δ 4.70 (2 H, m, 5, 5′), 4.44 (2 H, m, 10, 10′), 4.14 (2 H, t, J = ~2.5 Hz, 4, 4′), 4.03 (4 H, m, 8, 8′, 9, 9′), 3.95 (2 H, m, 3, 3′), 3.81 (2 H, m, 7, 7′), 3.32 (4 H, dd, J = 16-20 Hz, [1.1] CH_2), 1.25-2.15 (6 H, m, trimethylene CH_2).

3,3′-Trimethylene[1.1]ferrocenophane (IV). The same procedure was followed as for the preparation of III. In a typical experiment, 3.26 g (8.4 mmol) of VIII yielded 0.835 g (23%, maximum obtained was 29%) of IV. Recrystallization by vapor diffusion of hexanes into toluene gave gold leaflets: mp 218 °C dec; NMR (C_6H_6) δ 4.50 (2 H, m, 5, 5′), 4.21 (2 H, m, 10, 10′), 4.13 (4 H, m, 7, 7′, 9, 9′), 4.04 (2 H, m, 8, 8′), 3.88 (2 H, m, 2, 2′), 3.81 (2 H, m, 4, 4′), 3.32 (4 H, s, [1.1] CH_2), 1.81 (6 H, m, trimethylene CH_2).

Acknowledgment. We are indebted to Dr. J. J. Eisch for valuable discussions. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, D.C., under Contract No. DE-AC02-76CH00016.

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Supplementary Material Available: Tables of anisotropic thermal factors, isotropic thermal factors, and calculated and observed structure factors (24 pages). Ordering information is given on any current masthead page.

Reaction of SO_2 with Transition-Metal Hydrides. Synthesis and Structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$

G. D. Jarvinen* and R. R. Ryan

Los Alamos National Laboratory, University of California, Los Alamos, New Mexico 87545

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The reaction of SO_2 with the unsaturated cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ gives the adduct $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$. Crystals of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ are monoclinic of space group $P2_1/n$ with lattice parameters at 203 K of a = 11.503 (2) Å, b = 12.357 (2) Å, c = 12.090 (3) Å, β = 89.51 (1)°, and Z = 4. The molecule consists of a triangular arrangment of osmium atoms with one nonbridged edge (Os-Os = 2.848 (1) Å), one edge bridged by a hydride (Os-Os = 3.068 (1) Å), and the third edge bridged by a hydride and the SO_2 (Os-Os = 2.895 (1) Å). The structure of the SO_2 complex is closely related to that of the methylene complex $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}CH_2)$.

Introduction

The reduction of SO_2 with hydrogen-containing compounds over heterogeneous catalysts is used in a number of industrial processes whose importance is certain to increase with increased use of fossil fuels. Although to date there has been only limited attention given to the reduction of SO_2 mediated by transition-metal complexes, it is likely that the study of such systems will lead to an enhanced understanding of the mechanistic aspects of SO_2 reduction and may indeed lead to homogeneous catalysts. Transition-metal complexes containing SO_2 and hydride ligands would be likely intermediates in the reduction process. Since the first hydrido SO_2 complexes were described by Levison and Robinson in 1972,[1] only two such compounds have been characterized by X-ray crystal structures[2,3] and rather few reactions of metal hydrides with SO_2 have been reported.[4-7]

Our recent investigations of the reactions between transition-metal hydride complexes and SO_2 have produced several new systems that show interesting reactivity. The reaction of SO_2 with $(\mu\text{-H})_2Os_3(CO)_{10}$ was chosen for study because this unsaturated cluster has been shown to form adducts with a considerable number of Lewis bases[8] and to transfer hydrogen to unsaturated ligands in certain cases.[9] In addition, new bonding modes have been observed for SO_2 in multimetal systems[10] and others are likely to be found. We report here on the initial adduct formed between SO_2 and $(\mu\text{-H})_2Os_3(CO)_{10}$.

Experimental Section

All preparations were carried out under a nitrogen or SO_2 atmosphere. Osmium carbonyl was purchased from Strem Chemicals, Newburyport, MA, and used to prepare $H_2Os_3(CO)_{10}$ by a published procedure.[11] Infrared spectra were recorded on

(1) Levison, J. J.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1972**, 2013-17.
(2) Angoletta, M.; Bellon, P. L.; Manassero, M.; Sansoni, M. *J. Organomet. Chem.* **1974**, *81*, C40-C42.
(3) Ryan, R. R.; Kubas, G. J. *Inorg. Chem.* **1978**, *17*, 637-41.
(4) (a) Ghatak, I.; Mingos, D. M. P.; Hursthouse, M. B.; Abdul Malik, K. M. *Transition Met. Chem. (Weinheim, Ger.)* **1979**, *4*, 260-4. (b) Eliades, T. I.; Harris, R. O.; Zia, M. C. *J. Chem. Soc., Chem. Commun.* **1970**, 1709.
(5) Reed, J.; Soled, S. L.; Eisenberg, R. *Inorg. Chem.* **1974**, *13*, 3001-5.
(6) Komiya, S.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 784-7.
(7) The formation of $Fe_3S_2(CO)_9$ from acidified solutions of $HFe(CO)_4^-$ and SO_3^{2-} first reported by Hieber and Gruber may well involve intermediate hydrido SO_2 species. Hieber, W.; Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91-103.
(8) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304-10.
(9) (a) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056-7. (b) Jackson, W. G.; Johnson, B. F. G.; Kelland, J. W.; Lewis, J.; Schorpp, K. T. *J. Organomet. Chem.* **1975**, *87*, C27-C30. (c) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1975**, 1614-20. (d) Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *J. Am. Chem. Soc.* **1975**, *97*, 7172-4. (e) Laing, M.; Sommerville, P.; Dawoodi, Z.; Mays, M. J.; Wheatley, P. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1035-6. (f) Adams, R. D.; Golembeski, N. M. *J. Am. Chem. Soc.* **1979**, *101*, 2579-87.
(10) (a) Briant, C. E.; Theobald, B. R. C.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 963-5. (b) Briant, C. E.; Hughes, G. R.; Minshall, P. C.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *224*, C21-C24. (c) Kubas, G. J.; Jarvinen, G. D.; Ryan, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 1883-91.
(11) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942-7.
(12) (a) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014-18. (b) Templeton, L. K.; Templeton, D. H., Abstracts, American Crystallographers Associations Summer Meeting, Storrs, Conn., June 1973; No. E10.
(13) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Table 2.2A. Cromer, D. T. *Ibid.*, Table 2.3.1.

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Table I. Crystal Data and Collection Methods

space group	$P2_1/n$
a, Å	11.503 (2)
b, Å	12.357 (2)
c, Å	12.090 (3)
β, deg	89.51 (1)
cell refinement	12 high order reflections
temp, °C	−70
intensities	4613 measured; 4309 for which $I \geq 2\sigma(I)$
cryst morphology developed planes; dist from origin	(010), 0.035 mm; ($\bar{1}$11), 0.035; (101), 0.165
abs coeff, cm^{-1}	236
transmission (max, min)[12]	0.268, 0.212
scattering factors	neutral atom for all atoms[13]
diffractometer and counting technique	Picker FACS-I, Lenhert's disk operating system,[14] Wang encoders, graphite monochromater, 3.5° takeoff angle, (1.5 + dispersion) continuous scans, 20 s symmetric background counts, and Mo Kα radiation (λ = 7093 Å)

a Perkin-Elmer 683 and NMR spectra were recorded on a Varian EM390 or a Brüker WM300 wide bore spectrometer.

Preparation of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$. Solutions of $H_2Os_3(CO)_{10}$ in acetone, chloroform, benzene, toluene, and heptane when stirred under an SO_2 atmosphere react at a rate roughly proportional to the solubility of SO_2 in the solvent. At room temperature in acetone the $H_2Os_3(CO)_{10}$ had disappeared in about 1 h while more than 48 h were required in heptane. While NMR spectra indicate a 80–90% yield of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ in SO_2-saturated acetone after 1 h, a pure crystalline product has only been obtained to date by reacting $H_2Os_3(CO)_{10}$ and SO_2 in heptane/acetone mixtures. In a typical preparation, 247.1 mg of $H_2Os_3(CO)_{10}$ (0.290 mmol) was dissolved in a mixture of 2 mL of acetone (dried by distillation from P_2O_5) and 35 mL of heptane. A stream of SO_2 was passed through the purple solution for 5 min, after which the solution was left unstirred under an SO_2 atmosphere. Yellow crystals began to form on the flask wall after 1 h. Overnight the solution became a clear bright yellow, and a small amount of yellow powdery material was deposited along with the crystals. The crystals were isolated by decanting the solution, washing with 3 × 3 mL of 18:1 heptane/acetone, and 2 mL of heptane, and vacuum drying. The yield was 76.1 mg of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ (29%). The solid is soluble in acetone, slightly soluble in chloroform, dichloromethane, benzene, and toluene, and insoluble in heptane and tetrahydrofuran: IR (Nujol) ν(CO) 2143 (m), 2113 (s), 2080 (s), 2059 (s), 2050 (s), 2037 (s), 2026 (s), 2007 (s), 1991 (s) cm^{-1}, ν(SO) 1176 (s), 1035 (s) cm^{-1}; ^1H NMR ($CDCl_3$, shifts relative to $CHCl_3$ at δ 7.24) δ −14.52 (d), −19.11 (d, J_{H-H} = 0.9 Hz). Anal. (Galbraith Laboratories, Inc.) Calcd for $C_{10}H_2O_{12}SOs_3$: C, 13.10; H, 0.22, S, 3.50. Found: C, 13.23; H, 0.23; S, 3.56. In the solid probe of the mass spectrometer the compound decomposes upon heating to 100–150 °C and peaks are observed corresponding to $Os_3(CO)_{12}$ and SO_2.

Crystals suitable for a crystal structure determination were grown by dissolving 52.6 mg of $H_2Os_3(CO)_{10}$ in a mixture of 4:1 heptane/acetone that was saturated with SO_2 at 0 °C. The solution was warmed slowly to room temperature over 3 h. After 2 h at room temperature the flask was placed in the freezer (−20 °C) overnight. About 4 mg of crystals were obtained.

Additional Products from the Reaction of $H_2Os_3(CO)_{10}$ and SO_2. The complex $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ is the first product observed by NMR or IR spectroscopy from the reaction of $H_2Os_3(CO)_{10}$ and SO_2, but additional products form at rates dependent on variables such as the solvent and SO_2 concentration. The μ-SO_2 complex is itself unstable in solution, yielding a number of products. Characterization of these additional species is in progress.

(14) Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–70.

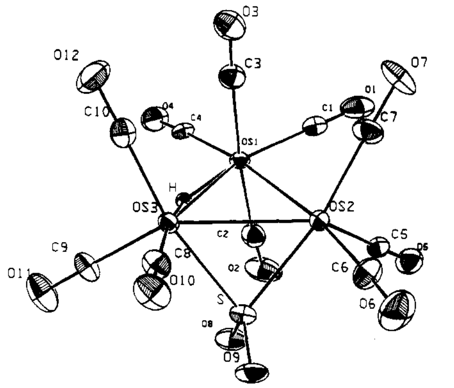

Figure 1. ORTEP plot of the $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ molecule with thermal ellipsoids scaled to 50% probability.

X-ray Measurements and Refinements. Pertinent information concerning the cell, crystal morphology, and intensity measurements is given in Table I. Two standard reflections, measured after every 50 intensity measurements, showed no sign of crystal degradation. The variance for F^2 was estimated from the formula $\sigma^2(F^2) = \sigma_c^2(F^2) + \sigma_n^2X(F^2)^2$ where $\sigma_c^2(F^2)$ is the variance due to accounting statistics, F^2 is the squared structure factor averaged over equivalent reflections, and σ_n^2 is taken to be 0.015.

The function minimized in the least-squares refinements was $\sum w(F_o - F_c)^2$ where $w = 4F_o^2/\sigma^2(F^2)$ and F_c includes a correction for secondary extinction.[15]

The structure was determined by standard Patterson and Fourier methods. Full-matrix least-squares methods were carried out by using the LANL system of crystal structure codes.[16] The position of one of the two hydrogen atoms was determined from Fourier difference maps (ρ_0 = 0.8 e/Å^3); refinements of the structure giving increased weight to the high angle data followed by difference maps failed to locate the second hydrogen atom. Refinements carried out with anisotropic thermal parameters for all atoms except for the hydrogen atom converged to an unweighted *R* value of 3.6% and a weighted *R* value of 4.0%. Final difference Fourier maps contained no peaks for which $\rho \geq 0.5$ e/cm^3.

Final atom positions and selected distances and angles are listed in Tables II and III, respectively.

Results

Purple solutions of $(\mu\text{-H})_2Os_3(CO)_{10}$ in various organic solvents turn yellow upon exposure to excess SO_2 at a rate roughly proportional to the solubility of SO_2 in the solvent. The first product that has been detected by IR or NMR spectroscopy has been isolated and found to have the composition $H_2Os_3(CO)_{10}(SO_2)$. The ^1H NMR data (δ −14.52 (d), −19.11 (d, J_{H-H} = 0.9 Hz)) suggest the presence of two bridging hydrides since all previously reported 1:1 adducts of $(\mu\text{-H})_2Os_3(CO)_{10}$ with simple Lewis bases contain one terminal hydride at δ −9 to −11 and one bridging hydride at δ −15 to −21.[8] However, the reaction of ethylene with $(\mu\text{-H})_2Os_3(CO)_9L$ (L = PPh_3 or PPh_2Et) appears to yield ethylene adducts with one terminal hydride (δ −14.31 and −14.20, respectively) and one bridging hydride (δ −20.33 and −19.89) where the terminal hydride resonance is in the "bridging" region.[17] To better define the nature of the bonding in the adduct, a single-crystal X-ray diffraction study was undertaken.

The molecular structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ is shown in Figure 1. The crystal contains discrete molecules

(15) (a) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558–64. (b) Larson, A. C. *Ibid.* **1967**, *23*, 664–5.

(16) Larson, A. C. Abstracts, American Crystallographers Association Proceedings, 1977.

(17) Brown, S. C.; Evans, J. *J. Chem. Soc., Dalton Trans.* **1982**, 1049–54.

Table II. Fractional Coordinates and Thermal Parameters[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Os(1)	0.88057 (3)	0.21458 (3)	0.55189 (3)	C(1)	0.8640 (8)	0.1079 (8)	0.6678 (7)
O(1)	0.8514 (6)	0.0456 (6)	0.7345 (6)	C(2)	0.8760 (8)	0.0969 (8)	0.4427 (8)
O(2)	0.8833 (8)	0.0212 (6)	0.3919 (6)	C(3)	0.8747 (8)	0.3271 (8)	0.6673 (8)
O(3)	0.8688 (7)	0.3883 (6)	0.7343 (6)	C(4)	1.0523 (7)	0.2147 (7)	0.5466 (7)
O(4)	1.1478 (6)	0.2085 (6)	0.5397 (6)	Os(2)	0.63450 (3)	0.22961 (3)	0.53294 (3)
C(5)	0.6245 (7)	0.0766 (7)	0.5375 (7)	O(5)	0.6229 (6)	−0.0162 (5)	0.5401 (6)
C(6)	0.4726 (7)	0.2590 (8)	0.5029 (8)	O(6)	0.3792 (6)	0.2769 (7)	0.4810 (7)
C(7)	0.6161 (9)	0.2534 (8)	0.6911 (8)	O(7)	0.6017 (7)	0.2668 (7)	0.7828 (6)
S(1)	0.6678 (2)	0.2456 (2)	0.3408 (2)	O(8)	0.7375 (6)	0.1655 (5)	0.2798 (5)
O(9)	0.5622 (6)	0.2776 (6)	0.2807 (5)	Os(3)	0.76566 (3)	0.39520 (3)	0.41732 (3)
C(8)	0.6428 (8)	0.4885 (7)	0.3707 (7)	O(10)	0.5671 (6)	0.5411 (6)	0.3454 (6)
C(9)	0.8569 (8)	0.4249 (8)	0.2867 (7)	O(11)	0.9105 (7)	0.4395 (7)	0.2098 (6)
C(10)	0.8344 (8)	0.5076 (8)	0.5088 (8)	O(12)	0.8787 (7)	0.5731 (6)	0.5613 (6)
H(1)	0.8734 (71)	0.2911 (67)	0.4479 (69)				

[a] Anisotropic thermal parameters are published as supplementary data except for H(1), B = 0.9 (17) Å^2.

Table III. Selected Distances (Å) and Angles (deg)

(a) Distances					
Os(1)-Os(2)	2.848 (1)	Os(1)-C(3)	1.97 (1)	Os(3)-C(8)	1.91 (1)
Os(1)-Os(3)	3.068 (1)	Os(1)-C(4)	1.98 (1)	Os(3)-C(9)	1.92 (1)
Os(2)-Os(3)	2.895 (1)	Os(2)-C(5)	1.89 (1)	Os(3)-C(10)	1.95 (1)
Os(1)-H	1.57 (8)	Os(2)-C(6)	1.93 (1)	Os(3)-S	2.358 (2)
Os(3)-H	1.82 (8)	Os(2)-C(7)	1.94 (1)	S-O(8)	1.468 (6)
Os(1)-C(1)	1.93 (1)	Os(2)-S	2.360 (2)	S-O(9)	1.474 (6)
Os(1)-C(2)	1.96 (1)				
(b) Angles about Os(1)					
Os(2)-Os(1)-Os(3)	58.46 (1)	Os(3)-Os(1)-C(1)	147.2 (3)	H-Os(1)-C(4)	92 (3)
Os(2)-Os(1)-H	81 (3)	Os(3)-Os(1)-C(2)	99.7 (3)	C(1)-Os(1)-C(2)	88.8 (4)
Os(2)-Os(1)-C(1)	90.6 (3)	Os(3)-Os(1)-C(3)	81.4 (3)	C(1)-Os(1)-C(3)	88.0 (4)
Os(2)-Os(1)-C(2)	87.8 (3)	Os(3)-Os(1)-C(4)	114.7 (2)	C(1)-Os(1)-C(4)	96.7 (4)
Os(2)-Os(1)-C(3)	89.0 (3)	H-Os(1)-C(1)	169 (3)	C(2)-Os(1)-C(3)	175.5 (4)
Os(2)-Os(1)-C(4)	172.5 (2)	H-Os(1)-C(2)	85 (3)	C(2)-Os(1)-C(4)	90.6 (4)
Os(3)-Os(1)-H	28 (3)	H-Os(1)-C(3)	98 (3)	C(3)-Os(1)-C(4)	92.9 (4)
(c) Angles about Os(2)					
Os(1)-Os(2)-Os(3)	64.58 (1)	S-Os(2)-C(5)	97.0 (3)	C(6)-Os(2)-C(7)	93.4 (4)
Os(1)-Os(2)-S	86.08 (5)	S-Os(2)-C(6)	87.0 (3)	Os(3)-Os(2)-S	52.13 (5)
Os(1)-Os(2)-C(5)	89.6 (2)	S-Os(2)-C(7)	166.2 (2)	Os(3)-Os(2)-C(5)	138.6 (3)
Os(1)-Os(2)-C(6)	170.5 (3)	C(5)-Os(2)-C(6)	97.7 (4)	Os(3)-Os(2)-C(6)	106.0 (3)
Os(1)-Os(2)-C(7)	91.8 (3)	C(5)-Os(2)-C(7)	96.7 (4)	Os(3)-Os(2)-C(7)	114.8 (3)
(d) Angles about Os(3)					
Os(1)-Os(3)-Os(2)	56.97 (1)	Os(2)-Os(3)-S	52.17 (5)	S-Os(3)-C(10)	168.4 (3)
H-Os(3)-Os(2)	24 (3)	Os(2)-Os(3)-C(8)	100.7 (3)	H-Os(3)-C(8)	171 (3)
Os(1)-Os(3)-S	81.20 (5)	Os(2)-Os(3)-C(9)	144.1 (3)	H-Os(3)-C(9)	86 (3)
Os(1)-Os(3)-C(8)	156.6 (3)	Os(2)-Os(3)-C(10)	116.2 (3)	H-Os(3)-C(10)	96 (3)
Os(1)-Os(3)-C(9)	109.9 (3)	S-Os(3)-H	82 (3)	C(8)-Os(3)-C(9)	92.4 (4)
Os(1)-Os(3)-C(10)	92.2 (3)	S-Os(3)-C(8)	90.0 (3)	C(8)-Os(3)-C(10)	92.4 (4)
Os(2)-Os(3)-H	76 (3)	S-Os(3)-C(9)	95.0 (3)	C(9)-Os(3)-C(10)	96.2 (4)
(e) Angles about Sulfur and H					
Os(2)-S-Os(3)	75.70 (6)	Os(3)-S-O(8)	117.7 (3)	O(8)-S-O(9)	112.5 (4)
Os(2)-S-O(8)	121.4 (3)	Os(3)-S-O(9)	112.4 (3)	Os(1)-H-Os(3)	129 (5)
Os(2)-S-O(9)	112.3 (3)				

of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ separated by normal van der Waals distances. The structure of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ is closely analogous to that determined for $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}CH_2)$[18] allowing for replacement of the bridging methylene by the larger bridging SO_2. A triangular arrangement of osmium atoms forms the framework of the molecule, and each osmium atom has a distorted octahedral coordination geometry if direct Os(1)–Os(3) and Os(2)–Os(3) bonds are not included. The edges of this triangle have either no bridging ligands [Os(1)–Os(2)], a bridging hydride [Os(1)–Os(3)], or a bridging hydride and SO_2 [Os(2)–Os(3)]. Only the hydride bridging Os(1) and Os(3) was located and refined. It appears to bridge in an unsymmetrical manner [Os(1)–H = 1.83 (8) Å and Os(3)–H = 1.58 (8) Å] although the difference in bond lengths is just over 2σ, 0.25 (11). The corresponding bridging hydride in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}CH_2)$ is unsymmetrical in the same fashion with the shorter Os–H distance to the osmium atom coordinated to four carbonyl ligands. The osmium-bridging hydride distances are consistent with the more precise values obtained by neutron diffraction studies of other triosmium clusters, 1.845 (3) Å (av) in $(\mu\text{-H})_2Os_3(CO)_{10}$,[19] 1.754 (8) and 1.883 (9) Å and 1.834 (11) and 1.808 (10) Å in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}CH_2)$,[18] and 1.813 (4) and 1.887 (4) Å in $(\mu\text{-H})Os_3(CO)_{10}(\sigma,\pi\text{-}CH{=}CH_2)$.[20] The somewhat smaller average Os–H distance of 1.71 Å for $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-}SO_2)$ may reflect the tendency of M–H distances

(18) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. *Inorg. Chem.* **1979**, *18*, 319–23.

(19) Broach, R. W.; Williams, J. M. *Inorg. Chem.* **1979**, *18*, 314–9.

(20) Orpen, A. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *Acta Crystallogr., Sect B* **1978**, *B34*, 2466–72.

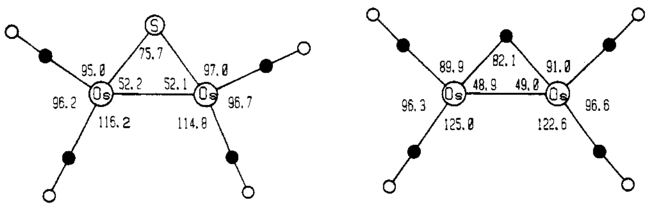

Figure 2. Comparison of the structures of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-L})$ (L = SO_2, left; L = CH_2, right) in the plane containing the doubly bridged Os atoms and the bridging S or C atom (angles in degrees). Open circles are oxygen atoms, and filled circles are carbons.

as determined by X-ray diffraction to be smaller than those determined by neutron diffraction.[21] The monobridged Os–Os distance is 0.220 (1) Å longer than the nonbridged distance. This compares with a 0.198 (3)-Å difference in the corresponding Os–Os bonds of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$. Such variations in M–M distances have been described in the literature for other hydrido–trimetal clusters.[22,23] The hydride lies 0.48 Å "below" the Os_3 plane on the same side of the triangle as the SO_2 ligand. The carbonyls trans to the hydride [C(1)–O(1) and C(8)–O(10)] are correspondingly "above" the Os_3 plane (0.39 and 0.25 Å for C(1) and C(8), respectively).

The arrangement of the carbonyl ligands about Os(2) and Os(3) is typical of triosmium clusters with a $(CO)_3Os(\mu\text{-H})(\mu\text{-X})Os(CO)_3$ bridge.[24] Thus the approximate position of the hydride bridging Os(2) and Os(3) is trans to both C(5) and C(9). Comparing the carbonyl geometry around Os(2) and Os(3) with the corresponding positions in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ shows that substituting SO_2 for methylene "rotates" the carbonyls that are roughly in the Os(2)–S–Os(3) plane away from the larger S atom and toward the bridging hydride (Figure 2). The variation of Os–CO distances is very similar to that found in the $\mu\text{-CH}_2$ complex.

The Os(2)–S–Os(3) bridge makes an angle of 105.9° with the Os_3 plane and is symmetrical within experimental error [Os(2)–S = 2.360 (2) Å; Os(3)–S = 2.358 (2) Å]. These Os–S distances are 0.04–0.06 Å smaller than those found for the Os(μ-H)(μ-S)Os bridges in $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-SEt})$ of 2.40 (1) Å,[25] in $(\mu\text{-H})Os_3(CO)_9(C_2H_4)(\mu\text{-SMe})$ of 2.402 (7) Å,[26] and in $[(\mu\text{-H})Os_3(CO)_{10}]_2(\mu\text{-SCH}_2\text{S-}\mu)$ of 2.421 (5) and 2.412 (6) Å.[27] This presumably reflects the smaller covalent radius of the relatively electron-deficient sulfur atom in SO_2 compared with the sulfur atoms of the EtS^-, MeS^-, and $CH_2S_2^{2-}$ ligands. A similar decrease in metal-bridging sulfur distance of about 0.06 Å was observed by Balch and co-workers upon oxidation of the bridging sulfide in $Pd_2(dpm)_2Cl_2(\mu\text{-S})$ to give a bridging SO_2 in $Pd_2(dpm)_2Cl_2(\mu\text{-SO}_2)$ [dpm = bis(diphenylphosphino)methane].[28]

The S–O bond lengths [1.468 (6) and 1.474 (6) Å] are equal within experimental error and are typical of $\mu\text{-SO}_2$ ligands.[29] The SO_2 plane makes an angle of 92.8° with the Os_3 plane and 88.6° with the Os(2)–S–Os(3) plane. The structural data suggest some steric interaction between O(8) and the carbonyl C(2)–O(2). The C(2)–O(8) distance of 2.681 (11) Å is somewhat less than the sum of the van der Waals radii of about 3.0 Å. The Os(1)–C(2)–O(2) angle of 169.3 (8)° is well outside the range of the remaining Os–C–O angles of 175–178°. Also there is significant asymmetry in the Os–S–O angles that could be explained by a repulsion between O(8) and C(2)–O(2) that distorts the coordination geometry about the sulfur atom: ∠Os(2)–S–O(8) = 121.4 (3)° and ∠Os(3)–S–O(8) = 117.7 (3)° vs. ∠Os(2)–S–O(9) = 112.3 (3)° and ∠Os(2)–S–O(9) = 112.4 (3)°.

Discussion

The complex $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-SO}_2)$ provides the first example of simple adduct formation between $(\mu\text{-H})_2Os_3(CO)_{10}$ and a two-electron donor ligand that does not yield the usual product containing bridging and terminal hydrides, with the donor ligand bound in an axial or equatorial position. The structurally similar cluster $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ does not result from simple adduct formation but from the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ and diazomethane that gives $(\mu\text{-H})Os_3(CO)_{10}(\mu\text{-CH}_3)$ as the first observed product.[30] Some of the factors that enter into the preference of the SO_2 adduct for a $(\mu\text{-H})_2(\mu\text{-SO}_2)$ configuration can be suggested. The SO_2 bridge can accommodate a considerable range of M–M distances from 2.6 to 3.9 Å (M–M single to no bond)[29] and thus can probably bridge the Os–Os bond more readily than the other donor ligands that have been used to form simple adducts with $(\mu\text{-H})_2Os_3(CO)_{10}$, e.g., CO, CNR, NCR, pyridines, PR_3, $P(OR)_3$, AsR_3, SbR_3, and X^-. (The halide anions are excellent bridging ligands but act as four-electron donors in that situation.) Also, a qualitative MO picture of the bonding in $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-CH}_2)$ that includes a four-center, six-electron $Os_2(\mu\text{-H})(\mu\text{-C})$ bond[18] can be used for the $\mu\text{-SO}_2$ complex. In this simple model donation of electron density into the π^* LUMO of SO_2 does not occur through the filled d_{xy}, d_{xz}, and d_{yz} orbitals that participate in back-bonding to the CO ligand. Thus, the competition between the CO ligands and SO_2 for π-electron density would be reduced relative to the case of the isomeric complex where the SO_2 ligand would be coordinated in the η^1-planar or η^2-bonding modes to a single $Os(CO)_3$ group.

The determination of the structures of $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-L})$ (L = CH_2, SO_2) allows only the second direct comparison of the effects of substituting a bridging SO_2 for a bridging methylene. Herrmann and co-workers noted the close similarities in the structures in the series $(\mu\text{-L})[\eta^5\text{-C}_5H_5)Rh(CO)]_2$ (L = CH_2, CO, SO_2.)[31] As in the Rh complexes, the osmium clusters show only small differences that can be largely attributed to the greater size of the $\mu\text{-SO}_2$ ligand relative to bridging methylene. This is perhaps not surprising, since the MO picture of SO_2 bonding in the η^1-planar and bridging forms is very similar to that of terminal and bridging carbenes.[29,32]

The ^1H NMR data suggest that $(\mu\text{-H})_2Os_3(CO)_{10}(\mu\text{-SO}_2)$ retains the observed solid-state molecular structure in solution. However, the $\mu\text{-SO}_2$ complex reacts over a period

(21) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1–82.
(22) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878–84. (b) Churchill, M. R.; DeBoer, B. G. *Ibid.* **1977**, *16*, 2397–403.
(23) (a) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R. *Acta Crystallogr. Sect. B* **1978**, *B34*, 3767–70. (b) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R.; Sheldrick, G. M.; Rouse K. D. *J. Chem. Soc., Dalton Trans.* **1979**, 616–18.
(24) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1580–84.
(25) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297–307.
(26) Johnson, B. F. G.; Lewis, J.; Pippard, D.; Raithby, P. R. *Acta Crystallogr., Sect. B* **1980**, *B36*, 703–5.
(27) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 546–55.
(28) Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996–3003.
(29) Ryan, R. R.; Kubas, G. J.; Moody, D. C.; Eller, P. G. *Struct. Bonding (Berlin)* **1981**, *46*, 47–100.
(30) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225–26.
(31) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Wülknitz, P. *Chem. Ber.* **1981**, *114*, 716–26.
(32) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585–91.

of hours to give a number of products depending on factors such as concentration, solvent, and temperature. Study of these additional species is in progress in the hope of observing intermediates in the reduction of coordinated SO_2.

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Supplementary Material Available: A table of anisotropic thermal parameters and a listing of calculated and observed structure factors (19 pages). Ordering information is given on any current masthead page.

Communications

Alkyne Insertion Reactions in Nickel Acyl Complexes. Occurrence of a 1,2-Trimethylphosphine Shift and the X-ray Structures of $Ni[C(Ph){=}C(H)(COCH_2SiMe_3)]Cl(PMe_3)_2$ and $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$

Ernesto Carmona,*[1a] Enrique Gutiérrez-Puebla,[1b] Angeles Monge,[1b] José M. Marín,[1a] Margarita Paneque,[1a] and Manuel L. Poveda[1a]

Departamento de Química Inorgánica, Facultad de Química Universidad de Sevilla, Sevilla, Spain Instituto de Química Inorgánica Elhuyar C.S.I.C., Serrano 113, Madrid and Departamento de Química, Facultad de Químicas Universidad Complutense, Madrid-3, Spain

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Summary: The facile formation of $Ni[C(Ph){=}C(H)(COR)]Cl(PMe_3)_2$ complexes (R = CH_3 (**1a**), CH_2SiMe_3 (**1b**), CH_2CMe_3 (**1c**), and CH_2CMe_2Ph (**1d**)) by insertion of PhC≡CH into the Ni—COR bond of the corresponding $NiCl(COR)(PMe_3)_2$ derivatives is reported. Complex **1d** reversibly rearranges in solution to yield the nickelacyclopropane complex $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMe_2Ph)]Cl(PMe_3)$, **2**, which contains a novel ketoylidic ligand. The X-ray structures of **1b** and **2** are also reported.

The insertion of unsaturated hydrocarbons into transition metal–carbon bonds is at present the subject of much academic and industrial research.[2] Recent elegant studies by Bergman et al.[3] have shown that the insertion of alkynes into the Ni–C bond of $Ni(acac)CH_3(PPh_3)$ takes place by a concerted cis addition process, with a reversible 1,3 dissociative shift of PPh_3 being suggested for the formation of trans addition products. In this paper we wish to communicate the facile formation of vinyl ketone complexes $Ni[C(Ph){=}C(H)(COR)]Cl(PMe_3)_2$ (R = CH_3 (**1a**), CH_2SiMe_3 (**1b**), CH_2CMe_3 (**1c**), CH_2CMe_2Ph (**1d**)) (in which the Ni center attains five-coordination by virtue of a strong interaction with the oxygen atom) by insertion of PhC≡CH into the Ni–COR bond of the corresponding *trans*-$Ni(COR)Cl(PMe_3)_2$ complexes.[4,5] In addition, with the reversible conversion of **1d** into $Ni[C(Ph)(PMe_3)C(H)(COCH_2CMePh)]Cl(PMe_3)$, **2**, which contains a novel ketoylidic ligand, we demonstrate that the 1,2 reversible shifts of phosphine ligands (see Scheme I) operate in systems related to those investigated by Bergman.[3] The X-ray crystal structures of **1b** and **2** are also reported.

The above acyls undergo a smooth reaction[6] with PhC≡CH to afford moderate yields (ca. 40–50%) of the vinyl complexes **1a–d**.

$$trans\text{-}NiCl(COR)(PMe_3)_2 \xrightarrow{PhC\equiv CH} trans\text{-}(Z)\text{-}NiCl[C(Ph){=}CH(COR)](PMe_3)_2$$

1a, R = CH_3
1b, R = CH_2SiMe_3
1c, R = CH_2CMe_3
1d, R = CH_2CMe_2Ph

The reactions are highly regio- and stereoselectives and seem to yield only the trans *Z* derivatives as indicated above. The new compounds are red crystalline solids that are moderately stable to air and soluble in common organic solvents. Spectroscopic data[7] are in accord with the proposed formulations. It is noteworthy to point out that the IR spectra of complexes **1** show ν(C–O) at ca. 1600 cm^{-1} (ca 40–50 cm^{-1} lower than in the parent acyls), suggesting that a change in the coordination mode of the acyl group

(1) (a) Universidad de Sevilla. (b) Instituto de Química Inorgânica Elhúyar y Universidad Complutense de Madrid.

(2) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; Kelly, A., Ed.; University Science Books: Mill Valley, CA, 1980.
(3) Huggings, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3002.
(4) (a) Carmona, E.; González, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2108. (b) Carmona, E.; Paneque, M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *Polyhedron* **1984**, *3*, 317.
(5) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 2524.

(6) To a stirred solution of $NiCl(COCH_2R)(PMe_3)_2$ (1.5 mmol) in a 2:1 Et_2O–acetone mixture (25 mL), was added an excess of PhC≡CH (ca. 0.2 mL) via syringe. After the mixture was stirred overnight at room temperature, the volatiles were removed in vacuo and the residue was extracted with Et_2O (30 mL). The resulting solution was centrifuged and the volume partially reduced until incipient crystallization. Cooling at −30 °C afforded the complexes **1a–c** (see ref 11 for **1d**) as red crystals, which were washed with petroleum ether and dried in vacuo; yield ca. 50%.

(7) For example, for **1b**: ^{1}H NMR (250 MHz, C_6D_6) δ 0.33 (s, 9 H, CH_2SiMe_3), 1.00 (pt, $J_{PH(app)}$ = 4 Hz, 18 H, PMe_3), 2.32 (s, 2 H, CH_2SiMe_3), 6.76 (t, $^4J_{PH}$ = 5.2 Hz, 1 H, C(Ph)=CH), 7.24 (m, 3 H, *m*-H and *p*-H of C_6H_5 group), 8.40 (d, $^3J_{HH}$ = 8.3 Hz, 2 H, *o*-H of C_6H_5 group); IR (Nujol mull, cm^{-1}) 1600 (ν(CO)), 1490 (ν(C=C)); molecular weight (crioscopically in C_6H_6, N_2), calcd for $C_{19}H_{35}OP_2ClSiNi$ 464, found 425. Anal. Calcd for $C_{19}H_{35}OP_2ClSiNi$: C, 49.2; H, 7.5. Found: C, 48.8; H, 7.5.

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