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The Proton Chemical Shift in Polycrystalline $H_2Os_3(CO)_{10}$, $H_4Ru_4(CO)_{12}$, and $H_4Os_4(CO)_{12}$

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Abstract: Multiple-pulse NMR techniques have been used to obtain estimates of the proton chemical shift tensors for protons directly bound to heavy metal atoms in $H_2Os_3(CO)_{10}$, $H_4Os_4(CO)_{12}$, and $H_4Ru_4(CO)_{12}$. The chemical shift anisotropy for these bridging protons was found to be less than 30 ppm, and the temperature-dependent spectra for $H_4Ru_4(CO)_{12}$ indicated the presence of anisotropic proton motion at room temperature.

Introduction

In recent years it has become possible to measure proton chemical shift tensors in solids by multiple pulse techniques.¹⁻⁶ Such measurements have included studies of organic compounds, hydrogen-bonded crystals, hydrated crystals, water itself, and one conducting system.⁶ This paper reports proton chemical shift spectra for protons directly bonded to transition metals via metal-hydrogen-metal bridge bonds. In solution such compounds, in contrast to other materials studied, exhibit a large positive chemical shift. For example, in their review Kaesz and Saillant⁷ cite an isotropic chemical shift range of $\tau \sim 15-30$ ppm ($\sigma \sim 5-20$ ppm) for hydrogens directly bonded to transition metals with those hydrogens bridging metal-metal bonds typically at even higher fields. The range for proton chemical shifts for organic liquids is typically $\tau \sim 0-10$ ppm ($\sigma \sim -10$ to 0 ppm) with similar isotropic values in the solid state.^{1,2} An early theoretical prediction by Buckingham and Stephens⁸ of the possibility of an unusually large chemical shift anisotropy for protons directly bonded to a transition metal (up to 500 ppm) has added speculation that such large upfield values for the isotropic values might be due to such large anisotropies.

Experimental Section

The spectra presented in this paper were obtained using a spectrometer⁹ and an eight-pulse sequence¹⁰ which have been discussed. A cycle time of 48 μ s was used for results reported here, although some data were taken with a cycle time of 36 μ s. It was necessary to signal average, and spectra were taken on both sides of resonance and reflected in order to determine the proper choice of phase. In some cases the resulting spectra were added to improve signal to noise. For $H_2Os_3(CO)_{10}$ and $H_4Ru_4(CO)_{12}$ runs were typically 1-2 h with 3-5-min pulse rates, while for $H_4Os_4(CO)_{12}$ data were accumulated over a 24-h period. Spin-lattice relaxation times ranged from somewhat under 1 min for the $H_4Ru_4(CO)_{12}$ to 5 min for the more rigid species, and pulse rates ranged from two to five times the relaxation time for a particular sample.

For temperature control a nitrogen-flow variable temperature probe was used, and the temperature was checked before and after each run and found constant to within ± 1 K. An acetyl chloride sample in a sealed spherical NMR tube was used for tuning and confirming proper

operation of the spectrometer since it is liquid over the temperature range of interest (liquid range: -112 to 50.9 °C). The chemical shift of acetyl chloride relative to a spherical sample of tetramethylsilane was determined at room temperature and the result used in assigning chemical shifts relative to tetramethylsilane at other temperatures.

In addition to studying the compounds under the eight-pulse sequence, two phase-altered¹¹ sequences were used, the effect of which is to sort out contributions to the line width coming from other than static field inhomogeneity.

The samples used in this study were kindly provided by Professor J. R. Shapley. They were prepared using the procedure of Knox et al.¹² and purified by chromatography on silica gel.

Results and Discussion

$H_2Os_3(CO)_{10}$. The structure of $H_2Os_3(CO)_{10}$ taken from the paper of Churchill, Hollander, and Hutchinson¹³ is shown in Figure 1a. The molecule is composed of an isosceles triangle of osmium atoms with the proton pair bridging the base. The carbonyls in the isolated molecules are symmetrically arranged so that the protons are equivalent, and thus the multiple-pulse NMR spectrum of a polycrystalline sample would furnish a single proton chemical shift tensor. However, in the solid state the molecular packing distorts the carbonyls slightly, and there are two different kinds of protons. Since the packing distortions are small¹³ and one does not expect intermolecular effects on the chemical shift tensor to be large, we have fit the spectra to a single proton chemical shift tensor. The fact that the isotropic chemical shift found ($\bar{\sigma}$ 9 ppm at 300 K and 11 ppm at 230 K) is close to the value observed in solution, $\bar{\sigma}$ 11.7 ppm (τ 21.7 ppm¹²), is evidence for the isolation of the molecular unit in the solid state.

Figure 2 shows the multiple pulse spectra for $H_2Os_3(CO)_{12}$ at 300 and 230 K along with the results of one of the phase-altered sequences.¹⁰ The similarity of spectra taken at 230 and 300 K indicates that the protons are not involved in a motional process sufficient to average the spectrum differently at these temperatures. In addition to an anisotropy in the proton chemical shift tensor, a variety of other phenomena could be contributing to the observed line widths of the spectra in Figure 2. An estimate of factors contributing to the line width other than inhomogeneity broadening was obtained by performing

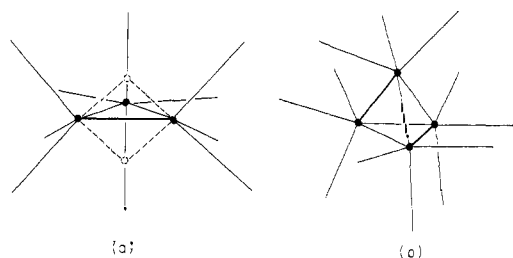


Figure 1. (a) The structure of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ as given by Churchill, Hollander, and Hutchinson;¹³ the shorter metal-metal distance is represented by a heavy line. Filled circles represent metal atoms and open circles represent expected hydrogen locations. Terminally bonded carbonyls are represented by straight lines. (b) The structure of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ as given by Wilson, Wu, Love, and Bau.¹⁵ Again, heavy lines indicate shorter metal-metal distances and terminally bonded carbonyls, directed over the faces of the near tetrahedron, are indicated by straight lines. Hydrogen positions are not indicated but are believed to edge bridge the four long metal-metal bonds.

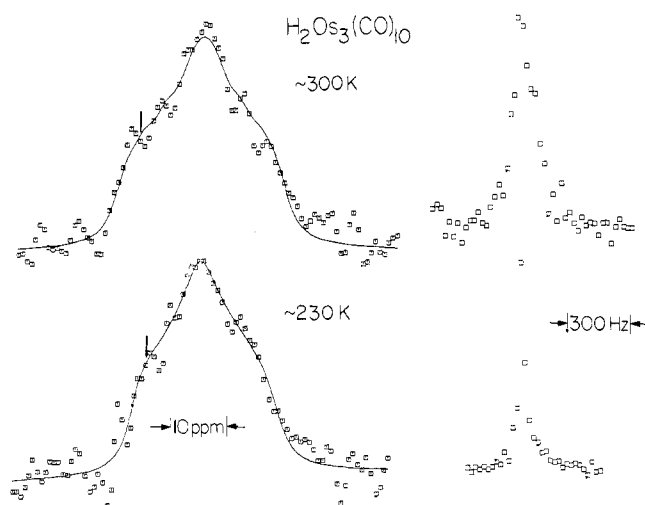


Figure 2. Multiple-pulse proton spectra for $\text{H}_2\text{Os}_3(\text{CO})_{10}$ at 300 and 230 K. Spectra on the left with the computer fit indicated were obtained using the standard eight-pulse sequence while the spectra on the right were obtained with the phase-altered sequence.

a phase-altered experiment¹¹ which has the property of suppressing inhomogeneity broadening. The suppression of inhomogeneity broadening was accomplished by establishing a vector Hamiltonian (I_y) perpendicular to the effective precession axis ($I_x + I_z$) with a phase error in the x pulses. The length of this vector Hamiltonian (the size of the phase error) was 2.5 kHz and thus sufficiently large to average out any inhomogeneity contribution to the line widths in Figure 2. The Fourier transform of the decay observed in the presence of the phase error is plotted on the right side of Figure 2 for both the 300 and 230 K spectra, and it is seen to be small compared to the multiple-pulse spectra widths. Thus, the contributions to the multiple-pulse spectrum can be limited to inhomogeneity broadening from the proton chemical shift tensor and the $^{189}\text{Os}-^1\text{H}$ heteronuclear dipolar interaction (16.1% of the osmium is ^{189}Os , a spin $3/2$ nuclei with a nonzero magnetic moment).

The line through the multiple-pulse spectra in Figure 2 is the result of a nonlinear regressional fit of a single chemical shift tensor with a uniform Lorentzian broadening function to the experimental points and furnishes principal values for the proton tensor of -4.4 , 9.9 , and 21.6 ± 1.5 ppm at 300 K¹⁴ and -2.5 , 9.8 , and 21.5 ± 1 ppm at 230 K. The Lorentzian broadening function obtained from the regressional fit had a 6-ppm width at half height; however, neither the quality of the fit nor the values of the reported principal values were a strong

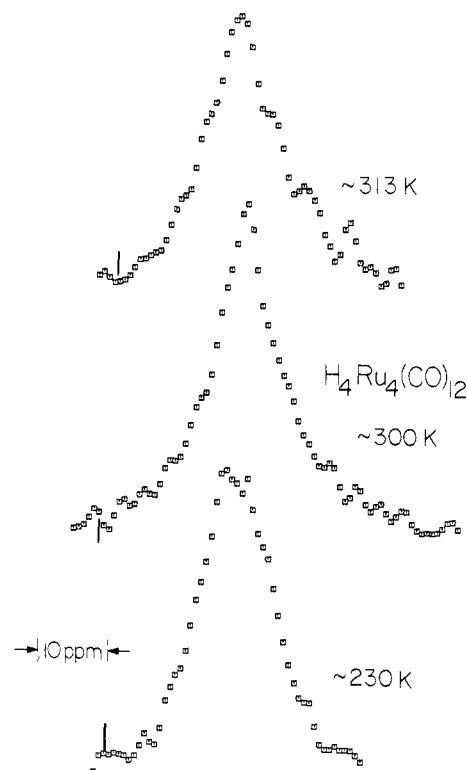


Figure 3. Multiple-pulse proton line shape for $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ as a function of temperature.

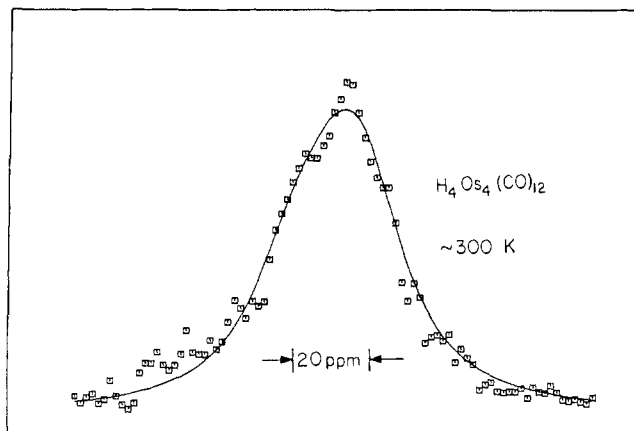


Figure 4. Multiple-pulse proton line shape for $\text{H}_4\text{Os}_4(\text{CO})_{12}$ at 300 K where the line represents a computer fit.

function of the width given this broadening function. Fitting the spectra in this fashion does not rigorously account for the $^{189}\text{Os}-^1\text{H}$ heteronuclear dipolar interaction, and the principal values obtained should be considered to furnish an upper limit to the anisotropy of the proton chemical shift tensor (we attempt a more complete separation of these effects in the discussion of $\text{H}_4\text{Os}_4(\text{CO})_{12}$ below).

$\text{H}_4\text{Ru}_4(\text{CO})_{12}$. The structure of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ as given by Bau et al.¹⁵ is indicated in Figure 1b. The structure is that of a distorted tetrahedron with two short and four long metal-metal bonds, and the carbonyls are directed over the faces of the near tetrahedron.¹⁵ Within the isolated molecule, the carbonyls are symmetrically disposed, and even in the solid state there is little distortion.¹⁵

Figure 3 shows multiple-pulse spectra for $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ taken as a function of temperature. The center of mass for all such spectra ranged from σ 18 to 20 ± 2 ppm in close agreement with the observed chemical shift for the molecule in so-

lution (τ 28 ppm or σ 18 ppm). One notes that the spectrum narrows from 230 K to room temperature and then broadens as the temperature goes higher. This same trend was observed in data taken over a slightly wider temperature range, 178–333 K, at a 36- μ s cycle time. ¹H dipolar spectra indicate the presence of proton motion¹⁴ in this temperature range, and the multiple-pulse spectra are characteristic of a chemical shift powder pattern averaged by a restricted motion of the protons.¹

H₄Os₄(CO)₁₂. Knox et al.¹² have concluded that the structure of H₄Os₄(CO)₁₂ is similar to that of H₄Ru₄(CO)₁₂ from spectroscopic data. Yet the dipolar spectra do not change from 100 to 300 K,¹⁴ and one concludes that the reorientational motion of the protons present in the H₄Ru₄(CO)₁₂ is not present in H₄Os₄(CO)₁₂. The multiple-pulse spectrum for H₄Os₄(CO)₁₂ at 300 K is reproduced in Figure 4. The center of mass of the spectra furnishes an isotropic chemical shift of near 20 ppm (τ 30 ppm) in agreement with our earlier estimate,¹⁴ and the solid line representing a nonlinear regression fit of the spectra to that expected from chemical shift tensor with uniform Lorentzian broadening function furnishes principal values indicating an axially symmetric tensor with an asymmetry of 26 ppm and a large Lorentzian broadening function of 11-ppm half-width.

As discussed above, both heteronuclear dipolar interactions with the ¹⁸⁹O_s and the proton chemical shift tensor contribute to the multiple-pulse spectrum, and thus the width of the multiple-pulse spectrum furnishes an upper limit to the proton chemical shift tensor. However, one expects the heteronuclear interaction to broaden the chemical shift spectra symmetrically, and thus the asymmetric tensor obtained from the computer fit to the H₄Os₄(CO)₁₂ can be associated with a proton chemical shift anisotropy. That is, since ¹⁸⁹O_s has a large quadrupole moment and is located in a molecular site of

less than cubic symmetry, one can assume that the spin ^{3/2} ¹⁸⁹O_s nuclei will be in Zeeman-perturbed quadrupolar state, and we have shown by explicit calculation¹⁶ that the heteronuclear interaction in this limit will broaden the proton spectra symmetrically.

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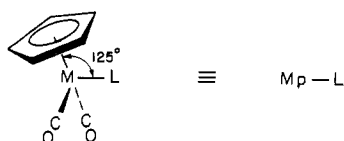
CpM(CO)₂(ligand) Complexes

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Abstract: The electronic structure of cyclopentadienyl metal dicarbonyl complexes of alkyls, carbenes, sulfur dioxide, acetylenes, and ethylenes is analyzed, with an emphasis on conformational preferences and rotational barriers.

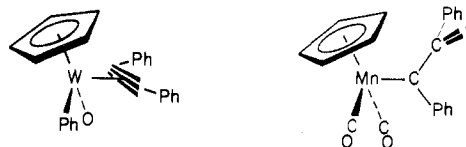
The cyclopentadienyl metal dicarbonyl fragment, CpM(CO)₂, is a common constituent of a large class of organometallic complexes CpM(CO)₂L, Mp-L, **1**. These molecules have found widespread utility in transition metal aided



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organic synthesis, especially so the iron variant Fp, CpFe(CO)₂L.^{2a} Structures have been determined for a range of CpM(CO)₂L complexes with L a σ -bonded ligand such as CO, PR₃, or CR₃,^{2b-e,3,4} including related systems CpMLL'-

L'',⁵ as well as complexes with conformationally more interesting ligands such as sulfur dioxide, carbenes, acetylenes, ethylenes, and allyls.⁶⁻⁹ Examples are shown in **2**^{7a} and **3**.^{6a}



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Several studies have been made of the orientational preferences of the attached ligand, giving us some information on barriers to rotation about the metal to ligand bond.^{10,11}

Systems containing more than one Mp unit can be put into two classes, those which contain the MpL moiety linked to