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Hydride Reduction of the Cations $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]PF_6$, $[(\eta\text{-}1,5\text{-}C_6H_7)Fe(CO)_3]BF_4$ and $[(\eta\text{-}1,5\text{-}C_7H_9)Fe(CO)_3]BF_4$: Evidence for the Iron Formyl $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CHO)$

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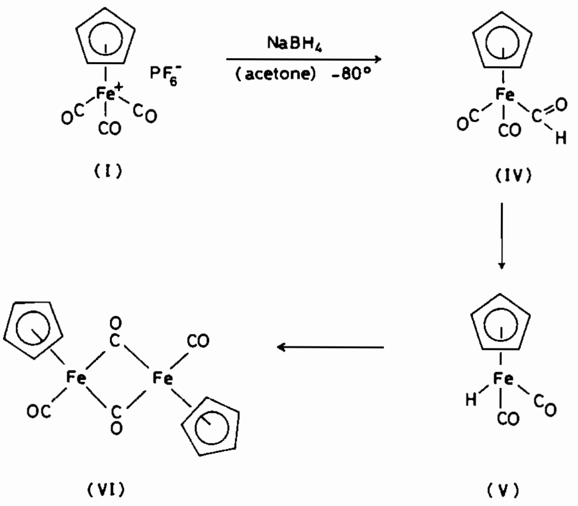
Hydride addition to the cation $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]PF_6$ favours attack at the $Fe(CO)_3$ group with $NaBH_4$ giving the iron formyl $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CHO)$, as an intermediate in contrast to the analogous cations $[(\eta\text{-}1,5\text{-}C_6H_7)Fe(CO)_3]BF_4$ and $[(\eta\text{-}1,5\text{-}C_7H_9)Fe(CO)_3]BF_4$ which favour simultaneous attack at the ring carbon atoms and the $Fe(CO)_3$ group.

Nucleophilic attack of the cations $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]PF_6$ (I), $[(\eta\text{-}1,5\text{-}C_6H_7)Fe(CO)_3]BF_4$ (II) and $[(\eta\text{-}1,5\text{-}C_7H_9)Fe(CO)_3]BF_4$ (III) can occur at a ring carbon atom, the iron atom and a carbonyl carbon atom [1]. Application of the perturbation theory of reactivity to this series [2] shows that the position of attack depends on the nucleophilicity of the reagent and solvent polarity, for example, a hard nucleophile changing from attack at the iron atom to the carbonyl with increasing solvent polarity.

In this note, the reactivity of I, II and III to the hydride donors $NaH > K[B(OiPr)_3H] > Li[BEt_3H] > Li[AlH_4] > Na[BH_4] > Na[BH_3CN]$ (in approximate order of hydride donor strength) is compared. Reactions were carried out in acetonitrile, dichloromethane and acetone solvents and the hydrides added either as solids or 1 M solutions in THF.

I undergoes ring attack to give 5-*exo* $C_5H_6Fe(CO)_3$ only with the weakest hydride donor, $Na[BH_3CN]$ [3] and reacts very rapidly with all other reagents to form $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$. To a d^6-acetone solution of I, cooled in liquid nitrogen, solid $NaBH_4(NaBD_4)$ was added and the mixture monitored by ^1H NMR spectroscopy (using a JEOL PS 100 FT instrument) as the temperature was raised slowly. At −80 °C, resonances developed at δ 14.25 ppm characteristic of a metal formyl proton [4] and δ 5.38 ppm assigned to the ring protons of the iron formyl $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CHO)$ (IV), shifted upfield by 0.67 ppm from those of the cation I. Between −50 and −20 °C these resonances decreased in intensity as new resonances appeared at δ −11.98 ppm (upfield from TMS $\delta = 0$) and δ 5.13 ppm arising from the metal hydride proton and ring protons respectively of $(\eta^5\text{-}C_5H_5)Fe(CO)_2H$ (V) [3]. On raising the temperature further, the resonances due to V decreased in intensity and were replaced by δ 4.95 ppm due to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (VI). Attempts to isolate the iron formyl (IV) were unsuccessful. An identical experiment with $NaBD_4$ gave initial development of the ring proton resonance at δ 5.40 ppm due to the deuteride of IV followed by its decrease and simultaneous growth of a resonance δ 5.15 ppm due to the deuteride of V and finally formation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (VI). Formation of the deuterides of IV and V eliminates a mechanism involving *exo*-attack on the cyclopentadienyl ring and subsequent transfer of the *endo*-hydrogen to the metal.



This result is significant because hydride addition to I is often stated to occur *exo* onto the cyclopentadienyl ring [5]; indeed, formation of the hydride V in earlier work [6] using $NaBH_4$ has been ascribed to the conversion of the initially formed *exo* compound to the hydride [1]. Our results show clearly that this pathway does not apply to the $NaBH_4$ reduction of I but rather that the formyl derivative IV is the active intermediate.

In contrast, cations II and III give the corresponding carbonyl-bridged dimers $[(\eta\text{-}1,5\text{-}C_5H_5(CH_2)_n)Fe(CO)_2]_2$, n = 1, 2, as sole products only with the powerful hydride donor, NaH, and the 5-*exo* $C_5H_6(CH_2)_nFe(CO)_3$ as sole product only with $NaBH_4$ [7] and $Na[BH_3CN]$ for II (n = 1). With other reagents, mixtures of ring products and dimers are formed [7, 8], indicating greater susceptibility to hydride attack of the ring in II and III compared to I and suggesting simultaneous ring and metal/carbonyl group attack since, by analogy with I, formation of a formyl derivative should lead to

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hydride transfer to the metal only and not to the ring. No NMR evidence was obtained for formyl intermediates from **II** and **III**.

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