Decacarbonyl(methyl)hydrotriosmium: NMR evidence for a carbon.cntdot..cntdot.hydrogen.cntdot..cntdot.osmium interaction

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Communications to the Editor

HOs₃(CO)₁₀CH₃:
NMR Evidence for a C··H··Os Interaction[1]

Sir:

Compounds involving methyl groups apparently bridging two transition metals are rare, but are becoming less so.[2] Definitive structural data are very scarce,[3] but structural proposals commonly have assumed a symmetrically bridging methyl group, as in 1. This structural element is now accepted for Al₂(CH₃)₆,[4] in contrast to the briefly controversial, unsymmetrical alternative II.[5] For lack of evidence to the con-

$$\text{III-H} \quad\longleftrightarrow\quad \text{III-D} \quad\longleftrightarrow\quad \text{III-H}$$
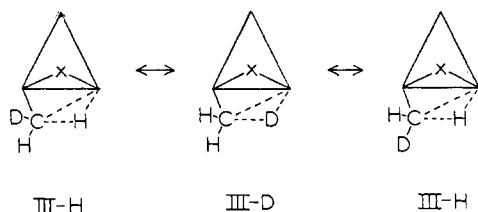
trary, we[2a] previously suggested a symmetrically bridging position for the methyl group in the cluster compound HOs₃(CO)₁₀CH₃. However, we now report novel NMR observations that support a significant C··H··Os interaction for this compound.

Treatment of D₂Os₃(CO)₁₀ with CH₂N₂ at room temperature provides "Os₃(CO)₁₀CH₂D₂", which in solution is an equilibrium mixture of partially deuterated methyl and methylene tautomers.[2a,6] We[2a] previously noted that the methyl ¹H NMR signal occurs at unusually high field. However, the spectrum of the deuterated material shows separate CH₂D and CHD₂ signals[7] displaced significantly to even higher field from the CH₃ signal (see Figure 1). The separations $\Delta_1 = \tau(CH_2D) - \tau(CH_3)$ and $\Delta_2 = \tau(CHD_2) - \tau(CH_2D)$ vary strongly with temperature, increasing from 0.34 and 0.39 ppm at 35 °C to 0.55 and 0.68 ppm at −76 °C. These large, temperature-dependent values of Δ_1 and Δ_2 are inconsistent with the relatively small effect commonly observed upon geminal substitution of H by D ($\sim$0.01 ppm)[8] and therefore require a different explanation.

A model involving a C··H··Os interaction rationalizes the observed effect. For the case in which the methyl group is CH₂D, three structures are possible as shown (X = H or D). An isotope effect on this equilibrium is to be expected, since the interacting (bridging) C–H or C–D bond should have a lower stretching force constant than the analogous noninteracting (terminal) bond. This implies a lower frequency,[9] and hence a lower zero-point energy, leading to a preference for the lighter nucleus in the bridging site.[6] Thus, each of the H-bridged forms (III-H) will be slightly more abundant than the D-bridged form (III-D). Since the bridging hydrogen atom

I   II

also should resonate at higher field than the terminal hydrogen atom, the nonrandom distribution results in a net upfield shift for the CH₂D signal relative to the CH₃ signal. As the temperature is lowered, the equilibrium shifts toward the lower energy H-bridged form, increasing the net shift.
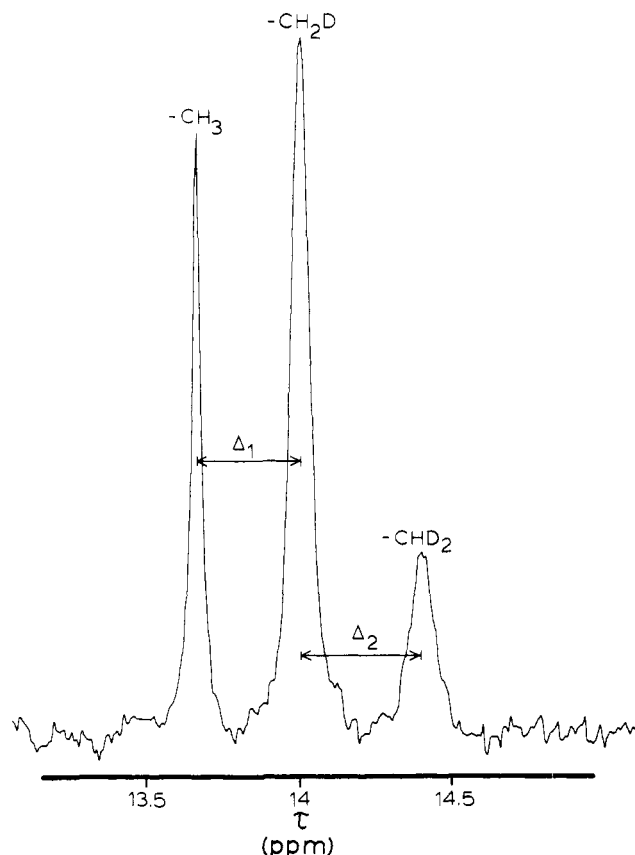
The positions of the CH₃, CH₂D, and CHD₂ resonances can

Figure 1. A portion of the ¹H NMR spectrum (35 °C) for a sample of "Os₃(CO)₁₀CH₂D₂", with some "Os₃(CO)₁₀CH₄" added as a reference.

be expressed quantitatively in terms of three parameters: τ_b and τ_t, the chemical shifts for the bridging and terminal methyl hydrogen atoms, respectively, and ΔE, the energy difference between the D-bridged and H-bridged forms.[10] Defining $A = \exp(-\Delta E/RT)$, the expressions resulting are the following:

$$\tau(CH_3) = (2\tau_t + \tau_b)/3 \tag{1}$$

$$\tau(CH_2D) = (\tau_t + A\tau_t + \tau_b)/(A + 2) \tag{2}$$

$$\tau(CHD_2) = (2A\tau_t + \tau_b)/(2A + 1) \tag{3}$$

Equations 1–3 may be solved at each temperature for the three parameters, the mean results of which are $\tau_b = 25 \pm 1$, $\tau_t = 8 \pm 1$, and $\Delta E = 130 \pm 10$ cal/mol.

An abnormally large and temperature-dependent isotope effect is also apparent for the methyl C–H coupling constant. The average value of $^1J(^{13}C-^1H)$ observed for each type of methyl group at 27 °C is 121.1 (CH₃), 118.9 (CH₂D), and 116.4 Hz (CHD₂), whereas at −80 °C it is 121.1 (CH₃), 116.7 (CH₂D), and 112.3 Hz (CHD₂).[13] These trends are qualitatively in accord with the interaction model as illustrated by III-H ↔ III-D. Quantitative analysis with a set of equations analogous to eq 1–3 leads to the values $J_t = 150 \pm 10$ Hz and $J_b = 60 \pm 20$ Hz.

Certain other models can be eliminated by further consideration of the NMR data. Thus, both the methyl and the methylene ¹³C NMR signals show normal chemical shift isotope effects, i.e., $\sim$0.2 ppm upfield per D atom.[7] This result

rules out the possibility that the methyl signal could arise from two different carbon sites in rapid equilibrium,[14] since an order of magnitude larger effect would be predicted. Furthermore, eq 1–3 predict that $\Delta_2 > \Delta_1$, as observed. A model involving two interactions per methyl group, as in IV, leads to closely related equations, which however predict that $\Delta_2 < \Delta_1$. Thus, the Δ_2/Δ_1 ratio allows configurations II and IV to be differentiated.

IV
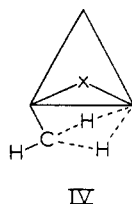
Cotton and co-workers[15] have shown that [EtB(pz)$_2$]-Mo(CO)$_2$(η^3-2-phenylallyl) has a C··H··Mo interaction involving an α-C–H bond of one ethyl group. The strength of the interaction was estimated to be ~19 kcal/mol from DNMR studies, but the barrier to exchange between the interacting and noninteracting methylene hydrogens was somewhat lower, ~14 kcal/mol.[15a] We have attempted to determine the barrier to bridge–terminal exchange in HOs$_3$(CO)$_{10}$CH$_3$, but the methyl ^{1}H NMR signal does not broaden relative to internal SiMe$_4$ down to −100 °C. From this result an upper limit to $\Delta G^{\ddagger}$ of ~5 kcal/mol can be estimated.[16] However, since bridge–terminal exchange could proceed via a doubly bridged configuration such as IV, the exchange barrier may represent only a lower bound for the strength of the C··H··Os interaction.

The general significance of our conclusion that the methyl ligand in HOs$_3$(CO)$_{10}$CH$_3$ adopts configuration II instead of I is not clear at this time. Neither the Os–Os separation, expected to be ~2.8 Å[6] in comparison with 2.61 Å for Al$_2$Me$_6$,[4a] 2.72 Å for (MgMe$_2$)$_n$,[17] 3.06 Å for (η^5-C$_5$H$_5$)$_2$YAlMe$_4$,[18] and ~3.5 Å for [(η^5-C$_5$H$_5$)$_2$YbMe]$_2$,[2c] nor steric crowding, which was proposed as determining the formation of Si··H··W bridges in W$_2$(CO)$_8$(SiHEt$_2$)$_2$,[19] appears to be a rational basis for the preference. Nevertheless, the new structural model for HOs$_3$(CO)$_{10}$CH$_3$ leads to a revised and clarified picture (shown) of the hydrogen transfer from carbon to osmium involved in the formation of H$_2$Os$_3$(CO)$_{10}$CH$_2$. Spin saturation transfer experiments confirm the selective exchange between the methyl group in HOs$_3$(CO)$_{10}$CH$_3$ and one hydride site in H$_2$Os$_3$(CO)$_{10}$CH$_2$.[20]
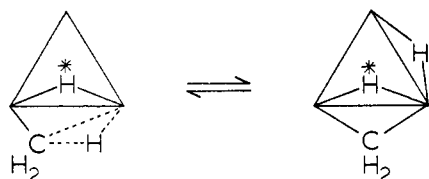
Partial deuteration should be a useful probe for C··H··M interactions in other cases.[21,22] It is noteworthy that the number of H bridges per ligand can be determined even with rapid bridge–terminal exchange. Extension of the method to borohydride–metal complexes should complement the IR technique[23] for determining whether the BH$_4$ ligand is mono-, bi-, or tridentate.

References and Notes

(1) This research was supported by National Science Foundation Grant No. CHE 75-14460. We acknowledge a loan of OsO$_4$ from Engelhard Industries.

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(7) Evidence for the assignment of these signals is the following. (a) Samples with a lower level of deuteration show the expected alteration in intensities; i.e., the CH$_3$ signal increases at the expense of the CHD$_2$ signal. (b) Near room temperature the line widths are in the order CH$_3$ < CH$_2$D < CHD$_2$, consistent with partially relaxed H–D coupling. As the temperature is lowered, quadrupolar relaxation apparently becomes more effective and by −60 °C all three signals have the same width. (c) The ^{13}C NMR spectrum of "Os$_3$(CO)$_{10}$^{13}CH$_2$D$_2$" shows overlapping triplet and quintet patterns due to ^{13}C–^{2}H coupling.

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(9) We have observed IR bands at 2985 (m), 2930 (s), 2840 (w), and 2520 (s, br) cm^{-1} for a carefully purified sample of the HOs$_3$(CO)$_{10}$CH$_3$–H$_2$Os$_3$(CO)$_{10}$CH$_2$ mixture in CCl$_4$ solution. The broad band near 2520 cm^{-1} appears to be a ν_{CO} + ν_{Os-C} combination band.[2a] The 2840-cm^{-1} band may be due to the C–H$_b$ moiety. However, we note that a similar band has been observed for Mn(CO)$_5$CH$_3$ and assigned as an overtone: A. B. Dempster, D. B. Powell, and N. Sheppard, *J. Chem. Soc. A*, 1129 (1970). We are attempting to assign the bending modes for "Os$_3$(CO)$_{10}$CH$_4$" and "Os$_3$(CO)$_{10}$CH$_2$D$_2$" in order to identify those associated with the perturbed C–H bond.

(10) Using only one chemical shift parameter for the terminal positions is an approximation, since the two sites are diastereotopic. However, the chemical shift difference between the two analogous sites in HOs$_3$-(CO)$_{10}$(CH$_2$CO$_2$Et)[11] is only 0.2 ppm, which is insignificant in comparison with the 17-ppm overall bridge-terminal shift difference in HOs$_3$(CO)$_{10}$CH$_3$. Furthermore, although ΔE and $\Delta \tau$ could be slightly different for the CH$_2$D compound than for the CHD$_2$ compound, separate analysis of the two sets of shifts as a function of temperature gave identical results within experimental error. A closely similar, though not identical, analysis has been applied in studying the effect of deuterium substitution on equilibrating carbonium ions.[12]

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(16) Approximating by use of two-site exchange expressions, for fast exchange $k_f = (\pi/2)(1/\Delta W) \times (\Delta \nu)^2$ and at coalescence $k_c = (\pi/\sqrt{2})(\Delta \nu)$. Assuming $\Delta \nu = 1700$ Hz and that $\Delta W \leq 1$ Hz at 163 K, the former expression leads to $\Delta G^{\ddagger}$ (163 K) ≤ 4.4 kcal/mol. The coalescence expression with $T_c \leq 143$ K leads to $\Delta G^{\ddagger}$ (143 K) ≤ 5.8 kcal/mol. An exchange barrier of 3.6 kcal/mol has been estimated from ^{13}C T_1 data: J. R. Norton and R. Jordan, personal communication.

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