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Role of Os−H- - -H−N Interactions in Directing the Stereochemistry of Carbonyl Cluster Hydride Derivatives

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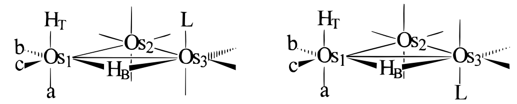
Summary: Unconventional hydrogen-bond interactions involving metal hydrides as proton acceptors from N−H bonds have been recently discovered in mononuclear organometallic systems. The work herein reported on $H_2Os_3(CO)_{10}L$ (L= NH_2Et, $NHEt_2$) suggests that this type of interaction may be even more important in cluster chemistry in directing the stereochemistry of the products as well as affecting the intramolecular ligand exchange processes.

It has been recently shown that unconventional hydrogen bonds with metal hydrides acting as proton acceptors[1] may significantly contribute to the stabilization of organometallic structures in mononuclear complexes.[2] One may envisage that the close proximity of ligands bound to the surface of metallic clusters may strongly prompt the formation of analogous interactions, thus directing the regiospecificity of a suitable entering ligand. To investigate this point further, we considered the reactions between the electronically unsaturated cluster $H_2Os_3(CO)_{10}$ and Lewis base ligands L (L = NH_2Et, $NHEt_2$, NEt_3). On the basis of a number of examples involving isonitriles[3,4] and nitrogen[5] bases as added ligands, we expected that the products of these reactions would be the coordinatively saturated $H_2Os_3(CO)_{10}L$ species containing L in either the *syn* (**A**) or *anti* (**B**) position with respect to the terminal hydride H_T.As the transformation from the violet $H_2Os_3(CO)_{10}$ to the yellow $H_2Os_3(CO)_{10}L$ is instantaneous, the amine coordination can be readily assessed. We found that (i) no reaction takes place in the case of L = NEt_3 and (ii) only one isomer is formed when L = NH_2Et, $NHEt_2$, characterized by the typical set of terminal and bridging hydride resonances, respectively (Table 1). The assignment of these products to structure **A** or **B** has been pursued by measuring the longitudinal relaxation time, T_1, of the bridging and terminal hydride resonances at the observation frequency of 400 MHz and at the temperature at which this parameter shows its minimum[6] (Table 1). In addition to the new adducts with NH_2Et and $NHEt_2$, in Table 1, T_1 values of the hydride resonances of the related $H_2Os_3(CO)_{10}(CNC(CH_3)_3)$ are also reported. As previously observed, the latter species is present as a mixture of **A** and **B** isomers in the approximate ratio of 1:4.

Chart 1



A **B**

Table 1. ^{1}H NMR Parameters of the Hydride Resonances of $H_2Os_3(CO)_{10}L$ Adducts at 208 K

L	$T_1(H_T)$ (ms)	$T_1(H_B)$ (ms)	$\delta(H_T)$ (ppm)	$\delta(H_B)$ (ppm)
$NHEt_2$	384	744	−10.4	−15.9
$NDEt_2$	751	883	−10.4	−15.9
NH_2Et	524	1071	−10.5	−16.2
ND_2Et	1174	1618	−10.5	−16.4
$CNC(CH_3)_3$	2082 (major)	1940 (major)	−10.3	−19.9
	1580 (minor)	1767 (minor)	−10.0	−19.7

At 208 K, the molecular reorientational time τ_c is equal to $0.6158/\omega_0$, where ω_0 is the observation frequency, *i.e.* $\tau_c = 2.45 \times 10^{-10}$ s. In the case of $H_2Os_3(CO)_{10}(CNC(CH_3)_3)$, whereas the bridging hydride resonances of the two isomers show relatively similar T_1 values, T_1 for the terminal hydride of the major isomer is smaller than that for the minor isomer. This reflects the closer proximity of the methyl groups to the terminal hydride, and the structure of the major isomer is then confirmed to be of **B** type.[3] In the case of both $H_2Os_3(CO)_{10}(NH_2Et)$ and $H_2Os_3(CO)_{10}(NHEt_2)$ the difference between the T_1 values of the bridging and terminal hydride resonances becomes much larger. Clearly, terminal hydrides are relaxed by a contribution additional to that acting on the bridging hydrides. In order to evaluate the contribution to the relaxation of H_T and H_B arising from N−H moieties, T_1 values of the adducts containing D_2NEt and $DNEt_2$ have been measured (Table 1). The difference between the relaxation rates of protio and deuterio species depends then on the contribution to the hydride resonances arising from amine protons. Clearly there is a substantial dipolar interaction between the terminal hydride and the amine hydrogen in both 1 and 2. Moreover, the knowledge of τ_c allows the determination of the H−H distance for this interaction by applying eqs 1 and 2:[7]

$$R_{1,D}{}^{H-H} = \left[\frac{1}{T_1(\text{protio})} - \frac{1}{T_1(\text{deuterio})}\right] \times 1.0625 \quad (1)^{8}$$

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[1] Richardson, T. B.; DeGala, S.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12875.

[2] Crabtree, R. H.; Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, *29*, 348.

[3] Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979**, *18*, 1909.

[4] Anslyn, E. V.; Green, M.; Nicola, G.; Rosenberg, E. *Organometallics* **1991**, *10*, 2600.

[5] Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304.

[6] Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

[7] Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: Oxford, U.K., 1973; Chapter 8.

[8] The factor 1.0625 accounts for the residual dipolar contribution arising from the interaction with the deuterium magnetic momentum.

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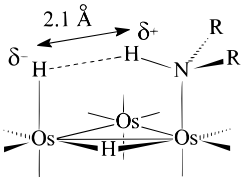
$$R_{1,\mathrm{D}}{}^{\mathrm{H-H}} = \frac{3\gamma_{\mathrm{H}}{}^{4}\hbar^{2}}{10r_{\mathrm{H-H}}{}^{6}}\left[\frac{1}{1+\omega_0{}^{2}\tau_{\mathrm{c}}{}^{2}} + \frac{4}{1+4\omega_0{}^{2}\tau_{\mathrm{c}}{}^{2}}\right] \quad (2)$$

From this evaluation, $r_{\mathrm{H-H}}$ was found to be 2.1 ± 0.05 Å in both complexes. This short contact strongly suggests the occurrence of an unconventional hydrogen bond in which the Os−H_T bond acts as proton acceptor from the N−H bond (Chart 2). Such strong intramolecular interactions are then responsible for the stabilization of isomer **A** and the lack of formation of isomer **B** for both $H_2Os_3(CO)_{10}(NH_2Et)$[9] and $H_2Os_3(CO)_{10}(NHEt_2)$. Furthermore, in the absence of such an “anchoring” link, as in the case of NEt_3, no product is formed. Likely the stereochemical nonrigidity too is markedly affected by the occurrence of this type of H- - -H interaction: Whereas in a number of $H_2Os_3(CO)_{10}L$ species[5] it has been shown that H_T/H_B exchange occurs with an activation energy in the range 11.5−13 kcal/mol, the adducts with NH_2Et and $NHEt_2$ display separate hydride resonances up to room temperature (*i.e.* $\Delta G^{\ddagger}$ for H_T/H_B exchange is >14 kcal/mol). At higher temperature an incipient transformation into other products takes place, thus preventing an accurate measurement of the H_T/H_B exchange rate. In summary, we think that this type of hydrogen-bond interaction may be very important in the elucidation of reaction pathways occurring on the surface of transition-metal clusters bearing hydride ligands as well as in the understanding of the structural determinants affecting the intramolecular ligand exchange.

Chart 2



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[9] Although this product can be isolated upon slow evaporation of the solvent and the excess amine, we have been unable to obtain until now suitable crystals for an X-ray diffraction study.

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