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Synthesis and Reactivity of the Polynuclear Formyl Cluster $PhCCo_3(CO)_8(CHO)^-$. Evidence for Facile Metalloformyl C–H Bond Scission

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Reducing agents (RLi and RMgX) and nucleophiles (amines and alcohols) have been reported to react with alkylidynetricobalt clusters $R'CCo_3(CO)_9$ to afford apically-substituted tricobalt clusters and/or $Co(CO)_4^-$, depending on the reaction conditions and the nature of the original R′ substituent [1–3]. These reactions are believed to proceed via an initial nucleophilic attack at a coordinated CO ligand [4, 5]. However, spectroscopic data (NMR and IR) for the proposed acyl intermediates are scarce, obscuring the course of such reactions. As part of our interest in CO-reduction pathways in polynuclear clusters [6], coupled with the uncertainty associated with the site of nucleophilic attack in $R'CCo_3(CO)_9$ clusters, we report our results on the hydridic reduction using $PhCCo_3(CO)_9$ (1) to give the thermally unstable formyl cluster $PhCCo_3(CO)_8(CHO)^-$ (2) and its decomposition to give $PhCCo_3(CO)_9{}^{\bullet -}$ (3) and $Co(CO)_4^-$ (5).

The reduction of $PhCCo_3(CO)_9$ (1) [7] with one equiv. of $LiEt_3BH$ in THF at −78 °C affords a brownish-green solution containing the polynuclear formyl complex 2 in quantitative yield. Complex 2 was characterized *in situ* by the standard techniques. The proton ^1H NMR spectrum of 2 (d_8-THF) at −78 °C exhibited a broad multiplet centered at δ 7.1, along with a broad resonance at δ 12.6 in a 5:1 integral ratio for the aromatic and formyl protons, respectively [8]. ^{13}C NMR analysis of 2 (−78 °C; d_8-THF), using ^{13}CO-enriched 1 [9] displayed two broad resonances at δ 247 and δ 206 in a 1:8 integral ratio. The low-field resonance is readily assigned to the formyl moiety, while the latter resonance is ascribed to the remaining eight carbonyl groups. The rapid equilibration of the terminal CO groups in 2 is not totally unexpected when one considers the facile rate of CO exchange in 1 and related derivatives [10]. The ^1H and ^{13}C NMR resonances gradually broaden as the temperature is raised to −50 °C, disappearing altogether upon the complete decomposition of 2 by −20 °C.

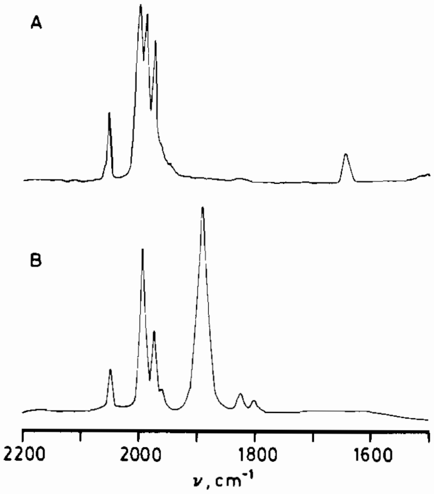

Fig. 1. Infrared spectra of the carbonyl region for (A) $PhCCo_3(CO)_8(CHO)^-$ (2) and (B) the decomposed formyl solution containing $PhCCo_3(CO)_9{}^{\bullet -}$ (3) and $Co(CO)_4^-$ (5). Both spectra were recorded in THF at −72 °C.

The decomposition of 2 was easily followed using variable-temperature FT-IR spectroscopy (THF solvent). Figure 1A shows the IR spectrum of 2 recorded at −72 °C. Particularly informative is the C–O stretching band at 1642 cm^{-1} that is readily assigned to the formyl moiety [8]. As the formyl solution is warmed, decomposition is observed starting at −40 °C and is complete by −20 °C (*vide supra*). The resulting IR spectrum (cooled back to −72 °C for comparative purposes) is shown in Fig. 1B, revealing the paramagnetic cluster $PhCCo_3(CO)_9{}^{\bullet -}$ (3) and $Co(CO)_4^-$ (5) [11] as the two major decomposition products. Quantitative FT-IR analysis indicated that 3 and 5 were formed in 38% and 41% yield, respectively. The identity of the compound(s) associated with the two minor C–O stretches (1820 and 1793 cm^{-1}; Fig. 1B) is currently unknown and attempts to isolate this material have been unsuccessful. Finally, additional proof for the presence of 3 was ascertained by EPR spectroscopy of the final reaction solution. A well-resolved, isotropic EPR spectrum centered at $g = 2.019$ was observed, in agreement with that published for $PhCCo_3(CO)_9{}^{\bullet -}$ [12]. The course of events for these reactions is depicted in eqn. (1).

Next we attempted to stabilize 2 towards decomposition by using the known hydrogen atom donors 9,10-dihydroanthracene and tri-n-butyltin hydride. Such additives have proven effective in retarding formyl decomposition in complexes that proceed by a metalloformyl C–H bond scission process [13]. However, our efforts proved unsuccessful as 2 decomposed at rates indistinguishable

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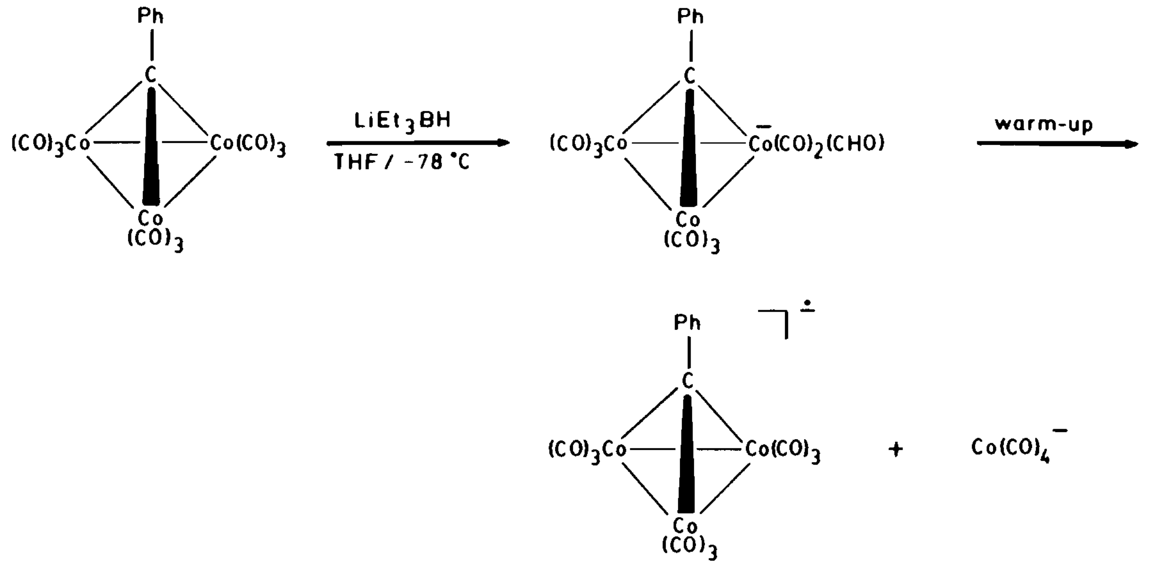

(1)

from reactions without these additives. The ability of **2** to function as a hydride donor was also examined, since many anionic formyl complexes reversibly release hydride faster than their decomposition rates [6b, 14]. When **2** (in THF) was treated with $Fe(CO)_5$ (1.1 equiv.) at −78 °C, no reaction was observed. Warming to room temperature led only to the formation of **3** and **5**; no $Fe(CO)_4(CHO)^-$ or $HFe(CO)_4^-$ were observed. The absence of transformylated products indicates that formyl **2** decomposes in preference to hydride liberation.

The observation of paramagnetic **3** is important in connection with alternative metalloformyl decomposition processes and the intervention of such radicals in catalytic cycles. Compound **3** represents the second unequivocal paradigm reported for a metalloformyl C–H bond scission process [15] we believe may be attributed to the redox stability associated with **3**. In comparison to related radical-chain decomposition reactions involving metalloformyl complexes [13, 16], **3** is unique because it is electrochemically stable. Typically, redox instability of the initial metalloradical drives the decomposition reaction in a chain-propagating fashion to the corresponding metal-hydride product [17]. However, once formed, $PhCCo_3(CO)_9^{\bullet -}$ (**3**) remains inert, a feature ascribed to the redox stabilization associated with the polynuclear cluster core [18].

The reaction of hydride with other $RCCo_3(CO)_9$ clusters (R = H, Cl, Br, Me) is currently being examined. These results along with our reduction studies with the heterometallic tetrahedrane clusters $PhCCo_2W(CO)_8Cp$ and $PhPFeCo_2(CO)_9$ will be reported shortly.

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