1404 *Organometallics* **1994,** *13,* 1404–1410

Solution Structure and Dynamics of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$. New ^1H and ^{13}C NMR Studies

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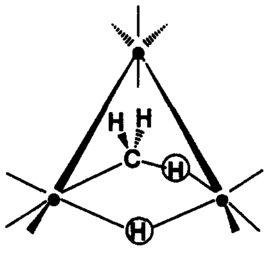
Received June 3, 1993[⊗]

A series of ^1H and ^{13}C NMR experiments was performed to investigate the solution structures and dynamics of the tautomeric pair of complexes $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$ and $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$. Proton and carbon NOE and T_1 relaxation studies enabled calculation of inter-proton distances in the methyl/methylene pair as well as in the closely related methylidyne complex $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$. A combination of $^{13}C\{^1H\}$ COSY and selectively ^1H-decoupled ^{13}C NMR experiments on ^{13}CO-enriched compounds allowed complete assignment of all the carbonyl resonances. ^{13}C spin saturation transfer experiments helped establish the overall interconversions of the four isomers constituting the methyl/methylene tautomer pair. The solution structure originally proposed for the methyl compound is supported over a more recent structural proposal, based on the calculated inter-proton distances, the time-averaged symmetry of the cluster, and the tautomerization process.

Introduction

The compounds $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$ and $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ derive from the interaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with diazomethane.[1] The methyl and methylene compounds exist in tautomeric equilibrium in solution, but only the methylene compound crystallizes from the solution. The structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ has been determined by combined X-ray and neutron diffraction studies,[2] which established that one hydride ligand bridges the same edge of the Os_3 triangle as the methylene ligand, whereas the second hydride ligand bridges an adjacent edge. In the absence of diffraction data, the methyl compound was proposed originally to have a very similar structure, structure A below, with the methyl group and hydride ligand bridging the same edge of the Os_3 triangle;[1a] the "agostic" [3] character of the bridging methyl group was shown by the effect of deuterium substitution on the ^1H NMR spectra.[1b] More recently, however, an alternative structure B was proposed for the methyl compound, in which the methyl carbon is coplanar with the triosmium framework.[4] This new structure was suggested by analogy with $(\mu\text{-H})_2Os_3(CO)_{10}Sn(CH(SiMe_3)_2)_2$,[5] in which the bridging tin atom is coplanar with the triosmium framework and displays a Sn–H–Os bridging interaction.

Here we present an extensive series of ^1H and ^{13}C NMR experiments on this pair of triosmium compounds as well as a more limited analysis of the product resulting from pyrolysis, namely, $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$.[1a] The solution structure of the methyl complex is deduced from a combination of inter-proton distances calculated from the T_1 relaxation times and nuclear Overhauser enhancements (NOE's), carbonyl ^{13}C NMR assignments, and the tautomerization mechanism. This organometallic cluster system features a relatively small number of protons, which provides a good test for using relaxation studies to determine inter-proton distances.[6] At the same time, the relatively large number of inequivalent carbonyl ligands in the tautomeric mixture provides an interesting challenge for complete assignment.



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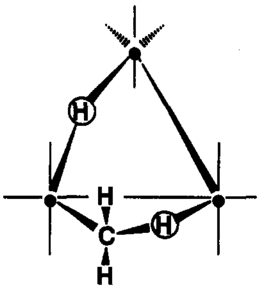

B

Experimental Section

Materials and Methods. The compounds were prepared by the literature method.[1a] A ^{13}C-labeled sample of the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ mixture in a sealed tube was heated briefly in an oven at 120 °C to generate a small amount of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}^{13}CH)$; this sample was used for the T_1 relaxation time measurements of the hydrocarbyl carbons and for the heteronuclear NOE studies. ^{13}CO enrichment was performed with $Os_3(CO)_{12}$ by stirring for 3 days at 120 °C in decalin in the presence of 12 equiv of 99% enriched ^{13}CO. Solutions for the NMR experiments were prepared in perdeuterated solvents, degassed by freeze-pump-thaw sequences, and sealed in tubes under vacuum.

All NMR experiments concerning the NOE and T_1 measurements were done on a Nicolet NT-360 spectrometer with an 1180 computer and a 293B pulse programmer. All T_1 experiments were performed with the fast inversion-recovery sequence, a symmetric five-element composite 180° pulse which compensates for offset effects and pulse length errors, alternating phase of the

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[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1994.

[1] (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977,** *99,* 5225. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978,** *100,* 7726.

[2] (a) Calvert, R. B.; Shapley, J. R.; Schultz, A. J.; Williams, J. M.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1978,** *100,* 6240. (b) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979,** *18,* 319.

[3] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983,** *250,* 395.

[4] Deeming, A. J. *Adv. Organomet. Chem.* **1986,** *26,* 1.

[5] Cardin, C. J.; Cardin, D. J.; Parge H. E.; Power, J. M. *J. Chem. Soc., Chem. Commun.* **1984,** 609.

[6] Aime, S.; Cisero, M.; Gobetto, R.; Osella, D.; Arce, A. J. *Inorg. Chem.* **1991,** *30,* 1614.

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90° pulse, and a nonlinear three-parameter least-squares fit. To obtain heteronuclear NOE's, ^1H gated-decoupled and ^1H broad-band decoupled ^{13}C NMR experiments were interleaved to minimize any difference in the two experiments. The simultaneous irradiation of two protons was performed with the addition of an external frequency synthesizer operating at about 140 MHz. A DANTE pulse was used for selective inversion in the methylene cluster. The NOE values were determined by difference techniques. All experimental measurements were assumed to be subject to errors of ±20%. ^1H chemical shifts are referenced to the residual methyl proton in toluene-d_8 at δ 2.09. ^{13}C chemical shifts are referenced to the methyl carbon in toluene-d_8 at δ 20.4.

^{13}C NMR spectra using ^{13}CO-enriched samples were recorded on a General Electric GN-500 spectrometer equipped with an NIC 1280 computer. When broad-band ^1H decoupling was applied for ^{13}C NMR experiments with a ^{13}CO-enriched sample, the decoupling frequency was set to δ −12 in the ^1H NMR region. Chemical shifts of carbonyl resonances were referenced to the $CDCl_3$ carbon resonance at δ 77.0.

For the $^{13}C\{^1H\}$ COSY spectrum a COSY pulse sequence with additional delays of 50 ms was used. The data matrix was acquired with 512 data points in t_1 and 1024 data points in t_2. A total of 64 1D spectra along the t_1 dimension were collected. Apodization was applied to all data sets with 0.5-Hz exponential line-broadening followed by 10° shifted sine bell. The frequency domain matrices were symmetrized along the $F_1 = F_2$ diagonal.

Selectively ^1H-decoupled ^{13}C NMR spectra were obtained by using a one-pulse sequence decoupler on during acquisition time to minimize the effects of the hydride hopping in the methylene tautomer. For the ^{13}C spin saturation transfer experiments, a directional coupler was inserted between the output of the transmitter and the probe, and the power reflected back from the probe due to ^{13}C decoupling was monitored. The ^{13}C decoupling power was adjusted by running selectively ^{13}C-decoupled and broad-band ^1H-decoupled ^{13}C NMR spectra so that resonances close to the site of selective irradiation remained unaffected. Selectivity less than 100 Hz was achieved.

Results

(1) Calculation of Inter-Proton Distances. Measurements of NOE's along with T_1 relaxation times allow calculation of inter-proton distances in the methylidyne, the methylene, and the methyl clusters in three steps. First, a correlation time for reorientation of these compounds is calculated from the T_1 relaxation times of the hydrocarbyl carbons. Then, the homonuclear dipolar relaxation rates are calculated from the T_1 relaxation times of the protons and the inter-proton NOE values in the three compounds. Finally, inter-proton distances are obtained by substitution of the two calculated parameters into the expression for homonuclear dipolar relaxation.[6,7]

NOE and T_1 Measurements by ^{13}C NMR Spectroscopy. The ^1H broad-band decoupled ^{13}C NMR spectrum of a mixture of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}^{13}CH_3)$, $(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}^{13}CH_2)$, and $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}^{13}CH)$ in toluene-d_8 at 18 °C shows three singlets at δ −59, 26, and 119 for the methyl, the methylene, and the methylidyne carbons, respectively (Table 1). Heteronuclear NOE's are obtained by comparing the intensities of these carbon resonances recorded under ^1H gated decoupled conditions with those recorded under ^1H broad-band decoupled conditions. The full NOE of 1.98 was observed in each of the three carbon signals. Therefore, the relaxation mechanism of the hydrocarbyl carbons in these three clusters is assumed to be completely dipolar in origin. In other words, the T_1 relaxation time of each of these carbon nuclei is simply equal to the dipolar component of the relaxation time, T_1^{dd}.

Table 1. ^{13}C NMR Data for the Triosmium Hydrocarbyl Clusters[a]

compound	δ[b]	NOE[c]	T_1,[d] s
$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}^{13}CH_3)$	−59	1.98	0.91
$(\mu\text{-}H)_2Os_3(CO)_{10}(\mu\text{-}^{13}CH_2)$	26	1.98	0.60
$(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}^{13}CH)$	119	1.98	1.20

[a] Toluene-d_8; 18 °C; 90.546 MHz. [b] Chemical shifts are referenced to the methyl carbon of toluene-d_8 at 20.4 ppm. [c] Heteronuclear NOE's were obtained by comparing intensities of hydrocarbyl carbon resonances recorded under ^1H gated decoupled conditions with those recorded under ^1H broad-band decoupled conditions. [d] A standard 180°–τ–90° inversion recovery method was used along with ^1H broad-band decoupling.

^{13}C T_1 inversion recovery experiments were performed at 18 °C in toluene-d_8 with ^1H broad-band decoupling, using the same sample as for the previous heteronuclear NOE measurements. The T_1 relaxation times of the methylidyne and the methylene carbons were measured to be 1.2 and 0.60 s, respectively. This 2:1 ratio is expected, since the methylene carbon has twice as many protons as the methylidyne carbon. The T_1 relaxation time of the methyl carbon in the methyl tautomer was found to be 0.91 s. In a brief previous study, Jordan and Norton reported T_1 values of 1.10 and 1.20 s (at 32 °C in CD_2Cl_2) for the methylene and methyl compounds, respectively.[8] As these authors noted, there is clearly some contribution to the methyl carbon relaxation from internal rotation of the methyl group. However, it is safe to assume that the correlation time for overall reorientation of the methyl compound is the same as that for the otherwise closely similar methylene and methylidyne compounds.

Assuming isotropic tumbling, the correlation time for molecular reorientation, τ_C, can be calculated from the equation describing heteronuclear dipole–dipole relaxation:[7]

$$(T_1^{dd})^{-1} = (\mu_0/4\pi)^2\gamma_C^2\gamma_H^2(h/2\pi)^2\tau_C/r_{C-H}^6 \qquad (1)$$

where T_1^{dd} is the dipolar component of the relaxation time for the hydrocarbyl carbon, the number of attached protons, μ_0 is the permeability of vacuum, γ_C and γ_H are the gyromagnetic ratios of carbon and hydrogen, respectively, and r_{C-H} is the C–H bond distance. The carbon–hydrogen bond distance determined by neutron diffraction studies of the methylene[2b] and the methylidyne[9] compounds is 1.09 Å. The slightly longer value of 1.107 Å was used to correct for systematic differences in vibrational averaging.[10] This correction increases the calculated correlation times by about 10% and the resulting inter-proton distances by about 0.05 Å. The calculated correlation time was 43 ps for both the methylene and the methylidyne complexes. Correlation times of 23 ps were calculated for the compounds $HOs_3(CO)_{10}(O_2CH)$ and $HOs_3(CO)_9(C_2H)$ in $CDCl_3$ at 25 °C with the assumption of a shorter r_{C-H} = 1.1 Å.[6] Correcting for the differences in viscosity and temperature gives values consistent with our results.[11]

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(7) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic Press: New York, 1971; pp 25, 50. (b) Harris, R. K. *Nuclear Magnetic Resonance Spectroscopy*; Pitman: London, 1983; p 88.

(8) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4853.

(9) Orpen, A. G.; Koetzle, T. F. *Acta. Crystallogr. B* **1984**, *40*, 606.

(10) Boeré, R. T.; Kidd, R. G. *Annu. Rev. NMR Spectrosc.* **1982**, *13*, 319.

(11) VanderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987**, *26*, 3077.

Table 2. ^1H NMR Data for the Mixture $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$[a]

proton[b]	δ	T_1,[c] s	T_1 (irr),[d] s
CH_3	−4.15	0.74	
μ-H	−15.45	15.3	17.1
H_2	5.12	0.90	1.28
H_1	4.26	0.90	1.28
H_4	−15.55	10.2	12.8
H_3	−20.89	8.8	10.4

[a] Toluene-d_8; 18 °C; 360.057 MHz. [b] For assignments, see Scheme 1. [c] Nonselective inversion recovery method was used, with a single-exponential for the data fitting. [d] Nonselective inversion with continuous irradiation of the methyl resonance in the methyl compound. Nonselective pulse with simultaneous irradiation of two nearby protons in the methylene compound.

Table 3. NOE Data for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$[a]

	$(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$:[b] irradiated proton			
enhanced signal	H_2	H_1	H_4	H_3
H_2		0.43		
H_1	0.43			
H_4		0.085		0.21
H_3	0.18		0.17	

	$(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$: irradiated protons	
enhanced signal	CH_3	μ-H
CH_3		0.013
μ-H	0.34	

[a] Toluene-d_8; 18 °C; 360.057 MHz. [b] For specific assignments, see Scheme 1.

Table 4. Homonuclear Dipolar Relaxation Rates and Inter-Proton Distances in the Triosmium Hydrocarbyl Clusters

compound	Ha–Hx	ρ(ax),[a] s^{-1}	NMR dist, Å	neutron dist, Å
$H_3Os_3(CO)_9CH$[b]	1–2	.013	3.8	3.61
$H_2Os_3(CO)_{10}CH_2$[c]	1–2	.67	2.0	1.75
	2–3	.035	3.2	3.03
	1–4	.013	3.8	3.28
	3–4	.033	3.2	2.88
$HOs_3(CO)_{10}CH_3$	1–2	.013	3.8	

[a] ρ(ax), homonuclear dipolar relaxation rates, were calculated by eq 2. The value for the methylidyne compound was corrected for the viscosity ratio (1.33) of xylene to toluene at 18 °C (see ref 11). [b] Neutron diffraction distances from ref 9. [c] Neutron diffraction distances from ref 2b.

T_1 and NOE Measurements by ^1H NMR Spectroscopy. The ^1H NMR spectrum of the methyl/methylene tautomers in toluene-d_8 at 18 °C shows two resonances for the methyl compound and four resonances, labeled H_1 to H_4, for the methylene compound (Table 2).[1] Nonselective T_1 inversion recovery experiments were performed at 18 °C with the same sample as before. For the methyl tautomer the T_1 relaxation times of 15.3 and 0.74 s were determined for the hydride and the methyl resonances, respectively, using a single-exponential data fit. The T_1 relaxation times for the four protons in the methylene tautomer were also measured by the same method. However, due to the presence of the cross relaxation, the inversion-recovery curves are actually biexponential, and thus the values obtained by a single exponential fit contain systematic errors.

This error is demonstrated by a separate nonselective inversion-recovery experiment performed while continuously irradiating the methyl protons in the methyl cluster. The saturation of the methyl spins nullifies the cross relaxation term, leaving the recovery curve single-exponential.[11] Under these conditions the T_1 relaxation time of 17.1 s was measured for the hydride ligand in the methyl tautomer. For the methylene compound the nonselective T_1 inversion recovery pulse sequence was applied along with the simultaneous irradiation of two nearby protons to offset the cross relaxations. Then a single exponential data fit was used to determine the T_1 relaxation times. These results are summarized in Table 2. Results from the application of this treatment to $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ have been reported previously.[11]

The NOE of one proton due to another proton was observed for the methyl/methylene mixture at 18 °C in toluene-d_8. The results are summarized in Table 3. For example, in the methyl complex the NOE of the hydride signal due to irradiation of the methyl spins was found to be 0.34. A similar study of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ showed NOE's of 0.32 and 0.02 at the C–H and μ-H sites, respectively.[11]

The two ^1H NMR parameters, T_1 relaxation times and homonuclear NOE's, are related to the homonuclear dipolar relaxation rate, ρ_{ax}, by

$$f_a(x) = n\rho_{ax}/2\rho_a \tag{2}$$

where $f_a(x)$ is the NOE observed when nucleus x is irradiated and a is observed, ρ_a is the total relaxation rate of a, that is, the inverse of the T_1 relaxation time without the contribution of the cross relaxation, and n is the number of x spins.[7] For example, the calculated value for the homonuclear dipolar relaxation rate between the two unequivalent spins, the hydride and the methyl in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$ is 0.013 s^{-1}. The list of ρ_{ax} determined for all three compounds is shown in Table 4.

The distance between two inequivalent protons in any of the clusters under discussion is given by the substitution of two calculated values, the correlation time of 43 ps and the homonuclear dipolar relaxation rate, into the expression for homonuclear dipolar relaxation:[7]

$$\rho_{ax} = (3/2)(\mu_0/4\pi)^2\gamma_H^{\,4}(h/2\pi)^2\tau_C/r_{H\text{-}H}^{\,6} \tag{3}$$

The calculated values for inter-proton distances in the methyl, the methylene, and the methylidyne compounds from this NMR method are shown in Table 4.

Errors in Calculated Inter-Proton Distances. From eqs 1–3 an inter-proton distance can be directly expressed by observable quantities:

$$r_{H\text{-}H} = r_{C\text{-}H}[{}^3/_4\gamma_H^{\,2}/\gamma_C^{\,2}]^{1/6}[T_1^{\,dd}\rho_a f_a(x)]^{-1/6} \tag{4}$$

From eq 4 the propagation of errors is derived:

$$|\Delta r/r| = (1/6)[|\Delta f_a(x)/f_a(x)| + |\Delta\rho_a/\rho_a| + |\Delta T_1^{\,dd}/T_1^{\,dd}|] \tag{5}$$

Thus, only one-sixth of the relative errors in $f_a(x)$, ρ_a, and T_1^{dd} contributes to the relative error in an inter-proton distance. However, comparison of the proton–proton distances that are calculated from the NMR method with those obtained from neutron diffraction data (Table 4) shows that the former are consistently 5–10% greater than the latter. For example, the average distance between the methylidyne proton and each of the three hydride ligands in $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-CH})$ is deduced to be 3.8 Å by the NMR method, whereas the neutron value is 3.61 Å. One systematic difference between the two approaches is reflected in the choice of a larger value of r_{CH} for the NMR data (vide supra), which, as eq 4 shows, directly increases the resulting value of r_{HH}. A possible source of experimental systematic error is in the determination of T_1^{dd}, since these measurements are very sensitive to the presence of trace amounts of oxygen. If our T_1 values were too short, implying that the derived correlation time is too long, then corrections would be in the direction of better agreement between the NMR and neutron values.

Assignment of the Proton Resonances in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$. The resonances at δ 5.12 and 4.26 are attributed to the methylene protons, whereas the resonances at δ −15.55 and −20.89 are clearly due to the two hydride ligands.[1] On the basis of chemical shift arguments,[1] the two hydride resonances have been assigned previously to the hydride ligands H_4 (bridging the same edge as the methylene ligand) and H_3 (bridging an adjacent edge), respectively, and this assignment is consistent with the ^{13}C NMR results given below. Also on the basis of chemical shift arguments,[14] the more downfield methylene signal can be assigned to the endo hydrogen located over the Os_3 triangle (H_2) and, conversely, the more upfield signal is due to the exo hydrogen (H_1). This assignment is consistent with the homonuclear NOE results that suggest methylene hydrogen H_2 is closer to hydride H_3 and methylene hydrogen H_1 is closer to hydride H_4 (see Table 3). Furthermore, these assignments are self-consistent in that the calculated inter-proton distances are all somewhat longer than the neutron diffraction distances (Table 4), whereas, reversing any of the pairs of assignments leads to calculated inter-proton distances that are strongly inconsistent with the neutron diffraction-derived distances.

(2) Carbonyl ^{13}C NMR Experiments. Assignment of Carbonyl Resonances. As shown in Figures 1 and 2, the $^{13}C\{^1H\}$ NMR spectrum of the ^{13}CO-enriched (ca. 40%) $(\mu\text{-H})Os_3(^*CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(^*CO)_{10}(\mu\text{-CH}_2)$ mixture at room temperature displays ten carbonyl resonances, with equal intensities, for the methylene tautomer, and six carbonyl resonances, with relative intensities of 2:2:2:2:1:1, for the methyl tautomer. The methylene compound resonances are labeled with Arabic numerals and the methyl compound resonances with Roman numerals. All of the resonances have been assigned by a combination of coupling constant analysis, $^{13}C\{^1H\}$ COSY, and selective proton-decoupling experiments.

Resonances 6 and 9 for the methylene compound as well as resonances V and VI for the methyl compound show triplet patterns, which are caused by partial ^{13}C incorporation of about 40% and large two-bond carbon–carbon trans couplings.[12–14] These resonances are readily assigned to the trans, axial carbonyls on the $Os(CO)_4$ unit in each of the tautomers. The fact that these two carbonyls are *inequivalent* in the case of $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$ immediately establishes that the methyl group is *not* in the same plane as the three osmium atoms, in contrast to the implication of structure B. The relative intensities of the carbonyl resonances observed for the methyl cluster indicate that the compound possesses a time-averaged plane of symmetry perpendicular to the plane defined by the three metal atoms but no symmetry plane that contains the metal triangle.

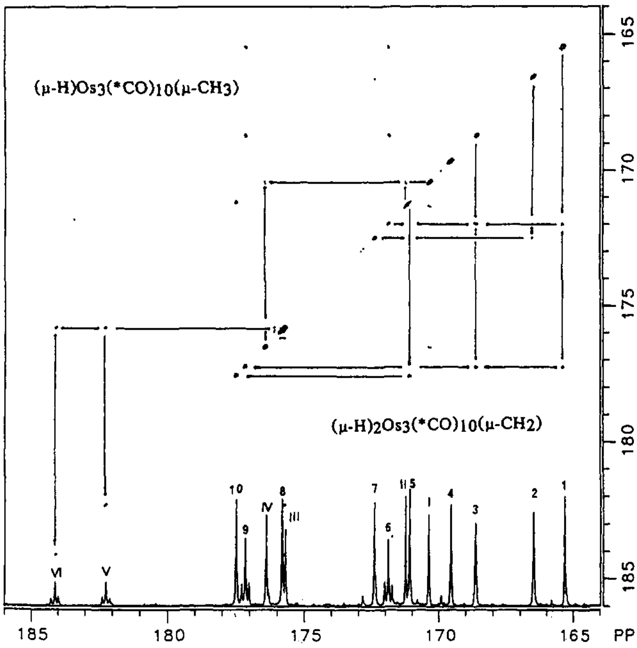

Figure 1. The $^{13}C\{^1H\}$ COSY spectrum of the mixture of $(\mu\text{-H})Os_3(^*CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(^*CO)_{10}(\mu\text{-CH}_2)$ in $CDCl_3$ at room temperature. Connectivities of the methyl and the methylene compounds are shown in the upper left and the lower right half triangles, respectively. The resonances due to the methylene and the methyl compounds are labeled in Arabic and Roman numerals, respectively.

The $^{13}C\{^1H\}$COSY spectrum of the $(\mu\text{-H})Os_3(^*CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(^*CO)_{10}(\mu\text{-CH}_2)$ tautomers is shown in Figure 1. Connectivities of the methyl and the methylene compounds are shown in the upper left and the lower right triangles, respectively. In triosmium carbonyl clusters two-bond couplings of 3–4 Hz are large enough to generate cross peaks, but three-bond couplings (1 Hz or less) are too small to be detected under these conditions.[15,16] In the methylene compound, resonances 1, 3, 6, and 9 are all mutually coupled. Since resonances 6 and 9 are assigned to the axial carbonyls on the $Os(CO)_4$ unit, resonances 1 and 3 correspond to the equatorial carbonyls of the same unit. Likewise, in the methyl compound, resonances III, V, and VI are mutually coupled, and since resonances V and VI are assigned to the axial carbonyls on the $Os(CO)_4$ unit, resonance III is assigned to the corresponding equatorial carbonyls. Resonances 2 and 7 generate cross peaks and so do resonances 5 and 10. Thus, each pair of these carbonyl signals corresponds to two carbonyls in one of the two $Os(CO)_3$ centers of the methylene compound.

Selectively ^1H-decoupled ^{13}C NMR experiments give the information necessary to assign the remainder of the carbonyl signals (Figure 2). The relative position of a carbonyl to a hydride ligand is deduced by the magnitude of the carbon–hydrogen coupling constant; a trans coupling

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(12) Tachikawa, M.; Richter, S. I.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *123*, C9.

(13) (a) Chi, Y.; Shapley, J. R.; Churchill, M. R.; Li, Y.-J. *Inorg. Chem.* **1986**, *25*, 4165. (b) Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1579.

(14) (a) Cree-Uchiyama, M.; Shapley, J. R.; St. George, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 1316. (b) Shapley, J. R.; Cree-Uchiyama, M.; St. George, G. M.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 140.

(15) (a) Hawkes, G. E.; Lian, L. Y.; Randall, E. W.; Sales, K. D.; Aime, S. *J. Chem. Soc. Dalton Trans.* **1985**, 225. (b) Aime, S.; Osella, D. *J. Chem. Soc., Chem. Commun.* **1981**, 300.

(16) Derome A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon: New York, 1987; p 222.

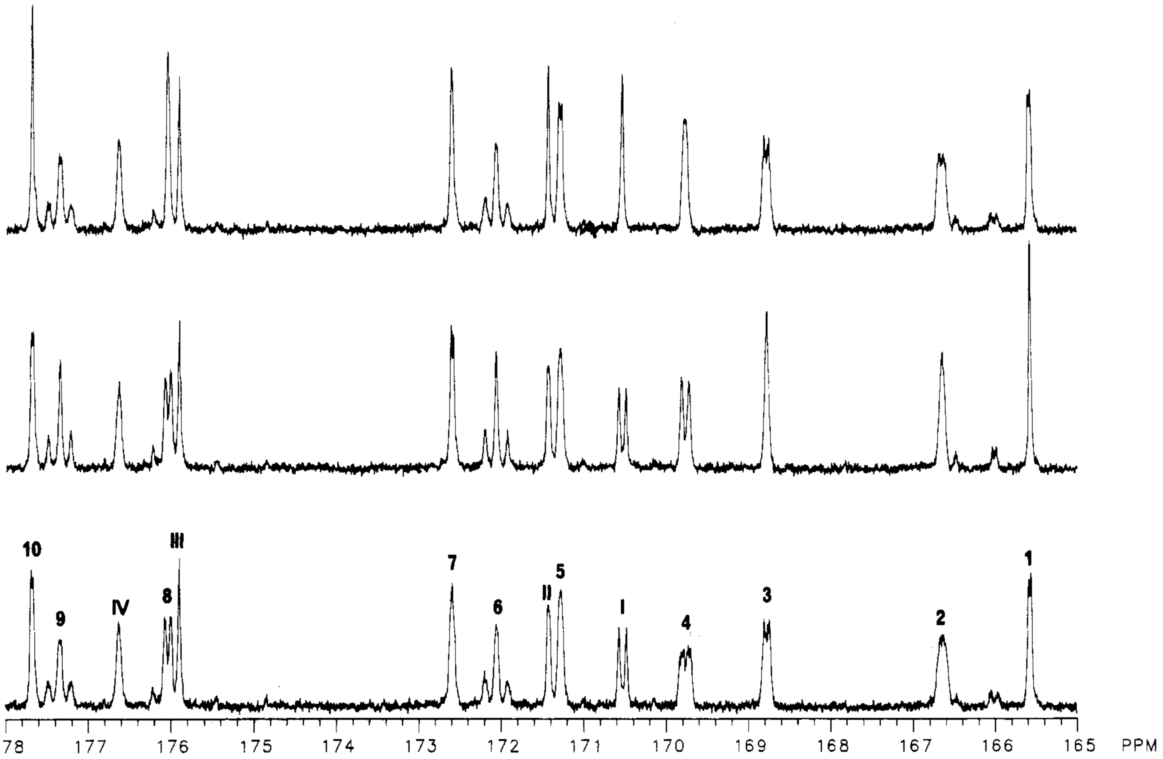
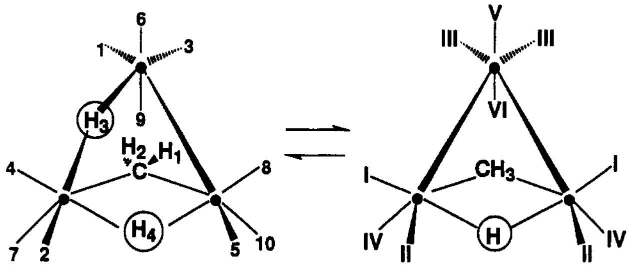


Figure 2. ^{13}C NMR spectra of $(\mu\text{-H})Os_3(^*CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(^*CO)_{10}(\mu\text{-CH}_2)$ in $CDCl_3$ at room temperature: (a) ^1H coupled ; (b) H_3 selectively irradiated; (c) H_4 selectively irradiated.

Scheme 1



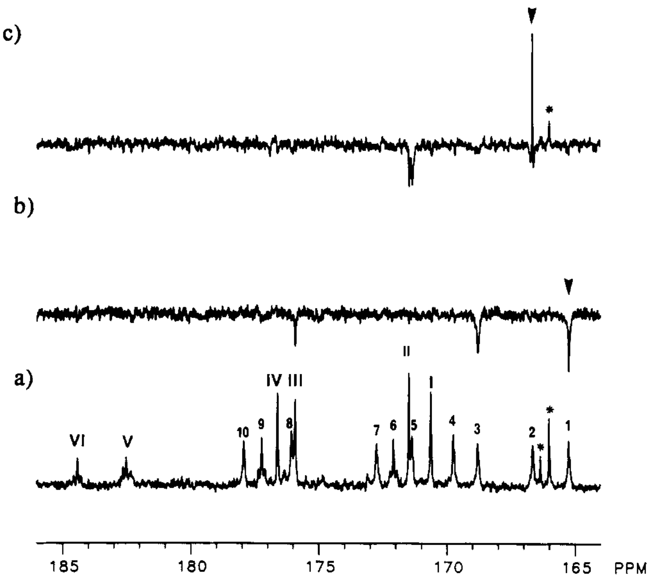


Figure 3. ^{13}C NMR spin saturation transfer experiments on $(\mu\text{-H})Os_3(^*CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(^*CO)_{10}(\mu\text{-CH}_2)$ in toluene-d_8 at 65 °C: (a) reference spectrum in which a noise region was irradiated; (b) difference spectrum when resonance 1 was irradiated; (c) difference spectrum when resonance 2 was irradiated. Signals due to decomposition species are labeled with an asterisk.

(10–12 Hz) is larger than a cis coupling (2.5 Hz or less).[14,15,17,18] For example, in the case of the two equatorial carbonyls corresponding to resonances 1 and 3, the coupling constant to H_3 is larger for 3 than for 1; therefore, resonances 3 and 1 are assigned to the carbonyls, respectively, trans and cis to H_3 on the $Os(CO)_4$ unit. On the other hand, resonances 5, 8, and 10 show coupling to H_4, but no coupling to H_3, so these three resonances are attributable to the $Os(CO)_3$ unit that is bonded only to H_4. Resonance 8 is assigned to the carbonyl trans to H_4 due to the large $^2J(CH)$ value. Resonance 10 is assigned to the pseudoaxial carbonyl due to its downfield chemical shift.[19,20] This leaves resonance 5 for the remaining carbonyl in the equatorial position *trans* to the unsupported metal–metal bond. The complete assignment of the carbonyl resonances is shown in Scheme 1.

^{13}C Spin Saturation Transfer. ^{13}C NMR spin saturation transfer experiments were carried out on the $(\mu\text{-H})Os_3(^*CO)_{10}(\mu\text{-CH}_3)/(\mu\text{-H})_2Os_3(^*CO)_{10}(\mu\text{-CH}_2)$ tautomers in toluene-d_8 at 65 °C and the results are shown in Figure 3. Resonances 1 and 2 for the methylene compound were chosen for irradiation because each of them is well separated from the other resonances. The selective irradiation of resonance 1 led to a significant decrease in the intensity of resonance III of the methyl compound but also in that of resonance 3. Analogous irradiation of resonance 2 caused a significant decrease in intensity of resonance II for the methyl tautomer but also in that of resonance 5. The saturation transfer from sites 1 and 2 of the methylene compound to sites III and II of the methyl

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(17) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; p 176.

(18) Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* 1988, 7, 294.

(19) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304.

(20) Farrugia, L. J. *J. Organomet. Chem.* **1990**, *394*, 515.

compound is entirely consistent with the assignments shown in Scheme 1. However, the intramolecular saturation transfer in the methylene compound, i.e., the exchange of carbonyls 1 and 2 with carbonyls 3 and 5, respectively, implies the generation of a time-averaged plane of symmetry perpendicular to the Os_3 triangle. This is presumably accomplished by migration of hydride ligand H_3 between the bridging sites on the two metal–metal bonds attached to the $Os(CO)_4$ unit. Moreover, this process is consistent with the selective line broadening that is observable at 65 °C (see Figure 3). All of the methylene carbonyl resonances, except those for the trans, axial carbonyls (6, 9), undergo broadening relative to the carbonyl resonances of the methyl compound. The axial carbonyl ligands lie on the plane that is created by the dynamic process and therefore do not undergo site exchange.

Discussion

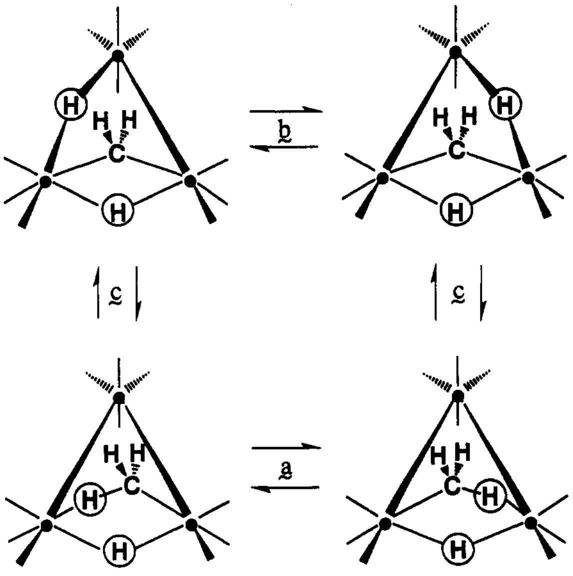
Solution Structure of (μ-H)$Os_3(CO)_{10}$(μ-CH_3). Our results strongly favor structure A rather than structure B for the solution structure of (μ-H)$Os_3(CO)_{10}$(μ-CH_3) on several grounds. First, the average distance between the methyl protons and the hydride ligand was calculated by the solution NMR method to be about 3.8 Å. In structure A the average inter-proton distance is expected to be approximately 3.5 Å. In structure B, however, regardless of the direction of the methyl agostic interaction with respect to the bridging hydride ligand, the average inter-proton distance would not be less than 4.5 Å, over 20% longer than the experimental value. Thus, the methyl-hydride distance determined by solution NMR techniques agrees reasonably well with A but not with B.

Secondly, the ^{13}C-NMR spectra recorded for the methyl tautomer supports structure A. Only six carbonyl resonances are observed for the methyl compound at room temperature as well as at −40 °C. The data clearly indicate the presence of a plane of symmetry perpendicular to the plane of the three metal atoms. In structure A the rapid methyl group rotation will create such a reflection plane (vide infra). In contrast, in structure B, which contains a plane of symmetry defined by the three metal atoms, seven carbonyl resonances with relative intensities of 2:2:2:1:1:1:1 would be expected. Moreover, couplings between the hydride ligand and the carbonyl carbons strongly favor A. In structure A none of the carbonyls on the $Os(CO)_4$ unit should couple to the hydride ligand, whereas in structure B the equatorial carbonyls on the $Os(CO)_4$ unit should show averaged cis and trans couplings of about 6 Hz. However, none of the resonances III, V, and VI, which are assigned to the carbonyls on the $Os(CO)_4$ unit, show any ^1H coupling.

Finally, the tautomerization process is explained more plausibly by structure A (vide infra). Previous ^1H spin saturation transfer experiments showed that the methyl protons exchange with the two methylene protons and the hydride ligand in the higher field site (H_3); the lower field site (H_4) is not directly involved in the interconversion.[1b] However, structure B would apparently decompose the methyl group into the methylene moiety and the hydride ligand (H_4) bridging the same edge of the metal triangle, contrary to what is observed.

Overall Interconversions among the Methyl/Methylene Tautomers. Since the structures of both the methyl and methylene compounds are chiral, each consists of two enantiomers. The overall dynamics of the four isomers constituting the pair of tautomers is summarized in Scheme 2.

Scheme 2



In the methyl tautomer, exchange among the protons in the methyl group involves formation and cleavage of a C–H bond together with an agostic C··H··Os interaction. This process (denoted as a) interconverts the two enantiomers of the methyl compound. Although the barrier for this process has not been measured directly, estimates of $\Delta G^\ddagger \approx$ 3–4 kcal/mol have been made on the basis of the reduced methyl carbon relaxation time.[11,21]

The second fastest process (b) involves interconversion of the two enantiomers of the methylene compound by transfer of the hydride ligand between the edges of the Os_3 triangle not bridged by the methylene group. This intramolecular process was most readily observed by the saturation transfer studies, but it could be detected by selective line broadening as well. The latter observation allows estimation of an exchange rate of ca. 30 s^{-1} at 65 °C, which corresponds to $\Delta G^\ddagger \approx$ 18 kcal/mol.

The tautomeric interconversion (c) is the slowest process observed. Direct measurement of the conversion of the methyl compound into the methylene compound at 14 °C provided an estimate of $\Delta G^\ddagger \approx$ 20 kcal/mol.[1b] This conversion involves hydrogen migration from a bridging site on the osmium–carbon bond to a bridging site on an osmium–osmium bond, i.e., a 3c, 2e Os–H–C bond and a 2c, 2e Os–Os bond are transformed into a 2c, 2e Os–C bond together with a 3c, 2e Os–H–Os bond. In the reverse direction the bridging hydrogen on the adjacent Os–Os bond transfers to an agostic site on the methyl moiety.

Analogous interconversions have been observed for the homologous ethyl/ethylidene tautomer pair,[14a] and similar hydrogen transfers from Os–H–Os to an adjacent Os–C, in some cases reversible, have been observed in several other triosmium hydrocarbyl compounds.[11,22,23] Related

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[21] Vander Velde, D. G. Ph.D. Thesis; University of Illinois at Urbana-Champaign, 1987.

[22] (a) Kneuper, H.-J.; Shapley, J. R. *New J. Chem.* **1988**, *12*, 479. (b) Kneuper, H.-J.; Shapley, J. R. *Organometallics* **1987**, *6*, 2455.

[23] Strickland, D. S.; Shapley, J. R. *J. Organomet. Chem.* **1991**, *401*, 187.

transformations are seen also in similar ruthenium and iron cluster compounds.[24,25]

Acknowledgment. This work was supported by National Science Foundation Grant CHE 89-15349 and its predecessor to J.R.S. M.K. thanks the Sankei Scholarship Foundation, the University of Illinois, and the Walter Brown Endowment Fund for fellowships. The GE GN-500 FT-NMR spectrometer was purchased in part with funds from National Science Foundation Grant CHE 85-14500 to the School of Chemical Sciences at the University of Illinois. We thank Dr. Vera Mainz for setting up the ^{13}C spin saturation experiments.

OM9303764

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(24) Duggan, T. P.; Golden, M. J.; Keister, J. B. *Organometallics* **1990**, *9*, 1656.

(25) Dutta, T. K.; Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1987**, *6*, 842.