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Journal of Organometallic Chemistry 593–594 (2000) 135–141

Journal of Organometallic Chemistry

# Facile oxidative addition/reductive elimination of HX (X = Cl, Br, I) on $(\mu\text{-H})_2Os_3(CO)_{10}$

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Received 27 May 1999; accepted 12 July 1999

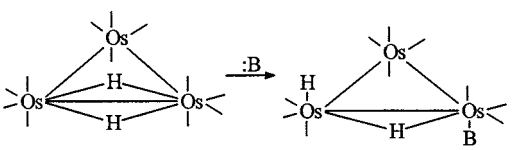
**Abstract**

The addition of an HX molecule (X = Cl, Br, I) to $(\mu\text{-H})_2Os_3(CO)_{10}$ yields four novel trihydride complexes of formula $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$, which differ in the position occupied by the terminal hydride on the osmium atom. The reaction takes place even at 183 K, and can be followed by NMR spectroscopy. At room temperature elimination of HX yields (partially) the original starting material. This reaction appears to be catalyzed by a base. This observation prompted us to investigate the reaction between $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ and ammonia. The product of the latter reaction is a mixture of isomers whose structures are related to those of the parent $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$. 

*Keywords:* Trihydride; Triosmium; NMR; Relaxation; Halogen coordination

## 1. Introduction

The coordinatively unsaturated 46 $e^-$ $(\mu\text{-H})_2Os_3(CO)_{10}$ cluster represents an ideal substrate for investigating the activation of small molecules on the surface of a trimetallic cluster moiety. The cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ reacts with basic reactants :B (either neutral or negatively charged) to yield the coordinatively saturated $H(\mu\text{-H})Os_3(CO)_{10}(B)$ species, which contain one terminal and one bridging hydride ligand (Scheme 1) [1]. The stability of the Os–B bond in the final adduct depends upon the nature of the base involved and, in general, the adduct 'survives' in the presence of an excess of added base [2]. The release of the base simply restores the starting $(\mu\text{-H})_2Os_3(CO)_{10}$ complex. When :B is a primary or secondary amine or an imine, the adduct appears to be stabilized by an intramolecular N–H···H–Os hydrogen bond [3]. It is expected that a strengthening of such an interaction may occur as the electronegativity of the donor atom X in the :X–H moiety increases. One may envisage that an enhanced polarization in the donor group may favour further reaction involving the heterolytic cleavage of the X–H bond and the addition of the proton to the cluster. If these processes were to take place, it is possible that an $\eta^2\text{-H}_2$ intermediate might be involved




Scheme 1.

In this work the interaction of HX (X = Cl, Br, I) with $(\mu\text{-H})_2Os_3(CO)_{10}$ is considered. One would expect the halogen electronegativity to cause the heterolytic cleavage of the X–H bond and subsequently the addition of the proton to the cluster. In an adduct derived by the addition of HX to $(\mu\text{-H})_2Os_3(CO)_{10}$ a competition between the loss of $H_2$ and the loss of HX may then occur.

## 2. Results and discussion

### 2.1. Synthesis and characterization of $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ (X = Cl, Br, I)

The violet 46 $e^-$ cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ reacts readily in $CD_2Cl_2$ solution at 183 K with HCl (gas or

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0022-328X/00/$ - see front matter 
PII: S0022-328X(99)00416-7

Table 1
$^1$H-NMR data for **I**, **II**, **III** and **IV** [a]

| Hydride | $\delta$ | $J_{^1H,^1H}$ (Hz) | $T_1$ (213 K) (s) |
|---|---|---|---|
| **IA** | −9.46 | 3.91; 2.93 | 1.00 |
| **IB** | −16.54 | 3.91 | 1.30 |
| **IC** | −19.24 | 2.93 | 1.31 |
| **IIA** * | −9.49 | 2.93 | 1.06 |
| **IIB** * | −17.39 | – | 1.55 |
| **IIC** * | −17.45 | 2.93 | 1.53 |
| **IIIA** | −8.54 | 14.16 | 0.56 |
| **IIIB** | −15.32 | 1.95 | 0.61 |
| **IIIC** | −16.29 | 14.16; 1.95 | 2.29 |
| **IVA** | −9.15 | 13.43 | 0.51 |
| **IVB** | −13.90 | 13.43; 1.95 | 3.76 |
| **IVC** | −17.00 | 1.95 | 0.56 |

[a] * indicates that $T_1$ were measured at 200 K (the minimum temperature needed to obtain sharp signals, due to chemical exchange).

aqueous solution) to yield a yellow product (**I**) which has been subsequently characterized by $^1$H-, $^{13}$C-NMR and IR spectroscopy.

The $^1$H-NMR spectrum at 183 K shows three resonances in the hydride region, which can be attributed to one terminal (A) and two bridging hydrides (B, C) on the basis of chemical shift considerations (Table 1). The $^{13}$C-NMR spectrum of a $^{13}$C enriched sample of **I** at 183 K (Fig. 1) shows ten different terminal carbonyl resonances at 171.70 ($J_{^{13}C,^1H_B} = 11.7$ Hz), 171.57 ($J_{^{13}C,^{13}C} = 35.7$ Hz), 170.02, 169.88 ($J_{^{13}C,^1H_A} = 27.4$ Hz), 169.39 ($J_{^{13}C,^{13}C} = 35.7$ Hz), 168.63 ($J_{^{13}C,^1H_B} = 2.9$ Hz), 167.32 ($J_{^{13}C,^1H_A} = J_{^{13}C,^1H_B} = J_{^{13}C,^1H_C} = 7.0$ Hz), 166.98 ($J_{^{13}C,^1H_C} = 6.8$ Hz), 166.82 ($J_{^{13}C,^1H_A} = J_{^{13}C,^1H_B} = J_{^{13}C,^1H_C} = 6.0$ Hz) and 164.53 ($J_{^{13}C,^1H_C} = 2.9$ Hz) ppm, respectively.

We can conclude from these data that the stoichiometry of the product is H(μ-H)$_2$Os$_3$(CO)$_{10}$(Cl), which represents the product of oxidative addition of HCl to (μ-H)$_2$Os$_3$(CO)$_{10}$. Although we have no direct evidence that the chlorine is coordinated to the cluster, the $[H_3Os_3(CO)_{10}]^+$ species exists and has different NMR [4].

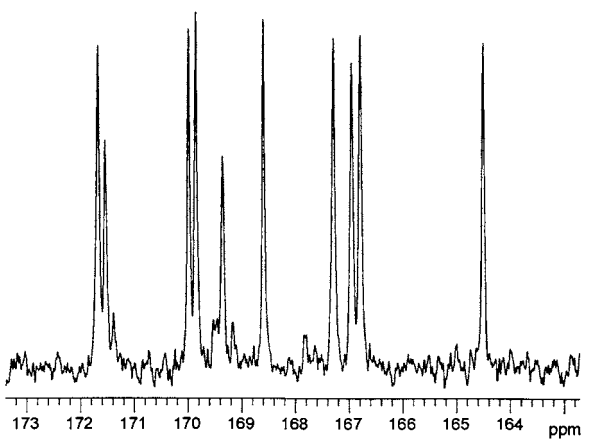



Fig. 1. {$^1$H}$^{13}$C-NMR spectrum of **I** obtained by the reaction between (μ-H)$_2$Os$_3$(CO)$_{10}$ and HCl in $CD_2Cl_2$ at 183 K.

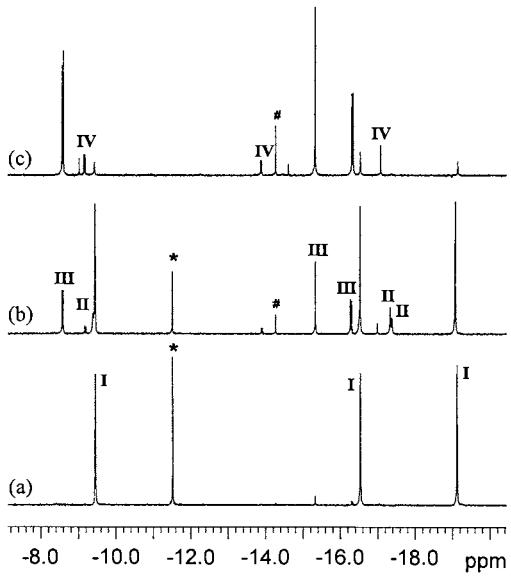



Fig. 2. $^1$H-NMR spectra ($CD_2Cl_2$, 183 K) of H(μ-H)$_2$Os$_3$(CO)$_{10}$(Cl) recorded (a) instantaneously; (b) after 2 h at RT; (c) after 5 h at RT (equilibrium). * = (μ-H)$_2$Os$_3$(CO)$_{10}$, # = (μ-H)(μ-X)Os$_3$(CO)$_{10}$.

After a few hours at room temperature, the signals of **I** disappear, while three other sets of three resonances increase (**II**, **III**, **IV**) (Fig. 2). The $^1$H chemical shifts and the $^1$H–$^1$H coupling constants for the three new sets of resonances are reported in Table 1.

Eventually, the most abundant species in the mixture is **III**, as shown in Fig. 2. This allowed us also to measure the $^{13}$C-NMR spectrum of a $^{13}$C enriched sample of this species: as in the case of **I**, it shows ten terminal carbonyl resonances at 165.25, 167.53, 169.08 ($J_{^{13}C,^{13}C} = 36.13$ Hz), 169.27, 170.67, 170.96, 170.76 ($J_{^{13}C,^1H_B} = 9.77$ Hz), 172.25 ($J_{^{13}C,^{13}C} = 32.67$ Hz), 172.77 ($J_{^{13}C,^{13}C} = 36.13$ Hz) and 173.98 ($J_{^{13}C,^{13}C} = 32.67$ Hz) ppm, respectively.

The fact that both **I** and **III** have the same type and number of ligands suggests that they are isomers of the same molecular formula H(μ-H)$_2$Os$_3$(CO)$_{10}$(Cl).

The quantities of **II** and **IV** in the mixture remain very low at any observation time; for this reason we could not measure their $^{13}$C-NMR spectra; however, on the basis of the similarity of their $^1$H patterns with those of **I** and **III**, respectively, we suggest that **II** and **IV** are also isomers of the H(μ-H)$_2$Os$_3$(CO)$_{10}$(Cl) species.

In principle, the number of possible isomers for this stoichiometry is high, depending on the relative positions of the four ligands (the three hydrides and the chlorine), and on the possibility for the terminal hydride to occupy both axial and equatorial coordination sites.

Since in the $^{13}$C-NMR spectrum of **I** only two signals show a $^{13}$C–$^{13}$C coupling, both the terminal hydride and the chlorine atom must occupy axial positions on two different osmium atoms, in a *syn* or *anti* arrangement. On the basis of this assumption one can envisage a total of six different isomers for this complex, depending on the relative positions of the two bridging hydrides on the metal triangle (Scheme 2).

Due to the dependence of the longitudinal relaxation times ($T_1$) on the relative interproton distances [5], the possibility of distinguishing between the six possible structures was pursued through the measurement of the $T_1$ of the three hydride signals at 213 K; the obtained values are reported in Table 1.

Since the relaxation times of the three resonances are similar, the terminal hydride having however the shortest value, we propose the assignment of *syn1* or *anti1* structures to complex **I**. Moreover, assuming that the molecular reorientational time ($\tau_C$) at 213 K is about $1.55 \times 10^{-10}$ s (as measured for other osmium derivatives having similar size in the same solvent [5]), the interproton distances $r_{AB}$, $r_{AC}$ and $r_{BC}$ have been calculated by solving the system of the three equations which describe the dipolar contributions to $T_1$ for the three protons A, B and C [6]:

$$\frac{1}{T_1^A} = K\left(\frac{1}{r_{AB}^6} + \frac{1}{r_{AC}^6}\right)$$

$$\frac{1}{T_1^B} = K\left(\frac{1}{r_{AB}^6} + \frac{1}{r_{BC}^6}\right)$$

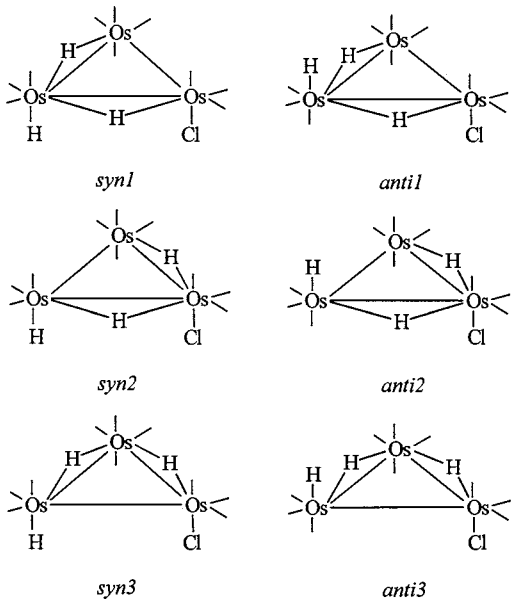
$$\frac{1}{T_1^C} = K\left(\frac{1}{r_{AC}^6} + \frac{1}{r_{BC}^6}\right)$$

where:

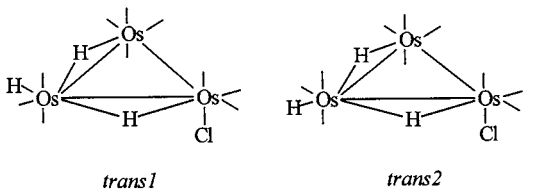
$$K = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 (\gamma_H^4 \hbar^2 \tau_C)\left(\frac{1}{1+\varpi_0^2\tau_C^2} + \frac{4}{1+4\varpi_0^2\tau_C^2}\right)$$

$\mu_0$ is the magnetic susceptibility in the vacuum, $\gamma_H$ is the gyromagnetic ratio for the proton, $\omega_0$ is the experimental resonance frequency. The obtained distances values are: $r_{AB} = 2.31$ Å, $r_{BC} = 2.56$ Å, $r_{AC} = 2.31$ Å. These values appear fully compatible with the proposed structure.

The $^{13}$C-NMR spectrum of **III** shows two pairs of carbonyl resonances displaying the characteristic $^{13}$C–$^{13}$C *trans*-coupling pattern. Therefore the chlorine atom and the terminal hydride can not longer be both in axial positions, but one of the two ligands must have shifted into the equatorial plane. The large $^1$H–$^1$H coupling constant (14.16 Hz) observed between the terminal and one of the bridging hydrides is peculiar to a terminal hydride directly *trans* to the bridge. Such an arrangement has been previously reported in the cases of $H_2(\mu\text{-}H)(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}NC_4H_6)Os_3(CO)_9$ [7], $H(\mu\text{-}H)_3(\mu_3\text{-}NCH_2CF_3)Os_3(CO)_8$ [8], and one of the minor isomers of $H(\mu\text{-}H)Os_3(CO)_{11}$[9]. Therefore, we can assign to **III** one of the two structures (*trans1*, *trans2*) depicted in Scheme 3, where the chlorine occupies the axial position. We cannot exclude a structure with an open metal–metal bond, but the $T_1$ measurements discussed below are more consistent with the closed structure.




Scheme 2.




Scheme 3.

The $T_1$ values measured for the signals corresponding to **III** confirm the assignment: the bridging hydride *trans* to the terminal one shows the longest $T_1$ due to the greater distance which separates it from the other hydrides. As for isomer **I**, we estimated the interproton distances, finding the following values (in accordance with the proposed structure): $r_{AB} = 1.92$ Å, $r_{BC} = 2.83$ Å, $r_{AC} = 2.52$ Å.

Since the chlorine atom occupies an axial position in both **I** and **III** and in some related triosmium $\eta^1$-Cl derivatives [10], we can assume a similar situation to be true also for **II** and **IV**. In fact, thermolysis of the previously reported HBr adduct $(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}NC_4H_6)Os_3(CO)_9(Br)$ leads to *syn* to *anti* isomerization as observed here [10c]. Thus the only difference between the four isomers of $H(\mu\text{-}H)_2Os_3(CO)_{10}(Cl)$ would be the coordination site of the terminal hydride on the Os atom.

Since **II** and **IV** resemble **I** and **III** with respect to the $^1$H–$^1$H coupling constants and the $T_1$ values, we can

conclude that the assignments of structure *anti1/syn1* and structure *trans2/trans1* to **II** and **IV,** respectively can be made.

Again, the interproton distances calculated for isomers **II** and **IV** support the proposed assignment. In fact, the obtained values are the following: $r_{AB} = 2.39$ Å, $r_{BC} = 2.82$ Å, $r_{AC} = 2.40$ Å for **II** and $r_{AB} = 2.64$ Å, $r_{BC} = 3.44$ Å, $r_{AC} = 1.87$ Å for **IV**.

In summary, NMR spectroscopy showed that the reaction between $(\mu\text{-H})_2Os_3(CO)_{10}$ and HCl affords the four isomers (**I**, **II**, **III**, **IV**) of the novel $H(\mu\text{-H})_2Os_3(CO)_{10}(Cl)$ species, which differ only in the position of the terminal hydride on the Os atom bound to the two bridging hydrides. The kinetically favored isomer is **I**, which then evolves towards the thermodynamically favored isomers, **II**, **III** and **IV**, the most stable appearing to be **III**. The reasons for this are still unclear.

The same results have been obtained by reacting $(\mu\text{-H})_2Os_3(CO)_{10}$ with both HBr and HI (aqueous solutions). The spectroscopic data for the products are reported in the experimental section.

It is worth noting that we were unable to observe the derivatives corresponding to the first step of the coordination of the HX molecule to $(\mu\text{-H})_2Os_3(CO)_{10}$. Even at the low temperatures employed in this work the first kinetic product detectable by NMR spectroscopy corresponds to the oxidative addition of the HX molecule to the cluster, whereas both $R_2NH$ and RSH allow the detection of intermediate species prior the oxidative addition reaction taking place [3a,11]. In any case, no significant differences are observed on going from HCl to HBr to HI. It then appears that simple arguments based only on the electronegativity of the X nucleus cannot be applied to explain the different reactivities of halogen with respect to N and S donor atoms. It is likely however that the acid/base properties of the coordinated H–X moiety need to be considered; in fact there is growing evidence that H···H interactions occurring on the surface of transition metal clusters play an important role in driving reaction steps further [3,11]. The observed behavior can then be accounted for in terms of two stages: (i) coordination of HX to form the saturated $H(\mu\text{-H})Os_3(CO)_{10}(\eta^2\text{-HX})$ species, characterized by a strong interaction between the negatively charged terminal hydride and the positively charged hydrogen in the HX ligand; (ii) the latter interaction promotes the heterolytic cleavage of the H–X bond with the formation of a new hydridic linkage, possibly through the intermediacy of an $\eta^2\text{-H}_2$ complex.

### 2.2. Reactivity of $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ (X = Cl, Br, I)

When the excess of HX and the $CD_2Cl_2$ are pumped off and the residue is redissolved in the same solvent, the formation of some amounts of $(\mu\text{-H})_2Os_3(CO)_{10}$ and $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ is detected, as shown by the presence in the RT $^1$H-NMR spectrum of two resonances at $-11.5$ ppm [12] and $-14.27$ (X = Cl) $-15.16$ (X = Br), $-17.60$ (X = I) ppm [13] respectively, in addition to those of the $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ systems.

These observations indicate that the $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ compounds undergo both $H_2$ and HX elimination at room temperature. The former process is irreversible ($(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ is unreactive towards $H_2$), while the latter simply corresponds to the reverse of the path which leads to the $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ formation. The overall behavior can be summarized in the following reaction scheme:

$$(\mu\text{-H})_2Os_3(CO)_{10} + HX \Leftrightarrow H(\mu\text{-H})_2Os_3(CO)_{10}(X) \rightarrow (\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10} + H_2$$

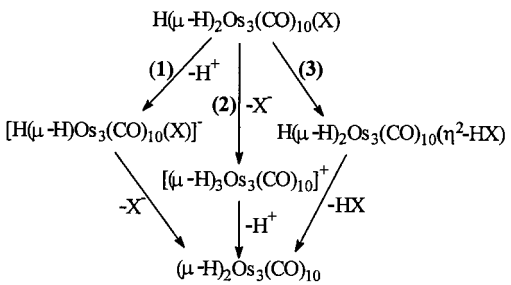
One may envisage three different pathways leading to HX elimination from $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ (Scheme 4):

1. deprotonation of $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ (promoted for instance by traces of water in the solvent) with the formation of the reported intermediate anionic cluster $[H(\mu\text{-H})Os_3(CO)_{10}(X)]^-$ [13], followed by halogen elimination;
2. halogen elimination with the formation of the cationic $[(\mu\text{-H})_3Os_3(CO)_{10}]^+$ [4] derivative, followed by deprotonation;
3. elimination of HX as a molecule via the formation of an $\eta^2$-HX intermediate.

If pathway (1) was the operating mechanism, the reaction rate should increase in the presence of a base. In pathway (2) the rate determining step should be the $X^-$ elimination because of the strong acid character of $[(\mu\text{-H})_3Os_3(CO)_{10}]^+$ [4]. In this case, as well as in the case of pathway (3), the reaction rate should not be affected by the presence of a base, since the rate-determining steps do not involve an acid/base process.

In order to obtain better insight into the operating mechanism, we decided to study the HX elimination from $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ in the presence of a base. We first chose $NEt_3$ in order to avoid any complications due to the reactivity of a coordinating base: in fact it is known that $NEt_3$ does not react at all with $(\mu\text{-H})_2Os_3(CO)_{10}$ due to steric hindrance [3a].

By adding $NEt_3$ to a frozen solution of $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ and allowing the sample to thaw di-




Scheme 4.

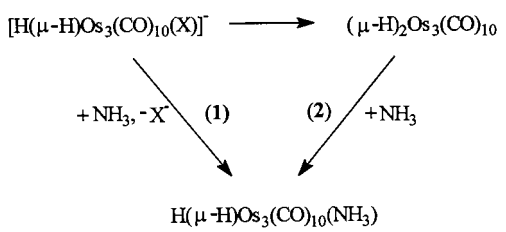
rectly inside the NMR spectrometer, we could follow the reaction as it started. This experiment showed that HX elimination occurs at temperatures close to 180 K, yielding an almost complete transformation of the starting material into $(\mu\text{-H})_2Os_3(CO)_{10}$. Only traces of $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ were observed. The observation that in the presence of $NEt_3$ the HX elimination occurs more rapidly provides strong support to the occurrence of mechanism (1).

On the basis of this result, it was decided to investigate the analogous reaction in the presence of ammonia. In addition to acting as a base, ammonia may act as a coordinating ligand: it may either substitute the halogen in the intermediate $[H(\mu\text{-H})Os_3(CO)_{10}(X)]^-$ (path 1, Scheme 5) or add to the unsaturated $(\mu\text{-H})_2Os_3(CO)_{10}$ (path 2).

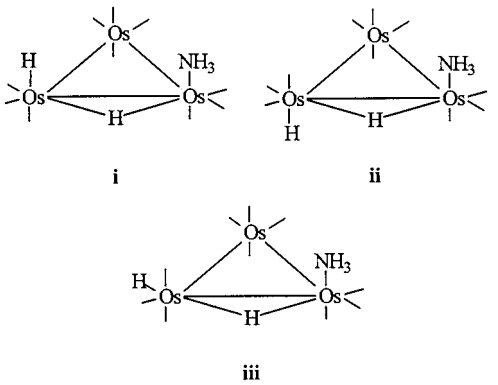
When the reaction with ammonia is performed on isomer **I** of $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ at 183 K, two hydride resonances are instantaneously observed in the $^1$H-NMR spectrum at $-10.41$ ($J_{^1H,^1H} = 2.44$ Hz) and $-16.58$ ($J_{^1H,^1H} = 2.44$ Hz) ppm, respectively, attributable to the known $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$ species (**i**) [2].

When the reaction is carried out on a mixture of the $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ isomers the low temperature allows the detection of some kinetic products, as shown by the $^1$H-NMR spectrum. In fact, in addition to the main hydride signals of $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$ (**i**), two other sets of resonances are observed at $-10.24$ ($J_{^1H,^1H} = 1.51$ Hz) and $-16.63$ ($J_{^1H,^1H} = 1.51$ Hz) ppm (**ii**), and at $-13.24$ ($J_{^1H,^1H} = 15.8$ Hz) and $-14.98$ ($J_{^1H,^1H} = 15.8$ Hz) ppm (**iii**), respectively. The two sets of signals disappear as the temperature is increased to 153 K, while those assigned to the known $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$ (**i**) increase, indicating the transformation of the two new species (**ii**) and (**iii**) into (**i**).

The data suggest that, carrying out the reaction in a mixture of the isomers of $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ at low temperature, two new isomers (**ii**) and (**iii**) of $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$ are formed, which then evolve towards the thermodynamically favoured isomer (**i**), having the terminal hydride in an axial position in a *syn* arrangement with respect to the $NH_3$ ligand. The $\delta$, $J_{^1H,^1H}$ and $T_1$ values (see Section 4) for these isomers are in accordance with the same type of isomerism depicted above for the parent $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$, i.e. they should differ from the main species solely in the terminal hydride position. In (**ii**) the terminal hydride should




Scheme 5.



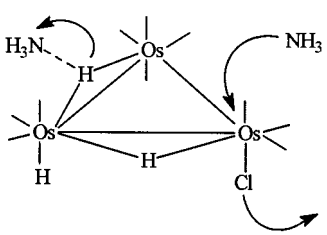

Scheme 6.

occupy the axial position anti with respect to the $NH_3$ group [2], while in (**iii**) it should occupy an equatorial position *trans* to the bridging hydride (Scheme 6).

Interestingly, when $(\mu\text{-H})_2Os_3(CO)_{10}$ is reacted with ammonia in the same conditions of temperature and pressure, only the isomer (**i**) of $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$ is formed. This observation excludes that the $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$ derives from the addition of $NH_3$ to $(\mu\text{-H})_2Os_3(CO)_{10}$ (path 2 in Scheme 3).

In order to get more insight into the operating mechanism, $[H(\mu\text{-H})Os_3(CO)_{10}(X)]^-$ was synthesized according to the literature method [10a], and reacted with ammonia under the same experimental conditions. Surprisingly, no reaction was observed up to 243 K; at higher temperatures only limited formation of $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$ occurred.

This observation suggests that, when the base has coordinating capability, the deprotonation of $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$ and the substitution of the halogen by the base are actually a single step concerted process involving two base molecules and the cluster, as tentatively depicted in Scheme 7. Moreover, the observation of different isomers of $H(\mu\text{-H})Os_3(CO)_{10}(NH_3)$, structurally related to the various isomers of the starting $H(\mu\text{-H})_2Os_3(CO)_{10}(X)$, suggests that the deprotonation step involves the bridging hydride between the 'rear' osmium atom and the one which bears the terminal hydride (Scheme 7)[1].



Scheme 7.

[1] The same reactions were performed by using $PPh_3$. In this case the reaction temperature is higher (273 K), due to the weaker base character of the phosphine with respect to amines, and does not allow the detection of any unusual isomer of the product $H(\mu\text{-H})Os_3(CO)_{10}(PPh_3)$.

## 3. Conclusions

The reactions of the unsaturated 46 $e^-$ cluster ($\mu$-$H)_2Os_3(CO)_{10}$ with HX (X = Cl, Br, I) afford the novel trihydride complexes $H(\mu\text{-}H)_2Os_3(CO)_{10}(X)$, which exist as four different isomers, depending on the position occupied by the terminal hydride on the osmium atom. The addition of HX is reversible, and the HX elimination appears to proceed via an acid/base mechanism.

When a base with coordinating capability such as ammonia is used to promote this process, further reactivity is observed, which leads to the formation of the $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$ derivative. The observation of kinetic isomers for the latter compound structurally related to isomers of $H(\mu\text{-}H)_2Os_3(CO)_{10}(X)$ suggests that ammonia does not simply add to the ($\mu$-$H)_2Os_3(CO)_{10}$ formed by HX elimination, but it attacks $H(\mu\text{-}H)_2Os_3(CO)_{10}(X)$, via a concerted mechanism, involving two ammonia molecules, which is based on the simultaneous cluster deprotonation and $X^-$ substitution.

## 4. Experimental

$^1$H- and $^{13}$C-NMR spectra were recorded on a JEOL EX-400 spectrometer operating at 399.65 and 100.25 MHz, respectively. The non selective inversion recovery pulse sequence [13] was used to obtain $T_1$ values.

($\mu$-$H)_2Os_3(CO)_{10}$ was synthesized according to the published method [13]. $^{13}$CO enriched samples were prepared by using $^{13}$C-enriched (about 40%) $Os_3(CO)_{12}$, obtained by direct exchange of $^{13}$CO with $Os_3(CO)_{12}$ (200 mg) in *n*-octane (100 ml) at 393 K for three days in a 250 ml sealed vial.

$^{13}$CO (99% enriched) was purchased from EURISOTOP (Saint Aubain, France). $NH_3$ was purchased from SIAD (Bergamo, Italy). Gaseous HCl was purchased from Fluka. Aqueous solutions of HCl (37%), HBr (48%) and HI (51%) were purchased from Aldrich Chemicals. All the solvents were stored over molecular sieves before use.

All the reactions were carried out directly in a reseal-able 5 mm NMR tube: the reactant was added to a frozen solution of the starting material, and the sample was allowed to reach the reaction temperature inside the NMR spectrometer. For the synthesis of the $H(\mu\text{-}H)_2Os_3(CO)_{10}(X)$ compounds, an excess of HX (about 1:10) was added to ($\mu$-$H)_2Os_3(CO)_{10}$. For the reactions of the $H(\mu\text{-}H)_2Os_3(CO)_{10}(X)$ complexes, the excess of HX was previously removed from the tube by pumping off the solvent and redissolving the residue. An equimolar quantity of base was used in the case of $NEt_3$ and $PPh_3$, while a 100 torr pressure was used in the case of ammonia.

### 4.1. Spectroscopic data for $H(\mu\text{-}H)_2Os_3(CO)_{10}(X)$

#### 4.1.1. X = Cl

Isomer **I**. IR ($CDCl_3$): 2141.9 (w), 2119.8 (sh), 2114.1 (m), 2093.9 (s), 2081.5 (w), 2067.0 (vs), 2061.7 (sh), 2036.4 (sh), 2025.0 (m). $^1$H-NMR ($CD_2Cl_2$, 183 K): $\delta = -9.46$ (A, $J_{^1H,^1H} = 3.91$, 2.93 Hz; $T_1 = 1.00$ s), $-16.54$ (B, $J_{^1H,^1H} = 3.91$ Hz; $T_1 = 1.30$ s), $-19.24$ (C, $J_{^1H,^1H} = 2.93$ Hz; $T_1 = 1.31$ s); $^{13}$C ($CD_2Cl_2$, 183 K): $\delta = 171.70$ ($J_{^{13}C,^1H_B} = 11.7$ Hz), 171.57 ($J_{^{13}C,^{13}C} = 35.7$ Hz), 170.02, 169.88 ($J_{^{13}C,^1H_A} = 27.4$ Hz), 169.39 ($J_{^{13}C,^{13}C} = 35.7$ Hz), 168.63 ($J_{^{13}C,^1H_B} = 2.9$ Hz), 167.32 ($J_{^{13}C,^1H_A} = J_{^{13}C,^1H_B} = J_{^{13}C,^1H_C} = 7.0$ Hz), 166.98 ($J_{^{13}C,^1H_C} = 6.8$ Hz), 166.82 ($J_{^{13}C,^1H_A} = J_{^{13}C,^1H_B} = J_{^{13}C,^1H_C} = 6.0$ Hz), 164.53 ($J_{^{13}C,^1H_C} = 2.9$ Hz).

Isomer **II**. $^1$H-NMR ($CD_2Cl_2$, 183 K): $\delta = -9.49$ (A, $J_{^1H,^1H} = 2.93$ Hz; $T_1$ (200 K) = 1.06 s), $-17.39$ (B, $T_1$ (200 K) = 1.55 s), $-17.45$ (C, $J_{^1H,^1H} = 2.93$ Hz; $T_1$ (200 K) = 1.53 s).

Isomer **III**. $^1$H-NMR ($CD_2Cl_2$, 183 K): $\delta = -8.54$ (A, $J_{^1H,^1H} = 14.16$ Hz; $T_1 = 0.56$ s), $-15.32$ (B, $J_{^1H,^1H} = 1.95$ Hz; $T_1 = 0.61$ s), $-16.29$ (C, $J_{^1H,^1H} =$ 14.16, 1.95 Hz; $T_1 = 2.29$ s). $^{13}$C-NMR ($CD_2Cl_2$, 183 K): $\delta = 173.98$ ($J_{^{13}C,^{13}C} = 32.67$ Hz), 172.77 ($J_{^{13}C,^{13}C} =$ 36.13 Hz), 172.25 ($J_{^{13}C,^{13}C} = 32.67$ Hz), 171.76 ($J_{^{13}C,^1H_B} = 9.77$ Hz), 170.96, 170.67, 169.27, 169.08 ($J_{^{13}C,^{13}C} = 36.13$ Hz), 167.53, 165.25.

Isomer **IV**. $^1$H-NMR ($CD_2Cl_2$, 183 K): $\delta = -9.15$ (A, $J_{^1H,^1H} = 13.43$ Hz; $T_1 = 0.51$ s), $-13.90$ (B, $J_{^1H,^1H} = 13.43$, 1.95 Hz; $T_1 = 3.76$ s), $-17.00$ (C, $J_{^1H,^1H} = 1.95$ Hz; $T_1 = 0.56$ s).

#### 4.1.2. X = Br

Isomer **I**. $^1$H-NMR ($CDCl_3$, 213 K): $\delta = -9.11$ ($J_{^1H,^1H} = 3.42$, 3.91 Hz), $-17.33$ ($J_{^1H,^1H} = 3.91$ Hz), $-19.17$ ($J_{^1H,^1H} = 3.42$ Hz).

Isomer **II**. $^1$H-NMR ($CDCl_3$, 213 K): $\delta = -8.96$ ($J_{^1H,^1H} = 3.61$ Hz), $-18.13$ ($J_{^1H,^1H} = 3.61$ Hz), $-18.22$.

Isomer **III**. $^1$H-NMR ($CDCl_3$, 213 K): $\delta = -8.62$ ($J_{^1H,^1H} = 13.67$ Hz), $-16.25$ ($J_{^1H,^1H} = 1.46$ Hz), $-16.38$ ($J_{^1H,^1H} = 13.67$, 1.46 Hz).

Isomer **IV**. $^1$H-NMR ($CDCl_3$, 213 K): $\delta = -9.35$ ($J_{^1H,^1H} = 12.70$ Hz), $-14.87$ ($J_{^1H,^1H} = 12.70$ Hz), $-17.08$.

#### 4.1.3. X = I

Isomer **I**. $^1$H-NMR ($CD_2Cl_2$, 180 K): $\delta = -8.73$ ($J_{^1H,^1H} = 2.93$ Hz, 2.93 Hz; $T_1 = 1.14$ s), $-18.72$ ($J_{^1H,^1H} = 2.93$ Hz; $T_1 = 1.50$ s), $-19.27$ ($J_{^1H,^1H} = 2.93$ Hz; $T_1 = 1.52$ s).

Isomer **II**. $^1$H-NMR ($CD_2Cl_2$, 180 K): $\delta = -8.69$ (broad; $T_1 = 1.33$ s), $-19.57$ (broad; $T_1 = 1.44$ s), $-19.74$ (broad; $T_1 = 1.66$ s).

Isomer **III**. $^1$H-NMR ($CD_2Cl_2$, 180 K): $\delta = -8.79$ ($J_{^1H,^1H} = 14.16$ Hz; $T_1 = 0.56$ s), $-16.46$ ($J_{^1H,^1H} =$ 14.16 Hz; $T_1 = 2.90$ s), $-17.95$ ($T_1 = 0.59$ s).

Isomer **IV**. $^1H$ ($CD_2Cl_2$, 180 K): $\delta = -9.65$ ($J_{^1H,^1H} = 13.18$ Hz; $T_1 = 0.42$ s), $-16.53$ ($J_{^1H,^1H} = 13.18$ Hz; $T_1 = 2.13$ s), $-17.19$ ($T_1 = 0.52$ s).

### *4.2. $^1H$-NMR data ($CD_2Cl_2$, 183K) for the three isomers of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$*

Isomer (**i**). $\delta = -10.41$ ($J_{^1H,^1H} = 2.44$ Hz; $T_1 = 0.60$ s), $-16.58$ ($J_{^1H,^1H} = 2.44$ Hz; $T_1 = 1.00$ s).

Isomer (**ii**). $\delta = -10.24$ ($J_{^1H,^1H} = 1.51$ Hz; $T_1 = 0.48$ s), $-16.63$ ($J_{^1H,^1H} = 1.51$ Hz; $T_1 = 0.77$ s).

Isomer (**iii**). $\delta = -13.24$ ($J_{^1H,^1H} = 15.80$ Hz; $T_1 = 4.53$ s), $-14.98$ ($J_{^1H,^1H} = 15.80$ Hz; $T_1 = 4.50$ s).

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