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Preliminary communication

Hydride addition to $[(\eta^5\text{-indenyl})Fe(CO)_3]BF_4$: evidence for η^3-indenyl intermediates

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Abstract

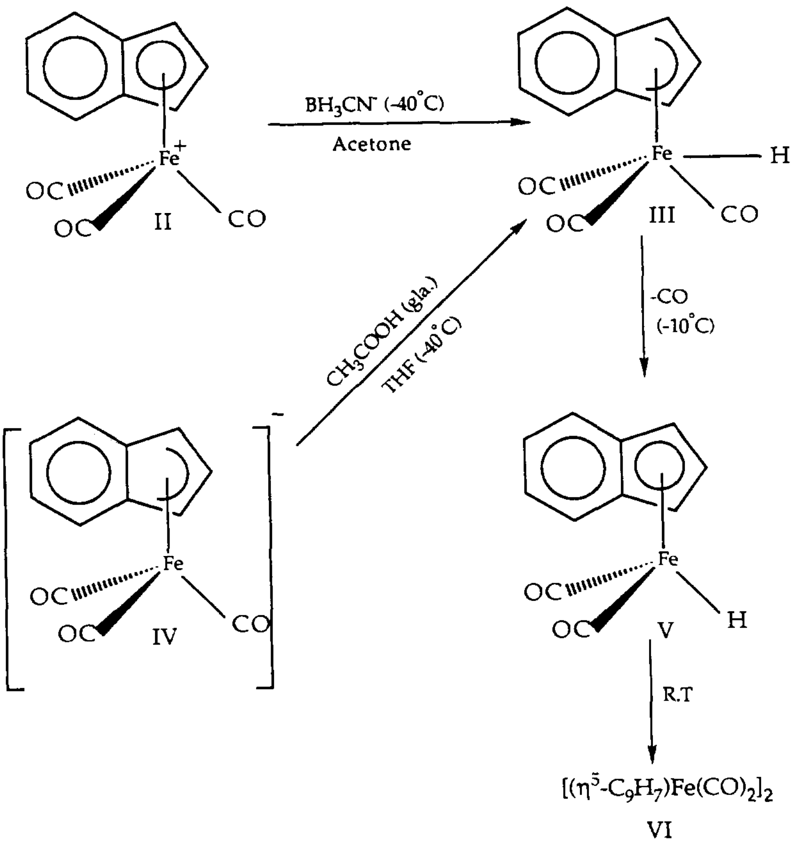
Spectroscopic evidence is presented for the formation at low temperatures of the η^3-indenyl intermediate $[(\eta^3\text{-}C_9H_7)Fe(CO)_3H]$, prior to formation of the normal hydride, $[(\eta^5\text{-}C_9H_7)Fe(CO)_2H]$, by reduction of the tricarbonylironindenyl cation with sodium cyanoborohydride in acetone.

Theoretical prediction of the point of attack by a nucleophile (e.g. hydride) on a ring metal carbonyl complex (e.g. $[(\eta^5\text{-indenyl})Fe(CO)_3]BF_4$) is difficult. Frontier orbital arguments may break down because of the occurrence of a band of unoccupied molecular orbitals rather than simply one frontier LUMO, as illustrated by the case of methoxide attack on $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$ [1]. Calculations of interaction energies predict initial attack by hard nucleophiles at the $M(CO)_3$ moiety in $(\eta\text{-ring})M(CO)_3$ complexes [2]. In the case of the $[(\eta^5\text{-}C_nH_m)Fe(CO)_3]^+$ cations, I ($n = m = 5$) and II ($n = 9$, $m = 7$), hydride addition from $NaBH_4$ proceeds via initial formation of the corresponding metal formyl, clearly observed in acetone at −50 °C by low-temperature NMR spectroscopy [3,4]. A recent publication [5] that described the formation of $[H_6Re_4(CO)_{12}]^{2-}$ by the reaction of $[(\eta^5\text{-}C_9H_7)Re(CO)_3]$ with $LiEt_3BH$ and postulated a reaction pathway involving initial metal attack and formation of $[(\eta^3\text{-}C_9H_7Re(CO)_3H]^-$ as intermediate, prompted us to report further studies on hydride attack on $[(\eta^5\text{-}C_9H_7)Fe(CO)_3]^+$ (II) by $NaBH_3CN$ in acetone. In this case, low-temperature ^1H NMR spectroscopy indicates initial attack at the metal by hydride and formation of $[(\eta^3\text{-}C_9H_7)Fe(CO)_3H]$ (III), rather than the $[(\eta^5\text{-}C_9H_7)Fe(CO)_2CHO]$ previously observed in the reaction with $NaBH_4$ [4].

The reactions between II and $NaBH_3CN$ (and $NaBD_3CN$) in acetone-d_6 were monitored by ^1H NMR spectroscopy by the method described previously [4]. $Na[(\eta^3\text{-}C_9H_7)Fe(CO)_3]$ (IV) was prepared by passing CO gas through a solution of $Na[(\eta^5\text{-}C_9H_7)Fe(CO)_2]$ (0.05 mg) in THF-d_8 (5 ml) [6]. The solution was cooled to −40 °C, three drops of glacial acetic acid were added, and the mixture was transferred under argon to an NMR tube. The ^1H NMR spectrum was recorded at

−40 °C on a JEOL GX 270 MHz spectrometer, although the ring resonance region was obscured by broad solvent absorptions.

In the reaction between $[(\eta^5\text{-}C_9H_7)Fe(CO)_3]^+$ (II) and $NaBH_3CN$ in acetone-d_6 new resonances developed at δ −8.75 (s), 5.55, 6.29 and 7.35 ppm. The resonance at δ −8.75 ppm could be reasonably assigned to either a metal-hydride (M–H) or an agostic hydrogen involving the interaction of an *endo*-ring hydrogen of a ring hydride addition product and the metal [7]. However, in the latter case coupling between the agostic hydrogen and adjacent ring protons would be expected [7]. No such coupling was observed, and so the resonance was assigned to the metal hydride of the 18-electron intermediate $[(\eta^3\text{-}C_9H_7)Fe(CO)_3H]$ (III), whilst the resonances at δ 5.55, 6.29 and 7.35 ppm were assigned to the allyl C protons and D proton and the A_2B_2 system of the six-membered ring of III, respectively. The deshielding of the central allylic proton (D) relative to the terminal allylic protons (C) is in accord with the observed X-ray structure of the allylic system in $[(\eta^3\text{-}C_9H_7)Fe(CO)_3]^-$, in which proton D lies 22° above the ring plane [6]. When the reaction temperature was raised to −10 °C, resonances due to the normal hydride $[(\eta^5\text{-}C_9H_7)Fe(CO)_2H]$ (V) appeared, identical with these reported previously, but no resonances due to the formyl appeared, in contrast to our previous



Scheme 1

observations when $NaBH_4$ was used [4]. Finally, at room temperature, the stable dimer $[(\eta^5\text{-}C_9H_7)Fe(CO_2)]_2$ (VI) was formed.

In a separate experiment, a solution of $Na[(\eta^3\text{-}C_9H_7)Fe(CO)_3]$ [6] in THF-d_8 was treated with the minimum amount of glacial acetic acid at −40 °C and the ^1H NMR spectrum recorded. Resonances appeared at δ −8.75, −15.35 and −5.56 ppm. The first resonance agrees closely with that for III, formed in this instance by protonation of the well-characterized $[(\eta^3\text{-}C_9H_7)Fe(CO)_3]^-$ anion [6], and provides supporting evidence for our formulation of the intermediate III as $[(\eta^3\text{-}C_9H_7)Fe(CO)_3H]$, as does comparison with the metal-hydride resonance in the isoelectronic $[(\eta^5\text{-}C_9H_7)V(CO)_3H]^-$, which lies at δ −6.10 ppm in THF-d_8 [8]. The resonance at δ −15.35 ppm is due to the normal hydride $[(\eta^5\text{-}C_9H_7)Fe(CO)_2H]$ (V) [4], and that at δ −5.56 is tentatively assigned to an agostic hydrogen in a species such as $[(\eta^4\text{-}C_9H_7)(\mu\text{-}H)Fe(CO)_3]$.

Finally, in the reaction with $NaBD_3CN$ in acetone-d_6 there were no detectable metal-hydride resonances due to either III or V, confirming that direct metal attack by hydride is the preferred reaction pathway (Scheme 1) and eliminating the alternative of initial *exo*-ring addition followed by intramolecular transfer of the *endo* hydrogen to give the above metal-hydride species. The result with $NaBD_3CN$ provides further support to our assignment of the δ −8.75 ppm resonance to the metal-hydride of III rather than to an agostic hydrogen, since the latter would involve a ring *endo* proton.

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