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Preliminary communication

Infrared evidence for competitive [Li^+] and Et_3B coordination to [$Fe(CO)_4CHO^-$] and thermodynamic evaluation of the ion pair equilibrium

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Abstract

The reaction between $Fe(CO)_5$ and [Et_3BH][Li], Super-Hydride, has been examined in THF over the temperature range −80 °C to room temperature by variable-temperature FT-IR spectroscopy. FT-IR studies reveal that the anionic formyl complex, [$Fe(CO)_4CHO^-$], exists in up to three chemically distinct contact ion pairs, one of which involves the termolecular formyl oxygen–BEt_3–lithium contact ion pair [$Fe(CO)_4CHOBEt_3$][Li]. From −80 °C to −55 °C, [$Fe(CO)_4CHOBEt_3$][Li] is shown to be in equilibrium with [$Fe(CO)_4CHOBEt_3^-$], while from −55 °C to room temperature, the dominant equilibrium involves the conversion of [$Fe(CO)_4CHOBEt_3^-$] into the known contact ion pair [$Fe(CO)_4CHO$][Li]. The temperature-dependent equilibrium constant associated with the different ion pairs has been determined by IR band-shape analysis and the values for ΔH and ΔS are reported. Proof for the proposed multiple ion pair equilibria between [$Fe(CO)_4CHO^-$] and Et_3B and [Li^+] is substantiated by the use of the hydride reagent LS-Selectride. Here, ion pairing is selective for [$Fe(CO)_4CHO$][Li] from −80 °C to room temperature as a result of trisiamylborane's inability to coordinate to the formyl oxygen.

Introduction

The reaction of neutral metal carbonyls, $M_x(CO)_y$, with trialkylborohydrides has been extensively studied as a route to anionic metal formyls, [$M_x(CO)_{y-1}CHO^-$] [1,2]. Typically, these formyls exist as either solvent-separated or contact ion pairs [3–9]. The latter ion pairs have been shown to involve an interaction between the formyl oxygen and the gegencation. Interestingly enough, no conclusive evidence exists for an interaction between an anionic metalloformyl and the generated Lewis acid R_3B [10,11]. However, Gladysz and coworkers have demonstrated that the presence of R_3B can modulate the stability of certain anionic metalloformyls,

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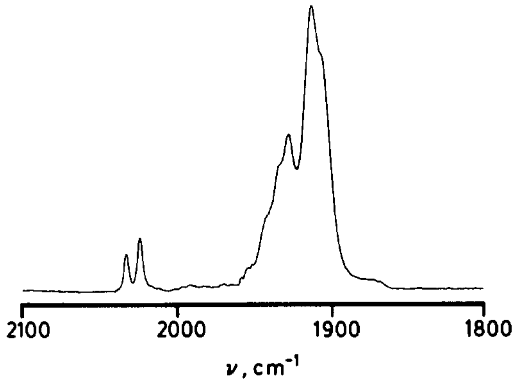

Fig. 1. Infrared spectrum of the terminal carbonyl region for the reaction of $Fe(CO)_5$ and $[Et_3BH][Li]$ in THF at −80 °C.

presumably through the formation of a discrete formyl oxygen–BR_3 contact ion pair [4b–e].

Recently, we had the need to prepare the formyl complex formed from $Fe(CO)_5$ and $[Et_3BH][Li]$ at −70 °C in connection with our studies dealing with the hydride-transfer properties of polynuclear formyl complexes [12]. To our surprise, low-temperature IR analysis exhibited more ν(CO) bands than expected for the known formyl complex $[Fe(CO)_4CHO][Li]$ [6,13]. Variable-temperature IR analysis revealed a clean conversion to $[Fe(CO)_4CHO][Li]$ as the temperature was raised, behavior indicative of an equilibrium between different ion pairs involving $[Fe(CO)_4CHO^-]$. On the basis of these observations, we report our results which demonstrate the existence of multiple equilibria involving the contact ion pairs $[Fe(CO)_4CHOBEt_3][Li]$ (**1**), $[Fe(CO)_4CHOBEt_3{}^-]$ (**2**), and $[Fe(CO)_4CHO][Li]$ (**3**), along with thermodynamics for the equilibrium for **2** ⇌ **3**.

Results and discussion

Treatment of $Fe(CO)_5$ with one equivalent of $[Et_3BH][Li]$ in THF at −78 °C affords the formyl complex $[Fe(CO)_4CHO^-]$ in quantitative yield [6,13]. Figure 1 shows the low-temperature IR spectrum in the terminal carbonyl region [14*]. The observation of two A_1 stretching bands at 2032 and 2024 cm^{-1} (Fig. 1) along with two formyl bands at 1488 and 1570 cm^{-1} (not shown) suggests that at least two types of contact ion pairs are present. The idealized C_{3v} symmetry displayed by these anionic formyls supports the existence of only formyl oxygen–$[Li^+/Et_3B]$ contact ion pairs [15,16]. On the basis of the effect of added Et_3B [17*], the former terminal and formyl ν(CO) bands are readily assigned to the formyl oxygen–BEt_3 contact ion pairs **1** and **2** (see below), while the latter two ν(CO) bands are assigned to known **3** [6,13].

Having established the nature of the ion pairs with $[Fe(CO)_4CHO^-]$, the effect of temperature on the equilibria between these ion pairs was next studied in order to quantify the thermodynamics associated with this system. Table 1 gives the K_{eq} values determined as a function of temperature [18*], while Fig. 2 shows the Van't

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

Table 1

Equilibrium parameters for the conversion of **3** into **2** and **2** into **1** [a]

$1000/T$, K^{-1}	$\ln K_{eq}$ [b]
3.80	4.20 [c]
3.95	3.59 [c]
4.12	2.68 [c]
4.29	2.21 [c]
4.48	1.67 [c]
4.69	1.24 [d]
4.81	1.07 [d]
4.93	0.900 [d]
5.05	0.730 [d]
5.18	0.620 [d]
$\Delta H_2 = 7.5 \pm 0.7$ kcal/mol [e]	$\Delta S_2 = 36.6 \pm 1.2$ e.u. [e]

[a] Prepared using equimolar amounts of $Fe(CO)_5$ ($\sim 3.66 \times 10^{-3}$ *M*) and $[Et_3BH][Li]$ in THF. The magnitude of K_{eq} was determined by following the changes in the area of the 2032 and 2024 cm^{-1} carbonyl bands. [b] Defined as the [area of **3**]/[area of **1**]+[area of **2**]. [c] Region defined by K_2. [d] Region defined by K_1. [e] Error limits at 95% confidence limits.

Hoff plot. Immediately apparent are two linear regions that are best explained by the equilibria given in eq. 1:

$$\underset{(1)}{Fe(BEt_3)^- Li^+} \overset{K_1}{\rightleftharpoons} \underset{(2)}{Fe(BEt_3)^- \| Li^+} \overset{K_2}{\rightleftharpoons} \underset{(3)}{Fe^- Li^+ \| BEt_3} \qquad (1)$$

The equilibrium represented by K_1 involves the intimate association of the lithium cation with **2** to give the termolecular ion pair **1**. To our knowledge, this

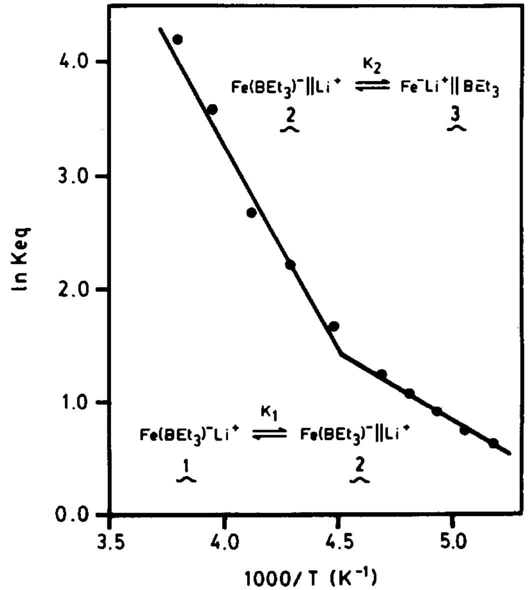

Fig. 2. Plot of $\ln K_{eq}$ vs $1/T$ illustrating the multiple ion pairing equilibria with $[Fe(CO)_4CHO^-]$ in THF.

phenomenon of multiple ion pairing has not been observed with anionic metal formyls. However, related triple ion equilibria are well-documented [3,19]. The complete expression for the relevant equilibria is given by $K_{\text{apparent}} = [\mathbf{3}]/[\mathbf{2}] + [\mathbf{1}]$, which leads to eq. 2.

$$\frac{1}{K_{\text{app}}} = \frac{[\text{Et}_3\text{B}]}{[\text{Li}^+]\left(\exp\frac{-\Delta H_2}{RT}\exp\frac{\Delta S_2}{R}\right)} + \frac{[\text{Et}_3\text{B}]}{\left(\exp\frac{-\Delta H_1}{RT}\exp\frac{\Delta S_1}{R}\right)\left(\exp\frac{-\Delta H_2}{RT}\exp\frac{\Delta S_2}{R}\right)} \tag{2}$$

Unfortunately, inadequate ν(CO) band resolution prevents an accurate assessment of ΔH_1 and ΔS_1 for the equilibrium associated with the conversion of **1** → **2**. The equilibrium between **2** and **3** is, however, easily evaluated above −55°C as [**1**] approaches zero. In this region eq. 3 dominates the equilibrium expression.

$$\frac{1}{K_{\text{app}}} = \frac{[\text{Et}_3\text{B}]}{[\text{Li}^+]\left(\exp\frac{-\Delta H_2}{RT}\exp\frac{\Delta S_2}{R}\right)} = \frac{[\mathbf{2}]}{[\mathbf{3}]} \tag{3}$$

Values of $\Delta H_2 = 7.5 \pm 0.7$ kcal/mol and $\Delta S_2 = 36.6 \pm 1.2$ e.u. are readily calculated for the conversion of **2** → **3**. Extrapolation of these data to room temperature predicts that only **3** should be observed, in agreement with earlier reports [6,13]. A full discussion of the relative importance of the enthalpic and entropic contributions to this latter equilibrium must await additional studies with different borohydrides and reaction solvents. Finally, these equilibria are readily reversible, provided that the solution is not warmed up above ~ 0°C. Extended warm-up leads to deleterious formyl deinsertion [6,13] and back hydride transfer to Et_3B to form $[\text{Et}_3\text{B–H–BEt}_3^-]$.

^{13}C NMR spectroscopy has been used to demonstrate the existence of cation ion pairing (i.e., $[\text{Li}^+]$, $[\text{Na}^+]$, $[\text{K}^+]$, and $[\text{PPN}^+]$) in $[\text{Fe(CO)}_4(\text{CHO})^-]$ [13]. Given the rapid solution equilibration associated with ion pairs ($\sim 10^{-8}$–10^{-10} s) [20], the slower ^{13}C NMR experiment gives only a single resonance, indicative of a population average. Thermodynamic parameters derived from temperature-dependent NMR chemical shifts can, in principle, be obtained in well-behaved systems as shown by Jackman et al. [21]. The situation becomes more complex when more than two species are in equilibrium or when the limiting chemical shifts cannot be obtained or accurately estimated. It is for these reasons we favor the use of variable temperature FT-IR spectroscopy for evaluation of ion pairing processes. Here each individual species can be spectroscopically detected on the IR time-scale ($\sim 10^{-13}$ s). Moreover, the use of variable-temperature FT-IR for ion pairing detection is especially attractive when dealing with limited quantities of material.

Confirmatory proof for the proposed Et_3B contact ion pairs was next established with the hindered borohydride LS-Selectride [22*]. Here only **3** was observed at all temperatures examined, consistent with trisiamylborane's inability to form a stable formyl oxygen-borane contact ion pair.

The observation of stable formyl oxygen–BEt_3 contact ion pairs suggests that similar ion pairs should be accessible for related iron acylate complexes, $[\text{Fe(CO)}_4\text{CRO}^-]$, and boranes. Although untested, such ion pairs could find use in the synthesis of unsymmetrical ketones [23] by directing the site of alkylation in much the same manner as the analogous lithium ion pairs [24]. The reaction of different borohydrides with $Fe(CO)_5$ and other metal carbonyls is planned along with detailed reactivity studies and thermodynamic evaluation of other formyl-borane contact ion pairs.

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