# Coordination of Imines on $Os_3$ Clusters: Effect of the Solvent in Addressing Isomer Formation

Silvio Aime,* Marta Férriz, Roberto Gobetto, and Esteve Valls

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

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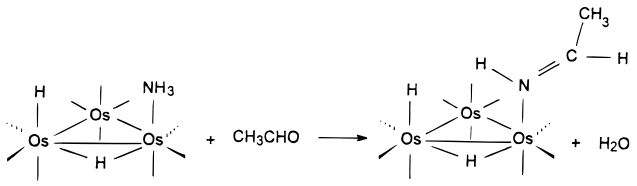
*Summary: Imine ligands terminally bound to triosmium clusters have been prepared by the reaction of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with $NH_3$ and a keto or aldhehydic substrate. However reactions in nonpolar solvents yield only one of the two possible isomers. In contrast, reactions in polar solvents, such as methanol, yield both isomers. Experimental methods are described that clearly demonstrate that the overall stereochemistry of the resulting complexes is dependent upon the competition between intra- and intermolecular hydrogen-bonding interactions. The isomers have been unambiguously assigned using $^{15}N$ and $^{13}C$ labeling as well as $T_1$ measurements.*



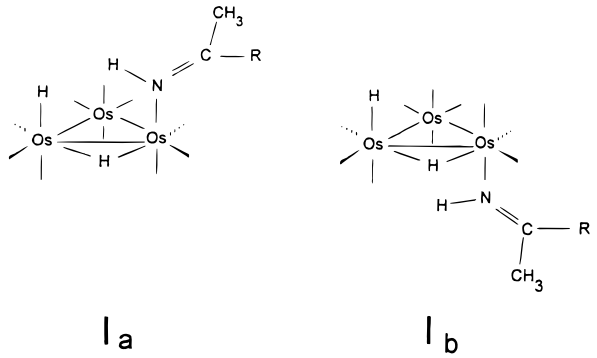
## Introduction

Although there are a number of reports of mononuclear imino complexes, the coordination of such ligands to metal clusters usually occurs by adopting $\eta^2$ or $\eta^3$ bonding modes.[1−5] The resultant imine moiety is often the result of extensive further reaction/rearrangement of the previously coordinated ligands such as nitriles, oximes, and amines.[6−10] Recently we have shown that terminally bound imine ligands (L) can be obtained by the reaction of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$ with aldehydes such as $CH_3CHO$ and $C_6H_5CHO$ directly in the NMR tube[11] (see Scheme 1). Derivatives of the general formula $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CR(H))$ containing the N-donor ligand in an axial position should be present in two isomeric forms, with the imine ligand either syn or anti to the terminal hydride[12] (see Scheme 2). However isomer $\mathbf{1_a}$ was observed as the only product in the case of the reaction of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$ and aldehydes. This has been interpreted in terms of a stabilization effect due to the formation of an intramolecular hydrogen bond between the N−H moiety and the terminal hydride ligand.[12]

**Scheme 1**




**Scheme 2**




R = H, $CH_3$

To extend this work to the synthesis of derivatives containing ketoimine moieties, we have considered the reaction of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$ with acetone. Surprisingly we found that both the $\mathbf{1_a}$ and $\mathbf{1_b}$ isomers were obtained in similar amounts. This led us to examine in detail the effects of solvent on isomer formation for this class of compound.

## Results and Discussion

The addition of $NH_3$ to a solution of $Os_3(\mu\text{-}H)_2(CO)_{10}$ in acetone causes an immediate color change from violet to yellow. This is typical of the formation of saturated adducts from the coordinatively unsaturated $Os_3(\mu\text{-}H)_2(CO)_{10}$ cluster. $^1H$ low-temperature NMR spectroscopy reveals a high yield of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$, which readily transforms into two products (A and B) which may be readily characterized by an analogous pattern in the hydride region (Table 1, Figure 1a). As well as the hydride resonances, each A and B derivative contains two distinct methyl resonances and an iminic N−H resonance at low field. On the basis of the behavior observed for the reaction of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$ with aldehydes,[11] it was concluded that acetone reacts with $NH_3$ to form the corresponding ketoimine, which

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**Table 1. $^1$H and $^{15}$N NMR Data for H($\mu$-H)Os$_3$(CO)$_{10}$(HN=C(CH$_3$)$_2$) and H($\mu$-H) Os$_3$(CO)$_{10}$(HN=CHCH$_3$) in Different Solvents**

| | | | $^1$H/ppm | | | | | $^{15}$N/ppm |
|---|---|---|---|---|---|---|---|---|
| ligand | isomer | solvent, $T$ (°C) | N*H* | C*H* | C*H*$_3$ | H$_T$ | H$_B$ | |
| HN=C(CH$_3$)$_2$ | A | $CDCl_3$, −55 | 8.60 | | 2.39, 2.25 | −10.39 $^2J_{1H,1H}$ = 3.4 Hz | −16.02 $^2J_{1H,1H}$ = 3.4 Hz | 189.41 $^1J_{15N,1H}$ = 74.3 Hz |
| HN=C(CH$_3$)$_2$ | A | $(CD_3)_2CO$, −55 | 10.64 | | 2.50, 2.48 | −9.69 $^2J_{1H,1H}$ = 3.4 Hz | −16.60 $^2J_{1H,1H}$ = 3.4 Hz | 180.96 $^1J_{15N,1H}$ = 71.8 Hz |
| HN=C(CH$_3$)$_2$ | B | $(CD_3)_2CO$, −55 | 10.54 | | 2.42, 2.37 | −9.82 $^2J_{1H,1H}$ = 3.8 Hz | −16.92 $^2J_{1H,1H}$ = 3.8 Hz | 177.79 $^1J_{15N,1H}$ = 71.8 Hz |
| HN=CHCH$_3$ | A | $CDCl_3$, −55 | 8.89 $^3J_{1H,1H}$ = 22.2 Hz | 7.93 $^3J_{1H,1H}$ = 4.9 Hz $^3J_{1H,1H}$ = 22.2 Hz | 2.26 $^3J_{1H,1H}$ = 4.9 Hz | −10.42 $^2J_{1H,1H}$ = 3.4 Hz | −16.09 $^2J_{1H,1H}$ = 3.4 Hz | 198.4 $^1J_{15N,1H}$ = 74.0 Hz |
| HN=CHCH$_3$ | A | $(CD_3)_2CO$, −55 | 10.60 $^3J_{1H,1H}$ = 21.4 Hz | 8.29 $^3J_{1H,1H}$ ≈ 5 Hz $^3J_{1H,1H}$ = 21.4 Hz | 2.37 $^3J_{1H,1H}$ ≈ 5 Hz | −9.70 $^2J_{1H,1H}$ = 3.4 Hz | −16.25 $^2J_{1H,1H}$ = 3.4 Hz | 191.91 $^1J_{15N,1H}$ = 74.4 Hz |
| HN=CHCH$_3$ | B | $(CD_3)_2CO$, −55 | 11.04 $^3J_{1H,1H}$ = 21.4 Hz | 8.39 $^3J_{1H,1H}$ ≈ 5 Hz $^3J_{1H,1H}$ = 21.4 Hz | 2.38 $^3J_{1H,1H}$ ≈ 5 Hz | −9.92 $^2J_{1H,1H}$ = 4.3 Hz | −16.54 $^2J_{1H,1H}$ = 4.3 Hz | 189.63 $^1J_{15N,1H}$ = 74.4 Hz |

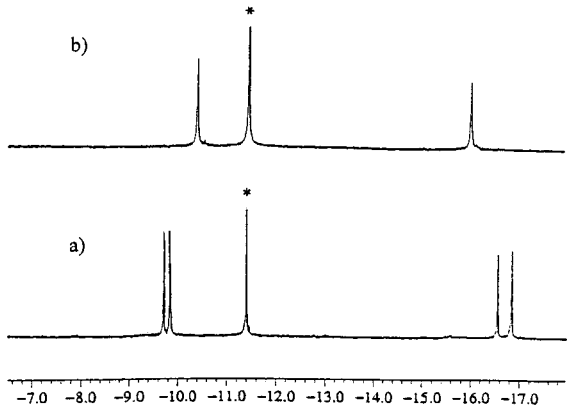


**Figure 1.** $^1$H NMR spectra of H($\mu$-H)Os$_3$(CO)$_{10}$(HN=C(CH$_3$)$_2$) recorded at 400 MHz: (a) in (CD$_3$)$_2$CO, −55 °C; (b) in $CDCl_3$, −55 °C. * denotes Os$_3$($\mu$-H)$_2$(CO)$_{10}$.

promptly coordinates at the vacant site on the osmium cluster. However, contrary to what is observed in the case of the aldimine derivatives, both theoretically possible isomers formed.

Further support for these assignments has been gained by the preparation of $^{15}$N-enriched samples, which show two doublets in the $^{15}$N NMR spectrum with the same couplings as those observed for the iminic proton resonances in the $^1$H NMR spectrum of the respective compounds (Table 1). Further the $^{13}$C NMR spectrum of a $^{13}$CO-enriched sample displays a number (and a pattern) of CO resonances consistent with the presence of both of the **1$_a$** and **1$_b$** forms of H($\mu$-H)Os$_3$(CO)$_{10}$(HN=C(CH$_3$)$_2$) (see Experimental Section). At higher temperatures (> −40 °C), all the $^1$H NMR resonances broaden progressively, indicating that isomeric exchange becomes fast on the NMR time scale. Indeed at 400 MHz there is complete collapse of the hydride resonances at +40 °C; however the observation of an average signal for the hydride resonances at higher temperatures is precluded by the incipient decomposition of the sample, which results in the release of the ketoimine moiety and re-formation of Os$_3$($\mu$-H)$_2$(CO)$_{10}$, as evidenced by the reappearance of a hydride resonance at $\delta$ −11.45. This isomerization process can also be followed by the observation of the coalescence of the imine proton resonances. The smaller separation of the latter resonances allows the observation of the time-averaged resonance, and the sharpening can be followed for almost 30 °C above the coalescence temperature. Line shape analysis either of the hydride or of the iminic resonances allowed us to estimate the $E_a$ of the isomerization process ($E_a$ = 52.6 kJ/mol). The value obtained is similar to those found in related H($\mu$-H)Os$_3$(CO)$_{10}$L species.[12]

To assess whether the origin of the discrepancy between the previous observations that the formation of only **1$_a$** for the aldimine-containing species and the present result, which shows the occurrence of both **1$_a$** and **1$_b$** isomers, lies with the nature of the compound or the polarity of the solvent, the acetone was completely evaporated from a solution of the H($\mu$-H)Os$_3$(CO)$_{10}$(HN=C(CH$_3$)$_2$) derivative and the residue was dissolved in $CDCl_3$.

The $^1$H (Figure 1b), $^{15}$N, and $^{13}$C NMR spectra of a chloroform solution of H($\mu$-H)Os$_3$(CO)$_{10}$(HN=C(CH$_3$)$_2$) at −55 °C were consistent with the presence of only one

**Table 2. Hydride Spin−Lattice Relaxation Times[a] Recorded at 400 MHz and Calculated NH- - -$H_t$ and NH- - -$H_b$ Distances Calculated According to Eqs 1 and 2**

| ligand | isomer | solvent | $T_1$ ($H_T$), s | $T_1$ ($H_B$), s | $r$($H_T$−NH), Å | $r$($H_B$−NH), Å |
|---|---|---|---|---|---|---|
| HN=C($CH_3$)$_2$ | A | $CD_2Cl_2$ | 0.43 (1.30) | 1.15 (1.53) | 2.0 | 2.8 |
| HN=C($CH_3$)$_2$ | A | ($CD_3$)$_2$CO | 1.06 (1.39) | 1.33 (1.69) | 2.6 | 2.9 |
| | B | | 2.10 (2.18) | 1.04 (1.18) | 4.2 | 3.0 |
| HN=CH$CH_3$ | A | $CD_2Cl_2$ | 0.52 (1.10) | 1.14 (1.61) | 2.1 | 2.7 |
| HN=CH$CH_3$ | A | ($CD_3$)$_2$CO | 0.89 (1.23) | 1.07 (1.27) | 2.6 | 2.9 |
| | B | | 2.22 (2.30) | 1.23 (1.43) | 4.3 | 3.1 |

[a] The $T_1$ values of the N−D isotopomers are shown in parentheses.

isomer (Table 1). An almost identical spectrum was observed when $CDCl_3$ was replaced with $CD_2Cl_2$; however, when methanol is used as the solvent, two isomers (in almost equal population) are observed. This result unambiguously demonstrates that solvent polarity is the controlling factor in the stereochemistry of these derivatives.

The assignment of structure **1a** or **1b** to the isomer present in $CDCl_3/CD_2Cl_2$ solutions was carried out by measuring the proton $T_1$ relaxation times of the hydride resonances (see Table 2). Using $T_1$ and $\tau_c$ it is possible to obtain an estimate of the distance between neighboring protons. In $CD_2Cl_2$, minimum $T_1$ values were observed at −65 °C. At this temperature $\tau_c$ is equal to $0.62/\omega_0$ ($\omega_0 = 2\pi 400 \times 10^6$ rad $s^{-1}$), i.e., $2.45 \times 10^{-10}$ rad $s^{-1}$. Further an accurate determination may be obtained by the isolation of the selective H,H dipolar term. In our system this goal is easily achieved by the comparison of the $T_1$ values of the two isotopomers, H($\mu$-H)$Os_3(CO)_{10}$(HN=C($CH_3$)$_2$) and H($\mu$-H)$Os_3(CO)_{10}$(DN=C($CH_3$)$_2$).[13−15]

$$R_{1,D}^{H-H} = \left[\frac{1}{T_1(protio)} - \frac{1}{T_1(deuterio)}\right] \times 1.0625 \quad (1)$$

$$R_{1,D}^{H-H} = \frac{3\gamma^4{}_H\hbar^2 \times 2.45 \times 10^{-10}}{10r_{H-H}^6}\left[\frac{1}{1+0.62^2} + \frac{4}{1+4\times 0.62^2}\right] \quad (2)$$

On this basis we have been able to evaluate the $r_{H,H}$ distance between $H_T$ and the imine proton as 2.0 Å, which is very similar to the value previously determined for the closely related cluster H($\mu$-H)$Os_3(CO)_{10}$(HN=CH-($CH_3$)). Therefore we conclude that in $CD_2Cl_2$ or in $CDCl_3$ solution, H($\mu$-H)$Os_3(CO)_{10}$(HN=C($CH_3$)$_2$) is present in the **1a** isomer with a distance between $H_T$ and the iminic proton that is strongly indicative of the presence of a hydrogen-bonding interaction.[16]

Measurement of the spin−lattice relaxation times at variable temperature for the two isomers **1a** and **1b** in acetone has also been carried out (Figure 2). From the data reported in Table 2, $T_{1(minima)}$ values for the terminal hydride of the syn isomer (A) are significantly longer in acetone than in $CD_2Cl_2$. Again by comparing the $T_1$ values of the two isotopomers H($\mu$-H)$Os_3(CO)_{10}$-(HN=C($CH_3$)$_2$ and H($\mu$-H)$Os_3(CO)_{10}$ (DN=C($CH_3$)$_2$ it is possible to obtain the selective H,H dipolar term, from which, using eqs 1 and 2 at $T_1$ minimum, the distances between neighboring protons may be estimated (Table 2).

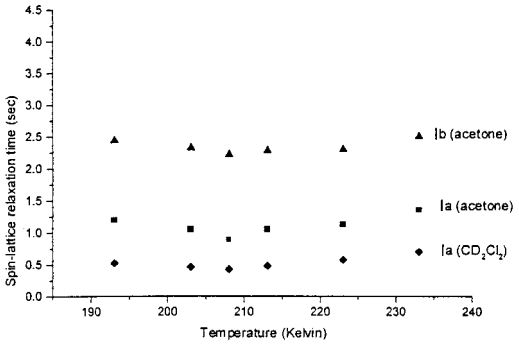


**Figure 2.** $^1$H spin−lattice relaxation times of terminally bound hydride ligands in H($\mu$-H)$Os_3(CO)_{10}$(HN=C($CH_3$)$_2$) (**1a** and **1b** isomers) measured as a function of temperature, in acetone-$d_6$ and $CD_2Cl_2$, respectively.

The long NH- - -$H_t$ distance of about 4.0 Å for **1b** is in agreement with the anti arrangement of the imine ligand. The distance between the imine proton and the terminal hydride is significantly longer for the syn isomer **1a** in ($CD_3$)$_2$CO than in $CD_2Cl_2$. This may be accounted for by a difference in the orientation of the imine ligand in the syn isomer in the two solvents. In solvents such as $CD_2Cl_2$ or $CDCl_3$, the presence of a hydrogen bond minimizes the distance between the imine proton and the terminal hydride, thus forcing the imine ligand to be aligned with the Os−Os bond containing the bridging hydride. Conversely when a polar solvent such as ($CD_3$)$_2$CO is used, the weak intramolecular hydrogen bond interaction is no longer operative, allowing the imine ligand to rotate into a different, low-energy, orientation with a longer NH- - -$H_t$ distance, thus maximizing the binding energy with the solvent molecules.

To assess whether the behavior of H($\mu$-H)$Os_3(CO)_{10}$-(HN=C($CH_3$)$_2$ is common to other imine systems bonded to the "H($\mu$-H)$Os_3(CO)_{10}$" type cluster framework, we investigated the stereochemistry of the adduct obtained by the addition of $CH_3CHO$ to H($\mu$-H)$Os_3(CO)_{10}NH_3$ to $Os_3(\mu$-H)$_2(CO)_{10}$ in different solvents. Again the $^1$H spectra (Table 1) give evidence for the formation of equivalent amounts of the syn and anti isomers when the H($\mu$-H)$Os_3$ $(CO)_{10}$(HN=CH$CH_3$) adduct is dissolved in acetone, whereas, as previously reported,[11] only isomer **1a** is present when $CDCl_3$ is used as the solvent. By measuring the hydride spin−lattice relaxation times of the two isotopomers H($\mu$-H)$Os_3(CO)_{10}$(HN=CH$CH_3$) and H($\mu$-H)$Os_3(CO)_3$(DN=CH$CH_3$) the distances reported in Table 2 were calculated. This result is analogous to that obtained when L = HN=C($CH_3$)$_2$ and

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demonstrates that comparable solvent effects take place when L is $HN{=}C(CH_3)_2$ or $HN{=}CHCH_3$.

## Conclusions

The results show that there is clear solvent control over the stereochemistry of the imine ligands bonded to the metallic framework in $H(\mu\text{-}H)Os_3(CO)_3$(imine) derivatives. Both isomeric forms are populated in solvents such as acetone and methanol due to the bonding of the solvent molecules, which effectively competes with the intramolecular hydrogen bonding between the terminal hydride and the imine moiety.

## Experimental Section

All solvents were dried and stored over molecular sieves. $Os_3(\mu\text{-}H_2)(CO)_{10}$[17] and $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CHCH_3)$[11] were prepared according to published procedures.

$^1H$, $^{13}C$, and $^{15}N$ NMR spectra were recorded on a JEOL EX-400 spectrometer operating at 399.65, 100.25, and 40.51 MHz, respectively. The scale reference for $^{15}N$ measurements was given with respect to nitromethane ($\delta = 0$, 303 K). $^{13}C$ NMR spectra were acquired from $^{13}CO$-enriched derivatives which were prepared by using $^{13}C$-enriched $Os_3(CO)_{12}$ obtained by direct exchange of 99% $^{13}CO$ (Isotec) with $Os_3(CO)_{12}$.[18]

Nonselective inversion recovery was used to obtain $^1H$ $T_1$ values.[19] Samples for $T_1$ measurements were degassed using freeze−pump−thaw techniques. The temperature was calibrated with a standard methanol $^1H$ thermometer sample. Errors in the reported $T_1$ values were estimated to be in the range ±2%.

**Synthesis of $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}C(CH_3)_2$. (1).** In a typical reaction 5 mg of $Os_3(\mu\text{-}H_2)(CO)_3$ ($5.9 \times 10^{-6}$ mol) in 0.5 mL of $CH_2Cl_2$ was transferred into a flask, and an excess of $NH_3$ was added. The solution immediately changed from purple to yellow. The solvent and excess $NH_3$ were rapidly removed under vacuum, and the residue was redissolved in acetone, which was in turn removed under vacuum. The yellow product finally dissolved in $CD_2Cl_2$ or $(CD_3)_2CO$.

$^{13}C$ NMR ($CDCl_3$, −55 °C, 100.25 MHz) $\mathbf{1_a}$: 186.4 ($^2J_{CC}$ = 36.6 Hz); 184.2 ($^2J_{CC}$ = 33.3 Hz; 180.7 ($^2J_{CH}$ = 22.6 Hz); 175.8 (d); 175.4; 175.2; 174.3; 173.5 ($^2J_{CH}$ = 10.7 Hz); 173.0; 172.7.

$^{13}C$ NMR ($(CD_3)_2CO$, −55 °C, 100.25 MHz) $\mathbf{1_a}$ and $\mathbf{1_b}$ mixture (integral in parentheses): 183.7 ($^2J_{CC}$ = 36.5 Hz) (2); 183.0, (2); 182.1 ($^2J_{CC}$ = 37.6 Hz) (2); 180.7 ($^2J_{CH}$ = 21.5 Hz) (1); 179.1 ($^2J_{CH}$ = 22.6 Hz) (1); 174.6 (2); 174.2 (1); 177.0 (1); 173.6 (1); 173.5 (1); 172.2 (1); 172.1 (1); 171.3 (1); 170.9 (1); 169.8 (1); 169.7 (1); 169.6 (2).

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