Notes

Coordination of an Imine Ligand on an Os_3 Cluster Stabilized by Intramolecular Os−H---H−N Hydrogen Bonding

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: The addition of CH_3CHO to a chloroform solution of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$ affords the new $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CHCH_3)$ derivative where the imine ligand occupies a terminal position. The stereochemistry of the adduct appears to be determined by the occurrence of an unconventional hydrogen-bond interaction involving the N−H moiety and the terminal hydride.

Introduction

Ammonia and primary amines can add to aldehydes or ketones to give imines. However, these products are often very unstable even at low temperature since they spontaneously polymerize; this is observed especially when the N−H moiety is present. Coordination to a metal can partially overcome the instability of such species; in fact a large array of mononuclear imino complexes have been reported.[1] In many cases, however, the imino metal complexes have been obtained by modification of a previously coordinated ligand such as nitriles, oximes, and amines. In binuclear and trinuclear metal derivatives the reactivity of coordinated ligands allows the formation of imino complexes[2] in which the organic ligand occupies a bridging position adopting several different bonding schemes.[3] Until now, there have been no examples of terminal imino ligands in polynuclear systems.

Herein we show that the stabilization of a coordinated imine may be obtained on the surface of a triosmium cluster eventually stabilized through the formation of an intramolecular hydrogen-bonding interaction between the N−H moiety and a terminal hydride ligand. Evidence for the occurrence of such unconventional hydrogen bonds has been recently gained in several systems, and it is expected that they may have a relevant role in addressing the stereochemistry of the products in a variety of organometallic reactions.[4]

Results and Discussion

The addition of a Lewis base (L) to the coordinatively unsaturated 46 e^- $(\mu\text{-}H)_2Os_3(CO)_{10}$ promptly yields the formation of the $H(\mu\text{-}H)Os_3(CO)_{10}(L)$ adduct.[5] In principle several isomers are possible for $H(\mu\text{-}H)Os_3(CO)_{10}(L)$ derivatives according to the coordination site occupied by the entering ligand (i.e., axial/equatorial; cis/trans to the terminal or to the bridging hydride, respectively).[6]

When L = NH_3, two isomers are formed with L in one of the axial coordination sites on the Os atom bearing the bridging hydride.[5h] In the largely dominant isomer the ammonia ligand is observed to be on the same side of the terminal hydride. This kind of structural isomer is the only species detected when L is a primary or secondary amine. Such behavior has been ascribed to the stabilization effect produced by a hydrogen-bonding interaction between the N−H moiety and the terminal hydride on the neighboring osmium.[4c]

The addition of CH_3CHO to a chloroform solution of $H(\mu\text{-}H)Os_3(CO)_{10}(NH_3)$ at room temperature causes the rapid disappearance of the NH_3-containing species with formation of a new derivative whose ^1H NMR spectrum (−55 °C) displays five signals at 8.89 ppm (1, $^3J_{H,H}$ = 22.2 Hz), 7.93 ppm (1, $^3J_{H,H}$ = 4.9 Hz; $^3J_{H,H}$ = 22.2 Hz),

(1) See for example: (a) Mehrota, R. C. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, pp 279−281. (b) Prenzler, D. P.; Hockless, D. C. R.; Heath, G. A. *Inorg. Chem.* **1997**, *36*, 5845. (c) Francisco, L. W.; White, P. S.; Templeton, J. L. *Organometallics* **1996**, *15*, 5127. (d) Balley, P. J.; Grant, K. J.; Pace, S.; Parsons, S.; Stewart, L. J. *J. Chem. Soc., Dalton Trans.* **1997**, 4263. (e) Esteruelas, M. A.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1995**, *14*, 2496.

(2) (a) Farmery, K.; Kilner, M.; Midcalf, C. *J. Chem. Soc. A* **1970**, 2279. (b) Kilner, M.; Midcalf, C. *J. Chem. Soc., Dalton Trans.* **1974**, 1620. (c) Andrews, M. A.; Van Burkirk, G.; Knobler, C. B.; Kaesz, H. D. *J Am. Chem. Soc.* **1979**, *101*, 7245. (d) Adams, R. D.; Katahira, D. A.; Yang, L. W. *J. Organomet. Chem.* **1981**, *219*, 241. (e) Kohler, J. U.; Lewis, J.; Raithby, P. R.; Rennie, M. A. *Organometallics* **1997**, *16*, 3851.

(3) Andreu, P. L.; Cabeza, J. A.; Del Río, I.; Riera, V. *Organometallics* **1996**, *15*, 3004.

(4) (a) Richaldson, T. B.; DeGaia, S.; Crabtree, R. H.; Siegbahn, P. E. M. J. *Am. Chem. Soc.* **1995**, *117*, 12875. (b) Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348. (c) Aime, S.; Gobetto, R.; Valls, E. *Organometallics* **1997**, *16*, 5140.

(5) (a) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1975**, *88*, C21. (b) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1976**, *114*, 313. (c) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304. (d) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; De Boer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145. (e) Churchill, M. R.; De Boer, B. G. *Inorg. Chem.* **1977**, *16*, 2397. (f) Churchill, M. R.; De Boer, B. G. *Inorg. Chem.* **1977**, *16*, 878. (g) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979**, *18*, 1909. (h) Aime, S.; Dastrù, W.; Gobetto, R.; Arce, A. J. *Organometallics* **1994**, *13*, 4232. (i) Aime, S.; Dastrù, W.; Gobetto, R.; Arce, A. J. *Organometallics* **1994**, *13*, 3737.

(6) See for example: Aime, S.; Gobetto, R.; Valls, E. *Inorg. Chim. Acta* **1998**, *275−276*, 521.

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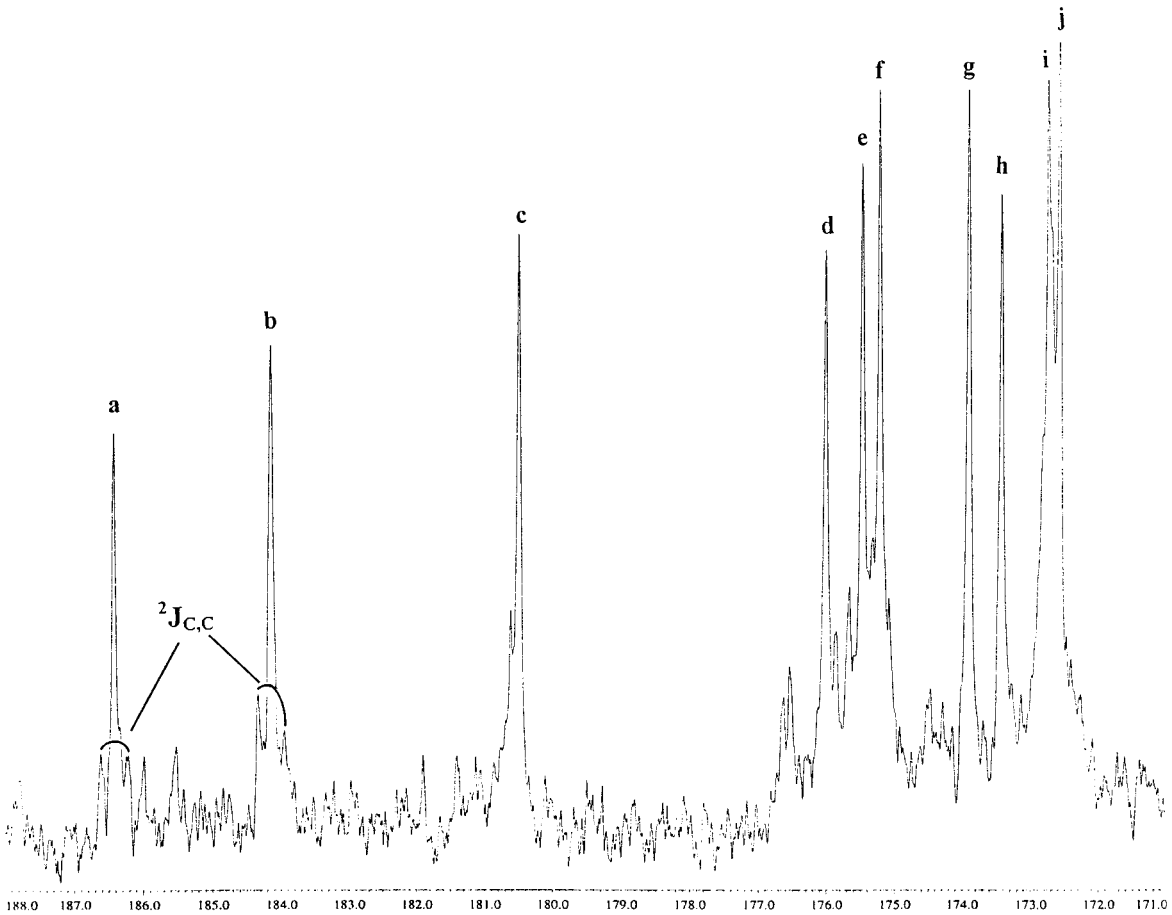
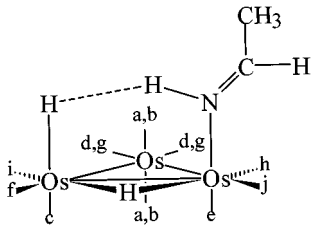


Figure 1. ^{13}C NMR spectrum of a ^{13}C-enriched sample of H(μ-H)$Os_3(CO)_{10}$(HN=CHCH$_3$). δ values expressed in ppm. Resonances are labeled according to the structure reported in Chart 1.

Chart 1



2.26 ppm (3, $^3J_{H,H}$ = 4.9 Hz), −10.42 ppm (1, $^2J_{H,H}$ = 3.4 Hz), and −16.09 ppm (1, $^2J_{H,H}$ = 3.4 Hz). The use of ^{15}N-enriched ammonia indicates that the ^1H resonance at 8.89 ppm is due to a hydrogen atom bound to nitrogen ($^1J_{15N,1H}$ = 74.0 Hz). The ^{15}N NMR spectrum shows a doublet at 198.4 ppm (**(**$^1J_{15N,1H}$ = 74.0 Hz), a value similar to that observed for Schiff base complexes.[7] The ^{13}C NMR spectrum (−55 °C, Figure 1) of a ^{13}CO-enriched specimen allows the detection of 10 carbonyl resonances at 186.43 ($^2J_{C,C}$ = 36.5 Hz) (a), 184.16 ($^2J_{C,C}$ = 36.5 Hz) (b), 180.50 ($^2J_{C,H}$ = 23.6 Hz) (c), 176.01 (d), 175.48 (e), 175.23 ($^2J_{C,Hterm}$ = 5.6 Hz) (f), 173.92 (g), 173.44 ($^2J_{C,Hbridg}$ = 11.3 Hz) (h), 172.75 ($^2J_{C,Hbridg}$ = 5.6 Hz, $^2J_{C,Hterm}$ = 4.2 Hz) (i), 172.59 (j). The assignment of the ^{13}CO resonances has been carried out on the basis of $^{13}C-^{13}C$ and $^{13}C-^1H$ coupling patterns and selective {$^1H_{term}$} and {$^1H_{bridging}$} decoupling experiments.

The assignment of carbonyl j and e has been made on the basis of the behavior for which axial carbonyls resonate at higher frequency than equatorial ones.[5c,i]

On the basis of the overall NMR information one can assign to this product a stoichiometry of H(μ-H)Os_3-$(CO)_{10}$(HN=CHCH$_3$) with the imine coordinated at an axial site as shown in Chart 1. The *trans*-H,H arrangement of the iminic protons is assigned on the basis of the large $^3J_{H-H}$ coupling of 22.2 Hz.[8]

The stereochemistry observed for H(μ-H)$Os_3(CO)_{10}$-(HN=CHCH$_3$) appears to be driven by the occurrence of an intramolecular interaction between the imine andthe hydride moieties analogous to those previously observed for primary and secondary amines.[4c] Support to this suggestion has been gained by evaluating the dipolar contribution of the NH moiety to the relaxation of the hydrides. The proton relaxation times were measured on H(μ-H)$Os_3(CO)_{10}$(HN=CHCH$_3$) and on H(μ-H)$Os_3(CO)_{10}$(DN=CHCH$_3$), respectively. The latter derivative was prepared by adding a few drops of D_2O to the reaction mixture.

The dependence of the T_1 values of both terminal and bridging hydrides versus 1/T displays a typical "v" shape in the temperature range from −90 to −30 °C with a minimum value at −65 °C (CD_2Cl_2). At this temperature, the T_1 value of the terminal hydride was 0.52 s

(7) Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987.

(8) A minor set of resonances (ca. 1:5 in respect to the major species) has been assigned to the isomeric derivative containing the imine protons in a cis-arrangement. ^1H NMR data: 9.36 ppm (1, $^3J_{H,H}$ = 12.8 Hz; $^1J_{H,N}$ = 74.4 Hz), 8.02 ppm (1, $^2J_{H,H}$ = 5.0 Hz; $^3J_{H,H}$ = 12.8 Hz), 2.29 ppm (3, $^2J_{H,H}$ = 5.0 Hz), −10.40 ppm (1, $^2J_{H,H}$ = 3.4 Hz) and −16.07 ppm (1, $^2J_{H,H}$ = 3.4 Hz). ^{15}N NMR: δ = 203.27 ppm ($^1J_{N,H}$ = 74.4 Hz).

and 1.10 s in the protio- and deuterio-derivatives, respectively. The T_1 of the bridging hydride showed a smaller variation in the two isotopomers (1.14 s and 1.61 s, respectively).

On these grounds, it was possible to evaluate the dipolar contribution of the imine proton to the relaxation of the terminal and bridging hydrides. From these values actual H−H distances can be estimated according to[9,10]

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

$$R_{1,D}^{H-H} = \frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_H{}^4\hbar^2\tau_c}{r^6}\left(\frac{1}{1+\omega_0{}^2\tau_c{}^2} + \frac{4}{1+4\omega_0{}^2\tau_c{}^2}\right)$$

where the molecular reorientational time τ_c is equal to $0.618/\omega_0$ ($\omega_0 = 2\pi 400 \times 10^6$ rad s^{-1}), i.e., 2.45×10^{-10} rad s^{-1}. The resulting $r_{H,H}$ distances were 2.1 ± 0.1 Å and 2.7 ± 0.1 Å for the terminal and the bridging hydride, respectively. The distance between the terminal hydride and the iminic proton is strongly suggestive of the occurrence of an unconventional hydrogen bond involving the metal hydride as proton acceptor from the N−H bond. One may envisage that such an interaction contributes either in the stabilization of the coordination of the imine ligand or in addressing the formation of a single stereoisomer of $H(\mu\text{-}H)Os_3(CO)_{10}(HN{=}CHCH_3)$.

Analogous results have been observed for imines obtained by reacting ammonia with benzaldehyde, isobutyraldehyde, and furfural as assessed by the characteristic pattern of their ^{1}H NMR spectra (see Experimental Section).

Experimental Section

All solvents were stored over molecular sieves. ^{13}CO (99% enriched) was purchased from Isotec Inc. (Miamisburg, OH). Acetaldeyde (Fluka), isobutyraldehyde (Fluka), and furfural (Sigma) were used without further purification. $H_2Os_3(CO)_{10}$ was prepared according to the published procedure.[11]

^{1}H, ^{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. ^{13}C NMR spectra were obtained from ^{13}CO-enriched derivatives which were prepared by using as starting material ^{13}C-enriched $Os_3(CO)_{12}$ obtained by direct exchange of ^{13}CO with $Os_3(CO)_{12}$.[12]

The nonselective inversion recovery pulse sequence was used to obtain ^{1}H-T_1 values[13] of previously degased samples. Errors in the reported T_1 values were estimated to be in the range ±5%.

In a typical reaction 5 mg of $H_2Os_3(CO)_{10}$ (5.9×10^{-6} mol) in 0.5 mL of CH_2Cl_2 was transferred into a 5 mm NMR tube, and excess NH_3 was added. The solution color readily turned from purple to yellow. The solvent and excess NH_3 were evaporated under vacuum, and the residue was again dissolved in CH_2Cl_2. Excess acetaldehyde was added and allowed to react for few minutes at room temperature. Finally the solvent and the excess of ammonia were evaporated and the residue was dissolved in the deuterated solvent (CD_2Cl_2 or $CDCl_3$).

The same procedure has been followed for the addition of isobutyraldehyde, furfural, and benzaldehyde. In these cases a longer reaction time was necessary (ca. 30 min at RT).

Characteristic ^{1}H NMR spectroscopic data for $H(\mu\text{-}H)Os_3(CO)_{10}$(1-furfuralimine) ($CDCl_3$, 400 MHz, 218 K): 9.15 (d, ^3J = 22.2 Hz, N*H*), 8.31 (d, ^3J = 22.2 Hz, C*H*), −10.35 (d, ^3J = 2.8 Hz, H_{term}), −16.11 (d, ^3J = 2.8 Hz, H_{bridg}).

Characteristic ^{1}H NMR spectroscopic data for $H(\mu\text{-}H)Os_3(CO)_{10}$(benzylimine) ($CDCl_3$, 400 MHz, 213 K): 9.42 (d, ^3J = 22.4 Hz, N*H*), 8.45 (d, ^3J = 22.4 Hz, C*H*), −10.26 (d, ^3J = 2.9 Hz, H_{term}), −15.88 (d, ^3J = 2.9 Hz, H_{bridg}).

Characteristic ^{1}H NMR spectroscopic data for $H(\mu\text{-}H)Os_3(CO)_{10}$(isobutylimine) ($CDCl_3$, 400 MHz, 218 K): 8.77 (d, ^3J = 22.2 Hz, N*H*), 7.94 (d, ^3J = 22.2 Hz, C*H*), −10.41 (d, ^3J = 2.6 Hz, H_{term}), −16.07 (d, ^3J = 2.6 Hz, H_{bridg}).

The excess of aldehyde present in the NMR tube prevents the observation of other resonances for the three derivatives.

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(11) Kaesz, H. D. *Inorg. Synth.* **1990**, *28*, 238.
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