Laursen and S. C. Hartman for the loan of pH stats and Professor L. Z. Zompa for providing us with a sample of tren.

Registry No. $[(en)_2Co^{III}(OH_2)_2]^{3+}$, 21247-59-6; $[(tn)_2Co^{III}(OH_2)_2]^{3+}$, 51286-38-5; $[(tren)Co^{III}(OH_2)_2]^{3+}$, 41884-78-0; $[(en)_2Co(CO_3)](ClO_4)$, 15155-12-1; $[(tn)_2Co(CO_3)](ClO_4)$, 31188-12-2; $[(tren)Co(CO_3)](ClO_4)$, 41593-06-0; $H_4P_2O_7$, 2466-09-3.

Supplementary Material Available: Figures 9–15, providing sample spectra, detailed results for pH 0–12 at both 1:1 and 2:1 molar ratios of $(tn)_2Co^{III}(aq)$ to orthophosphate, and a summary of related literature data[12,13] (7 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and University of Illinois, Urbana, Illinois 61801

Structural Studies on Polynuclear Osmium Carbonyl Hydrides. 15.[1] Preparation and X-ray Crystal Structure of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me)$, a Complex with an $Os(\mu\text{-}H)(\mu\text{-}N)Os$ Bridge

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The complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me)$ has been synthesized from $(\mu\text{-}H)_2Os_3(CO)_{10}$ and $MeC_6H_4SO_2N_3$. This species crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.246$ (1) Å, $b = 8.668$ (1) Å, $c = 18.572$ (3) Å, $\alpha = 89.92$ (1)°, $\beta = 98.61$ (1)°, $\gamma = 113.05$ (1)°, $V = 1205.4$ (2) Å^3, $\rho_{calcd} = 2.82$ g cm^{-3} for mol wt 1021.95, and $Z = 2$. Diffraction data (4.5° < 2θ < 50°; Mo Kα) were collected with a Syntex $P2_1$ diffractometer, and the structure was solved by standard Patterson, Fourier, and least-squares refinement techniques. The resulting discrepancy indices were $R_F = 4.0\%$ and $R_{wF} = 2.9\%$ for all 4276 reflections (none rejected) and $R_F = 3.2\%$ and $R_{wF} = 2.8\%$ for those 3786 data with $|F_o| > 3\sigma(|F_o|)$. The molecule contains a triangular arrangement of osmium atoms; Os(1) and Os(2) are each linked to three terminal carbonyl groups, while Os(3) is linked to four. Atoms Os(1) and Os(2) are additionally bridged by a hydride ligand (which was located and refined) and by a $>NHSO_2C_6H_4Me$ ligand. Osmium–osmium bond lengths are Os(1)–Os(3) = 2.858 (1) Å and Os(2)–Os(3) = 2.847 (1) Å (unbridged) and Os(1)–Os(2) = 2.814 (1) Å (μ-H,μ-N bridged). Within the Os(1)–H(br)–Os(2) system, interatomic paramters are Os(1)–H(br) = 1.91 (8) Å, Os(2)–H(br) = 1.96 (8) Å, and Os(1)–H(br)–Os(2) = 93.5 (34)°. Within the Os(1)–N–Os(2) system, parameters are Os(1)–N = 2.162 (7) Å, Os(2)–N = 2.145 (7) Å, and Os(1)–N–Os(2) = 81.6 (2)°.

Introduction

The unsaturated cluster compound $(\mu\text{-}H)_2Os_3(CO)_{10}$ has been shown to react with certain diazo compounds $RHC^-{-}N^+{\equiv}N$ (R = H[4], CO_2Et[5]) with loss of dinitrogen to give the insertion products $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CH_2R)$. These results prompted us to examine the interaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with an analogous dipolar compound, an azide $RN^-{-}N^+{\equiv}N$. This article describes the characterization of the insertion product $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me)$ that results from reaction with *p*-toluenesulfonyl azide.

Experimental Section

$Os_3(CO)_{12}$ was prepared by the method of Nyholm[6] from osmium tetraoxide. The synthesis of $H_2Os_3(CO)_{10}$ is described by Kaesz et al.[7] Tosyl azide was prepared by a literature procedure.[8]

Infrared spectra were obtained on a Perkin-Elmer 467 spectrophotometer. Proton NMR spectra were recorded on a Varian HA-100 spectrometer. Electron-impact mass spectra were obtained by Mr. Joe Wrona with a Varian MAT CH-5 instrument at 70 eV. Elemental analyses were performed at the University of Illinois by the microanalytical laboratory of the School of Chemical Sciences.

Table I. Experimental Data for the Diffraction Study of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me)$

(A) Crystal Parameters at 25 °C[a]

$a = 8.2462$ (14) Å	$V = 1205.4$ (2) Å^3
$b = 8.6681$ (14) Å	$Z = 2$
$c = 18.5723$ (28) Å	mol wt 1021.95
$\alpha = 89.923$ (13)°	ρ(calcd) = 2.82 g cm^{-3}
$\beta = 98.614$ (13)°	μ(calcd) = 168.6 cm^{-1}
$\gamma = 113.046$ (12)°	space group $P\bar{1}$

(B) Measurement of Intensity Data

radiation: Mo Kα ($\bar{\lambda} = 0.710\,730$ Å)
monochromator: highly oriented graphite, $2\theta_{mono} = 12.2°$, equatorial mode
rflctns measd: $+h, \pm k, \pm l$
2θ range: 4.5–50.0°
scan type: coupled θ(cryst)–2θ(detector)
scan speed: 3.0°/min in 2θ
scan width: $[2\theta(\text{Mo K}\alpha_1) - 0.85]° \rightarrow [2\theta(\text{Mo K}\alpha_2) + 0.85]°$
bkgd measmt: stationary crystal–stationary counter at beginning and end of each scan, each for one-third of the total scan time
std rflctns: 0,0,13, $2\bar{6}3$, and 403; these were measured after every 97 rflctns. No decay in intensity was observed
rflctns collected: 4267 unique data

[a] Unit cell parameters were derived from a least-squares fit to the setting angles at the unresolved Mo K$\bar{\alpha}$ components of 12 Friedel pairs of reflections well scattered in reciprocal space with 2θ values between 25 and 30°.

Synthesis of $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}NHSO_2C_6H_4Me)$. To a stirred solution of $(\mu\text{-}H)_2Os_3(CO)_{10}$ (30 mg) in chloroform (5 mL) was added an excess (4 drops, ca. 60 mg) of *p*-toluenesulfonyl azide. After 24 h the bright yellow solution was evaporated to dryness, and the residue was extracted with a small amount of diethyl ether. This solution was cooled to −25 °C for several hours, and the yellow precipitate was collected. Recrystallization from dichloromethane and drying

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[1] For previous parts in this series, see the following. (a) Part 12: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 1926–30. (b) Part 13: Churchill, M. R.; Lashewycz, R. A. *Ibid.* **1979**, *18*, 3261–7. (c) Part 14: Churchill, M. R.; Hollander, F. J. *Ibid.* **1980**, *19*, 306–310.
[2] SUNY at Buffalo.
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under vacuum provided bright yellow crystals (14 mg, 39%). No other product was observed. IR (C_6H_{12}): ν(CO) 2110 (vw), 2078 (vs), 2060 (m), 2024 (vs), 2011 (m), 2004 (s), 1990 (w), 1974 (w) cm^{-1}. IR (CCl_4): ν(NH) 3325 (vw) cm^{-1}. Mass spectrum: m/e 1027 (^{192}Os, M$^+$). ^{1}H NMR ($CDCl_3$, 25 °C): τ 2.22 (d, 2 H_a), 2.61 (d, 2 H_b), 4.20 (br, 1 H_c), 7.55 (s, 3 H_d), 25.31 (d, 1 H_e); J_{ab} = 8.1 Hz, J_{ce} = 2.2 Hz. Anal. Calcd for $C_{17}H_9NO_{12}SOs_3$: C, 19.96; H, 0.89; N, 1.37; Os, 55.84. Found: C, 20.06; H, 0.89; N, 1.40; Os, 55.81.

Collection of X-ray Diffraction Data for (μ-H)Os_3(μ-$NHSO_2C_6H_4Me$). The complex crystallizes as clear yellow prisms with well-developed faces. Several crystals were mounted and examined via precession photographs which revealed no symmetry other than the Friedel condition. The crystal selected for data collection was a triangular prism (triangular edge dimensions 0.10 × 0.14 × 0.13 mm and 0.20 mm in length); this was mounted on a glass fiber with GE varnish. The fiber was set into an aluminum pin with beeswax and was mounted on our Syntex $P2_1$ automated diffractometer with the long axis of the crystal aligned approximately along the ϕ axis of the goniometer. Crystal alignment, determination of the orientation matrix and accurate cell parameters, and data collection were all carried out as described previously.[9] Details specific to the present analysis are given in Table I.

All crystallographic computations were performed by using our in-house Syntex XTL system, including the XTL interactive crystallographic program package[10] as modified by our research group at SUNY at Buffalo. Data were corrected for absorption (μ = 168.6 cm^{-1}) by the empirical method previously described.[11] Reflections used, their 2θ values, and their maximum-to-minimum intensity ratios were as follows: 006, 13.33°, 1.28:1; $00\bar{6}$, 13.33°, 1.31:1; $0\bar{1}8$, 18.22°, 1.33:1; $01\bar{8}$, 18.22°, 1.32:1; 0,0,11, 24.58°, 1.28:1; $0,0,\bar{1}\bar{1}$, 24.58°, 1.26:1; 0,0,13, 29.14°, 1.25:1; $0,\bar{1},15$, 33.82°, 1.32:1; $1,\bar{1},16$, 37.14°, 1.32:1.

Analysis of the standard reflections showed no evidence of decay. Data were converted to unscaled $|F_o|$ values, following correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$. The esd's, $\sigma_c(|F_o|)$, were based on counting statistics.

Solution and Refinement of the Structure. The analytical form[12a] of the scattering factors for neutral osmium, sulfur, oxygen, nitrogen, carbon, and hydrogen were used throughout the analysis. Both the real and imaginary components of anomalous dispersion[12b] were included for all nonhydrogen atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized by least-squares refinement. Here the weight, w, is defined in eq 1; p, the "ignorance factor ", was set to a value of 0.01.

$$w = [[\sigma_c(|F_o|)]^2 + (p|F_o|)^2]^{-1} \qquad (1)$$

Data were placed on an approximate absolute scale by means of a Wilson plot, which also yielded an overall temperature factor of $\bar{B}$ = 2.47 Å^2. A three-dimensional Patterson map was easily interpreted to yield the positions of the three independent osmium atoms. A difference Fourier synthesis (R_F = 15.7%) revealed unambiguously the positions of all remaining nonhydrogen atoms. Full-matrix least-squares refinement of positional and anisotropic thermal parameters converged with R_F = 4.2%, R_{wF} = 3.3%, and GOF = 1.55 (307 parameters, 4267 data).

A difference Fourier synthesis revealed clearly the positions of all hydrogen atoms other than H(2). The positional parameters of these atoms were included in the least-squares refinement, H(2) being inserted in its idealized position (regular trigonal geometry about C(2), with d(C–H) = 0.95 Å).[13]

Inspection of the $|F_o|$ and $|F_c|$ values for the complete model showed that a correction for secondary extinction was necessary. (The worst disagreement was for the $1\bar{1}\bar{1}$ reflection, with $|F_c|/|F_o|$ = 1.19.) The $|F_o|$ values of all reflections were now corrected for secondary extinction as shown in eq 2; the value of g, determined by a least-squares analysis of high-intensity reflections, was 1.86 × 10^{-7}.

$$|F_o|_{cor} = |F_o|_{uncor}(1.0 + gI_o) \qquad (2)$$

Table II. Final Positional Parameters (with Esd's) for (μ-H)$Os_3(CO)_{10}$(μ-$NHSO_2C_6H_4Me$)

atom	x	y	z	B, Å^2
Os(1)	0.221 60 (4)	0.102 70 (4)	0.182 51 (2)	
Os(2)	0.482 97 (4)	0.393 99 (4)	0.260 13 (2)	
Os(3)	0.507 41 (4)	0.320 67 (4)	0.113 72 (2)	
S	0.3905 (3)	0.0317 (3)	0.347 89 (11)	
N	0.4352 (9)	0.1342 (9)	0.2718 (4)	
O(1)	0.2747 (7)	0.0865 (8)	0.3799 (3)	
O(2)	0.3378 (8)	−0.1437 (8)	0.3293 (3)	
C(1)	0.6019 (11)	0.1080 (10)	0.4043 (4)	
C(2)	0.6321 (13)	0.2051 (12)	0.4666 (5)	
C(3)	0.8012 (14)	0.2663 (12)	0.5098 (5)	
C(4)	0.9374 (13)	0.2300 (11)	0.4892 (5)	
C(5)	0.9017 (13)	0.1281 (13)	0.4258 (6)	
C(6)	0.7332 (14)	0.0667 (13)	0.3835 (5)	
C(7)	1.1166 (16)	0.2874 (16)	0.5374 (7)	
O(11)	−0.0462 (9)	0.1257 (9)	0.0562 (4)	
O(12)	−0.0853 (8)	−0.1055 (9)	0.2626 (4)	
O(13)	0.2315 (9)	−0.1951 (9)	0.0998 (4)	
O(21)	0.5083 (9)	0.7361 (8)	0.2135 (4)	
O(22)	0.4025 (11)	0.4787 (10)	0.4066 (4)	
O(23)	0.8846 (9)	0.5161 (10)	0.2995 (4)	
O(31)	0.2447 (10)	0.4905 (9)	0.0699 (4)	
O(32)	0.7339 (9)	0.1305 (9)	0.1800 (4)	
O(33)	0.8304 (10)	0.6433 (10)	0.0988 (4)	
O(34)	0.4229 (9)	0.1414 (9)	−0.0371 (4)	
C(11)	0.0561 (11)	0.1197 (11)	0.1041 (5)	
C(12)	0.0341 (11)	−0.0230 (11)	0.2367 (5)	
C(13)	0.2257 (11)	−0.0863 (12)	0.1319 (5)	
C(21)	0.4959 (11)	0.6087 (12)	0.2309 (5)	
C(22)	0.4294 (12)	0.4369 (12)	0.3547 (5)	
C(23)	0.7369 (13)	0.4735 (12)	0.2855 (5)	
C(31)	0.3403 (13)	0.4261 (11)	0.0864 (5)	
C(32)	0.6519 (12)	0.2004 (12)	0.1545 (5)	
C(33)	0.7107 (13)	0.5228 (13)	0.1047 (5)	
C(34)	0.4531 (11)	0.2062 (11)	0.0187 (5)	
H(br)	0.227 (10)	0.308 (9)	0.222 (4)	4.0
H(1)	0.506 (13)	0.100 (13)	0.254 (5)	6.0
H(2)	0.556 (13)	0.245 (12)	0.478 (5)	6.0
H(3)	0.812 (12)	0.345 (12)	0.548 (5)	6.0
H(5)	1.004 (13)	0.133 (13)	0.412 (5)	6.0
H(6)	0.713 (13)	0.008 (12)	0.341 (5)	6.0
H(7A)	1.191 (15)	0.231 (15)	0.516 (6)	8.0
H(7B)	1.088 (14)	0.230 (14)	0.593 (6)	8.0
H(7C)	1.173 (16)	0.381 (15)	0.531 (7)	8.0

Four cycles of full-matrix least-squares refinement led to final convergence with R_F = 4.0%, R_{wF} = 2.9%, and GOF = 1.39 for 334 parameters refined against all 4276 reflections (*none rejected*). For comparision, we may note that the residuals for those 3786 data with $|F_o| > 3\sigma_c(|F_o|)$ were R_F = 3.2%, R_{wF} = 2.8%, and GOF = 1.43.

A final difference Fourier synthesis showed no significant features. The function $\sum w(|F_o| - |F_c|)^2$ showed no abnormal dependency on $|F_o|$, $(\sin\theta)/\lambda$, sequence number, and identity or parity of crystallographic indices; the weighting scheme is thus satisfactory.

Final positional and thermal parameters are collected in Tables II and III.

Results and Discussion

The crystal consists of discrete ordered units of (μ-H)-$Os_3(CO)_{10}$(μ-$NHSO_2C_6H_4Me$), which are mutually separated by normal van der Waals distances. The closest two contacts involving nonhydrogen atoms are O(13)···O(31)(x, y − 1, z) = 2.829 (11) Å and O(11)···O(34)(−x, −y, −z) = 3.029 (11) Å. The atomic labeling scheme is illustrated in Figures 1 and 2; a stereoscopic view of the molecule appears as Figure 3. Interatomic distances and angles are collected in Tables IV and V, while principal planes appear in Table VI.

As shown in Figure 4, the triosmium cluster approximates an isosceles triangle in which the two nonbridged osmium–osmium bond lengths are Os(1)–Os(3) = 2.858 (1) Å and Os(2)–Os(3) = 2.847 (1) Å, while the μ-hydrido-μ-(substituted amide)-bridged Os(1)–Os(2) linkage is reduced to 2.814 (1) Å. [For comparison we note that the average osmium–osmium

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Table III. Final Anisotropic Thermal Parameters (Å^2) for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$[a]

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Os(1)	2.257 (13)	2.392 (14)	2.831 (14)	0.725 (11)	0.588 (10)	0.057 (11)
Os(2)	2.888 (14)	2.735 (15)	2.411 (14)	0.823 (11)	0.457 (11)	−0.223 (11)
Os(3)	2.846 (14)	2.656 (15)	2.519 (14)	0.712 (11)	0.800 (11)	0.071 (11)
S	3.46 (9)	3.80 (11)	3.01 (9)	1.39 (8)	1.10 (8)	0.79 (8)
N	2.8 (3)	3.6 (3)	3.0 (3)	1.3 (3)	0.61 (24)	0.5 (3)
O(1)	3.9 (3)	5.4 (3)	3.9 (3)	2.3 (3)	1.68 (23)	1.11 (25)
O(2)	4.6 (3)	3.9 (3)	4.4 (3)	1.38 (25)	1.01 (25)	0.70 (25)
C(1)	3.4 (4)	3.6 (4)	2.6 (4)	1.6 (3)	0.1 (3)	0.4 (3)
C(2)	5.2 (5)	4.6 (5)	2.7 (4)	2.9 (4)	0.9 (4)	−0.0 (3)
C(3)	6.0 (6)	4.3 (5)	2.6 (4)	2.4 (4)	0.5 (4)	−0.1 (3)
C(4)	4.9 (5)	3.3 (4)	3.9 (5)	1.4 (4)	−0.1 (4)	0.5 (4)
C(5)	4.1 (5)	5.6 (6)	4.4 (5)	2.7 (4)	0.3 (4)	0.0 (4)
C(6)	5.4 (5)	5.5 (5)	2.9 (4)	3.0 (4)	−0.0 (4)	−0.9 (4)
C(7)	5.3 (6)	5.2 (6)	6.1 (7)	1.5 (5)	−0.6 (5)	1.3 (5)
O(11)	4.2 (3)	6.9 (4)	4.8 (4)	2.3 (3)	−0.5 (3)	0.8 (3)
O(12)	3.7 (3)	5.9 (4)	6.0 (4)	0.7 (3)	2.2 (3)	1.8 (3)
O(13)	5.5 (4)	5.2 (4)	8.3 (5)	2.8 (3)	0.1 (3)	−2.4 (4)
O(21)	5.5 (4)	2.4 (3)	6.1 (4)	1.0 (3)	0.5 (3)	−0.2 (3)
O(22)	9.4 (5)	6.7 (4)	3.4 (3)	3.8 (4)	2.0 (3)	−0.8 (3)
O(23)	3.3 (3)	7.3 (5)	7.8 (5)	0.5 (3)	−0.8 (3)	−1.5 (4)
O(31)	6.4 (4)	5.0 (4)	4.9 (4)	3.4 (3)	0.1 (3)	0.4 (3)
O(32)	5.3 (4)	7.2 (4)	5.3 (4)	4.3 (3)	1.4 (3)	1.3 (3)
O(33)	5.2 (4)	5.5 (4)	7.3 (5)	−1.6 (3)	2.1 (3)	0.4 (3)
O(34)	5.8 (4)	6.2 (4)	3.9 (3)	1.1 (3)	0.7 (3)	−1.8 (3)
C(11)	2.9 (4)	3.5 (4)	4.3 (5)	1.1 (3)	0.4 (3)	−0.5 (3)
C(12)	3.3 (4)	3.7 (4)	4.3 (5)	1.5 (3)	1.1 (3)	0.1 (4)
C(13)	3.1 (4)	4.2 (5)	4.6 (5)	1.5 (4)	0.7 (3)	0.4 (4)
C(21)	3.2 (4)	3.8 (5)	3.7 (4)	0.7 (3)	0.4 (3)	−0.7 (4)
C(22)	4.1 (4)	4.3 (5)	3.7 (5)	1.5 (4)	0.5 (4)	0.0 (4)
C(23)	4.0 (5)	3.7 (5)	4.7 (5)	1.0 (4)	−0.3 (4)	−0.7 (4)
C(31)	4.9 (5)	3.0 (4)	3.9 (4)	1.1 (4)	1.0 (4)	0.3 (3)
C(32)	4.2 (5)	4.4 (5)	3.5 (4)	1.8 (4)	1.4 (4)	0.1 (4)
C(33)	4.7 (5)	5.2 (5)	3.2 (4)	1.7 (4)	1.4 (4)	−0.4 (4)
C(34)	3.3 (4)	3.7 (4)	4.1 (5)	0.8 (3)	0.9 (3)	0.6 (4)

[a] The anisotropic thermal parameters enter the equation for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

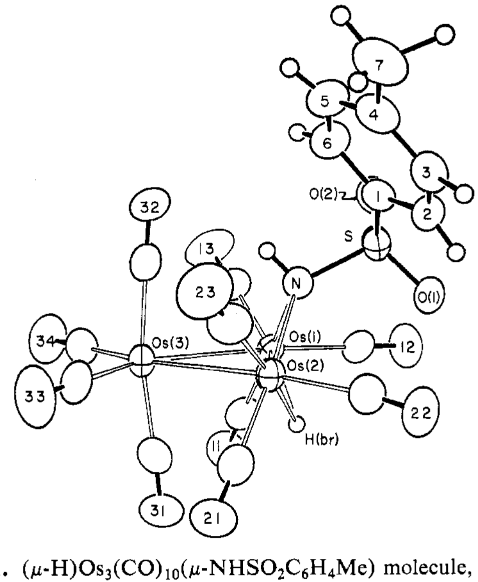

Figure 1. $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$ molecule, showing the atomic labels. Oxygen atoms of carbonyl groups and carbon atoms of tolyl groups are given by numbers only.

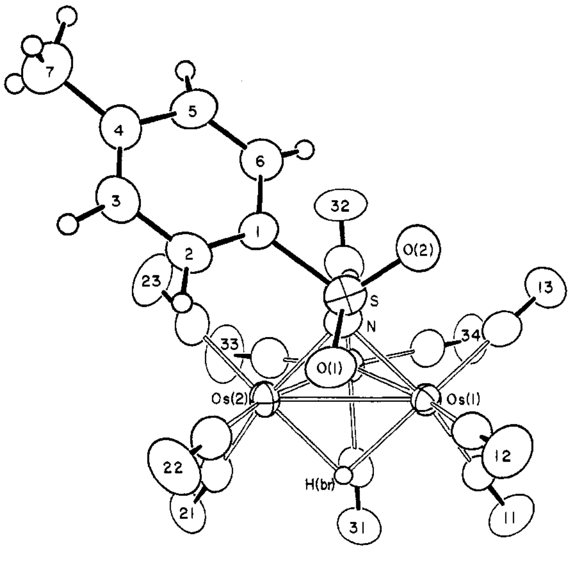

Figure 2. $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$ molecule, showing atom labels and the conformation about the N–S bond.

bond length in $Os_3(CO)_{12}$, the parent carbonyl, is 2.877 (3) Å.[14])

The net *shortening* of the dibridged $Os(\mu\text{-H})(\mu\text{-N})Os$ linkage relative to the nonbridged osmium–osmium bonds is characteristic of $Os(\mu\text{-H})(\mu\text{-X})Os$ systems containing relatively small X atoms (the covalent radius of nitrogen is ~0.70 Å[15]). We note that the corresponding values for $Os(\mu\text{-H})(\mu\text{-C})Os$ systems (r(C) = 0.772 Å[15]) are 2.785 (2) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH{=}NEt}_2)$[16] and 2.800 (1) Å in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CHCH}_2\text{PMe}_2\text{Ph})$.[17] The effects of the nature of

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(14) Part 1: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.

(15) Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7-2, p 224.

(16) Part 11: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 848.

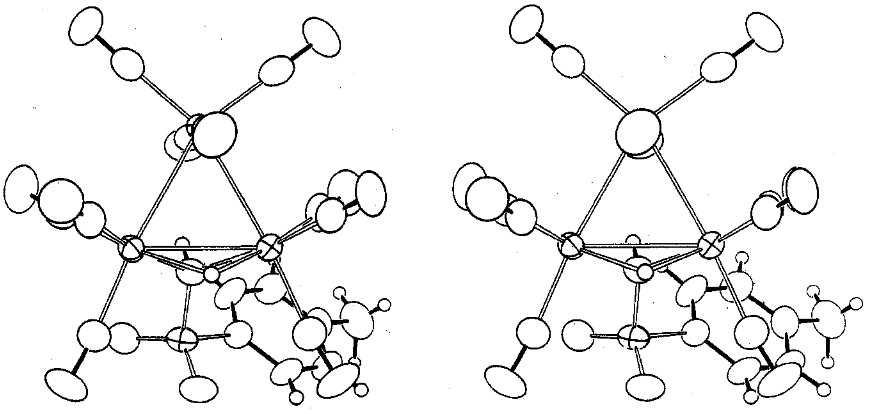

Figure 3. Stereoscopic diagram of the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$ molecule.

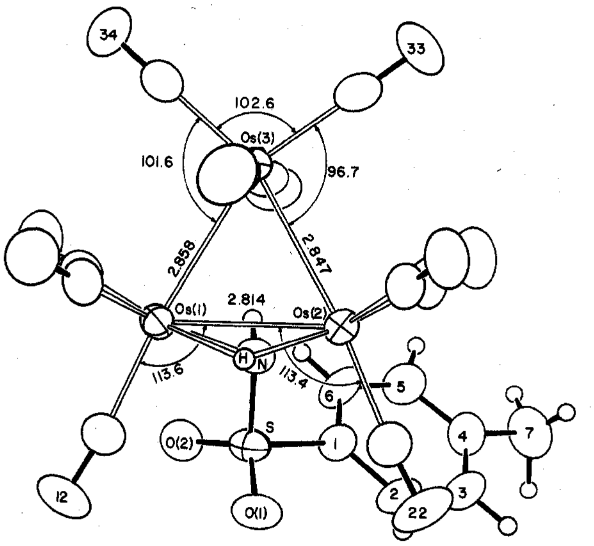

Figure 4. Distances and angles within the equatorial plane of the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$ molecule.

Table IV. Interatomic Distances (Å) within the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$ Molecule[a]

A. Osmium–Osmium Distances			
Os(1)–Os(2)	2.814 (1)	Os(1)–Os(3)	2.858 (1)
		Os(2)–Os(3)	2.847 (1)
B. Osmium–Bridge Atoms			
Os(1)–H(br)	1.91 (8)	Os(1)–N	2.162 (7)
Os(2)–H(br)	1.96 (8)	Os(2)–N	2.145 (7)
C. Osmium Carbonyl			
Os(1)–C(11)	1.889 (10)	Os(1)–O(11)	3.035 (7)
Os(1)–C(12)	1.932 (9)	Os(1)–O(12)	3.069 (7)
Os(1)–C(13)	1.905 (10)	Os(1)–O(13)	3.040 (8)
Os(2)–C(21)	1.905 (10)	Os(2)–O(21)	3.025 (6)
Os(2)–C(22)	1.945 (10)	Os(2)–O(22)	3.051 (7)
Os(2)–C(23)	1.912 (11)	Os(2)–O(23)	3.026 (8)
Os(3)–C(31)	1.941 (11)	Os(3)–O(31)	3.080 (8)
Os(3)–C(32)	1.945 (10)	Os(3)–O(32)	3.072 (8)
Os(3)–C(33)	1.922 (11)	Os(3)–O(33)	3.062 (8)
Os(3)–C(34)	1.928 (10)	Os(3)–O(34)	3.053 (7)
D. Carbon–Oxygen			
C(11)–O(11)	1.146 (12)	C(23)–O(23)	1.114 (14)
C(12)–O(12)	1.141 (12)	C(31)–O(31)	1.140 (13)
C(13)–O(13)	1.136 (13)	C(32)–O(32)	1.128 (13)
C(21)–O(21)	1.120 (12)	C(33)–O(33)	1.141 (14)
C(22)–O(22)	1.113 (12)	C(34)–O(34)	1.125 (12)
E. Distances within $\mu\text{-NHSO}_2C_6H_4Me$ Ligand			
S–N	1.679 (7)	N–H(1)	0.85 (11)
S–O(1)	1.420 (7)		
S–O(2)	1.434 (6)		
S–C(1)	1.769 (9)		
C(1)–C(2)	1.363 (12)	C(2)–H(2)	0.88 (11)
C(2)–C(3)	1.399 (15)	C(3)–H(3)	0.96 (10)
C(3)–C(4)	1.383 (16)	C(5)–H(5)	0.90 (11)
C(4)–C(5)	1.395 (14)	C(6)–H(6)	0.90 (10)
C(5)–C(6)	1.388 (16)	C(7)–H(7A)	1.04 (13)
C(6)–C(1)	1.370 (15)	C(7)–H(7B)	1.16 (11)
C(4)–C(7)	1.504 (18)	C(7)–H(7C)	0.78 (12)
F. Intramolecular Contacts			
H(1)···O(32)	2.43 (11)	O(1)···O(12)	3.245 (10)
H(1)···C(32)	2.34 (10)	O(1)···O(22)	3.155 (10)
N···O(32)	3.208 (11)	O(1)···C(12)	2.976 (11)
H(br)···C(31)	2.87 (8)	O(1)···C(22)	2.865 (11)
G. Average Distances			
Os–C	1.922 [19][b]	C–H	0.95 [12]
Os–O	3.051 [19]	C–C(phenyl)	1.383 [14]
C–O	1.130 [12]		

[a] Estimated standard deviations of the least significant digit(s) are given in parentheses as calculated from the esd's of the atom parameters. [b] Esd calculated by $[\Sigma(x_i - \overline{x})^2/(n-1)]^{1/2}$.

X on dimensions within $Os(\mu\text{-H})(\mu\text{-X})Os$ bridges have been summarized previously.[1a,b]

The μ_2-hydride ligand was located directly in the present analysis, and its positional parameters were refined. The Os(1)–H(br)–Os(2) angle is 93.5 (34)°, and the individual osmium–hydrogen distances are Os(1)–H(br) = 1.91 (8) Å and Os(2)–H(br) = 1.96 (8) Å.

The $\mu\text{-NHSO}_2C_6H_4Me$ ligand occupies a symmetrically bridging site with Os(1)–N = 2.162 (7) Å, Os(2)–N = 2.145 (7) Å, and Os(1)–N–Os(2) = 81.6 (2)°. The sulfonate group takes up an exo configuration on the nitrogen atom, leaving the N–H system in such an orientation as to permit weak hydrogen bonding with O(32) (see Figure 1). Appropriate dimensions are as follows: N···O(32) = 3.208 (11) Å, N–H(1) = 0.85 (11) Å, H(1)···O(32) = 2.43 (11) Å, N–H(1)···O(32) = 153 (9)°. The substitutents on the nitrogen and sulfur atoms provide an approximately staggered conformation about the N–S bond (cf. Figure 2). The plane of the phenyl group makes an angle of 52.67° with the triosmium system.

The $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-N})$ portion of the molecule has approximate C_s symmetry. It is interesting to note that the equatorial carbonyl ligands do not lie strictly in the triosmium plane but are mainly displaced toward the bridging hydride ligand. Thus, the nitrogen atom lies −1.549 (8) Å and the hydride ligand lies +1.21 (8) Å from the triosmium plane; displacements of oxygen atoms of the equatorial carbonyl ligands are as follows: +0.436 (9) Å for O(22), +0.151 (7) Å for O(12), +0.244 (8) Å for O(33), and −0.019 (8) for O(34). This results from two factors: (i) direct steric interaction of the sulfonate group with some equatorial carbonyl

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(17) Part 2: Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141.

Table V. Intramolecular Angles (Deg) for $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$

A. Os-Os-Os			
Os(1)-Os(2)-Os(3)	60.63 (1)	Os(3)-Os(1)-Os(2)	60.27 (1)
Os(2)-Os(3)-Os(1)	59.10 (1)		
B. Os-Os-C (Cisoid)			
Os(2)-Os(1)-C(11)	120.3 (3)	Os(3)-Os(2)-C(21)	87.4 (3)
-C(12)	113.6 (3)	-C(23)	90.0 (3)
-C(13)	134.9 (3)	Os(1)-Os(3)-C(31)	81.9 (3)
Os(3)-Os(1)-C(11)	89.5 (3)	-C(32)	89.1 (3)
-C(13)	89.9 (3)	-C(34)	101.6 (3)
Os(1)-Os(2)-C(21)	119.3 (3)	Os(2)-Os(3)-C(31)	85.4 (3)
-C(22)	113.4 (3)	-C(32)	86.8 (3)
-C(23)	133.2 (3)	-C(33)	96.7 (3)
C. Os-Os-C (Transoid)			
Os(3)-Os(1)-C(12)	173.4 (3)	Os(1)-Os(3)-C(33)	155.5 (3)
Os(3)-Os(2)-C(22)	171.5 (3)	Os(2)-Os(3)-C(34)	160.7 (3)
D. Os-C-O Angles			
Os(1)-C(11)-O(11)	178.3 (8)	Os(2)-C(21)-O(21)	178.1 (9)
Os(1)-C(12)-O(12)	173.5 (8)	Os(2)-C(22)-O(22)	172.4 (9)
Os(1)-C(13)-O(13)	177.5 (9)	Os(2)-C(23)-O(23)	178.2 (9)
Os(3)-C(31)-O(31)	178.7 (9)	Os(3)-C(33)-O(33)	179.4 (9)
Os(3)-C(32)-O(32)	178.0 (9)	Os(3)-C(34)-O(34)	179.0 (9)
E. C-Os-C			
C(11)-Os(1)-C(12)	92.2 (4)	C(31)-Os(3)-C(32)	170.2 (4)
-C(13)	89.6 (4)	-C(33)	92.9 (4)
C(12)-Os(1)-C(13)	96.5 (4)	-C(34)	92.6 (4)
C(21)-Os(2)-C(22)	91.0 (4)	C(32)-Os(3)-C(33)	93.8 (4)
-C(23)	92.2 (4)	-C(34)	92.9 (4)
C(22)-Os(2)-C(23)	98.4 (4)	C(33)-Os(3)-C(34)	102.6 (4)
F. Os-Os-Bridge			
Os(3)-Os(1)-N	83.0 (2)	Os(3)-Os(1)-H(br)	83.7 (24)
Os(3)-Os(2)-N	83.6 (2)	Os(3)-Os(2)-H(br)	83.1 (23)
G. C-Os-Bridge			
N-Os(1)-C(11)	169.2 (3)	N-Os(2)-C(21)	168.4 (4)
-C(12)	94.4 (3)	-C(22)	96.9 (4)
-C(13)	98.2 (4)	-C(23)	95.1 (4)
H(br)-Os(1)-C(11)	86.3 (24)	H(br)-Os(2)-C(21)	87.3 (23)
-C(12)	90.1 (24)	-C(22)	88.5 (23)
-C(13)	172.4 (24)	-C(23)	173.1 (23)
H. Os-Bridge-Os			
Os(1)-N-Os(2)	81.6 (2)	Os(1)-H(br)-Os(2)	93.5 (34)
I. Other Angles in μ-NHSO$_2$C$_6$H$_4$Me Ligand			
Os(1)-N-S	120.1 (4)	C(5)-C(4)-C(7)	120.4 (10)
Os(2)-N-S	125.3 (4)	C(4)-C(5)-C(6)	120.6 (10)
Os(1)-N-H(1)	105.1 (71)	C(5)-C(6)-C(1)	119.3 (10)
Os(2)-N-H(1)	115.7 (71)	H(2)-C(2)-C(1)	124 (7)
S-N-H(1)	106.3 (71)	-C(3)	116 (7)
N-S-O(1)	108.1 (4)	H(3)-C(3)-C(2)	112 (6)
-O(2)	107.5 (4)	-C(4)	127 (6)
-C(1)	102.5 (4)	H(5)-C(5)-C(4)	111 (7)
O(1)-S-O(2)	119.8 (4)	-C(6)	126 (7)
-C(1)	108.8 (4)	H(6)-C(6)-C(5)	120 (7)
O(2)-S-C(1)	108.8 (4)	-C(1)	120 (7)
S-C(1)-C(2)	120.5 (7)	C(4)-C(7)-H(7A)	108 (7)
-C(6)	118.0 (7)	-H(7B)	106 (6)
C(2)-C(1)-C(6)	121.4 (9)	-H(7C)	109 (10)
C(1)-C(2)-C(3)	119.5 (9)	H(7A)-C(7)-H(7B)	107 (9)
C(2)-C(3)-C(4)	120.3 (10)	-H(7C)	99 (11)
C(3)-C(4)-C(5)	118.8 (9)	H(7B)-C(7)-H(7C)	127 (11)
C(3)-C(4)-C(7)	120.6 (10)	N-H(1)· · ·O(32)	153 (9)

Table VI. Principal Planes (and Atomic Deviations Therefrom) and Torsional and Dihedral Angles in the $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-NHSO}_2C_6H_4Me)$ Molecule[a]

atom	dev, Å	atom	dev, Å
A. Triosmium Plane			
$-0.7737X + 0.5402Y - 0.3310Z + 1.5299 = 0$			
Os(1)*	0.000	C(33)	0.146 (11)
Os(2)*	0.000	O(33)	0.244 (8)
Os(3)*	0.000	C(34)	−0.017 (10)
C(12)	0.079 (10)	O(34)	−0.019 (8)
O(12)	0.151 (7)	N	−1.549 (8)
C(22)	0.210 (10)	H(br)	1.21 (8)
O(22)	0.436 (9)		
B. C_2Os_2N Plane			
$0.7663X + 0.0797Y - 0.6376Z + 1.3398 = 0$			
Os(1)*	0.0000 (3)	Os(3)	2.3345 (3)
Os(2)*	0.0002 (4)		
N*	0.046 (7)		
C(11)*	0.012 (10)	O(11)	0.020 (7)
C(21)*	0.067 (10)	O(21)	0.136 (7)
C. C_2Os_2H Plane			
$0.0219X + 0.5304Y - 0.8475Z + 2.4905 = 0$			
Os(1)*	0.0000 (3)	Os(3)	2.0723 (3)
Os(2)*	0.0000 (3)		
H(br)*	0.21 (7)		
C(13)*	0.036 (10)	O(13)	0.103 (8)
C(23)*	−0.035 (10)	O(23)	−0.057 (8)
D. Phenyl Ring			
$0.0345X + 0.8504Y - 0.5249Z + 3.4435 = 0$			
C(1)*	0.008 (8)	C(7)	−0.073 (13)
C(2)*	−0.001 (9)	S	0.043 (2)
C(3)*	−0.008 (10)	O(1)	0.034 (6)
C(4)*	0.009 (9)	O(2)	−0.942 (6)
C(5)*	−0.002 (11)	N	1.554 (7)
C(6)*	−0.007 (10)		

E. Torsional Angles

atoms	angle, deg	atoms	angle, deg
Os(1)-N-S-C(1)	176.7	N-S-C(1)-C(2)	113.5

F. Dihedral Angles

planes	angle, deg	planes	angle, deg
A/B	109.80	B/C	126.83
A/C	123.37	A/D	52.67

[a] Atoms marked with an asterisk were assigned weights = $1/\sigma^2$. All other atoms were given zero weight in the calculation.
[b] Orthonormal coordinates (Å).

groups (O(1)···C(22) = 2.865 (11) Å, O(1)···(22) = 3.155 (10) Å, O(1)···C(12) = 2.976 (11) Å, O(1)···O(12) = 3.245 (10) Å) and (ii) the smaller cone angle of space taken up by the bridging hydride ligand (vis à vis bridging nitrogen ligand; see Figure 1).

The ten carbonyl groups are in five distinct chemical environments. While the range of osmium–carbonyl distances is relatively small (1.889 (10)–1.945 (10) Å), they can, to some extent, be broken down into classes on the basis of their chemical environment. The shortest pairs are Os(1)–C(11) = 1.889 (10) Å and Os(2)–C(21) = 1.905 (10) Å (trans to N) and Os(1)–C(13) = 1.905 (10) Å and Os(2)–C(23) = 1.912 (11) Å (trans to H); the longest pair, Os(3)–C(31) and Os(3)–C(32) [1.941 (11) and 1.945 (10) Å], involve mutually trans axial carbonyl groups on Os(3); the remaining two pairs [Os(1)–C(12) = 1.932 (9) Å and Os(2)–C(22) = 1.945 (10) Å, Os(3)–C(33) = 1.922 (11) Å and Os(3)–C(34) = 1.928 (10) Å] are trans to osmium atoms. In accordance with this we note that the longest osmium···oxygen distances are Os(3)···O(31) = 3.080 (8) Å and Os(3)···O(32) = 3.072 (8) Å, i.e., those associated with the mutually trans carbonyl groups on Os(3).

Carbon–oxygen distances are all reasonable, ranging from 1.113 (12) to 1.146 (12) Å, and the Os–C–O systems are all close to linear, with angles ranging from 172.4 (9) to 179.4 (9)°.

The presence of two semiaxial bridging ligands across the Os(1)–Os(2) bond causes some asymmetry in the disposition of carbonyl groups within the equatorial plane. Thus, the Os(2)–Os(1)–C(12) and Os(1)–Os(2)–C(22) angles [113.6 (3) and 113.4 (3)°] are some 12–16° larger than the analogous angles at Os(3), i.e., Os(1)–Os(3)–C(34) and Os(2)–Os-

(3)–C(33) [101.6 (3) and 96.7 (3)°].

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Registry No. (μ-H)$Os_3(CO)_{10}$(μ-$NHSO_2C_6H_4Me$), 73017-56-8; (μ-H)$_2Os_3(CO)_{10}$, 41766-80-7; $MeC_6H_4SO_2N_3$, 941-55-9.

Supplementary Material Available: A table of data-processing formulas and a listing of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and University of Illinois, Urbana, Illinois 61801

Synthesis, Crystal Structure, and Dynamic Behavior of Tetra-μ-hydrido-μ-[1,2-bis(diphenylphosphino)ethane]-decacarbonyltetraruthenium, an Isomer of (μ-H)$_4Ru_4(CO)_{10}$(diphos) with a *Bridging* diphos Ligand[1,2]

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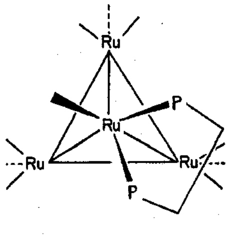
In the presence of trimethylamine oxide the substitution of (μ-H)$_4Ru_4(CO)_{12}$ by 1,2-bis(diphenylphosphino)ethane (diphos) occurs rapidly at room temperature and leads to (μ-H)$_4Ru_4(CO)_{10}$(μ-diphos) as the major product. Upon being heated, this compound (isomer II) rearranges to the previously characterized compound (μ-H)$_4Ru_4(CO)_{10}$(diphos) (isomer I). Isomer II crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 16.845$ (3) Å, $b = 14.644$ (2) Å, $c = 17.469$ (3) Å, $\beta = 116.48$ (1)°, ρ(obsd) = 1.865 (10) g cm^{-3} and ρ(calcd) = 1.872 g cm^{-3} for $V = 3857$ Å^3, mol wt 1086.85, and $Z = 4$. Diffraction data were collected with Mo Kα radiation on a Syntex $P2_1$ diffractometer, and the structure was solved by conventional methods, using the Syntex XTL system. The final discrepancy indices were $R_F = 5.9\%$ and $R_{wF} = 4.6\%$ for those 2446 reflections with $|F_o| > \sigma(F_o)$. All atoms, including the four bridging hydrides, were located directly. Positional parameters of the hydride ligands were refined, the resulting Ru–(μ-H) bond lengths averaging 1.70 ± 0.12 Å and the Ru–(μ-H)–Ru bond angles averaging 124 ± 9°. The hydrido-bridged ruthenium–ruthenium vectors range from 2.923 (2) to 3.048 (2) Å, while the nonhydrido-bridged Ru–Ru bonds are 2.779 (2) and 2.782 (2) Å. The diphos ligand takes up a bridging position between Ru(1) and Ru(2), the two ruthenium–phosphorus bond lengths being 2.356 (4) and 2.335 (5) Å. The (μ-H)$_4Ru_4$ core of the molecule takes up the asymmetric (idealized C_s symmetry) form, as found in (μ-H)$_4Ru_4(CO)_{10}$(diphos) (isomer I), rather than the symmetric (D_{2d}) configuration found in other $H_4Ru_4L_{12}$ species. The hydride ligands in (μ-H)$_4Ru_4(CO)_{10}$(μ-diphos) are fluxional. Complete equilibration is evident at room temperature (τ 27.3, triplet, $J = 3$ Hz). Various stages of the equilibration are observable at lower temperatures, but a static spectrum was not achieved even at −131 °C. Spectral changes below −70 °C can be interpreted in terms of edge-to-edge movement of one hydride ligand ($\Delta G^* = 7.2$ kcal/mol) together with conformational changes in the backbone of the diphos ligand ($\Delta G^* = 9.1$ kcal/mol).

Introduction

We have previously reported the crystal structure and dynamic ^{1}H NMR spectra of (μ-H)$_4Ru_4(CO)_{10}$(diphos).[2,4] The X-ray study showed that the diphos ligand chelates to one ruthenium atom (see I) and that the (μ-H)$_4Ru_4$ core of the molecule adopts configuration III (idealized C_s symmetry) rather than the more symmetrical configuration IV (idealized D_{2d} symmetry) inferred for (μ-H)$_4Ru_4(CO)_{12}$, (μ-H)$_4Ru_4(CO)_{11}[P(OMe)_3]$, and ($\mu$-H)$_4Ru_4(CO)_{10}(PPh_3)_2$.[5] The NMR spectra showed that the hydride ligands scramble over the metal framework, and the spectral changes were interpreted in terms of an edge–terminal–edge scrambling mechanism. The previous compound (I) was prepared from the direct reaction of (μ-H)$_4Ru_4(CO)_{12}$ and diphos at 60 °C. Subsequently, we have found that in the presence of trimethylamine *N*-oxide substitution occurs at 25 °C[6] but that it leads to an isomeric product shown herein to be (μ-H)$_4Ru_4(CO)_{10}$(μ-diphos) (see II). In addition we now report



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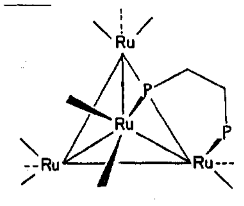

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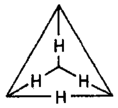

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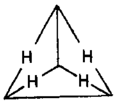

IV

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[1] This article constitutes part 4 of our series "Crystallographic Studies on Ruthenium Carbonyl Hydrides". For the previous contribution, see ref 2.

[2] Part 3: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1950.

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