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Preliminary communication

Hydride addition to $Ru_3(CO)_{12}$. Synthesis and characterization of the transient formyl cluster complex $Ru_3(CO)_{11}(CHO)^-$

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Abstract

The reaction of $Ru_3(CO)_{12}$ (1) with $LiEt_3BH$ at −78 °C affords the transient cluster formyl complex $Ru_3(CO)_{11}(CHO)^-$ (2) which is observed to decompose by CO loss to give the known hydride cluster $Ru_3(CO)_{11}(H)^-$ (3) rapidly at temperatures above −50 °C. The formyl cluster has been characterized by low temperature FT-IR, ^1H and ^{13}C NMR measurements. Formyl trapping experiments and the effect of Bu_3SnH on the rate of formyl decomposition are briefly described.

Polynuclear formyl complexes continue to receive attention as possible intermediates in the homogeneously and heterogeneously catalyzed reduction of carbon monoxide to industrially important commodity chemicals [1,2]. Our interest in the hydridic reduction of $Ru_3(CO)_{12}$ (1) stems from earlier reports where it was suggested that formation of the known hydride cluster $Ru_3(CO)_{11}(H)^-$ (3) was preceded by the intermediacy of the corresponding formyl cluster $Ru(CO)_{11}(CHO)^-$ (2) [3]. Since the anticipated formyl cluster was not observed in solution by NMR measurements, this raised the question of whether a formyl intermediate was actually involved in the reductive transformation of $Ru_3(CO)_{12}$ (1) to $Ru_3(CO)_{11}(H)^-$ (3).

Herein we report the solution characterization and reactivity of the previously unreported formyl cluster $Ru_3(CO)_{11}(CHO)^-$ (2).

Results and discussion

Treatment of a tetrahydrofuran (THF) solution of $Ru_3(CO)_{12}$ (1) at −78 °C with a stoichiometric amount of $LiEt_3BH$ affords a red solution containing the spectroscopically identified formyl cluster **2**. Analysis of this solution using low temperature FT-IR techniques revealed the complete absence of $Ru_3(CO)_{12}$ (1) and the presence of CO stretching bands at 2034, 1988, 1966, 1948, 1918, 1897, 1883, and 1621 cm^{-1}. This latter band is readily assigned to that of the formyl moiety [4],

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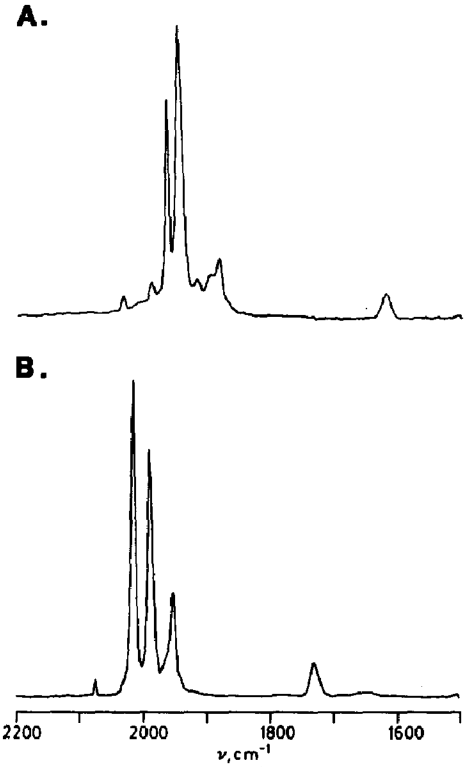


Fig. 1. Infrared spectra of the carbonyl region for (a) $Ru_3(CO)_{11}(CHO)^-$ (2), (b) $Ru_3(CO)_{11}(H)^-$ (3) in THF at −70 °C.

while the shifting of the terminal carbonyl bands to lower energy is consistent with the formation of an anionic ruthenium cluster. Upon warming to −50 °C, the solution darkens and acquires the blood-red color of the corresponding hydride cluster **3** (Eq. 1) [5]. Such a formyl-to-hydride transformation has been noted by others and presumably derives from a reductive decarbonylation reaction [6]. Figure 1 shows the low temperature IR spectra of clusters **2** and **3**.

$$\underset{(1)}{Ru_3(CO)_{12}} + LiEt_3BH \xrightarrow{THF} \underset{(2)}{[Ru_3(CO)_{11}(CHO)]^-} \rightarrow \underset{(3)}{[Ru_3(CO)_{11}(H)]^-} \qquad (1)$$

^1H NMR analysis of $Ru_3(CO)_{12}$ (**1**) in THF-d_8 at −78 °C with $LiEt_3BH$ showed the expected low-field resonance for **2** at 13.9 ppm. Warm-up to room temperature led to **3**, identified by its characteristic high-field ^1H NMR resonance at −12.8 ppm [5,7]. In order to glean information concerning the stereochemical disposition of the formyl moiety (i.e., equatorial or axial substitution), a ^{13}CO enriched sample of $Ru_3(CO)_{12}$ was treated with $LiEt_3BH$ at −78 °C and examined by ^{13}C NMR.

The ^{13}C NMR spectrum of **2** is shown in Fig. 2a. The two resonances at 215 and 282 ppm are assigned to the eleven terminal carbonyls and the formyl resonance, respectively. The assignment of the formyl resonance is ascertained by a gated decoupling ^{13}C NMR experiment, the results of which are shown in Fig. 2b. Here the formyl resonance appears as a doublet with $J(^{13}C-^1H)$ 135 Hz consistent with

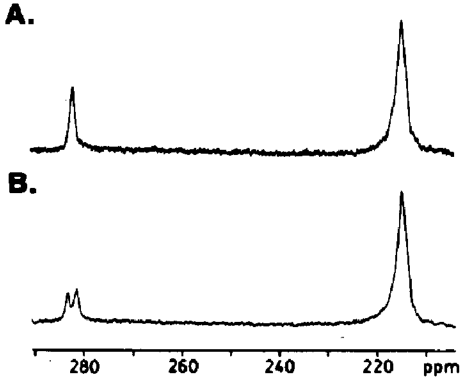
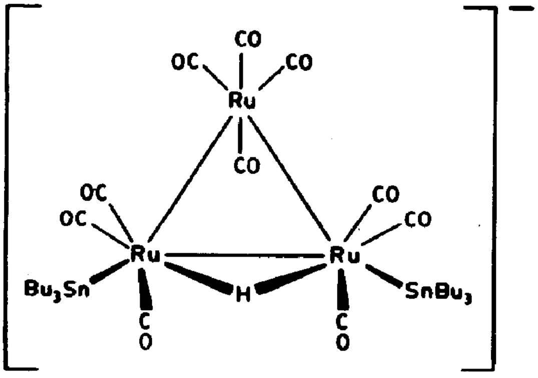


Fig. 2. (a) The $^{13}C\{^1H\}$ NMR spectrum of $Ru_3(CO)_{11}(CHO)^-$ (2) in THF-d_8 at −78 °C; (b) The ^{13}C gated decoupled NMR spectrum of the same solution.

the ascription of this resonance as that of the formyl moiety [4,8]. The rapid equilibration of the eleven carbonyl groups in **2** is not unexpected when one considers the facile rate of carbonyl exchange in $Ru_3(CO)_{12}$ and its substituted derivatives [9,10]. Unfortunately, such facile carbonyl exchange prevents us from assigning the stereochemistry of the formyl group in **2**. However, we note that analogous osmium acyl complexes display equatorial substitution [11].

Because of the extreme lability of **2** we next performed in situ trapping experiments designed to convert the anionic formyl complex **2** into neutral carbene derivatives. Treatment of **2** in THF at −78 °C with either methyl triflate or ethyl fluorosulfonate failed to yield the expected carbene clusters. The use of trifluoroacetic acid gave similar results. In all cases, only regenerated $Ru_3(CO)_{12}$ was observed and the nature of the hydride based products were not investigated further. These results suggest that **2** can function as a hydride transfer agent as observed in other formyl complexes [2,12].

Attempts to retard the decarbonylation in eq. 1 were unsuccessful when the hydrogen atom donor tri-n-butyltin hydride was used. This additive has proven effective in retarding the rate of formyl decomposition in complexes that proceed via a free radical chain mechanism initiated by formyl C–H bond scission [13]. **2** decomposed in THF above −50 °C in the presence of Bu_3SnH to initially afford **3**, which then reacted slowly with Bu_3SnH to give $HRu_3(CO)_{10}(SnBu_3)_2^-$ (**4**) based on



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IR and NMR analyses. Hydrogen which accompanies the formation of **4** was detected by GC, but no attempt was made to quantify it. The IR spectrum of **4** is particularly informative as the bridging CO stretching band of **3** is absent, being formally replaced by two tri-n-butyltin moieties in **4**. Similar silyl, germyl, and stannyl complexes of this genre have been reported from the reaction of **3** with R_3SiH, R_3GeH, and R_3SnH compounds, respectively [14].

The formyl cluster **2** has been shown to be the direct precursor to $Ru_3(CO)_{11}(H)^-$ (**3**). Further characterization of the tri-n-butyltin adduct derived from **3** is currently under investigation and will be reported in due course.

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