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Equilibrium Isotope Effect on Hydrogen Distribution between Carbon- and Metal-Bound Sites. A Neutron Diffraction Study of Partially Deuterated Decacarbonyldihydridomethylenetriosmium

Sir:

Neutron diffraction studies allow accurate location of light atoms in transition metal compounds, as recently reported examples have shown.^{2,3} As part of a program involving the use of neutron diffraction to define carefully the geometries of small hydrocarbon moieties bound to one or more metal atoms, we now report results for a partially deuterated sample of $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$.⁴ Because of the differences in sign and magnitude between the neutron scattering lengths of hydrogen and deuterium,⁵ we have been able to determine the abundance of H and D at each site in the partially deuterated molecule. These population data, supported by analogous data from solution NMR spectra, reflect an equilibrium isotope effect on the H/D distribution that favors the incorporation of deuterium in the methylene group and, conversely, hydrogen in the osmium hydride positions. This effect is readily interpreted in terms of vibrational zero point energies and is general for any case involving exchange of hydrogen and deuterium between carbon- and metal-bound sites.

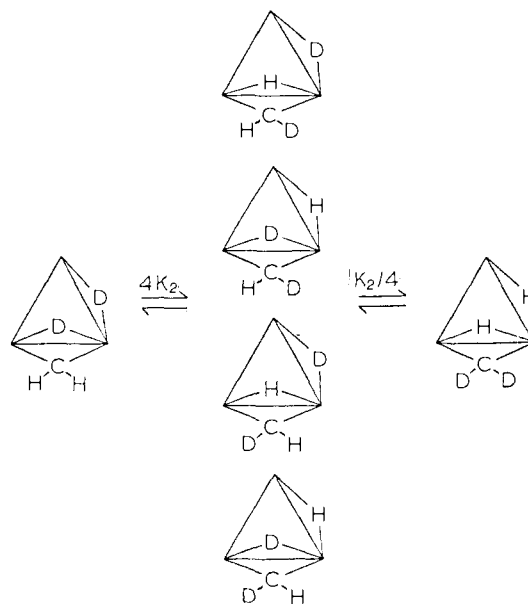
The combination of $\text{D}_2\text{Os}_3(\text{CO})_{10}$ and CH_2N_2 provides " $\text{Os}_3(\text{CO})_{10}\text{CH}_2\text{D}_2$ ", a mixture in solution of hydridomethyl and dihydridomethylene tautomers.⁴ A dichloromethane solution of this mixture in an NMR tube held at -2°C yielded a crystal which was used for neutron data collection. The crystal had dimensions of $2.0 \times 2.0 \times 0.55$ mm and weighed 5 mg, which is relatively small for neutron diffraction, after being dried under vacuum. A smaller crystal of $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$ (undeuterated) with dimensions $0.24 \times 0.17 \times 0.06$ mm was used for X-ray diffraction measurements.

The details of the procedure used for the measurement of the X-ray⁶ and neutron⁷ diffraction data have been described previously. A total of 2258 reflections to $2\theta = 55^\circ$ ($\lambda = 0.71069$ Å) were measured on a full-circle Picker X-ray diffractometer at Illinois and 731 reflections to $2\theta = 60^\circ$ ($\lambda = 1.142$ (1) Å) were determined at room temperature on an Electronics and Alloy four-circle diffractometer at the CP-5 reactor at Argonne National Laboratory. Based on the Laue symmetry and the systematic absences, the two possible space groups are $Pnma$ (D_{2h}^{10} , No. 62)⁸ or the nonstandard $Pn2_1a$ ($Pna2_1$, C_{2v}^9 , No. 33).⁸ The lattice parameters of $a = 18.692$ (4), $b = 10.250$ (5), and $c = 8.918$ (8) Å were determined by least-squares refinement of 12 reflections in the range $20^\circ < 2\theta < 40^\circ$ using Mo $K\alpha$ X-radiation. The structure was solved by the conventional heavy-atom method in the space group $Pnma$ using the X-ray data and independently by direct methods (MULTAN) using the neutron diffraction data. However, attempted refinement of the structure in the space group $Pnma$ was un-

successful owing to the disorder imposed by the mirror plane and subsequent refinement was based on an ordered structure in the space group $Pn2_1a$. Full-matrix least-squares refinement of the neutron data, including hydrogen and deuterium atoms, converged and yielded discrepancy indices of $R(F_o) = 0.089$, $R(F_o^2) = 0.075$, and $R_w(F_o^2) = 0.097$. The molecular structure is shown in Figure 1. The hydrogen atom scattering amplitudes were treated as variables in the least-squares refinement, which resulted in derived scattering amplitudes of $b_{\text{H}(1)} = 0.23$ (1), $b_{\text{H}(2)} = 0.24$ (1), and $b_{\text{H}(3)} = -0.06$ (1). The atom at the site of H(4) was not located⁹ on a final difference Fourier, and, therefore, its scattering length is estimated to be 0.00 ± 0.03 . The percentage of ^1H in each of the hydrogen sites is 42 (1) for H(1), 41 (1) for H(2), 70 (1) for H(3), and 64 (3) for H(4) based on the above scattering amplitudes.

The methylene carbon atom is equidistant from Os(1) and Os(2) even though these latter two atoms are chemically nonequivalent. The geometry of the CH_2 ligand ($\angle\text{H-C-H} = 106$ (1) $^\circ$) suggests that the CH_2 fragment is best described in terms of sp^3 hybridization. This situation is in contrast to that for heterocyclopropanes in which the exocyclic H-C-H angles are 114° or greater.¹⁰ The X-ray structures of two related molecules, $\text{Ru}_2(\text{CH}_2)_3(\text{PMe}_3)_6$ ¹¹ and $\text{Cp}_2\text{Rh}_2(\text{CO})_2(\text{CH}_2)$ ¹² have been reported. A point of interest in these systems, all of which contain methylene ligands bridging two metal atoms bonded by a metal-metal single bond, is that the M-C-M angle is nearly constant at $80 \pm 2^\circ$.

The solution ^1H NMR spectrum of " $\text{Os}_3(\text{CO})_{10}\text{CH}_2\text{D}_2$ " also shows a preference for H over D in the metal hydride sites of both the methylene and the methyl tautomers. For the methylene isomer no difference in intensity between the two hydride sites or between the two methylene sites could be established after repeated integration. The methylene/hydride intensity ratio was 0.75 (10). If a single parameter K_2 is defined as the equilibrium constant for a pairwise H/D interchange in the methylene isomer, then the possible configurations for a dideuterated (d_2) species are related as shown. A similar set



of monodeuterated (d_1) configurations also will contribute to the observed intensities. For the methyl isomer at each level of deuteration there are only two configurations, which are related by the equilibrium constant K_1 . The best set of parameters was determined by minimizing the difference between experimental and calculated intensities, with K_1 , K_2 , K_{eq} (relating the methyl and methylene tautomers), d_1 , and d_2 as variables.¹³ The results were $K_1 = 1.74$ (23), $K_2 = 1.58$ (21),

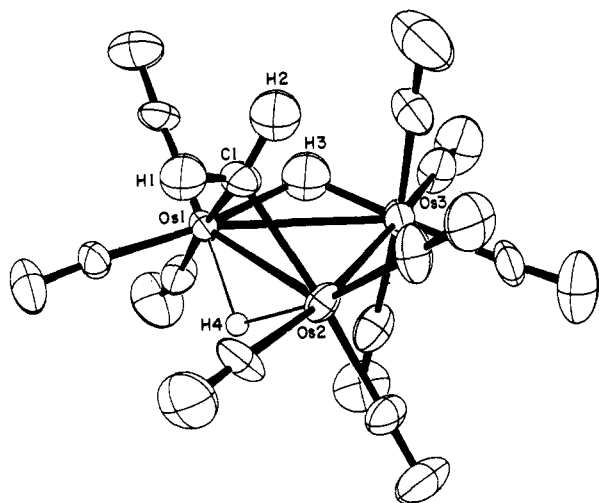


Figure 1. The $\text{H}_2\text{Os}_3(\text{CO})_{10}\text{CH}_2$ molecule, with thermal ellipsoids scaled to 50% probability. The atom labeled H(4) was not located (see text). The intramolecular bond distances include Os(1)–Os(2) = 2.834 (6), Os(2)–Os(3) = 2.870 (7), Os(1)–Os(3) = 3.066 (6), Os(1)–C(1) = 2.15 (1), and Os(2)–C(1) = 2.15 (1) Å. The H–C–H angle is 106 (1)°.

$K_{\text{eq}} = 2.45$,¹⁴ and $d_1/d_2 = 0.20$. The site populations determined by neutron diffraction were analyzed similarly with K_2 , d_1 , and d_2 variables.¹⁵ The results were $K_2 = 2.30$ (10) and $d_1/d_2 = 0.17$. The apparent difference in the K_2 values determined by NMR and by neutron diffraction is not statistically significant.¹⁶

The equilibrium isotope effect observed for the partially deuterated tautomers is readily understood qualitatively in terms of zero-point energies. The C–H group has significantly higher vibrational frequencies than the Os–H–Os group, so that partial replacement by deuterium will lead to preferential placement of the lighter nucleus in the lower frequency site.¹⁷ The vibrational data required for precise calculation of the isotope effect is not available; modes for bridging hydrogen are especially difficult to identify.¹⁸ However, consideration of estimated frequencies leads to a range of calculated values from ~ 1.5 to 3.5,¹⁹ which is consistent with the experimental results. More importantly, because of the large disparity in zero-point energies, a value in this range should be characteristic of a fully equilibrated H/D distribution among carbon (or nitrogen or oxygen) and metal sites.²² Therefore, the effect should be an important tool for detecting reversible hydrogen-transfer processes in organometal cluster compounds.²³ It should also be considered for such processes occurring on metal surfaces.

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- (13) All possible configurations of partially deuterated methyl and methylene tautomers were considered and their relative concentrations expressed in terms of K_1 , K_2 , K_{eq} , d_1 , and d_2 . Expected ^1H NMR intensities for a given site were then expressed as linear combinations of the appropriate configurations. The best values of the five variables were generated by computer minimization of the difference between the calculated and empirical ^1H NMR intensities. The minimization program utilized was STEPT, J. P. Chandler, Computer Science Department, Oklahoma State University, Stillwater, Okla. Such a fit was required since K_2 does not equal the inverse of the observed methylene/hydrate intensity ratio.
- (14) $K_{\text{eq}} = 2.65 \pm 0.16$ (CDCl_3 , 35 °C) was obtained by direct measurement on an undeuterated sample.
- (15) In this analysis the hydride site populations were averaged so that only one value of K_2 was necessary.
- (16) It may be significant that the neutron crystal was grown at -2 °C and the NMR data collected at $+35$ °C. Adjusting the value of 2.30 obtained by neutron diffraction to reflect the value expected at $+35$ °C, we obtained $K_2 = 2.08$.
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Reactions of Dioxygen Platinum(II) Complexes with Activated Acetylenes

Sir:

Recently, we have synthesized a series of dioxygen platinum complexes, containing phosphine ligands having various degrees of bulkiness and basicity, which are useful intermediates in the preparation of the corresponding dihydrides.¹ We now wish to describe the interesting behavior of these dioxygen complexes toward activated acetylenes.

Dioxygen platinum complexes, $\text{Pt}(\text{PR}_3)_2(\text{O}_2)$ ($\text{PR}_3 = \text{PCy}_3$, P^iPr_3 , $\text{P}^i\text{Bu}_2^i\text{Bu}$, $\text{P}^i\text{Bu}_2\text{Me}$, PPh_3), react readily under ambient conditions with acetylenes such as hexafluorobut-2-yne (C_4F_6) and dimethyl acetylenedicarboxylate (DMA) to give 1,2 addition of the dioxygen molecule across the acetylenic $\text{C}\equiv\text{C}$ bond (eq 1).