Stereochemical Nonrigidity in (μ_2-H)(H)$Os_3(CO)_{11}$. Evidence for the Occurrence of a Racemization Process at Low Temperature

Silvio Aime,* Walter Dastrù, and Roberto Gobetto

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7, 10125 Torino, Italy

Alejandro J. Arce

Centro de Quimica, Instituto Venezolano de Investigationes Cientificas, Apartado 21827, Caracas 1020-A, Venezuela

Received March 16, 1994[⊗]

Summary: A ^{13}C-2D EXSY experiment on a ^{13}C-enriched sample of $H_2Os_3(CO)_{11}$ at 220 K and at the observation frequency of 100.25 MHz indicates that this compound is involved in an intramolecular exchange between two enantiomeric structures prior to undergoing the axial/equatorial hydride motion typical of this type of adduct.

Introduction

The electron-deficient cluster $H_2Os_3(CO)_{10}$ (I) reacts with a wide variety of Lewis bases L to form[1,2] the electron-precise adducts (μ_2-H)(H)$Os_3(CO)_{10}$L (II).

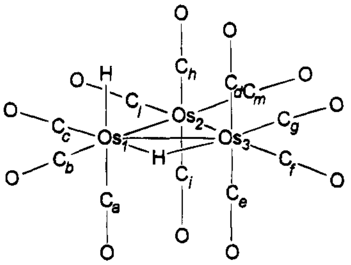
$$\underset{\text{I}}{H_2Os_3(CO)_{10}} + L \rightleftharpoons \underset{\text{II}}{(\mu_2\text{-}H)(H)Os_3(CO)_{10}L}$$

When L = CO (Chart 1), the formation of II is favored by the presence of a partial pressure of CO.[3]

The X-ray structure of the title compound has been reported, but the extensive crystal disorder prevented the direct localization of the hydride ligands. Their positions were assigned on the basis of (a) the isostructurality with $Os_3(CO)_{12}$[4] and (b) the low-temperature neutron diffraction study of the analogous (μ_2-H)(H)$Os_3(CO)_{10}PPh_3$ derivative.[5]

The solution structure and dynamics of (μ_2-H)(H)$Os_3(CO)_{10}$L have been investigated in detail for a number of added Lewis bases.[6–9] Invariably the fluxional process involves a concerted rotational movement of the two hydrides and pivoting of carbonyls a and c along the $(CO)_b$—Os_1—Os_2 vector. The averaging process of the two hydrides was observed also in the case of (μ_2-H)(H)$Os_3(CO)_{11}$, and the associated free activation energy as a result is quite similar to those measured for the other related adducts.[7] However, its variable-temperature (VT) ^{13}C NMR behavior is quite different from those of the analogous adducts with L = phosphine, isonitriles, etc., thus implying a more complex fluxional pathway for this compound.

Chart 1



Results and Discussion

The low-temperature limiting spectrum of a ^{13}C-enriched sample (~55% enrichment) of (μ_2-H)(H)$Os_3(CO)_{11}$ in CD_2Cl_2 in the presence of free CO is shown in trace A of Figure 1. The complete assignment has been accomplished on the basis of ^{13}C—^{13}C and ^{13}C—^{1}H coupling constants and NOE (nuclear Overhauser effect) measurements. In fact, the occurrence of a large $^2J_{C,C}$ ($^2J_{CC}$ = 35 Hz) coupling constant[10] between the two sets of related axial carbonyls (d and e; h and i) allows their easy localization in the spectrum. The fifth axial CO (carbonyl a) is unambiguously assigned to the resonance at 178.9 ppm on the basis of the large $^1J_{C,H}$ coupling ($^1J_{C,H}$ = 23 Hz) with the trans hydride ligand. Carbonyls c and g, trans to the bridging hydride, show a smaller $^2J_{C,H}$ coupling, as shown by the resonances at 171.2 ($^2J_{C,H}$ < 5 Hz) and 163.0 ($^2J_{C,H}$ = 9 Hz) ppm.

A powerful tool to get a complete assignment was provided by the measurement of the differential NOE's as the bridging and the terminal hydride resonances were selectively irradiated.[11] Then, the final assignment of the 11 resonances is as follows (δ ppm): 182.6 (CO_e), 181.3 (CO_d), 178.9 (CO_a), 173.8 (CO_i), 173.6 ($CO_{b/l}$), 173.5 ($CO_{l/b}$), 172.6 (CO_h), 171.2 (CO_c), 170.0 (CO_m), 164.8 (CO_f), 163.0 (CO_g).

The ^1H NMR spectrum at 200 K agrees well with those reported earlier by Deeming[1] and Shapley.[2] Inspection into the ^{187}Os satellite subspectra shows a

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

[1] (a) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1975,** *88,* C21. (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976,** *114,* 313.

[2] Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975,** *97,* 4145.

[3] Poë, A. J.; Sampson, C. N.; Smith, R. T.; Zheng, Y. *J. Am. Chem. Soc.* **1993,** *115,* 3174.

[4] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977,** *16,* 878.

[5] Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977,** *16,* 2397.

[6] Aime, S.; Osella, D.; Milone, L.; Rosenberg, E. *J. Organomet. Chem.* **1981,** *213,* 207.

[7] Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982,** *21,* 3304.

[8] Rosenberg, E.; Anslyn, E. V.; Barner-Thorsen, C.; Aime, S.; Osella, D.; Gobetto, R.; Milone, L. *Organometallics* **1984,** *3,* 1790.

[9] Keister, J. B.; Frey, U.; Zbinden, D.; Merbach, A. E. *Organometallics* **1991,** *10,* 1497.

[10] Aime, S.; Gobetto, R.; Osella, D.; Milone, L.; Rosenberg, E.; Anslyn, E. V. *Inorg. Chim. Acta* **1986,** *111,* 95.

[11] Farrugia, L. J.; Chi, Y.; Tu, W.-C. *Organometallics* **1993,** *12,* 1616.

0276-7333/94/2313-3737$04.50/0

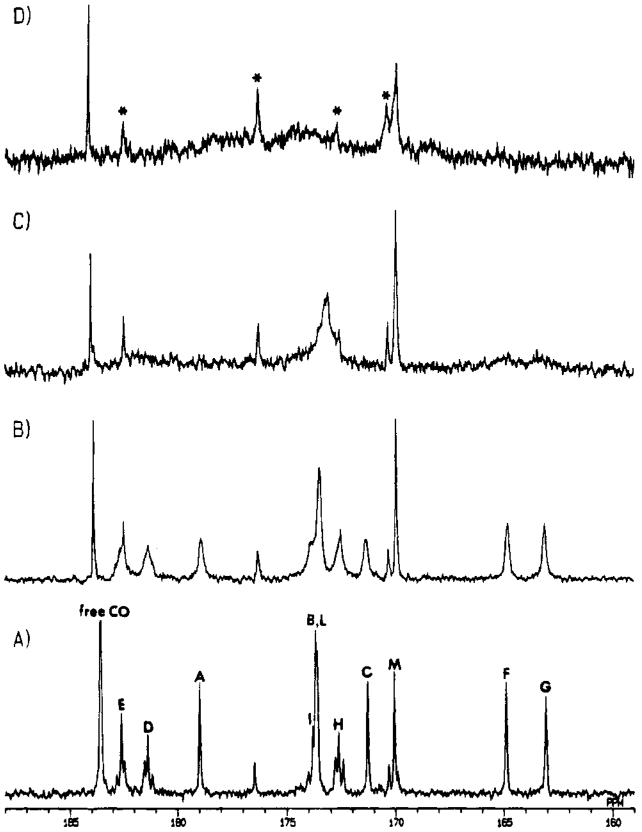


Figure 1. Variable-temperature ^{13}C NMR spectra of (μ_2-H)(H)$Os_3(CO)_{11}$ in CD_2Cl_2: (A) 200 K; (b) 240 K; (c) 270 K; (d) 300 K. The asterisks denote impurities.

$^1J_{^{187}Os,H}$ coupling of 38.1 Hz with the terminal hydride, whereas the bridging hydride is coupled to the two inequivalent osmium nuclei by 29.4 and 34.5 Hz, respectively. This latter observation is fully consistent with other asymmetrically bridging hydrides in Os_3-containing moieties.[12]

As the temperature is increased to 220 K, the ^{187}Os satellites of the bridging hydride broaden and collapse; in the same temperature interval a marked broadening is also observed for the ^{187}Os satellites flanking the terminal hydride resonance. At higher temperatures (from 230 K) the incipient bridge–terminal hydride exchange induces an overall broadening which prevents the observation of the ^{187}Os satellites.

Interestingly, in the 200–230 K temperature interval, no change occurs in the ^{1}H resonances of the main isotopomer. The observed behavior suggests an exchange process which averages out the structural differences between the two front Os_1 and Os_3 atoms without involving any exchange between bridging and terminal hydrides.

More helpful in the elucidation of the underlying exchange was consideration of the ^{13}C NMR spectrum. When the temperature is increased (traces B and C, Figure 1), the ^{13}C NMR spectrum shows a progressive broadening of all the resonances but one at 170.0 ppm (assigned above as CO_m on Os_2); this resonance broadens only at higher temperature (trace D, Figure 1).

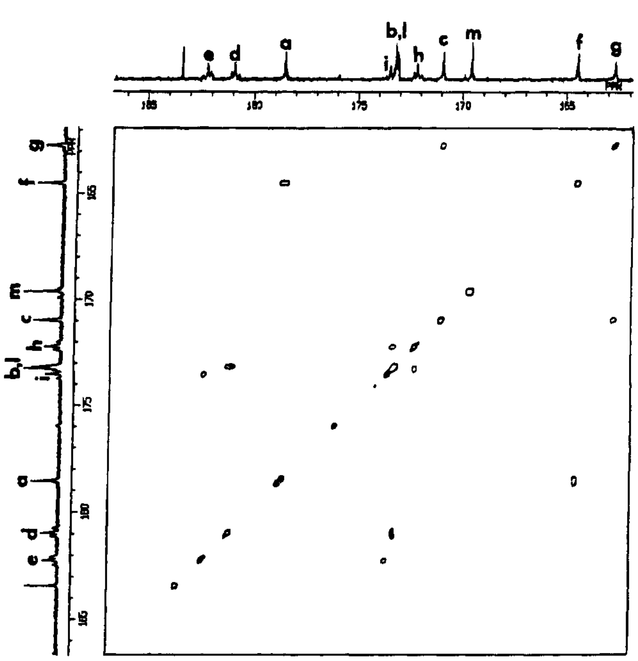


Figure 2. Contour plot of a ^{13}C-2D-EXSY experiment (100.25 MHz, CD_2Cl_2, 200 K, τ_m = 0.5 s) for (μ_2-H)(H)Os_3-$(CO)_{11}$.

Very informative in the elucidation of the exchange pathway was the ^{13}C-2D-EXSY[13] experiment carried out at 220 K in CD_2Cl_2 (Figure 2), which shows that all CO's exchange pairwise, except for one at 170.0 ppm. On the basis of the assignment reported above, the following pairwise exchange takes place: a $\rightleftarrows$ f, b $\rightleftarrows$ d, c $\rightleftarrows$ g, e $\rightleftarrows$ i, h $\rightleftarrows$ l. On the grounds of the observation made on the ^{187}Os subspectra in the ^{1}H VT spectra in the low-temperature range, we conclude that the reversible motion of the terminal hydride from Os_1 to Os_3 is coupled with the pairwise rearrangement of the carbonyl ligands.

Two possible mechanisms may be proposed to account for the observed behavior:

Mechanism I (Scheme 1) involves the reversible motion of the terminal hydride from Os_1 to Os_3, not directly through the bond connecting them but through Os_2 as the result of two successive "single-step merry-go-round" processes,[14] the first involving carbonyls a, b, h, m, and i and the terminal hydride and the second the terminal hydride and carbonyls d, f, e, m, and l. Such a single-step merry-go-round process is reminiscent of the dynamic behavior shown by the $[HFe_3(CO)_{11}]^-$ anion, where two carbonyls exchange by pairwise opening and closing of the hydride and carbonyl bridge units.[15] On the other hand, some similarity exists also with the exchange pathway described by Alex and Pomeroy[16] in $Os_3(CO)_{12-x}[P(OMe)_3]_x$ (x = 1–4) derivatives; all these clusters exhibit a pairwise terminal–bridge carbonyl exchange in a plane perpendicular to the Os_3 plane coupled with a restricted trigonal-twist mechanism exchanging a $P(OMe)_3$ ligand of an $Os(CO)_3$-$[P(OMe)_3]$ unit from one equatorial site to the other.

Mechanism II (Scheme 2) involves the exchange of the terminal hydride between Os_1 and Os_3 through an intermediate containing a μ_3-bridging hydride, accom-

---

[12] Farrugia, L. J. *Organometallics* **1989**, *8*, 2410 and references therein.

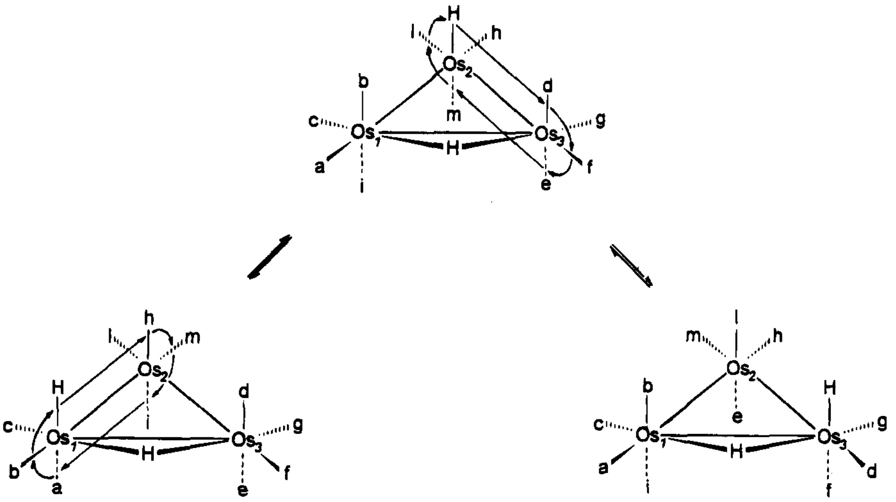
[13] Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

[14] Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

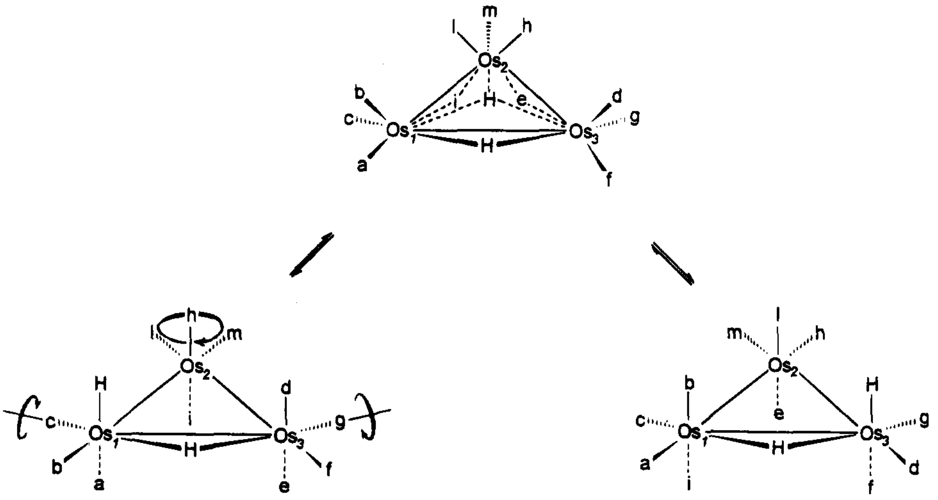
[15] Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1976**, *118*, 199.

[16] Alex, R. F.; Pomeroy, R. K. *Organometallics* **1987**, *6*, 2437.

Scheme 1



Scheme 2



panied by a concerted motion of carbonyls a, b, d, e, f, h, i, l, and m. In this process the motion of the terminal hydride and carbonyls a and b is pivoted along the Os_1-CO_c vector and the vacant site created at Os_1 by this rotation is readily filled up by the migration of CO_i from Os_2 to Os_1. At the Os_2 center a trigonal-twist rotation[17] of CO_h, CO_l, and CO_m takes place; this process involves the movement of the equatorial CO_m to the other equatorial site and axial–equatorial exchange between carbonyls l and h. Then, rotation at Os_3 to pivot along the Os_3-CO_g vector allows CO_e to move to Os_2 (to fill the vacancy left by CO_i) and the μ_3-hydride to occupy the terminal position at Os_3.

Interestingly, the rapid switch forward and backward along the pathways of both mechanisms leads to the exchange between the enantiomeric structures of $(\mu_2\text{-H})(H)Os_3(CO)_{11}$.

Although the various coordination modes of ligands such as hydride, PR_3, etc. may frequently give rise to chiral clusters, it is often difficult to sort out experimental procedures which unambiguously show their occurrence.[12,18] This appears to be an interesting case where the presence of the enantiomeric forms is revealed through the elucidation of the underlying exchange process.

Experimental Section

^{13}CO (99% enriched) was purchased from Isotec (Miamisburg, OH). $H_2Os_3(^{13}CO)_{10}$[19] and $(\mu_2\text{-H})(H)Os_3(^{13}CO)_{11}$[1] were prepared according to the published methods by using as starting material $Os_3(^{13}CO)_{12}$, obtained by direct exchange of ^{13}CO with $Os_3(CO)_{12}$ in *n*-octane at 110 °C for 3 days in sealed vials (250 mL); the level of enrichment was ~55% as judged from the isotopomer populations.

^{13}C NMR spectra were obtained on a JEOL EX400 spectrometer operating at 100.25 MHz.

The 2D EXSY experiment was acquired in the absolute mode at 220 K by using 512 words in the f_2 dimension and 256 words (doubled by zero-filling) in the f_1 dimension; the mixing time was 500 ms.

OM940204M

---

[17] Gavens, P. D.; Mays, M. *J. Organomet. Chem.* **1978**, *162*, 389.

[18] (a) Farrugia, L. J. *Organometallics* **1990**, *9*, 105. (b) Farrugia, L. J.; Rae, S. E. *Organometallics* **1991**, *10*, 3919.

[19] Kaesz, H. D. *Inorg. Synth.* **1990**, *28*, 238–239.