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# Investigating Pathways of Molecular $H_2$ Exchange in $(\mu\text{-H})_2Os_3(CO)_{10}$

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*Summary: The occurrence of two pathways responsible for the reaction of* $(\mu\text{-H})_2Os_3(CO)_{10}$ *with molecular hydrogen has been elucidated by comparing the results obtained from* $H_2/D_2$ *isotopic exchange experiments and para-*$H_2$ *effects observed in the cluster's* $^1H$ *NMR spectrum. The most efficient exchange process is based on an associative mechanism that leads to the formation of the elusive* $(\eta\text{-*}H_2)(H)(\mu\text{-H})Os_3(CO)_{10}$ *species (**$H_2$ *is either a* $D_2$ *or a para-*$H_2$ *molecule), which undergoes *H−H elimination. The other pathway (whose efficiency increases with temperature) is based on the dissociation of* $H_2$ *from* $(\mu\text{-H})_2Os_3(CO)_{10}$ *to form the highly unsaturated "*$Os_3(CO)_{10}$*" moiety, which promptly adds a **$H_2$ *molecule, yielding the asymmetrical* $\text{*}H(\mu\text{-*}H)Os_3(CO)_{10}S$ *intermediate (where S is a stabilizing solvent molecule), which releases the S molecule to re-form* $(\mu\text{-*}H)_2Os_3(CO)_{10}$*.*

## Introduction

A better understanding of the molecular hydrogen activation and of the hydrogen atoms' mobility in transition metal complexes represents a key step in the mechanism interpretation in many catalytic reactions. A number of approaches have been exploited for the investigation of the intimate mechanisms in catalytic hydrogenations. In recent years interesting new insights have been provided by the use of para-hydrogen. In fact, it has been shown that para-$H_2$ allows the detection of hydrogenation reaction intermediates even when they are present at very low concentrations, thanks to the extraordinary enhancement of the NMR signals due to the para hydrogen induced polarization (PHIP effect).[1−9]

Recently we reported that by reacting $(\mu\text{-H})_2Os_3(CO)_{10}$ with $D_2$ the formation of the three isotopomers $(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$, and $(\mu\text{-D})_2Os_3(CO)_{10}$ occurs.[10] A mechanism involving the reversible oxidative addition and reductive elimination of molecular hydrogen on $(\mu\text{-H})_2Os_3(CO)_{10}$ via the formation of a fluxional tetra(hydride, deuteride) intermediate has been proposed; however, such an intermediate has not been detected.

Moreover, some years ago, Pöe et al. reported that $(\mu\text{-H})_2Os_3(CO)_{10}$ may release molecular hydrogen to form the highly reactive "$Os_3(CO)_{10}$" intermediate, possibly stabilized by a solvent molecule.[11]

We deemed it of interest to gain more insights into the pathways leading to association/dissociation of molecular hydrogen in $(\mu\text{-H})_2Os_3(CO)_{10}$ by comparing the results from $H_2/D_2$ exchange with the effects in the $^1H$ NMR spectra obtained by reacting the cluster with para-$H_2$.

## Results and Discussion

It has been reported[12,13] that a para-$H_2$ effect can be detected as a strongly enhanced signal also in compounds containing two equivalent protons. The enhancement is observed if such species are generated in hydrogenation reactions via asymmetrical intermediates whose CSA (chemical shift anisotropy) and/or CSA/DD (interference term between the chemical shift anisotropy and the dipolar interactions) contributions to the relaxation are significantly different for the two added protons. The hydride resonance of $(\mu\text{-H})_2Os_3(CO)_{10}$ has already been observed as an enhanced emission signal when the compound was produced by reacting $Os_3(CO)_{10}(NCCH_3)_2$ and para-$H_2$, via the intermediate $H(\mu\text{-H})Os_3(CO)_{10}(NCCH_3)$ species.[12] Furthermore, a strong emission signal was observed for free molecular hydrogen in the case of the reversible interaction of para-$H_2$ with $H(\mu\text{-H})Ru_3(\mu\text{-CO})(CO)_{10}$.[13]

On the basis of this knowledge and by carefully considering the mechanism previously proposed for the $H_2$ exchange reaction on $(\mu\text{-H})_2Os_3(CO)_{10}$ (Scheme 1), some para-$H_2$ effects on the resonances of both the cluster and molecular $H_2$ are expected in their reaction. In fact, statistically all of the three possible pathways reported in Scheme 1 could occur. An enhanced signal for $(\mu\text{-H})_2Os_3(CO)_{10}$ is expected when both the hydrogen atoms of the para-$H_2$ molecule remain on the cluster (path i), while when they are both eliminated as

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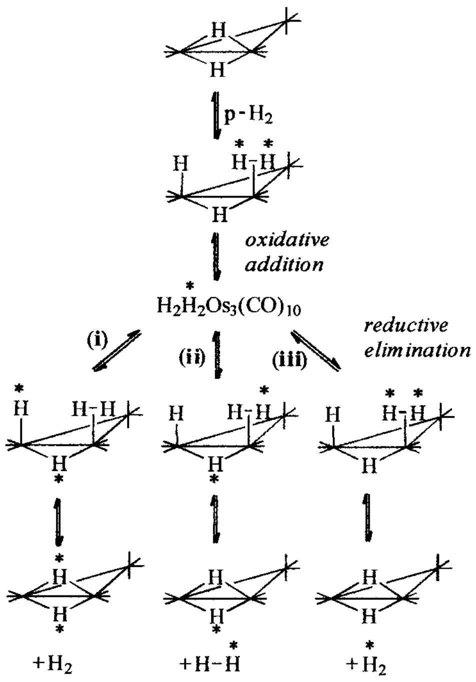
**Scheme 1**



molecular hydrogen (path iii), they should give rise to an enhanced signal for free molecular hydrogen, as in the case of the reversible interaction of para-$H_2$ with $H(\mu\text{-}H)Ru_3(\mu\text{-}CO)(CO)_{10}$.[13] Path ii would not contribute to any para-$H_2$ effect because of the loss of spin correlation that occurs when only one of the hydrogen atoms of the original para-$H_2$ molecule remains on the cluster.[1]

A toluene-$d_8$ solution of $(\mu\text{-}H)_2Os_3(CO)_{10}$ was then allowed to react with para-$H_2$ in a resealable 5 mm NMR tube. The sample was shaken and introduced into the magnet. No polarized signal was detected at room temperature. Likely, the fast relaxation of the hypotized tetrahydride intermediate[10] may be responsible for the absence of para-$H_2$-induced polarization on the $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $H_2$ resonances, or, alternatively, the rate of inclusion of para-$H_2$ in the cluster at room temperature is not high enough to allow the observation of any effect in the NMR spectrum.

To increase the process rate, the reaction between $(\mu\text{-}H)_2Os_3(CO)_{10}$ and para-$H_2$ was then carried out at 353 K: under these conditions a strong emission signal at −12.5 ppm, assigned to polarized $(\mu\text{-}H)_2Os_3(CO)_{10}$, appeared in the $^1H$ NMR spectrum (Figure 1). The peak recovered the normal intensity in about 10 min.

Since no polarized signal has been detected for free molecular hydrogen in the NMR spectrum (Figure 1), we must conclude that the mechanism reported in Scheme 1 does not explain the experimental data, as it seems unlikely that only route i is operative.

A few years ago Pöe et al. showed that a mechanism involving a first-order dissociation of $H_2$ from $(\mu\text{-}H)_2Os_3(CO)_{10}$ is possible, with the formation of the "$Os_3(CO)_{10}$" species, possibly stabilized by the coordination of a solvent molecule (S).[11] If a para-$H_2$ molecule is added to the "$Os_3(CO)_{10}(S)$" species, it yields polarized $H(\mu\text{-}H)Os_3(CO)_{10}(S)$, which undergoes solvent elimination leading to polarized $(\mu\text{-}H)_2Os_3(CO)_{10}$ (Scheme 2).

Further support to the occurrence of a stabilized "$Os_3(CO)_{10}$" transition state as responsible for the observed para-$H_2$ effect has been found by reacting para-$H_2$ with $H(\mu\text{-}H)Os_3(CO)_{11}$, which is known to form $(\mu\text{-}H)_2Os_3(CO)_{10}$ upon loss of CO and to undergo dissociative $H_2$ exchange (Scheme 3).[11] In this case a remarkable increase in the intensity of the polarized $(\mu\text{-}H)_2Os_3(CO)_{10}$ signal was detected at 100 °C,[14] ca. 6 times with respect to that found for the reaction of the same amount of $(\mu\text{-}H)_2Os_3(CO)_{10}$ at the same temperature (this means that the observed polarization is due to the direct $H_2$ exchange on $H(\mu\text{-}H)Os_3(CO)_{11}$, and not on the $(\mu\text{-}H)_2Os_3(CO)_{10}$, which derives from its decarbonylation). The observed increment is related to the higher rate of $H_2$ exchange on $H(\mu\text{-}H)Os_3(CO)_{11}$ with respect to $(\mu\text{-}H)_2Os_3(CO)_{10}$, as previously found by Pöe and co-workers ($k_{(CO)11}/k_{(CO)10} \approx 7$),[11] due to the greater stabilization of the transition state "$Os_3(CO)_{10}(L)$" achieved when L = CO with respect to the previous case, where L = solvent.

Nevertheless, if the previously reported results for the $H_2/D_2$ exchange in $(\mu\text{-}H)_2Os_3(CO)_{10}$ are concerned, the occurrence of the dissociative mechanism depicted in

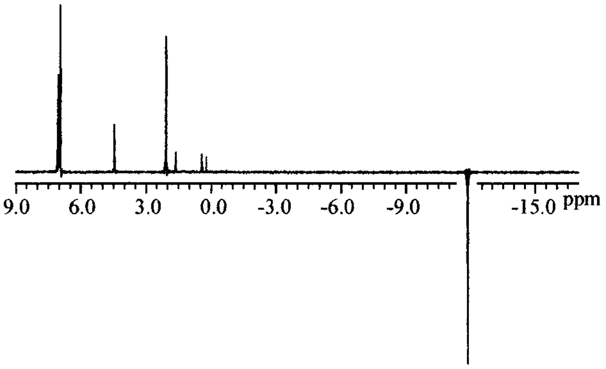
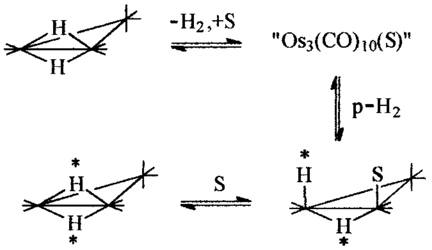
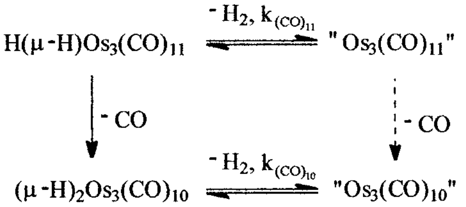


**Figure 1.** Single scan $^1H$ NMR spectrum of polarized $(\mu\text{-}H)_2Os_3(CO)_{10}$, obtained by reacting nonpolarized $(\mu\text{-}H)_2Os_3(CO)_{10}$ with para-$H_2$ at 353 K (400 MHz, toluene-$d_8$).

**Scheme 2**



**Scheme 3** [a]



[a] The dotted arrow indicates that this path does not lead to any detectable para-$H_2$ effect.

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[14] The signal enhancement also depends on the intermediate $H(\mu\text{-}H)Os_3(CO)_{10}(L)$ (L = solvent, CO) lifetime, which has to be short with respect to its relaxation time in order to maintain the hydrogen polarization. When L = CO, a higher temperature is required to hasten the release of the ligand and then shorten the intermediate lifetime.

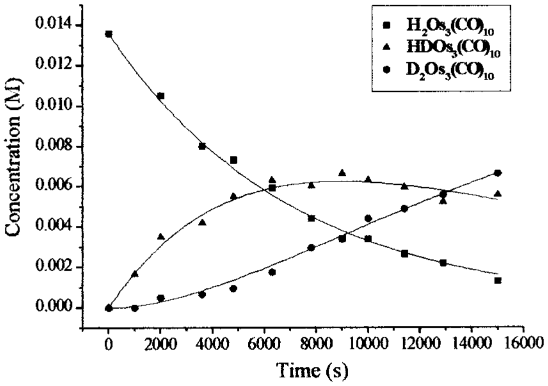

**Figure 2.** Concentrations of the three isotopomers ($\mu$-H)$_2$Os$_3$(CO)$_{10}$, ($\mu$-H)($\mu$-D)Os$_3$(CO)$_{10}$, and ($\mu$-D)$_2$Os$_3$(CO)$_{10}$ vs time (toluene, 353 K). The dotted lines represent the calculated curves obtained by applying the consecutive reactions' model kinetics.

Scheme 2 would account solely for the incorporation of a deuterium molecule, leading to the formation of ($\mu$-D)$_2$Os$_3$(CO)$_{10}$.[10] Clearly the reported observation of large amounts of the H,D isotopomer indicates that an associative mechanism, based on the formation of a tetrahydrido intermediate, should also occur, and indeed the process reported in Scheme 2 may have a really small role in the overall $H_2$ exchange process, since para-$H_2$ allows the detection of species that are present in solution at very low concentrations.

To assess whether the two mechanisms have more or less the same importance or if the dissociative one is responsible for the exchange just for a small part, we reconsidered the $H_2/D_2$ exchange under the same conditions used for the para-$H_2$ exchange, i.e., by using a $D_2$ pressure of 4 atm, in toluene at 80 °C. If, under these experimental conditions, the secondary dissociative mechanism was as active as the associative one, the formation of ($\mu$-D)$_2$Os$_3$(CO)$_{10}$ should markedly be faster than that previously reported. The plot of concentrations of the three isotopomers vs time (Figure 2) shows the same shape found previously in chloroform solutions under milder conditions;[10] that is, the rate of formation of ($\mu$-D)$_2$Os$_3$(CO)$_{10}$ is not greater than what is found in that case. This finding demonstrates that the dissociative mechanism is really much less active than the associative one, and its occurrence can be evidenced just by means of the extraordinary signal enhancements generated by the use of para-$H_2$.

Anyway, the occurrence of the mechanism depicted in Scheme 1 and the lack of observation of any polarization on the signal attributed to free $H_2$ are incompatible. We have to conclude that, even at 353 K, the associative mechanism is too slow to allow the detection of some para-$H_2$ effects or, alternatively, that a mechanism somewhat different from that previously reported must be found in order to explain both the $H_2/D_2$ exchange and the para-$H_2$ data.

In the latter case, we probably have to invoke the formation of $H_2$ and ($\mu$-H)$_2$Os$_3$(CO)$_{10}$ both containing one polarized and one normal hydrogen atom, i.e., a loss of spin correlation and, as a consequence, no detectable para-$H_2$ effect. The mechanism proposed in the previous paper for the $H_2$ exchange may then be revised according to the consecutive reactions model. This can be done simply by disregarding the oxidative addition which leads to the classical tetrahydride intermediate (see Scheme 1); that is, the intermediate species would be a nonfluxional, $\eta^2$-$D_2$ derivative (Scheme 4). A weak hydrogen bonding interaction between the hydride and one of the hydrogen or deuterium atoms of the para-$H_2$ or $D_2$ molecule may contribute to the stabilization of the intermediate. In this case the replacement of hydrogen atoms by deuterium (or para-$H_2$) atoms on the triosmium cluster would occur in two different steps. In the reaction with para-$H_2$ the two hydrogen atoms of the parent para-$H_2$ molecule would be transferred to two different cluster molecules, with loss of spin correlation, and no hyperpolarization effect could then be detected either on the cluster resonance or on the molecular hydrogen one. This would also explain the lack of any enhanced signal when the reaction is carried out at room temperature, when only the associative mechanism is operating.

If the mechanism depicted in Scheme 4 was operating, the formation of the ($\mu$-H)($\mu$-D)Os$_3$(CO)$_{10}$ and ($\mu$-D)$_2$Os$_3$(CO)$_{10}$ isotopomers in the reaction with $D_2$ would follow the consecutive reactions kinetics and would not be (as stated before) simply based on statistics. Evidence can be found by carefully inspecting the plot of the concentrations of the three isotopomers ($\mu$-H)$_2$Os$_3$(CO)$_{10}$, ($\mu$-H)($\mu$-D)Os$_3$(CO)$_{10}$, and ($\mu$-D)$_2$Os$_3$(CO)$_{10}$ formed in the reaction of $H_2Os_3(CO)_{10}$ with $D_2$ (Figure 2). The plot is typical of a reaction that occurs in two different steps, according to the consecutive reactions model:

$$(1) \qquad (\mu\text{-H})_2\text{Os}_3(\text{CO})_{10} + {}^*\text{H}{-}\text{H}^* \xrightarrow{k_1} (\mu\text{-H})(\mu\text{-}^*\text{H})\text{Os}_3(\text{CO})_{10} + {}^*\text{H}{-}\text{H}$$

$$(2) \qquad (\mu\text{-H})(\mu\text{-}^*\text{H})\text{Os}_3(\text{CO})_{10} + {}^*\text{H}{-}\text{H}^* \xrightarrow{k_2} (\mu\text{-}^*\text{H})_2\text{Os}_3(\text{CO})_{10} + {}^*\text{H}{-}\text{H}$$

(*$H_2$ is either a $D_2$ or a para-$H_2$ molecule). The two reactions can be considered as irreversible since there is a great excess of $D_2$ in the reaction mixture. The data are indeed well fitted by the corresponding equations,[15] yielding the following rate constants values: $k_1 = 3.7 \pm 0.3\ 10^{-5}\ s^{-1}$ (in good accordance with the value of $3.9 \times 10^{-5}\ s^{-1}$, which can be obtained by extrapolation to 80 °C of the data previously obtained in chloroform)[10] and $k_2 = 2.2 \pm 0.2\ 10^{-5}\ s^{-1}$.

The difference between $k_1$ and $k_2$ is rather unexpected, since the same types and number of bonds are involved in the two reactions, and therefore no isotopic effect should be observed.[16-18] Anyway it may be explained on a statistical basis, taking into account that in reaction 2 the incoming *H−H* molecule can add to the cluster both on the H side and on the H* one (see Scheme 3). Only in the former case would the final products ($\mu$-*H)$_2$Os$_3$(CO)$_{10}$ and H−H* be formed, while in the latter one *H−H* would be eliminated, without any observable transformation. It follows that just one-half of the actually reacting ($\mu$-H)($\mu$-*H)Os$_3$(CO)$_{10}$ mol-

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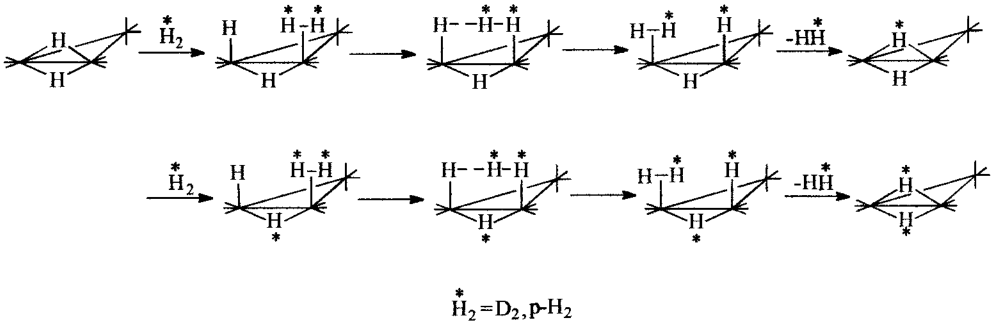
**Scheme 4**



ecules can be detected, and as a consequence, the $k_2$ value obtained appears to be smaller than expected. In other words, this is an "apparent" rate constant, the "real" constant value being about two times $k_2$.

## Experimental Section

All solvents were stored on molecular sieves and purged with nitrogen before use. $H_2$ and CO were purchased from SAPIO (Milano, Italy) and used without further purification. $D_2$ (99.8%) was purchased from EURISO-TOP (Saint Aubin, France). Para-enriched hydrogen (about 50%) was prepared by storing $H_2$ over $Fe_2O_3$ at 77 K for 3−4 h.

$^1H$ and $^{13}C$ spectra were obtained on a JEOL EX-400 spectrometer operating at 399.65 and 100.25 MHz, respectively. $(\mu\text{-H})_2Os_3(CO)_{10}$ and $H(\mu\text{-H})Os_3(CO)_{11}$ were prepared according to the published methods.[19,20]

$^{13}C$ NMR experiments were performed with $^{13}CO$-enriched $(\mu\text{-H})_2Os_3(CO)_{10}$, which was 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.[21]

The reactions with para-$H_2$ and deuterium were carried out in a 5 mm resealable NMR tube. Para-$H_2$ (or deuterium) was added to 0.6 mL of 10.00 mM frozen solutions of the cluster; the sample was introduced into the magnet and then warmed to the desired temperature. In the para-$H_2$ case single scan $^1H$ spectra were recorded by using 45° pulses. In the deuterium case the kinetics of the $H_2/D_2$ exchange were studied by using $^{13}C$-enriched samples, as described before:[10] the reaction was followed by detecting the $^{13}C\{^1H\}$ NMR spectra every hour. Each spectrum consisted of 600 transients, and the following parameters were used: pulse width 12 $\mu$s (60°), pulse delay 5.5 s, 32 000 sampled points, observed range 25 000 Hz. The quantification of the relative amounts of $(\mu\text{-H})_2Os_3(CO)_{10}$, $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$, and $(\mu\text{-D})_2Os_3(CO)_{10}$ was made by integration of the radial carbonyl resonance in the $^{13}C\{^1H\}$ NMR spectra. The observed integrals for $(\mu\text{-H})_2Os_3(CO)_{10}$ and $(\mu\text{-H})(\mu\text{-D})Os_3(CO)_{10}$ were decreased by an amount corresponding to 6% and 3%, respectively, due to the nuclear Overhauser effect (which is not present in $(\mu\text{-D})_2Os_3(CO)_{10}$).

Since $D_2$ was always present in great excess with respect to the cluster, its concentration was considered to be constant during the reaction and therefore included in the rate constant $k'$ for the fits of the data. The rate constant values reported therein are corrected for this factor and therefore represent the "true" rate constant $k$ values. For example,

$$\frac{d[H_2Os_3(CO)_{10}]}{dt} = k'[H_2Os_3(CO)_{10}], \qquad \text{where } k' = k_1 p_{D_2}$$

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