Journal of Organometallic Chemistry, 213 (1981) 207—213
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

LIGAND DYNAMICS IN $H_2Os_3(CO)_{10}$ AND $H_2Os_3(CO)_{10}L$ *

S. AIME *, D. OSELLA

Istituto di Chimica Generale ed Inorganica, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino (Italy)

L. MILONE *

Istituto di Chimica Generale ed Inorganica, Università di Pavia, Viale Taramelli, 12, Pavia (Italy)

E. ROSENBERG *

Department of Chemistry, California State University, Northridge (U.S.A.)

(Received January 13th, 1981)

Summary

The variable temperature ^{13}C NMR spectra of $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_{10}L$ ($L = P(C_6H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(i\text{-}C_3H_7)_3$) have been recorded and the results interpreted in terms of a localized exchange process involving concerted motion of the hydride and carbonyl ligands. Taken along with previously reported variable temperature ^1H NMR data the results provide a complete picture of the ligand dynamics in these systems.

Introduction

In recent years there has been a growing interest in the study of stereochemical nonrigidity in metal cluster derivatives, based in the hope that a knowledge of ligand exchange processes in these systems would shed some light on the mobility of chemisorbed species on a metal surface [1].

A number of processes have been observed for intramolecular exchange of coordinated carbon monoxide in trimetallic clusters, ranging from localized axial—radial exchange at a single metal atom to delocalized "merry-go-round" process which can involve up to eight carbonyl ligands. The study of the variable temperature ^{13}C NMR spectra of metal carbonyl hydrides can give additional insight into the mechanisms of hydride exchange and its relation to CO migra-

---

* Dedicated to the memory of Professor Paolo Chini.

tion. In the case of $H_2Os_3(CO)_{10}$ the equivalence of the two hydrides prevents evaluation of their stereochemical rigidity by ^1H NMR [2].

In the case of $H_2Os_3(CO)_{10}L$ [3] two hydride signals are observed in the low temperature limiting ^1H NMR spectrum and these merge into a single resonance at room temperature, but the pathway for this exchange and its relationship to possible motions of the CO groups could not be defined. We report here the results of our studies on the variable temperature ^{13}C NMR spectra of ^{13}CO enriched samples of $H_2Os_3(CO)_{10}$ (I) and $H_2Os_3(CO)_{10}L$ (II) ($L = P(C_6H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(i\text{-}C_3H_7)_3$), which give a more complete picture of the ligand dynamics in these systems.

Results and discussion

The ^{13}C NMR spectrum of I, at room temperature, shows four resonances in the CO region at 182.7, 181.8, 176.3 and 175.2 ppm (rel. int. = 1 : 1 : 1 : 2), when ^1H decoupling is used. In the ^1H-coupled spectrum the resonance at 175.2 ppm appears as a doublet of doublets ($^2J(H{-}C)$ = 10.7 Hz and 0.8 Hz). We assign this resonance to the four CO groups in the plane perpendicular to the plane of the metal triangle and on the metal atoms bridged by the hydrides. The larger coupling is probably due to the *trans* H—CO interaction and the smaller to the *cis*. These observations demonstrate that the hydrides and CO groups are rigid at room temperature. As the temperature is increased the resonances at 176.3 and 175.2 ppm broaden and merge to a slightly broadened singlet (in the ^1H-coupled spectrum) at 175.6 ppm (at 113°C) while the downfield resonances remain unchanged. These changes in the spectrum can be interpreted in terms of a CO site exchange on the osmium atoms bridged by the hydrides. The loss of the large hydrogen coupling can be associated with an intermolecular ligand exchange, since a partial decomposition of the sample is observed after a prolonged heating at these temperatures. In order to further investigate the relationship between CO and hydride mobility in this type of system we then examined the variable temperature ^{13}C NMR spectra of three adducts of $H_2Os_3(CO)_{10}$.

From the solid state structure of $H_2Os_3(CO)_{10}2(P(C_6H_5)_3)$ (IIa) [4] ten different CO resonances would be expected in the low temperature limiting ^1H-decoupled ^{13}C NMR spectrum. As is shown in Fig. 1, only six resonances are detected, in intensity ratios of 4 : 1 : 1 : 1 : 1 : 2 (Table 1). In the ^1H-coupled spectrum the resonances at 180.2 ppm appear as a doublet ($^2J(H{-}C)$ = 24 Hz) while the resonances at 172.0, 174.9 and 170.4 ppm are noticeably broadened. As the temperature is increased to −40°C the resonances centered at 180.2 and 172.0 ppm broaden and disappear into the baseline. At 30°C these resonances merge to a single resonance at 176.1 ppm. In this range of temperature other minor changes in the spectrum are observed. The resonance of relative intensity 2 at 170.4 ppm is resolved into two resonances as a result of a small temperature dependence of the chemical shifts.

The ^{13}C NMR spectrum of $H_2Os_3(CO)_{10}P(O\text{-}i\text{-}C_3H_7)_3$ (IIb) shows seven resonances at the low temperature limit (−50°C), in intensity ratios of 2 : 2 : 1 : 1 : 1 : 2 : 1 (Table 1). As with IIa the ^1H-coupled spectrum shows a resolved doublet at 180.4 ppm and broadening of the resonances at 171.7 and

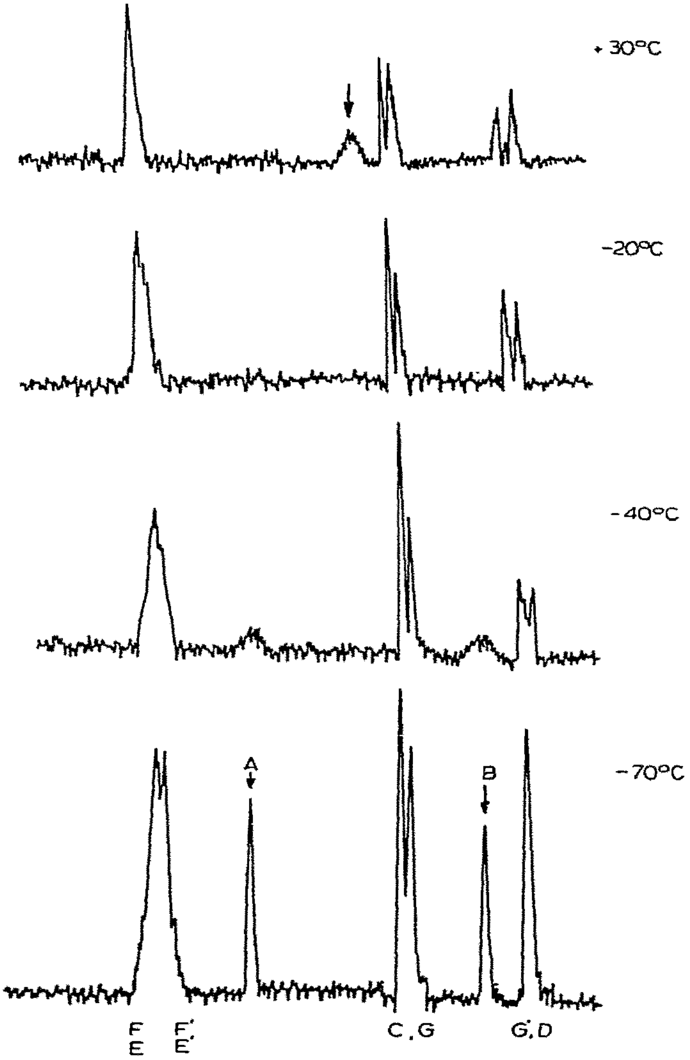


Fig. 1. ^{13}C NMR variable temperature spectra of the CO region of $H_2Os_3(CO)_{10}P(C_6H_5)_3$.

168.8 ppm. Again, two resonances at 180.4 and 171.7 ppm (the latter is partially obscured by overlap in the —50°C spectrum) broaden, collapse and merge to a single resonance as the temperature is increased to 26°C. In this temperature range, the signals centered at 183.5 and 181.2 ppm, which appear as broadened and complex resonances in the —50°C spectrum sharpen and appear as a singlet and a doublet at 26°C. The remaining resonances are unchanged in this temperature range except for a slight downfield shift of the resonance at 168.8 ppm.

The unfortunate overlap of four and three resonances in IIa and IIb, respectively, prompted us to examine yet another complex, $H_2Os_3(CO)_{10}P(i\text{-}C_3H_7)_3$ (IIc), in the hope that the combination of a more basic and bulkier phosphine

TABLE 1

^{13}C NMR CHEMICAL SHIFTS FOR $H_2Os_3(CO)_{11}L$ (δ, ppm)

	L	T (°C)	CO_A	CO_B	CO_C	CO_D	$CO_{E,E'}$	$CO_{F,F'}$	CO_G	$CO_{G'}$
IIa	$P(C_6H_5)_3$	−70	180.2	172.0	174.9	170.4	183.5	183.5	174.5	170.4
IIb	$P(O\text{-}i\text{-}C_3H_7)_3$	−50	180.4	171.7	175.2	168.8	181.2	183.5	174.9	171.7
IIc	$P(i\text{-}C_3H_7)_3$	−60	179.9	171.1	174.7	172.1	183.0	184.2	174.1	170.8

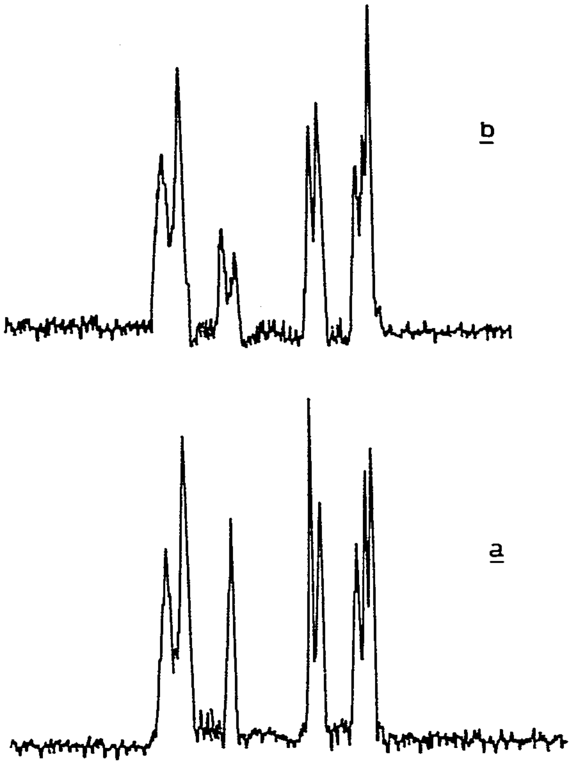
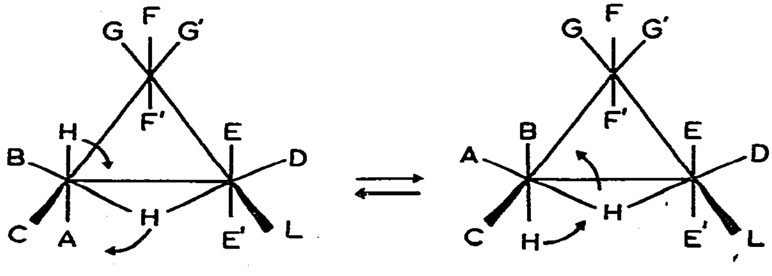


Fig. 2. Proton decoupled (a) and proton coupled (b) ^{13}C NMR spectra of the CO region of $H_2Os_3(CO)_{10}$-$P(i\text{-}C_3H_7)_3$ at −60°C.

would change the chemical shifts enough to give better resolution of the resonances at the low temperature limit. This hope was realized in that overlap between only two sets of the ten expected resonances occurs. The coupling and averaging patterns of IIc are virtually identical with those of IIa and IIb (Table 1, Fig. 2).

The low temperature limiting spectrum of IIa—IIc and their observed dynamic behaviour in the temperature range examined are consistent with only a localized CO and hydride exchange at the osmium atom bearing the terminal



SCHEME 1

hydride. Recognition of this exchange process allows an unambiguous assignment of almost all of the CO resonances in IIa—IIc. The CO resonances at 180.2, 180.4 and 179.9 ppm in IIa, IIb and IIc, respectively, can be assigned to CO_A (Scheme 1) *trans* to the terminal hydride on the basis of the observed large hydrogen carbon coupling. This resonance averages with only CO_B or CO_C as the temperature is increased. We propose that CO exchange is concerted with bridge—terminal hydride exchange where oscillatory motion of CO_A and CO_B with the terminal and bridging hydrides in the octahedral plane defined by these four atoms, site exchanges CO_A and CO_B (172.0 ppm in IIa, 171.7 ppm in IIb and 171.1 ppm in IIc) and brings the terminal and bridging hydrides to opposite faces of the metal triangle. This process simultaneously averages CO_F with $CO_{F'}$ and CO_E with $CO_{E'}$ and can thus be assigned to the resonances in the 181—184.0 ppm region, all of which sharpen as the high temperature limit is reached. This assignment is also consistent with the fact that axial CO groups are generally found at lower field than radial CO groups [5]. In IIb we can specifically assign the resonance at 181.2 ppm to the average of CO_E and $CO_{E'}$, based on the observed phosphorous—carbon two-bond coupling of 7.0 Hz, which is in good agreement with the results reported for other phosphine-substituted derivatives [5]. The resonances at 174.9 ppm in IIa, 175.2 ppm in IIb and 174.7 ppm in IIc can be assigned to CO_C, which remains virtually unchanged throughout the temperature range examined. The resonances at 170.4 ppm in IIa, 168.8 ppm in IIb and 172.1 ppm in IIc can be assigned to CO_D by virtue of the fact that increasing phosphine basicity would be expected to result in an increasing downfield shift of this resonance. We cannot rigorously exclude the possibility that CO_C and not CO_B is exchanging with CO_A, but we propose that cyclic motion of four ligands within a plane would be a lower energy process than any exchange pathway involving CO_C.

These findings clearly demonstrate that localized CO site exchange and bridge—terminal hydride interchange are interdependent processes in IIa—IIc. The mechanism proposed here is supported by the similar free energies of activation estimated for CO_A—CO_B site exchange and for bridge—terminal hydride exchange evaluated by ^1H NMR spectra [*]. The results also suggest that a similar interdependence of CO site exchange with hydride bridge opening may operate in other μ_2-hydride carbonyl complexes. We are currently investigating this point.

Experimental

Complexes I—IV were prepared according to literature procedures [3]. The ^{13}CO enrichment was performed with $Os_3(CO)_{12}$ by stirring for 4 days at 110°C (solvent toluene) in the presence of <1 atmosphere of 90% enriched ^{13}CO.

^{13}C NMR spectra were recorded on a Jeol-PFT-100 operating at 25.1 MHz.

---

[*] The ^1H NMR spectra of IIa, IIb and IIc in the hydride region show, in the low temperature limit, two resonances respectively at 19.9τ ($^2J(H,H) = 4$ Hz) and 29.3τ ($^2J(P,H) = 11$), 20.1τ ($J(H,H) =$ 4 Hz) and 30.3τ ($^2J(P,H) = 12$ Hz), 19.7τ ($^2J(H,H) = 4.5$ Hz) and 30.6τ ($^2J(P,H) = 11.0$ Hz). Estimated values for the free energy of activation are the following: $\Delta G^{\ddagger}_{253} = 12.1$ kcal mol^{-1} for IIa, $\Delta G^{\ddagger}_{250} = 11.9$ kcal mol^{-1} for IIb ahd $\Delta G^{\ddagger}_{262} = 12.3$ kcal mol^{-1} for IIc.

Solutions of I—IV in $CDCl_3$ were sealed under vacuum in 10 mm tubes with the addition of 0.05 *M* $Cr(acac)_3$ as an inert relaxation reagent. Accumulations of 200—500 transients were performed at each temperature at a spectral width of 1250 Hz. The temperature was monitored by a Jeol JNM-DB-TP-5-H100E temperature control unit with a termocouple approximately 1 cm below the sample (outside the RF and decoupling coils).

Acknowledgement

We thank Johnson and Matthey Co., London, for a loan of OsO_4 (L.M.). We also acknowledge support from NATO (L.M. and E.R., grant 1649/79), C.N.R. (S.A., Grant 79.02343.64) and PRF (E.R., Grant 9631 G4).

References

1 E.L. Muetterties, T.N. Rhodin, E. Band, C.F. Brucker and W.R. Pretzer, Chem. Rev., 79 (1979) 91.
2 R.W. Broach and J.M. Williams, Inorg. Chem., 18 (1979) 314, and references therein.
3 a) A.J. Deeming and S. Hasso, J. Organometal. Chem., 88 (1975) C21. b) A.J. Deeming and S. Hasso, J. Organometal. Chem., 114 (1976) 313.
4 M.R. Churchill and B.G. De Boer, Inorg. Chem., 16 (1977) 2397.
5 S. Aime and L. Milone, Progr. NMR Spectr., 11 (1977) 183 and references therein.