Organometallics **1996,** *15,* 4967−4970

H/D Isotopic Exchange on the Surface of a Triosmium Carbonyl Cluster

Silvio Aime,* Walter Dastrù, Roberto Gobetto, Jochen Krause,[†]
Lluisa Matas,[‡] and Alessandra Viale

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali,
Università di Torino, via Pietro Giuria 7, 10125 Torino, Italy

Received July 2, 1996[⊗]

The reactions of both $Os_3(CO)_{10}(NCCH_3)_2$ and $Os_3(CO)_{11}(NCCH_3)$ with HD or with a mixture of H_2/D_2 in chloroform solution at room temperature afford a mixture of $H_2Os_3(CO)_{10}$ (**Ia**), $HDOs_3(CO)_{10}$ (**Ib**), and $D_2Os_3(CO)_{10}$ (**Ic**). The three isotopomers are also obtained by reacting $H_2Os_3(CO)_{10}$ with D_2. By measurement of the rates of disappearance of **Ia** in the latter reaction at four different temperatures, the thermodynamic parameters have been estimated ($E_a = 43.7$ kJ/mol, $\Delta H^\ddagger = 41.2$ kJ/mol, $\Delta S^\ddagger = -0.17$ kJ/(mol K)). No H/D isotopic exchange has been observed after heating **Ia** and **Ic** in toluene for several hours. A mechanism involving the reversible oxidative addition and reductive elimination of molecular hydrogen on $H_2Os_3(CO)_{10}$ via the formation of a fluxional tetra(hydrido, deuterio) intermediate is proposed.

Introduction

It is well-known that the reaction of molecular hydrogen at transition-metal centers may result in both oxidative addition (leading to classical hydrides) or η^2-H_2 coordination (leading to nonclassical hydrides).[1−6] No example of the latter class of complexes has yet been reported among the vast array of hydrido cluster compounds. However, the η^2-coordination mode can be envisaged as an activated state or intermediate in hydrogenation reactions involving polymetallic systems.

In a typical reaction pathway the addition of H_2 to a cluster requires first the formation of a vacant coordination site (by ligand dissociation) to which H_2 subsequently binds in a η^2 fashion, followed quickly by an internal oxidative addition to form, in most cases, stable M−H−M bonds:

$$M_xL_y \xrightarrow{-L} M_xL_{y-1} \xrightarrow{+H_2} (\eta^2\text{-}H_2)M_xL_{y-1} \rightarrow H_2M_xL_{y-1}$$

Often the organometallic chemist has resorted to stable coordinatively unsaturated organometallic systems[7−9] to overcome the difficulties associated with ligand dissociation. For instance, the coordinatively unsaturated $H_2Os_3(CO)_{10}$ has been observed[10−16] to undergo a number of addition reactions with a variety of Lewis bases, L, according to the equation

$$(\mu\text{-H})_2Os_3(CO)_{10} + L \rightarrow (\mu\text{-H})HOs_3(CO)_{10}L$$

However, attempts to add H_2 to form the $48e^-$ $H_4Os_3(CO)_{10}$ species have been unsuccessful. Whether H_2 could not react with $H_2Os_3(CO)_{10}$ or whether the saturated $H_4Os_3(CO)_{10}$ is not stable enough to be isolated remains an open question. In this paper we report the results of H_2−D_2 exchange studies, which provide strong support for the view that $H_4Os_3(CO)_{10}$ is indeed formed in this reaction, although it cannot be isolated.

Results and Discussion

Some years ago it was shown that a convenient synthesis of $H_2Os_3(CO)_{10}$ involves the reaction at room temperature of the lightly stabilized $Os_3(CO)_{10}(NCCH_3)_2$ derivative with H_2. Poe and co-workers studied in detail the kinetics of this reaction, which proceeds through dissociation of the acetonitrile ligand and subsequent competition between MeCN and H_2.[17]

In an attempt to obtain the compound $HDOs_3(CO)_{10}$ at room temperature by reacting a chloroform solution of $Os_3(CO)_{10}(NCCH_3)_2$ with gaseous HD, we produced, after 12 h, a mixture of $H_2Os_3(CO)_{10}$ (**Ia**), $HDOs_3(CO)_{10}$ (**Ib**), and $D_2Os_3(CO)_{10}$ (**Ic**) in the approximate relative ratio of 1:2:1. When the reaction was stopped at shorter

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* To whom correspondence should be addressed. E-mail: aime@silver.ch.unito.it.

[†] Present address: Hoechst Aktiengesellschaft, Zentralforschung C 487, D-65926 Frankfurt am Main, Germany.

[‡] Permanent address: Dept. de Quimica, Universitat de Girona, Girona 17071, Spain.

[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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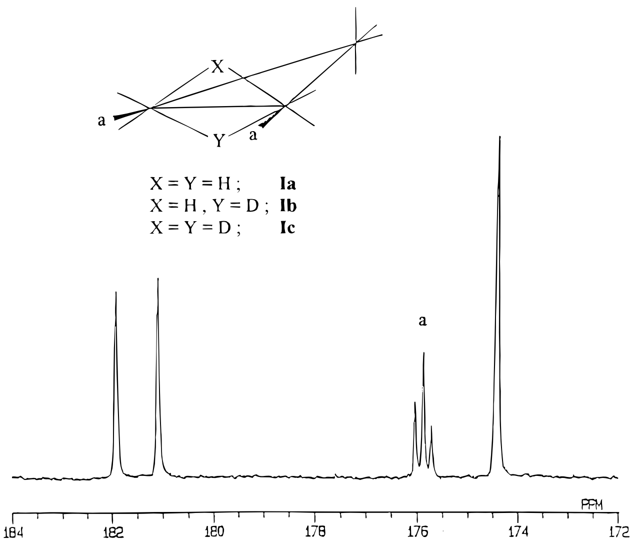

Figure 1. Proton-decoupled ^{13}C NMR spectrum of the mixture of $H_2Os_3(CO)_{10}$ (**Ia**), $HDOs_3(CO)_{10}$ (**Ib**), and $D_2Os_3(CO)_{10}$ (**Ic**) isotopomers obtained by reacting a ^{13}CO-enriched sample of $Os_3(CO)_{10}(NCCH_3)_2$ and HD ($CDCl_3$, room temperature, 100.25 MHz).

times, the amount of $HDOs_3(CO)_{10}$ formed was higher but invariably some $H_2Os_3(CO)_{10}$ and $D_2Os_3(CO)_{10}$ were present. The quantification of the three isotopomers has been possible by integrating the relative areas of the radial carbonyl resonance a (Figure 1), whose ^{13}C chemical shift is strongly affected by isotopic substitution.[18] In fact, the ^{13}C chemical shift of carbonyl a (solvent $CDCl_3$) appears at 176.09 ppm in **Ia**, at 175.89 ppm in **Ib** and at 175.73 ppm in **Ic**. The origin of such large isotopic shifts is not yet clear; certainly it appears much higher than that expected on changes in anharmonic vibrations upon changes in the atomic mass. Rather, it may imply structural effects associated with the high degree of stereochemical rigidity of this complex. At an observation frequency of 100 MHz no isotopic shift was observed for the other carbonyl resonances.

The quantification of the relative amounts of **Ia**, **Ib**, and **Ic** from the $^{13}C\{^1H\}$ NMR spectrum does not exactly correspond to the computed values of the areas of each resonance, since there is signal enhancement in the cases of **Ia** and **Ib** due to the nuclear Overhauser effect (NOE), which is not present in **Ic**. After careful measurement of the NOE contribution to the resonances of the proton-containing isotopomers, we found that the observed integrals for **Ia** and **Ib** have to be decreased by an amount corresponding to 6% and 3%, respectively.

The relative amounts of the **Ia** and **Ib** isotopomers may also be determined by ^1H NMR, since they show different ^1H chemical shifts (the hydride resonance of **Ib** is 0.007 ppm to lower field than **Ia** in $CDCl_3$ at room temperature).

Closely related results are obtained when the starting material is $Os_3(CO)_{11}(NCCH_3)$. In fact, when this compound is reacted with H_2 in chloroform solution at room temperature, there is first the formation of $H_2Os_3(CO)_{11}$ (characterized by two hydride resonances at −20.02 and −10.30 ppm, respectively; −60 °C, $CDCl_3$), followed by its slow transformation into $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$.[17] Again, the use of HD afforded the mixture of the three isotopomers **Ia**, **Ib**, and **Ic**, in a way analogous to that observed in the case of the reaction with $Os_3(CO)_{10}(NCCH_3)_2$.

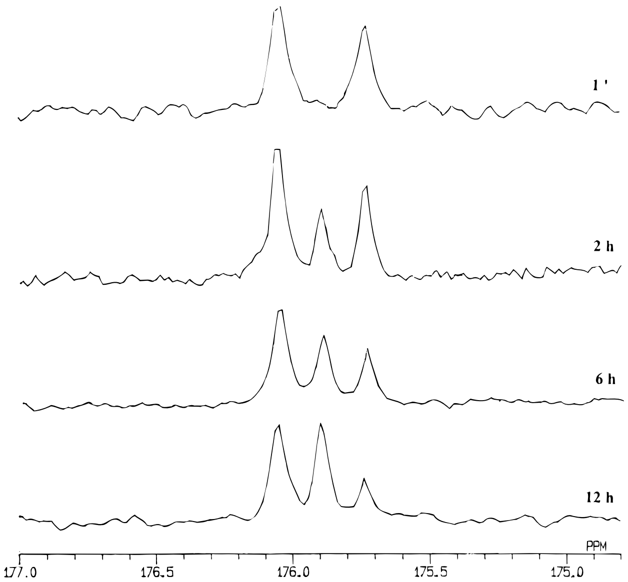

Figure 2. Stacked plot of proton-decoupled ^{13}C NMR spectra (carbonyl a only) showing the formation of **Ia**, **Ib**, and **Ic** isotopomers from the reaction of a ^{13}CO-enriched sample of $Os_3(CO)_{10}(NCCH_3)_2$ and a 40:60 mixture of H_2/D_2 ($CDCl_3$, room temperature, 100.25 MHz).

The mixture of **Ia**, **Ib**, and **Ic** isotopomers was also obtained when $Os_3(CO)_{10}(NCCH_3)_2$ or $Os_3(CO)_{11}(NCCH_3)$ was reacted with 50:50 mixture of H_2 and D_2 at room temperature in chloroform solution. Actually, when the reaction between the H_2/D_2 mixture and $Os_3(CO)_{10}(NCCH_3)_2$ is carried out in the NMR tube, there is rapid formation of **Ia** and **Ic** (after ca. 1 min), followed by a slow increase in the amount of **Ib**. The yields of **Ia** and **Ic** from $Os_3(CO)_{10}(NCCH_3)_2$ do not correspond to the ratio expected from the composition of the H_2/D_2 mixture. As shown in Figure 2, by using a ratio of 40:60 for the H_2/D_2 mixture we found a ratio of 55:45 in the formation of **Ia** and **Ic**, respectively, as a result of an higher reactivity of H_2 than D_2. Interestingly, as the H/D exchange reaction proceeds, this kinetic effect determines the faster disappearance of **Ic** than **Ia**. From the stack-plot of the spectra reported in Figure 2, it is apparent that the formation of **Ib** occurs mainly from the reaction of **Ic** and H_2 rather than from **Ia** and D_2. The possibility that the observed H/D exchange is the result of bimolecular exchange between **Ia** and **Ic** species has been ruled out by the observation that no formation of $HDOs_3(CO)_{10}$ was obtained when an equimolar mixture of **Ia** and **Ic** was heated in toluene for 4 h.

On the basis of these observations we decided to undertake a detailed study of the H_2-D_2 equilibration brought about by $H_2Os_3(CO)_{10}$. As shown in Figure 3, the reaction of D_2 with a ^{13}CO-enriched sample of $H_2Os_3(CO)_{10}$ in a sealed vial at 25 °C using chloroform as solvent slowly yields a mixture of **Ia**, **Ib**, and **Ic**.

Analogous experiments were carried out at 30, 40, and 50 °C, and the natural logarithms of the rate constants obtained by measuring the decrease of **Ia** have been plotted vs 1000/T (Figure 4). Analysis of these data gives an estimate of the thermodynamic parameters involved in this transformation ($E_a = 43.7$ kJ/mol; $\Delta H^{\ddagger} = 41.2$ kJ/mol; $\Delta S^{\ddagger} = -0.17$ kJ/(mol K)).

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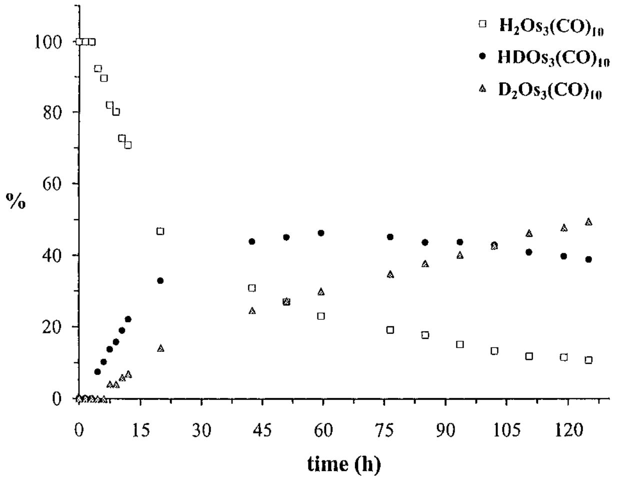


Figure 3. Plot of the percentages of **Ia**, **Ib**, and **Ic** isotopomers formed in the reaction of $H_2Os_3(CO)_{10}$ and D_2 (in chloroform solution at room temperature) versus time.

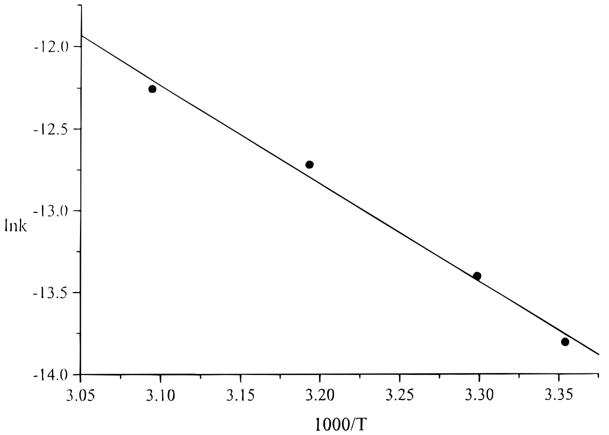


Figure 4. Arrhenius plot of ln *k* vs 1000/*T* for the reaction between $H_2Os_3(CO)_{10}$ and D_2 in chloroform solution ($R = 0.998$).

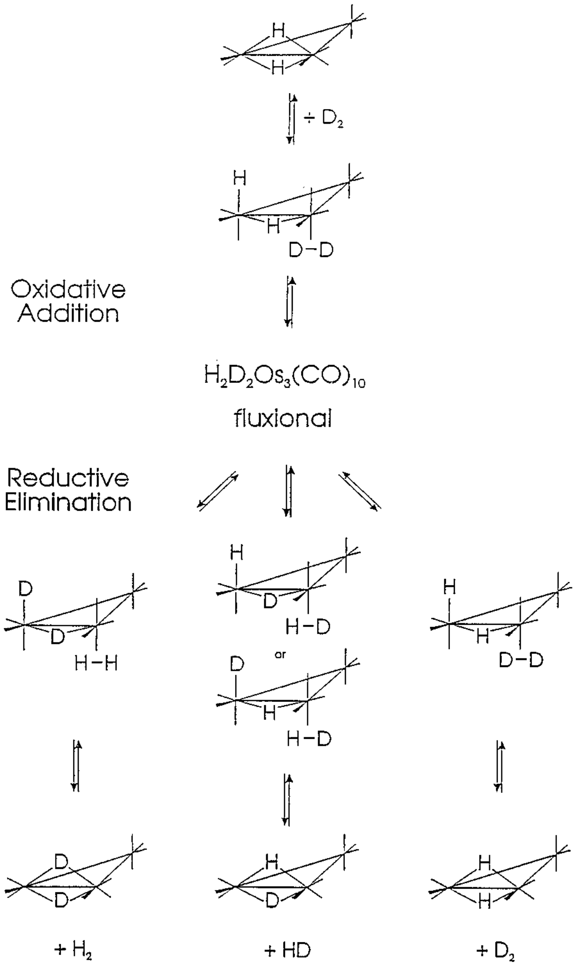
Another set of experiments was carried out by reacting $H_2Os_3(CO)_{10}$ with a mixture of H_2 and D_2, in order to assess whether the rates of formation of **Ib** and gaseous HD were the same. The percents of HD in the head space of the reaction vessel (measured by mass spectrometry) correspond well to those expected from the relative intensity ratio of **Ib** in the ^{13}C NMR spectrum at any given time of the reaction.

The observation of **Ib** and HD in the reaction of $H_2Os_3(CO)_{10}$ and a H_2/D_2 mixture may be accounted for in terms of several reaction pathways: (i) the formation of HD molecules by heterogeneous catalysis promoted by the presence of traces of metal, (ii) the formation of a tetra(hydrido, deuterio) species, followed by its heterolytic dissociation by proton abstraction due to traces of water, and (iii) the formation of a fluxional tetra(hydrido, deuterio) species, followed by a reductive elimination of an hydrogen molecule.

Process i has been ruled out by careful assessment of the purity of $H_2Os_3(CO)_{10}$ solutions before and after the reactions with H_2/D_2 mixtures. Furthermore, rates were highly reproducible for different preparations of $H_2Os_3(CO)_{10}$.

Process ii has been reported to cause H/D exchange in several nonclassical iridium hydride complexes, and such a process has been reported to be catalyzed by the addition of a number of bases.[19] A related mechanism has been reported in the case of a Pt/Au cluster in pyridine, where the catalytic cycle involves the addition of an H_2/D_2 molecule followed by its heterolytic dissociation, forming protonated solvent molecules.[20] The reversibility of both stages allows the H/D isotopic exchange to take place. We ruled out the occurrence of such a mechanism because no enhancement of H/D exchange was observed when H_2O or a base such as *t*-BuOH was added to the solution.

Scheme 1. Proposed Mechanism for the H/D Exchange on the Surface of $H_2Os_3(CO)_{10}$



On the other hand, the addition of a few drops of CF_3COOH to the solution of $H_2Os_3(CO)_{10}$ causes a decrease of H/D exchange, likely as a consequence of the formation of the $[H_3Os_3(CO)_{10}]^+$ species, as established by the observation of two new resonances at −12.05 and −14.20 ppm (relative ratio 2:1) in the ^1H NMR spectrum.[21] Since the structure of this species is not known, we cannot speculate as to why protonation slows down the H/D exchange. However, these observations certainly exclude catalysis by traces of H^+ as a mechanism for this exchange.

The observed behavior may then be accounted for in terms of process iii. We think that the H/D isotopic exchange occurs on the faces and edges of the cluster

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after the formation of the tetra(hydrido,deuterio) saturated adduct $H_2D_2Os_3(CO)_{10}$. On the basis of the known structures of $H_2Os_3(CO)_{10}L$ species we suggest an η^2-coordinated H_2 or HD or D_2 molecule, quickly followed by an internal reversible oxidative addition, as shown in Scheme 1.

Tentatively, we think that $H_4Os_3(CO)_{10}$ should be highly fluxional via a bridge−terminal exchange, as found in the series of the analogous $H_2Os_3(CO)_{10}L$ adducts. Thus, although the compound $H_4Os_3(CO)_{10}$ cannot be isolated, the observation of H/D exchange reported here strongly testifies to its formation.

Support for this suggestion may be drawn from the kinetic data. In fact, the small negative $\Delta S^‡$ value is consistent with the occurrence of a reaction pathway leading to the formation of the intermediate tetra(hydrido, deuterio) species and a unimolecular rate-determining step. The positive $\Delta H^‡$ value reflects the strong energy demand associated with the cleavage of H−H or D−D bonds, compensated only in part by the formation of Os−H or Os−D bonds.

To some extent the proposed mechanism resembles that recently proposed by Pignolet et al.[22] to explain the H/D exchange on the surface of coordinatively saturated clusters such as $[Pt(H)(PPh_3)(AuPPh_3)_7](NO_3)_2$, with the important difference that in that system the coordination of the D_2 molecule requires the dissociation of a PPh_3 ligand to create the vacant coordination site. Thus, it appears that such an ability to promote H/D exchange shown by $H_2Os_3(CO)_{10}$ should be shared by other unsaturated hydride derivatives or by systems able to provide vacant coordination sites under mild experimental conditions.

Experimental Section

All solvents were stored over molecular sieves and purged with nitrogen before use. CH_3CN was distilled from P_2O_5. ^{13}CO (99% enriched) was purchased from ISOTEC (Miamisburg, OH). HD (97%) and D_2 (99.8%) were purchased from EURISO-TOP (Saint Aubin, France). $Os_3(CO)_{11}(NCCH_3)$, $Os_3(CO)_{10}(NCCH_3)_2$, and $H_2Os_3(CO)_{10}$ were prepared according to the published methods.[23,24]

^1H and ^{13}C spectra were obtained on a JEOL EX-400 spectrometer operating at 399.65 and 100.25 MHz, respectively. ^{13}C NMR experiments were performed with ^{13}CO-enriched metal carbonyl complexes, which were prepared by using ^{13}C-enriched (40%) $Os_3(CO)_{12}$, obtained by direct exchange of ^{13}CO with $Os_3(CO)_{12}$ as starting material.[25]

In the reactions of $Os_3(CO)_{11}(NCCH_3)$, $Os_3(CO)_{10}(NCCH_3)_2$, and $H_2Os_3(CO)_{10}$ with gases, 0.75 mL of a 1.17×10^{-2} M $CDCl_3$ solution of the organometallic compounds was transferred into a 5 mm resealable NMR tube having a total volume of 3 mL. The solution was frozen and the air pumped off. After addition of the gas (1 atm), the solution was refrozen with liquid N_2 and the tube was sealed and quickly introduced into the NMR probe. The sample was then warmed to the desired temperature. The reaction was followed by detecting the ^{13}C NMR spectra every 1 h. Each spectrum consists of 600 transients, and the following parameters were used: pulse width 12 μs (60°), pulse delay 5.5 s, 32 000 sampled points, observed range 25 000 Hz.

Mass spectra of the head space gas mixtures were obtained on a VG Micromass quadrupole spectrometer.

Acknowledgment. We thank the Ministero dell' Università e della Ricerca Scientifica e Tecnologica (MURST) and the Consiglio Nazionale delle Ricerche (Comitato 03) for financial support. The European Community (Commission-DG XII, HCM program) is gratefully acknowledged for providing a postdoctoral grant to J.K. L.M. thanks the University of Girona for financial support to her stay at the University of Torino.

OM960527D

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