Journal of Organometallic Chemistry, 182 (1979) C57—C60
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Preliminary communication

METAL FORMYL COMPLEXES. HYDRIDE TRANSFER TO GROUP VIII TRANSITION METAL CARBONYL CLUSTERS

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(Received July 16th, 1979)

Summary

The reaction of $LiBH(C_2H_5)_3$ with $Os_3(CO)_{12}$ or $Ir_4(CO)_{12}$ leads to the formation of spectroscopically detectable formyl complexes. In the latter case, the complex is smoothly converted to $[Ir_4(CO)_{11}H]^-$, an expected decomposition complex of the corresponding polynuclear formyl complex, $[Ir_4(CO)_{11}CHO]^-$.

Introduction

The synthesis, characterization, and chemical behavior of formylmetal complexes have served as focal points for a number of recent studies [1]. Complexes of this type have been implicated in the conversion of carbon monoxide and hydrogen to petrochemicals [2,3]. In addition, polynuclear metal carbonyl clusters have been suggested as possible catalysts or catalyst precursors in a number of these reactions [3,4]. Implicitly, metal clusters may be responsible for sustaining, or participating in the generation of, kinetically significant quantities of intermediate formyl complexes. We now wish to report the results of an investigation directed towards the preparation of polynuclear formyl-transition metal complexes.

Results and discussion

A variety of anionic formylmetal complexes have been generated via the reaction of hydride donors with neutral mono- and di-nuclear metal carbonyl complexes, (Eq. 1, $x = 1$ or 2) [5].

$$M_x(CO)_y + H^- \rightarrow [M_x(CO)_{y-1}CHO]^- \tag{1}$$

The generation of an isolable formyl complex with nuclearity greater than

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two has not been reported. We now wish to provide evidence which indicates that spectroscopically detectable formyl complexes can be generated via hydride attack on $Os_3(CO)_{12}$ or $Ir_4(CO)_{12}$. In the case of $Ir_4(CO)_{12}$, the results strongly suggest that the starting metal nuclearity has been retained in the formyl complex.

The reaction of a slight molar excess of $LiBH(C_2H_5)_3$ in THF with $Ir_4(CO)_{12}$ proceeds smoothly at 0°C under N_2 resulting in the formation of a clear orange red solution. Analysis of this solution revealed the presence of new bands in the IR (THF) 1590—1610 cm^{-1}, and NMR (THF, δ (ppm), 0°C) 14.2 (s, Ir—CHO). These signals disappeared as the solution was heated to 40°C over a 30 min period. The only new signal present in the NMR was detected at δ −15.2 (external TMS) (Fig. 1).

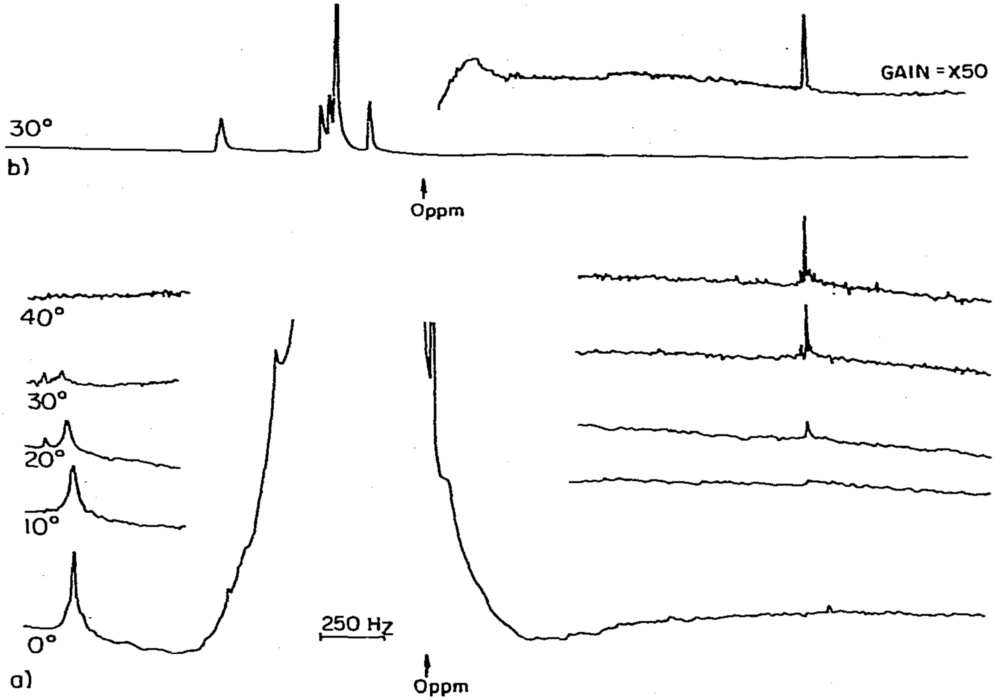

Fig. 1. ^1H FT-NMR spectra (100 MHz) of: (a) the solution from the reaction of $Ir_4(CO)_{12}$ with $LiBH(C_2H_5)_3$ in THF; (b) the THF solution of the complex, $[Ir_4(CO)_{11}H]^-$, prepared by the procedure of Malatesta [6].

The NMR and IR spectra were identical to those found for $[Ir_4(CO)_{11}H]^-$ which was prepared independently by the reaction of K_2CO_3 with $Ir_4(CO)_{12}$ as described by Malatesta [6]. These results are consistent with the formation of an intermediate formyl complex, $[Ir_4(CO)_{11}CHO]^-$.

The reaction of a slight molar excess of $LiBH(C_2H_5)_3$ in THF with $Os_3(CO)_{12}$ proceeds rapidly (10—20 min) at −20 to −30°C under N_2 with formation of a clear deep red solution. Spectral analysis reveals the appearance of a characteristic band in the IR (THF) 1590—1610 cm^{-1}, which in conjunction with ^1H FT-NMR (THF, δ (ppm), −20°C) 14.9 (s, Os—CHO) suggests that a pendant formyl moiety has been generated (Fig. 2). The solution was then warmed to 0°C over a 20 min period during which the NMR signal at δ 14.9 disappeared with concomitant appearance of several new signals with chemical shifts in the range of δ −13 to −23. These signals are indicative of a mixture of hydrido-osmium carbonyl complexes. Hydrides are likely decomposition products of the presumed formyl complex, $[Os_3(CO)_{11}CHO]^-$. The identity of the material(s) giving rise to these signals has not been established, although $[HOs_3(CO)_{11}]^-$, $[H_2Os_4(CO)_{12}]^{2-}$, and $[H_3Os_4(CO)_{12}]^-$ are candidates [7a,b].

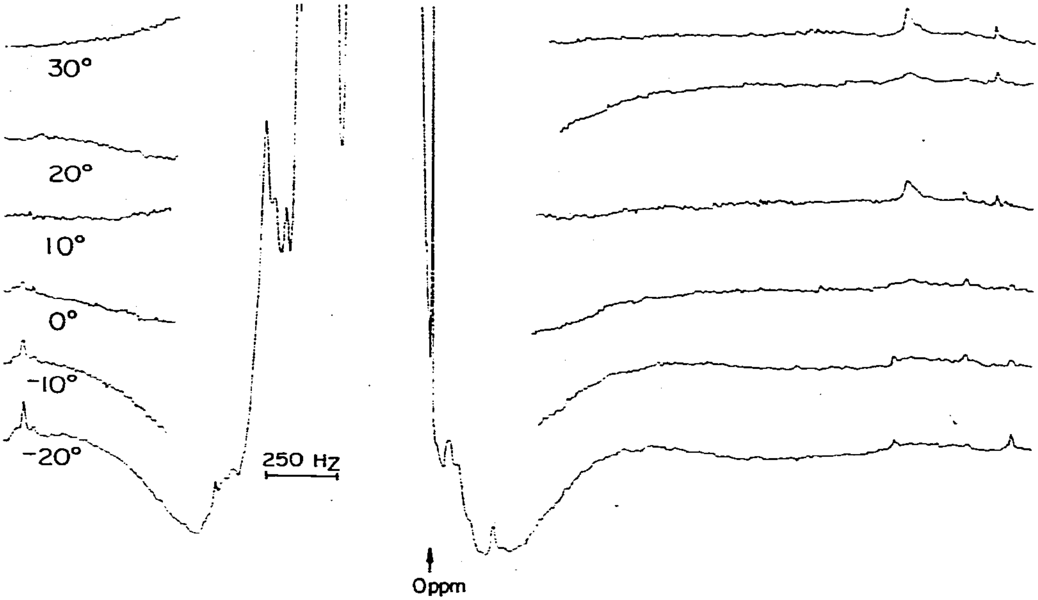

Fig. 2. ^{1}H FT-NMR spectra (100 MHz) of the solution from the reaction of $Os_3(CO)_{12}$ with $LiBH(C_2H_5)_3$ in THF.

The reaction of $LiBH(C_2H_5)_3$ with $Ru_3(CO)_{12}$ was also examined at temperatures from −20 to 0°C. In all cases the only detectable reaction product was $[Ru_3(CO)_{11}H]^-$ [7c]. The anticipated formyl complex, $[Ru_3(CO)_{11}CHO]^-$ appears to undergo facile decarbonylation, even under these relatively mild conditions. The ^{1}H FT-NMR spectra are shown in Fig. 3.

Small amounts of methanol (ca. 20—30% based on $M_x(CO)_y$) were detected when the solutions containing the initial formyl complexes were quenched with CF_3COOH. Casey has previously noted a similar result in the direct reaction of Et_3N^+ $[(C_6H_5O)_3P(CO)_3FeCHO]^-$ with CF_3COOH [5b]. The binuclear formyl complex, $[Re_2(CO)_9CHO]^-$ Li^+, prepared by Gladysz, gave methanol only after reaction with excess hydride [5a]. Attempts to isolate the polynuclear formyl complexes listed above have proved unsuccessful. As a result, it is difficult to establish which of the methanol forming sequences most closely represents that occurring with these formyl complexes.

Determination of the approximate half lives for the proposed polynuclear formyl complexes indicates the following stability trend, $Re_2(CO)_9CHO^- >$ $Ir_4(CO)_{11}CHO^- > Os_3(CO)_{11}CHO^- > Ru_3(CO)_{11}CHO^-$. It appears that the stability trend does not correlate with the nuclearity, metal—metal, or metal—carbon monoxide bond strengths of the starting metal carbonyl complexes [8]. Additional comments regarding the features responsible for this trend must await a more thorough definition of the hydride—formyl interconversion mechanism.

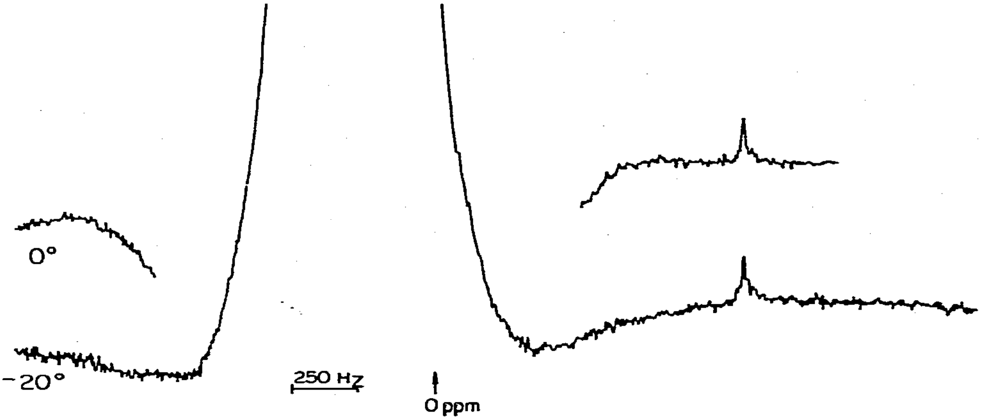

Fig. 3. ^{1}H FT-NMR spectra (100 MHz) of the solution from the reaction of $Ru_3(CO)_{12}$ with $LiBH(C_2H_5)_3$ in THF.

Acknowledgements

The authors are grateful to Union Carbide Corporation for allowing publication of this work.

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