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Spectroscopic studies of hydride addition to the tricarbonylcyclopentadienyliron cation

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Abstract

Hydride addition to $[CpFe(CO)_3]BF_4$ by $NaBH_3CN$ in THF was monitored in the temperature range −60°C to +40°C by IR and ^1H NMR spectroscopy. At low temperatures, initial attack occurred both at the carbonyl group, to give the formyls $[CpFe(CO)_2CHO:BH_2CN]$ and $[CpFe(CO)_2CHO]$, and at the metal centre to give $[CpFe(CO)_3H]$ (probably best formulated as $[(\eta^3\text{-}C_5H_5)Fe(CO)_3H]$). At higher temperatures these intermediates decompose to leave $[CpFe(CO)_2H]$, which dimerizes to $[CpFe(CO)_2]_2$ at +40°C. In addition $[CpFe(CO)_2CH_2OH]$, $[CpFe(CO)_2CH_3]$ and $[CpFe(CO)_2COOH]$ are formed. Finally the thermodynamically stable ring adduct $[(5\text{-exo-}\eta^4\text{-}C_5H_6)Fe(CO)_3]$ is observed even at low temperatures.

Key words: Iron; Cyclopentadienyl; Hydride

1. Introduction

For nearly two decades, there has been interest in the hydride reduction of metal carbonyl complexes, motivated at least in part by interest in the Fischer-Tropsch reaction involving hydrogenation of carbon monoxide catalysed by transition metal compounds [1]. The addition of hydride to $[CpFe(CO)_3]^+$, (I) and $[Cp^*Fe(CO)_3]^+$ (II) has been widely studied [2]. In the former case, only the ring addition product $[(\eta^4\text{-}C_5H_6)Fe(CO)_3]$ (III) and the dimer $[CpFe(CO)_2]_2$ (IV) (formed from the hydride, $[CpFe(CO)_2H]$ (V) are obtained as stable final products. However, low-temperature ^1H NMR studies showed this reaction with BH_4^- proceeded by initial attack at a metal carbonyl group to give the metal formyl, $[CpFe(CO)_2CHO]$ (VI) at about −50°C, and on raising the temperature this gave the metal hydride V, which subsequently dimerized to IV. No other intermediates were observed. Permethylation leads to greatly increased stability of a number of reduction products such as $[Cp^*Fe(CO)_2CH_2OH]$, (VII) and $[Cp^*Fe(CO)_2CH_3]$, (VIII) [2]. A detailed study of the reactions of $[Cp^*Fe(CO)_2L]PF_6$ ($L = CO$, PR_3) with $NaBH_4$ in a range of solvents and various temperatures followed by ^1H NMR spectroscopy revealed a complex situation but provided clear evidence for initial CO attack in most cases and formation of metal formyls such as $[Cp^*Fe(CO)(PPh_3)(CHO)]$ (IX) and its Lewis adduct with BH_3, $[Cp^*Fe(CO)(PR_3)CHO:BH_3)$ (X). Subsequent reduction products depend on the molar ratio of hydride to substrate and the nature of the solvent [2]. Removal of the stabilizing influence of permethylation means most of the above species are unstable and can only be observed spectroscopically at low temperatures, as in our earlier studies of the borohydride reduction of I [3]; however, the use of the milder nucleophile BH_3CN^- in methanol with I, enabled Cutler *et al.* [4] to isolate $[CpFe(CO)_2CH_2\text{-}OMe]$ as a stable product formed via the intermediate $[CpFe(CO)_2CH_2OH]$, (XI), whose presence was confirmed by trapping with PhNCO [4]. In contrast, reaction of I with $NaBH_3CN$ in THF led simply to ring addition and formation of III [5].

We have recently [6] performed *ab initio* MO calculations on the following species: $[CpFe(CO)_3]^+$ (I), $[CpFe(CO)_3H]$ (XII), $[CpFe(CO)_2CHO]$ (VI), $[(\eta^4\text{-}C_5H_6)Fe(CO)_3]$ (III), and $[(\eta^3\text{-}C_5H_5)Fe(CO)_3H]$ (XIII). These calculations showed that III was the thermodynamically stable product and XII and VI less stable. The last two complexes were of similar stability although XII turns out to be a weak complex between

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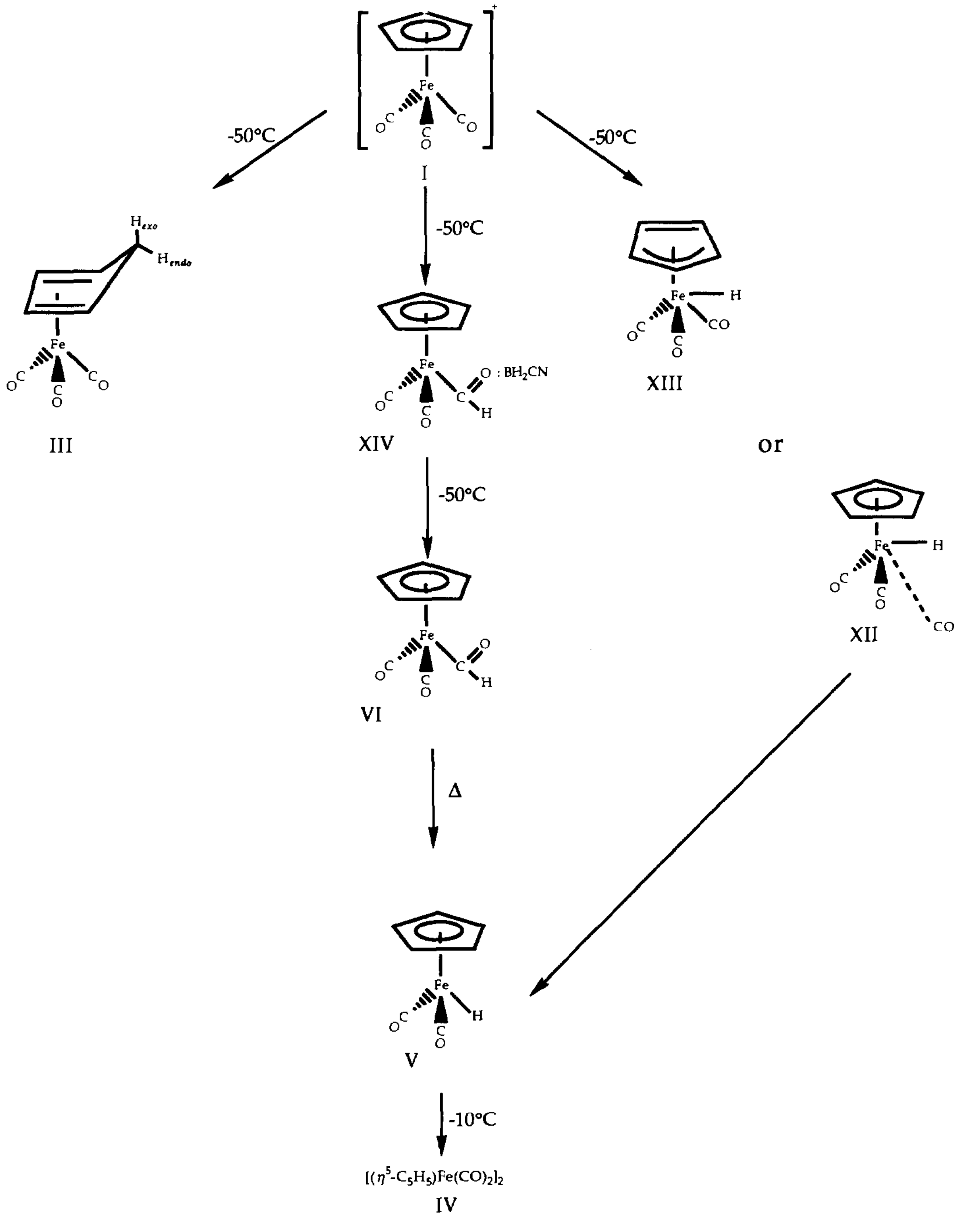
[CpFe(CO)$_2$H] and CO with a long Fe–CO bond. Interestingly XIII is the least stable of the above products of hydride attack.

In this paper we report a low temperature spectroscopic study of the reaction of NaBH$_3$CN with I in THF in order to determine whether the use of the milder nucleophile BH$_3$CN$^-$ yields more intermediates and reaction paths than is the case with BH$_4^-$ [3].

2. Results and discussion

A solution of [CpFe(CO)$_3$]BF$_4$ (I) in THF-d_8 was treated with NaBH$_3$CN in THF-d_8 in 1:1 molar ratio as described above, and the ^{1}H NMR spectrum recorded over the temperature range, −60°C to +40°C. The first intermediate appeared at −50°C, with a broad resonance at δ 12.35 ppm assigned to the formyl



Scheme 1.

proton of [CpFe(CO)$_2$CHO : BH$_2$CN] (XIV) (by analogy with the corresponding BH$_3$ formyl adduct observed by Astruc and coworkers [2]) and a resonance for the corresponding Cp ring protons at δ 5.32 ppm. When the mixture was kept at -50°C, the previously reported formyl [CpFe(CO)$_2$CHO] (VI) appeared, with the formyl proton at δ 14.15 and ring protons at δ 5.42 ppm. In addition, an upfield resonance grew at δ -5.98 with resonances at δ 5.48 (1H), δ 5.08 (2H), and δ 4.65 ppm (2H). Clearly, a metal hydride species is formed which is quite different from the normal hydride [(η^5-C$_5$H$_5$)Fe(CO)$_2$H] (V), which is observed at the same temperature as a single resonance at δ -11.95 with the corresponding Cp ring protons at δ 4.95 ppm. The signal from the intermediate hydride at δ -5.98 ppm is close to that observed for the analogous [(η^3-C$_9$H$_7$)Fe(CO)$_3$H] [7], and very close also to that for [(η^5-C$_5$H$_5$)V(CO)$_3$H] [8]; it is consequently assigned to [(η^3-C$_5$H$_5$)Fe(CO)$_3$H] (XIII), although in view of the theoretical work [6], the formulation of this intermediate as [(η^5-C$_5$H$_5$)Fe(CO)$_3$H] cannot be excluded particularly in view of the difficulty of making unambiguous assignments in the δ 4–6 ppm region because of the complexity of the spectrum. As the temperature was raised, the intensity of the formyl adduct [CpFe(CO)$_2$CHO : BH$_2$CN], (XIV) decreased while that of the normal formyl [CpFe(CO)$_2$CHO], (VI) increased. When the temperature was raised further to -25°C, both formyl signals disappeared as well as that of the intermediate hydride at δ -5.98 ppm, leaving the normal hydride [(η^5-C$_5$H$_5$)Fe(CO)$_2$H] (V), which is relatively stable and remains present up to $+40$°C. At higher temperatures, this hydride undergoes dimerization with formation of [CpFe(CO)$_2$]$_2$, (IV). Interestingly, along with these intermediates that were formed only at low temperatures, the thermodynamically stable ring addition product [(η^4-C$_5$H$_6$)Fe(CO)$_3$, III, was also formed and characterized by a triplet at δ 5.87 ppm due to the inner diene protons (H$_3$, H$_4$), a doublet at δ 3.06 ppm due to the outer protons (H$_2$, H$_5$) and with the methylene protons (H$_{\text{exo}}$, H$_{\text{endo}}$) as two clear doublets at δ 2.68 (H$_{\text{endo}}$) and δ 2.34 ppm (H$_{\text{exo}}$), in agreement with previous data [5]. This assignment of the methylene protons in III is supported by the use of long-range ^{1}H–^{31}P spin–spin coupling constants in the closely related [(η^4C$_5$H$_6$)Fe(CO)$_2$(PPh$_3$)]$^+$ cation [9].

2.1. Deuteration studies

The reaction was repeated using NaBD$_3$CN under the same conditions (-50°C). Again, the signals from the Cp ring protons of the corresponding deuterated forms of V, VI, XIV and XIII were observed, together with peaks for the deuterated ring product, [(η^4-C$_5$H$_5$-exo-D)Fe(CO)$_3$]. In this case, the signals from the inner and outer diene protons have identical shifts to those from III, but with the methylene proton as a single resonance at δ 2.64 due to H$_{\text{endo}}$ [5,9], consistent with exo ring attack by deuteride. However, when the temperature was raised slowly to -45°C another singlet grew in intensity at δ 2.28, and then progressively decreased with increasing temperature. These observations suggest intermolecular exo ring attack by deuteride, followed by formation of the endo deuteride, which is stable over a very limited temperature range and is probably formed intramolecularly from either the metal formyl [CpFe(CO)$_2$CDO] or the unstable tricarbonyl deuteride [(η^3-C$_5$H$_5$)Fe((CO)$_3$D]. The reaction pathways consistent with these observations are shown in Scheme 1.

2.2. Other products

A peak at δ 7.60 with an associated Cp ring peak at δ 5.83 ppm which also appeared at -50°C is assigned to the carboxylic acid derivative [CpFe(CO)$_2$COOH], XV, presumably formed by nucleophilic attack at a carbonyl carbon by residual water (or OH$^-$) in the solvent. XV was previously prepared directly from I and KOH yielding a product with δ 8.6 ppm [10]. When the temperature is raised XV decomposes to the hydride V and thence IV. The hydroxymethyl derivative [CpFe(CO)$_2$CH$_2$OH] (XI) is also formed, as indicated by resonances at δ 4.97, CH$_\alpha$ at δ 5.16, CH$_\beta$ at δ 4.60 and OH at δ 1.03 ppm (J(H–H) = 6.6 Hz). As suggested by Graham [11] the formyl VI should be susceptible to nucleophilic attack at the formyl carbon.

3. Experimental section

^{1}H NMR spectra were recorded on a JEOL GX 270 spectrometer. Analyses were performed by the microanalytical laboratory of the Chemical Services unit of University College Dublin. [CpFe(CO)$_3$]BF$_4$ (I), (η^4-C$_5$H$_6$)Fe(CO)$_3$ (III), (η^4-C$_5$H$_5$-exo-D)Fe(CO)$_3$ (III-D), and (η^5-C$_5$H$_5$)Fe(CO)$_2$CH$_3$ (XVI) were prepared by published procedures [12,5,13].

3.1. Low temperature reactions of [(η^5-C$_5$H$_5$)Fe(CO)$_3$]BF$_4$ with NaBH$_3$CN

The hydride addition reaction of [(η^5-C$_5$H$_5$)Fe(CO)$_3$]BF$_4$ with NaBH$_3$CN in a 1 : 1 molar ratio was carried out in tetrahydrofuran (THF) under nitrogen or argon at various temperatures. The reaction was monitored by IR spectroscopy in the carbonyl region, and also by ^{1}H NMR spectroscopy using a JEOL GX 270 spectrometer. In this case separate solutions of NaBH$_3$CN (0.01 mg, 0.16 mmol) in THF-d_8 (0.3 ml)

[14*] and $[CpFe(CO)_3]BF_4$ (0.03 mg 0.10 mmol) in THF-d_8 (0.3 ml) were prepared in separate stoppered 5 mm NMR tubes under argon. Both tubes were cooled to −90°C in a dry-ice/acetone bath. The hydride solution was then added to the cation solution under argon at −90°C. The NMR tube containing the reaction mixture was then placed in the probe of the NMR spectrometer at −80°C.

^1H NMR spectra were recorded immediately and subsequently every 10°C as the temperature was allowed to rise to room temperature.

Deuteride addition reactions ($NaBD_3CN$) were carried out similarly.

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14 Some commercial sources of this solvent contained trace impurities with signals at δ 11.38 and δ 11.08 ppm, probably due to peroxides. In these cases a very rapid reaction occurred even at −60°C with direct formation of $CpFe(CO)_2H$ without any formyl resonances being observed. Only when the trace impurities were used up did the sequence of reactions involving formyls and hydrides, subsequently discussed appear. All the results reported were obtained with THF-d_8 free of such impurities.

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[*] Reference number with asterisk indicates a note in the list of references.