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Reactions of Iron–η^1-Allyl Complexes with Mercury (II) Chloride

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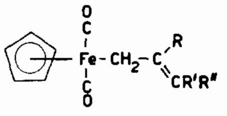
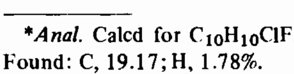
Transition metal–carbon σ bonds are cleaved by the action of various electrophilic reagents [1]. Such scission reactions using mercury(II) salts, in particular, have been the subject of considerable current interest [2].

We have previously reported [3] that the course of reaction between metal alkyls and aryls of the type η^5-$C_5H_5Fe(CO)_2R$ and $HgCl_2$ is markedly influenced by the nature of R. Three types of products were observed: (1) η^5-$C_5H_5Fe(CO)_2Cl$ and RHgCl, (2) η^5-$C_5H_5Fe(CO)_2HgCl$ and RCl, and (3) Hg_2Cl_2 and materials derived from the decomposition of oxidized η^5-$C_5H_5Fe(CO)_2R$. We now report still another type of behavior which occurs when R = η^1-allyl.



Ia R = R′ = R″ = H
Ib R = CH_3, R′ = R″ = H
Ic R = R′ = H, R″ = CH_3
Id R = H, R′ = R″ = CH_3
Ie R = R′ = H, R″ = C_6H_5

A solution of Ia (0.64 g, 2.9 mmol) in THF (5 ml) was added dropwise to a slight deficiency of $HgCl_2$ (0.56 g, 2.1 mmol) in THF (20 ml) at 25 °C, the resulting mixture was treated with additional THF (25 ml), and the clear yellow solution was stirred for 1 hr under Ar. Filtration and addition of pentane (400 ml) to the filtrate afforded a yellow–orange precipitate which was collected and washed with acetone (5 ml) to give 0.75 g of a yellow solid. An additional 0.22 g of the product was obtained from the THF–pentane filtrate, total yield 95% based on a 1:1 adduct, η^5-$C_5H_5Fe(CO)_2C_3H_5 \cdot HgCl_2$, IIa. IIa was treated with an equimolar amount of NH_4PF_6 in acetone to afford IIIa* as yellow crystals, dec. 145 °C without melting, soluble in acetone but insoluble in CH_2Cl_2 and benzene, and a 1:1 electrolyte in nitrobenzene.**

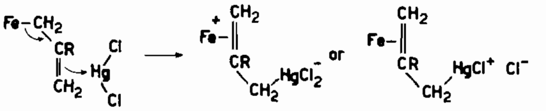


IIIa R = H
IIIb R = CH_3

Additional evidence for the proposed structure IIIa derives from the infrared and mass spectra. The infrared spectrum of IIIa in the ν_{CO} region (Nujol mull, CsI plates) shows bands at 2064 and 2032 cm^{-1} (2072 and 2036 cm^{-1} in acetone soln.), consistent with the presence of a positively charged η^5-$C_5H_5Fe(CO)_2$ species [5]. The appearance of a C_5H_5 resonance at 4.23 τ in the ^1H NMR spectrum of IIIa in acetone-d_6 also points to such a cation [5]. The mass spectrum contains peaks due to $C_5H_5Fe(CO)C_3H_5^+$ and various isotopic species $C_3H_5HgCl^+$ and $C_3H_5Hg^+$: *e.g.*, calcd for $C_3H_5\,{}^{202}Hg^{35}Cl$ m/e 277.97859, found m/e 277.97894.

A similar reaction of Ib with $HgCl_2$, followed by treatment with NH_4PF_6, produced IIIb.* In contrast, Ic and $HgCl_2$ react more slowly to afford a small amount of what may be η^5-$C_5H_5Fe(CO)_2C_4H_7 \cdot HgCl_2$, IIc, analogous to IIa, with the main organometallic product (65% yield) being η^5-$C_5H_5(CO)_2$-HgCl. Corresponding reactions of Id and Ie with $HgCl_2$ likewise proceed more slowly to yield also η^5-$C_5H_5Fe(CO)_2HgCl$ but none of the appropriate 1:1 adduct.

Complexes II likely result from electrophilic attack at the double bond of the η^1-allyl ligand by $HgCl_2$:



II

Such interaction of $HgCl_2$ would be strictly analogous to the reported protonation [6] and reaction with SO_2 [5] of the η^1-allyl fragments. The rapid rate of this addition indicates that it represents the most favorable path for electrophilic attack at these iron complexes by $HgCl_2$. The slower reactivity of and a different organometallic product derived from Ic, Id, and Ie may be best rationalized as consequences of steric inhibition to electrophilic attack at the double bond of the η^1-allyl group in these complexes by $HgCl_2$. The formation of η^5-$C_5H_5Fe(CO)_2HgCl$ in these reactions indicates, by analogy with the behavior of the previously studied alkyls [3], that the electrophilic interaction of $HgCl_2$ is with the iron. Dissociation of the η^1-allyl ligand as a carbonium ion would then lead to the observed products, as described by us earlier [3].

**Anal.* Calcd for $C_{10}H_{10}ClF_6FeHgO_2P$: C, 20.05; H, 1.68. Found: C, 19.17; H, 1.78%.

**Λ_M = 32.0 cm^2/ohm *M* (*ca.* 10^{-3} *M soln.*). For typical conductivities of 1:1 electrolytes in nitrobenzene see ref. 4.

**Anal.* Calcd for $C_{11}H_{12}ClF_6FeHgO_2P$: C, 21.55; H, 1.98. Found: C, 21.48; H, 1.84%.

Acknowledgment

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