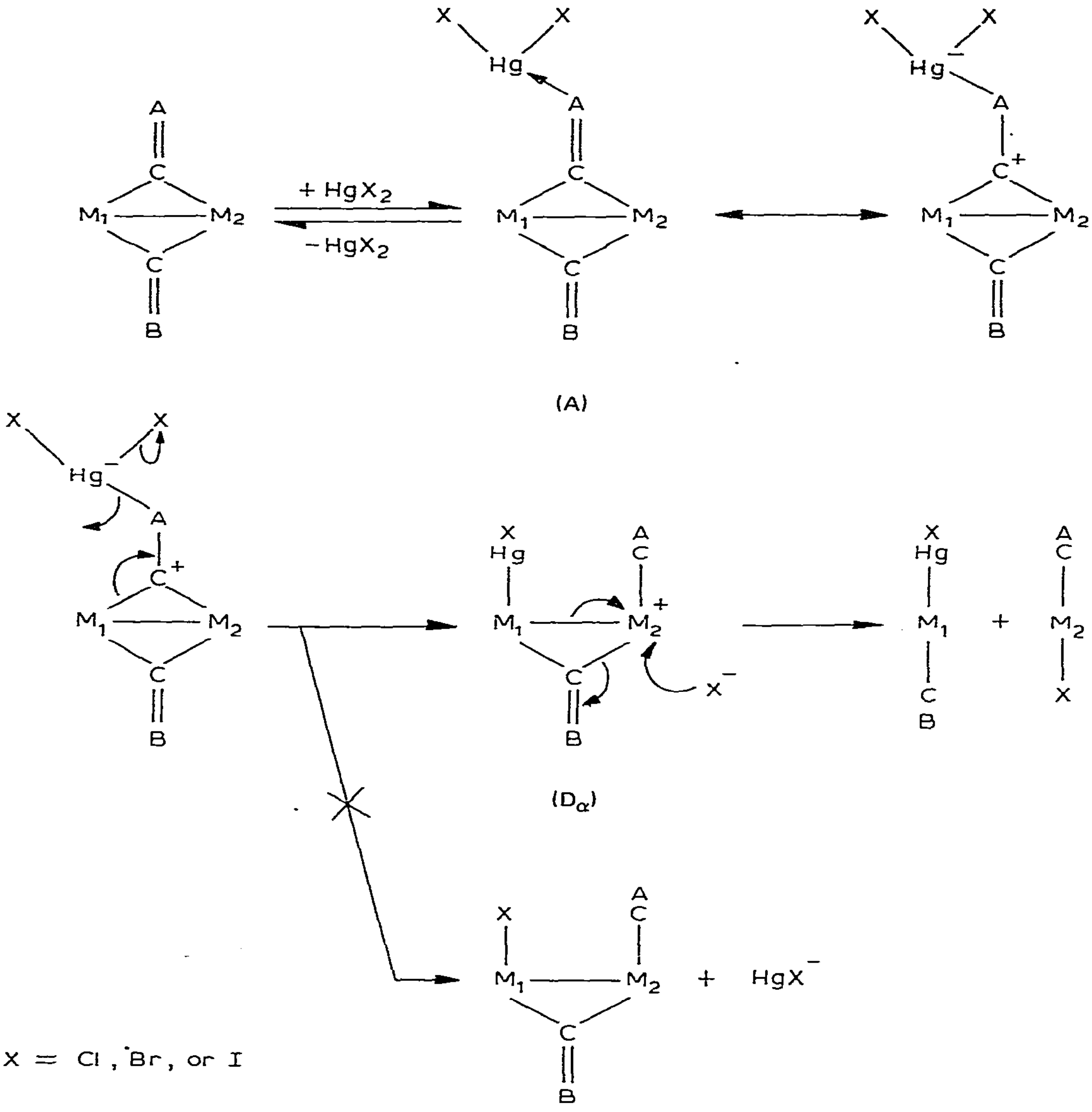
Summary

The reactions of $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)]$ (L = CO or CNMe) with HgX_2 (X = Cl, Br or I) give $[Fe(\eta\text{-}C_5H_5)(CO)_2HgX]$ and $[Fe(\eta\text{-}C_5H_5)(L)(CNMe)X]$ as the sole products in ca. quantitative yields; this is consistent with the previously proposed mechanism for the reactions of electrophiles with polynuclear metal carbonyl derivatives.

Previously, one of us has suggested that polynuclear metal carbonyl complexes containing actual or potential μ-CO, μ-CNR, μ-CS or related ligands react with electrophiles, E, by way of adducts containing μ-$\{CA\rightarrow E\}$ moieties (A = O, NR, S etc.) [1]. These adducts may or may not be observed. They may breakdown with loss of the electrophile as E^{2-}, as shown in Scheme 1 for E = HgX_2, to cationic intermediates. These may incorporate all, part or none of E^{2-}, and undergo subsequent reactions (usually nucleophilic attack) with the formation of the final products or their obvious precursors which, in most instances, do not contain metal—metal bonds. It is an important feature of the proposed mechanism that the E^{2-}, or its incorporated fragment, and the μ-ligand to which it was originally bonded, CA, should be coordinated to different metal atoms in the final products. Here we report an unambiguous confirmation of this prediction and, hence, add weight to the original proposal.

Equimolar amounts of HgX_2 (X = Cl, Br, or I) and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_4]$ react very rapidly (> 1 min at 20°C) in C_6H_6/MeOH solution to give $[Fe(\eta\text{-}C_5H_5)(CO)_2HgX]$ and $[Fe(\eta\text{-}C_5H_5)(CO)_2X]$. IR spectroscopy shows that the reactions are virtually quantitative and that the two products are obtained in equal amounts. Under the same conditions $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(L)(CNMe)]$ (L = CO or CNMe) give only $[Fe(\eta\text{-}C_5H_5)(CO)_2HgX]$ and $[Fe(\eta\text{-}C_5H_5)(L)(CNMe)X]$; again the reactions appear to be quantitative and the products to be formed in equal amounts. It should be mentioned that product purification



X = Cl, Br, or I

M_1, CB = Fe(η-C_5H_5)(CO), CO

M_2, CA = (i) Fe(η-C_5H_5)(CO),CO

(ii) Fe(η-C_5H_5)(CO),CNMe

(iii) Fe(η-C_5H_5)(CNMe),CNMe

SCHEME 1

and separation becomes increasingly difficult as the number of isocyanide ligands increases, partly because the initial reaction is followed by ligand redistribution. However, it is possible to state that [Fe(η-C_5H_5)$(CO)_2$X] were not formed in either of the last two reactions.

The mechanism we propose for these reactions (Scheme 1) is similar to those suggested previously for related reactions of the same substrates with other electrophiles [1]. It is reasonable to suppose that for the isocyanide complexes, the adducts, A, should have the structure $[Fe_2(\eta\text{-}C_5H_5)_2(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)HgX_2\}]$ (cf. $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CN(Me)H\}]^+$ in ref. 2). Because the reactions are so fast, the proposed adducts have not been observed, but the closely related $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}CS \rightarrow HgCl_2\}]$ has been isolated [3]. The adduct decomposes by loss of X^-, migration of HgX from CA to M_1 and cleavage of the M_1—CA bond to an intermediate D_α which then undergoes nucleophilic attack at M_2 by X^- to give the final products. An alternative pathway which involves migration of X^- from Hg to M_1 and loss of HgX^- is discounted. The free HgX^- anion would be expected to decompose rapidly to X^- and Hg metal under our conditions, and this is not observed.

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