Journal of Organometallic Chemistry, 206 (1981) C43—C48
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

FORMYL COMPLEXES OF TRANSITION METAL CARBONYL CLUSTERS

II*. SPECTROSCOPIC STUDY BY ^2H NMR OF THE SYNTHESIS OF $[Ir_4(CO)_{12-x}(CHO)_x]^{x-}$, $[Os_3(CO)_{11}(CHO)]^-$ AND $[Ru_3(CO)_{11}(CHO)]^-(x = 1,2)$

R.C. SCHOENING*, J.L. VIDAL and R.A. FIATO

Union Carbide Corporation, Research and Development Department, P.O. Box 8361, South Charleston, WV 25303 (U.S.A.)

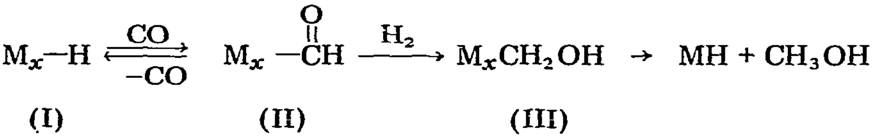
(Received August 12th, 1980)

Summary

The reactions of $LiHB(C_2H_5)_3$ and $LiDB(C_2H_5)_3$ with $Re_2(CO)_{10}$, $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Rh_4(CO)_{12}$ have been studied by ^1H, ^2H and ^{13}C NMR techniques. Results suggest the formation of formaldehyde and methanol in these systems, as well as the existence of previously unreported formyl complexes. A ^2H isotope effect is noted in the apparent increase in stability of cluster formyl complexes.

Introduction

A reaction scheme describing participation of metal formyl (II) and hydroxymethyl (III) complexes in the hydrogenation of carbon monoxide to alcohols is shown below (eq. 1).



$$M_x{-}H \underset{-CO}{\overset{CO}{\rightleftarrows}} M_x{-}\overset{\overset{O}{\|}}{C}H \xrightarrow{H_2} M_xCH_2OH \rightarrow MH + CH_3OH \qquad (1)$$

(I) (II) (III)

The existence of mono- and binuclear complexes (x = 1,2) containing these functional groups is well established [1,2].

Activation of carbon monoxide by clusters has been proposed [3a], and the presence of clusters in several catalytic systems [3b] suggests the existence of

---

*For part I see ref. 3d.

polynuclear complexes II and III ($x \geqslant 3$). Cluster hydride complexes (I) are known [3c]; we recently prepared [3d] the related formyl species (II) and studied their thermal stability (summarized in Table 1 below).

Reactions of hydride donors with $Re_2(CO)_{10}$, $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, $Ru_3(CO)$ and $Rh_4(CO)_{12}$ have been studied with ^2H and ^{13}C NMR techniques. Results suggest the formation of formaldehyde and methanol in these systems as well as the existence of previously unreported formyl complexes.

TABLE 1

THERMAL STABILITY OF TRANSITION METAL CLUSTER FORMYL COMPLEXES

Initial cluster	Formyl species δ (ppm)	Decomposition product δ (ppm)	Thermal range of formyl stability (1 atm Ar)
$Ir_4(CO)_{12}$	$Ir_4(CO)_{11}(CHO)^-$; 14.2	$Ir_4(CO)_{11}H^-$; −15.2	$\leq$+20°C
$Os_3(CO)_{12}$	$Os_3(CO)_{11}(CHO)^-$; 14.9	$Os_3(CO)_{11}H^-$; −13.6	$\leq$−10°C
$Ru_3(CO)_{12}$	—	$Ru_3(CO)_{11}H^-$; −12.9	$\leq$−40°C

Results and discussion

The reactions were conducted as in our previous report [3d] but using $LiDB(C_2H_5)_3$ (Ventron, Alfa Products) instead of $LiHB(C_2H_5)_3$.

A well characterized formyl-metal complex, $[Re_2(CO)_9CHO]^-$ [2], was studied initially. The ^1H NMR shift (THF, δ, amb.) of $[Re_2(CO)_9(CHO)]^-$ is reported at 15.78 ppm and 15.97 ppm with "in-situ" and isolated samples, respectively. A shift of 16.04 ppm (THF, δ, −40°C) was found by us during "in-situ" preparations, with the slight differences in shifts being probably caused by temperature and by the presence of $B(C_2H_5)_3$ in this case. A sample of $Re_2(CO)_{10}$ (1 mmol) in THF was treated with a 10% excess of similar solution of $LiDB(C_2H_5)_3$ under nitrogen. ^2H NMR spectra of this solution (THF, δ, −40°C) immediately after filtration show a resonance at 14.3 ppm (s, Re—CDO). Upon warming in the NMR tube over a period of 1 h, this signal gradually decreased and a new band (s, Re—D) appeared at δ −10.8 ppm (external TMS). The relative intensity of this band indicates that the conversion of the initial formyl to the hydride is not quantitative. This suggests that the formyl complex may be decomposing by a non-hydride-forming sequence, e.g., formation of methanol and formaldehyde. The chemical shift of this "deutero-formyl" resonance (δ 14.3 ppm) is different from that reported for $[Re_2(CO)_9(C\mathit{H}O)]^-$ (δ 16.04 ppm) [2], but in agreement with that reported for some bis-formyl complexes [4]. ^{13}C NMR spectra (THF, δ, −40°C) of the above reaction sequence using $LiHB(C_2H_5)_3$ showed the same shift, 281.4 ppm, and $J(^{13}C{-}H) = 128$ Hz as previously reported for $[Re_2(CO)_9(C\mathit{H}O)]^-$ [2], but a similar study using $LiDB(C_2H_5)_3$ gave a formyl-assignable resonance at 285.2 ppm with no detectable carbon—deuterium coupling. This evidence supports the existence of a deuterium analog to the bis-formyl complex proposed by Gladysz [4].

The reaction of $Ir_4(CO)_{12}$ with $LiDB(C_2H_5)_3$ proceeds smoothly at −10°C. ^2H NMR analysis of this solution shows a signal at δ 13.7 ppm (s, Ir—C*D*O) which on warming gradually transforms into a resonance at δ −16.2 ppm (s, Ir—*D*) which, by comparison to an independently prepared sample of this anion [5], can be assigned to $[Ir_4(CO)_{10}D_2]^{2-}$ (Fig. 1). Analogous systems with $LiHB(C_2H_5)_3$ did not exhibit this behavior. We suggest, from this study and from the known decarbonylation of II into I, that $[Ir_4(CO)_{10}(CDO)_2]^{2-}$ could be the source of $[Ir_4(CO)_{10}D_2]^{2-}$ in our system (eq. 2).

$$[Ir_4(CO)_{10}(CDO)_2]^{2-} \longrightarrow [Ir_4(CO)_{10}D_2]^{2-} + 2CO \qquad (2)$$

^{13}C NMR studies conducted with a ^{13}CO enriched sample of $Ir_4(CO)_{12}$ con-

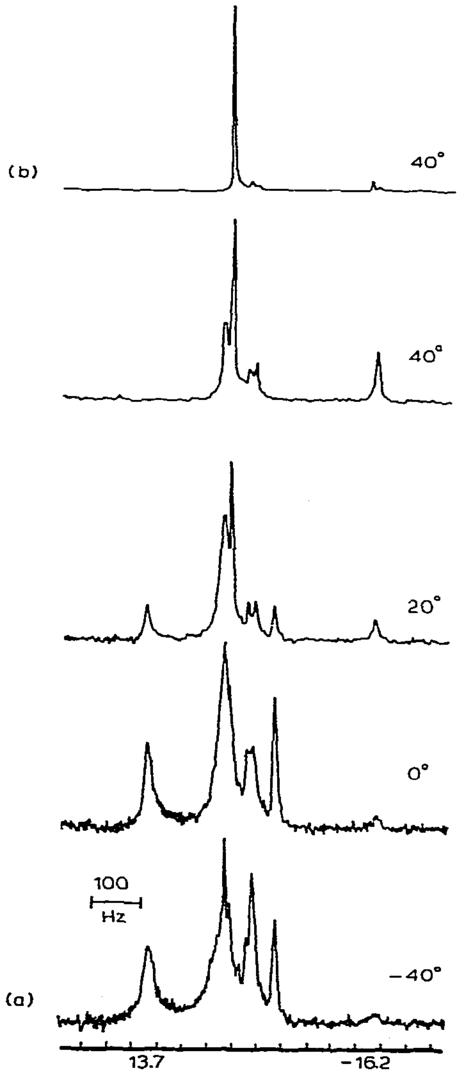


Fig. 1. ^2H NMR spectra of the reaction between $Ir_4(CO)_{12}$ and $[DB(C_2H_5)_3]^-$ (a) as a function of temperature, (b) after addition of one drop of CD_3OD.

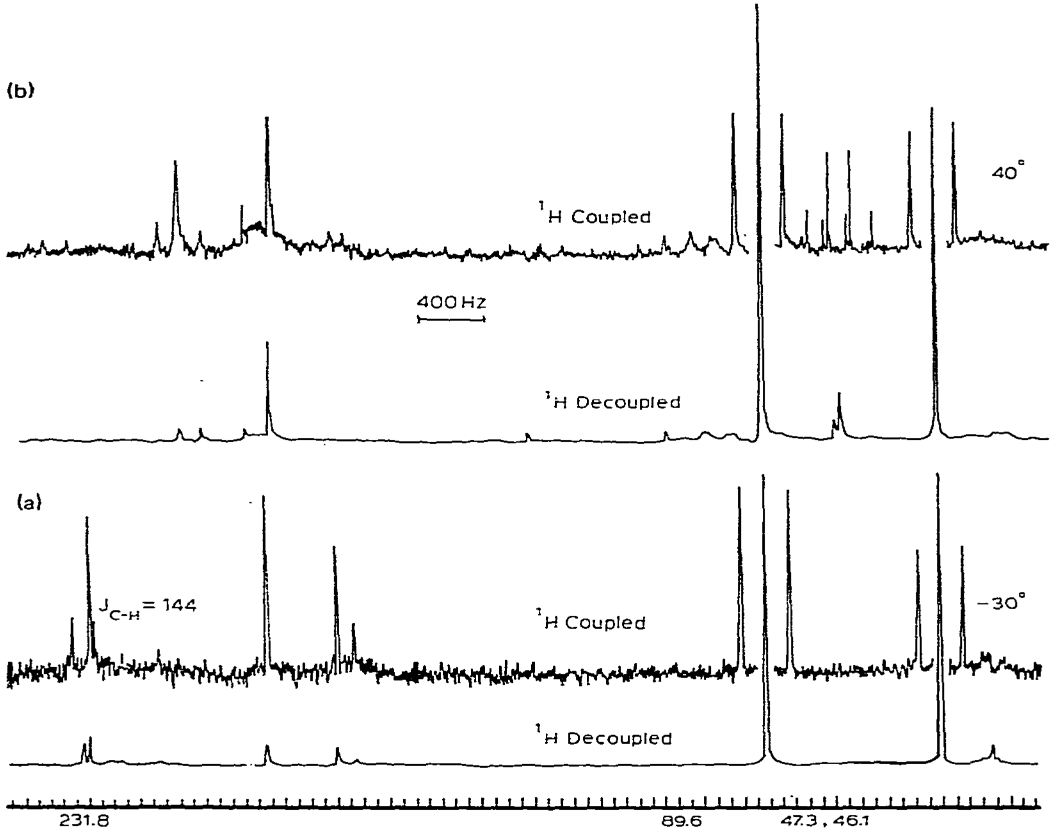


Fig. 2. ^{13}C NMR spectra of the reaction of $Ir_4(CO)_{12}$ with $HB(C_2H_5)_3^-$ after a 2.5 h contact time at (a) −30°C and (b) 40°C.

firmed the presence of only one formyl species in the borohydride system (THF, −30°C), 231.8 ppm and J (^{13}C—H) = 144 Hz (Fig. 2). On warming to 40°C, resonances assignable to methanol (q, 46.1 ppm), methoxy (q, 47.3 ppm) and formaldehyde (t, 89.6 ppm) were generated. NMR analysis of natural abundance carbon-13 samples [3d] gave no detectable resonances. Similar studies with the borodeuteride mixture (THF, −30°C) showed the presence of a different formyl resonance (s, Ir—C*D*O) at 266.0 ppm without evidence for C—D coupling. We noted multiplets consistent with D_2CO (89.6 ppm), CD_3OD (46.1 ppm) and CD_3O^- (47.3 ppm) as in the case of $Re_2(CO)_{10}$. The presence of methoxy-containing species was confirmed by GC/MS trapping of CD_3OD and by the increase of ^{13}C and ^{2}H NMR signals, δ 46.1 and 3.03 ppm, respectively, upon addition of methanol-d_4. The appearance of a ^{2}H NMR signal (s, 40°C) at δ −15.2 ppm on addition of methanol-d_4 is consistent with the presence of $[Ir_4(CO)_{11}D]^-$ and confirmed by comparison with independent preparation of authentic samples of this complex [5]. This transformation can be explained (eq. 3) by the ability of formyl complexes to transfer hydride with subsequent formation of $[Ir_4(CO)_{11}]^{2-}$. The intermediacy of a bis-formyl species as a precursor to formaldehyde and methanol is consistent with previous proposals by Gladysz et al. [4]. The detection of $[Ir_4(CO)_{10}(CDO)_2]^{2-}$ and $[Re(CO)_8(CDO)_2]$

in our case is a probable consequence of the increased kinetic stability of the bis-formyl complexes with respect to their non-deuterated analogues, as recently found by Gladysz et al. [6] with mononuclear complexes.

$$[Ir_4(CO)_{10}(CDO)_2]^{2-} \xrightarrow{-D_2CO} [Ir_4(CO)_{11}]^{2-} \xrightarrow{CD_3OD} [Ir_4(CO)_{11}D]^- + CD_3O^- \quad (3)$$

The blood-red solution obtained by mixing $Ru_3(CO)_{12}$ with $LiDB(C_2H_5)_3$ at −70°C did not exhibit ^2H NMR bands corresponding to metal formyl or hydride complexes. A signal δ 12.8 ppm (s, Ru—C*D*O), is noted, however, upon increasing the temperature to −50°C with a new band at δ −12.9 ppm (s, Ru—*D*) appearing upon further warming. The signal at high field is consistent with $[Ru_3(CO)_{11}D]^-$ while the formyl resonance at δ 12.8 ppm probably corresponds to $[Ru_3(CO)_{11}(CDO)]^-$. In contrast to earlier results (vide supra), the enhanced stability of this complex over its ^1H analog may have facilitated its detection.

The reactions of $Os_3(CO)_{12}$ with borohydride or deuteride gave results similar to $Ru_3(CO)_{12}$ [3d]. The appearance of other M—H(D) resonances, in addition to that of $[Os_3(CO)_{11}H]^-$, were noted, however, in the deuterium experiments. In the case of $Rh_4(CO)_{12}$ the hydride and deuteride systems are also similar. The reaction proceeded smoothly at −100°C giving a blood-red solution for which a ^2H NMR formyl resonance was undetectable, although a signal δ −14.6 ppm (−60°C, Rh—*D*), was noted upon warming. We have not yet determined whether these results should be attributed to the decarbonylation of rhodium-formyl species or to direct hydride transfer to the metal.

The reported [3d] series of polynuclear formyl complex decarbonylation rates can now be expanded: Re>Ir>Os>Ru. Our results also suggest that an isotope effect may have increased the stability and allowed detection of the bis-formyl complexes of Re and Ir as well as the mono-formyl Ru complex. The absence of C—D coupling in the ^{13}C NMR of the Re and Ir complexes may be due to ^2H quadrupolar relaxation; a $J(C—D) \simeq 20—24$ Hz was expected. The presence of five major ^2H NMR resonances at varying intensities relative to temperature in the δ 0—10 ppm region for all the cases (Fig. 1) is indicative of species derived from $DB(C_2H_5)_3^-$ and probably related to reaction sequences involving I or II. Within the reactant concentration range studied (cluster: $DB(R_3)^-$ molar ratios, 0.8 to 1.2) no significant variation of product distribution was observed.

Acknowledgement

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

References

1 H. Pichler and H. Schultz, Chem. Ing-Tech., 42 (1970) 1162; C. Masters, Adv. Organometal. Chem., 17 (1979) 61.

2 C.P. Casey, M.A. Andrews and J.E. Rinz, J. Amer. Chem. Soc., 101 (1979) 741; W. Tam, W.K. Wong and J.A. Gladysz, ibid., 101 (1979) 1585; T.J. Collins and W.R. Roper, J. Organometal. Chem., 159 (1978) 73; B.N. Chaudret, D.J. Cole-Hamilton, R.S. Nohr and G. Wilkinson, J. Chem. Soc. Dalton Trans., (1977) 1546; J.P. Collman and S.R. Winter, J. Amer. Chem. Soc., 95 (1973) 4089; J.A. Gladysz and J.C. Selover, Tetrahedron Lett., (1978) 319; J.A. Gladysz, G.M. Williams, W. Tam and D.L.

Johnson, J. Organometal. Chem., 140 (1977) C1; W.K. Wong, W. Tam and J.A. Gladysz, J. Amer. Chem. Soc., 101 (1979) 5440; C.P. Casey, M.A. Andrews and D.R. McAlister, ibid., 101 (1979) 3371.

3 (a) E.L. Muetterties and J. Stein, Chem. Revs., 79 (1979) 479; E.L. Muetterties, T.N. Rhodin, E. Band, C.F. Brucker and W.R. Pretzer, Chem. Revs., 79 (1979) 91; E.L. Muetterties, Science, 196 (1977) 839; E.L. Muetterties, Bull. Soc. Chim. Belg., 84 (1975) 959.
(b) K.G. Caulton, M.G. Thomas, B.A. Sosinsky and E.L. Muetterties, Proc. Natl. Acad. Sci., USA, 73 (1976) 4274; G.C. Demitras and E.L. Muetterties, J. Amer. Chem. Soc., 99 (1977) 2796; M.G. Thomas, B.F. Beier and E.L. Muetterties, J. Amer. Chem. Soc., 98 (1976) 1296; C.U. Pittman and R.C. Ryan, Chem. Tech., (1978) 170 and references therein; J.L. Vidal, W.E. Walker, R.A. Fiato, R.L. Pruett and R.C. Schoening, Fundament. Res. Homog. Catal., 3 (1980) 499 and references therein;
(c) P. Chini and B.T. Heaton, Topics Current Chemistry, Vol. 71, Springer-Verlag, Berlin, 1977, p. 1; A.P. Humphries and H.D. Kaesz, Prog. Inorg. Chem., 25 (1979) 145.
(d) R.L. Pruett, R.C. Schoening, J.L. Vidal and R.A. Fiato, J. Organometal. Chem., 182 (1979) C57.

4 J.A. Gladysz and W. Tam, J. Amer. Chem. Soc., 100 (1978) 2545.

5 M. Angoletta, L. Malatesta and G. Gaglio, J. Organometal. Chem., 94 (1975) 99; L. Malatesta and G. Caglio, Chem. Commun., (1967) 420; G. Ciani, M. Manassero, V.G. Albano, F. Canziani, G. Giordano, S. Martinengo and P. Chini, J. Organomet. Chem., 150 (1978) C17.

6 J.C. Selover, M. Marsi, D.W. Parker and J.A. Gladysz, J. Organometal. Chem., 206 (1981) 317.