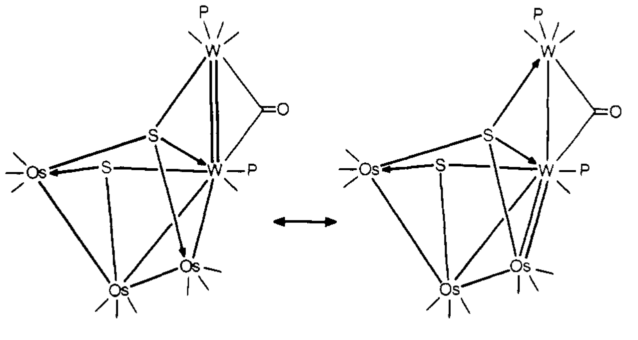
and 4 is that they employ different bonding mechanisms. 2 utilizes a delocalized bonding mechanism (PSEP theory) and 4 utilizes a localized bonding mechanism (i.e., all bonds are of a two-center-two-electron type). Except for this difference in the structures of the clusters the only difference between 2 and 4 is in the identity of one of the ligands. 4 contains PMe_2Ph in place of one of the carbonyl ligands (e.g., C(11)–O(11) in Figure 1). It is not possible at this time to prove which factors are most responsible for the change in structure, but both steric and electronic effects could be important. Most simply, the substitution of a bulky phosphine for a carbonyl ligand should lead to enhanced ligand–ligand nonbonded repulsions. These might be sufficiently large in 4 that they cannot be offset by the formation of the additional metal–metal bond. Electronically, the replacement of a poorly electron-donating CO ligand by a good donor like phosphine would lead to an increase in the electron density on the tungsten atom. This could lead to a strengthening of the tungsten–osmium bonds, perhaps at the expense of the osmium–osmium bonds, and one of the latter is then broken. All of the metal–metal bonds in 4 are shorter than the corresponding bonds in 2, but the greatest contractions are for those which involve metal atoms which have lower coordination numbers as a result of the bond cleavage. Although it is electron precise, 4 does add CO to yield 3. Unfortunately, it is not possible to compare accurately the relative rates of CO addition to 2 and 4 because the addition of CO to 2 leads to degradation of the cluster, but the rates must be somewhat similar because the CO addition to 4 and the CO degradation of 2 seem to occur at similar rates.

When irradiated in the presence of $W(CO)_5PMe_2Ph$, 2, adds a second tungsten-containing moiety across one of its tungsten–sulfur bonds. 5 appears to possess an unusual electronic structure since there are not enough ligands in the complex to allow all the metal atoms to achieve 18-electron configurations. Eighteen-electron configurations could be achieved by employing a metal–metal double bond and assuming that the quadruply bridging sulfido ligand serves as a 6-electron donor. The resonance structures 5A and 5B could be viable representations of its bonding and would explain the observed shortening of the indicated tungsten–osmium and tungsten–tungsten bonds. The pentaosmium cluster $HOs_5(CO)_{13}(\mu\text{-}PhNC_6H_4N)$ is also unsaturated by the amount of 2 electrons and shows a selective shortening of two of the osmium–osmium bonds to 2.60 Å.[24] In spite of its apparent unsaturation, we have not been successful in performing ligand additions to 5.



5A 5B

In all of the new compounds 2–5 the tungsten atoms are bonded to one or more of the bridging sulfido ligands. It is, thus, believed that the sulfido ligands play a key role in their stabilization and probably an important role in directing their synthesis as well.

Acknowledgment. This research was supported by the National Science Foundation. NMR studies were supported by Grant CHE-7916210 to the Northeast Regional NSF-NMR Facility from the National Science Foundation. We thank Engelhard Industries for a loan of osmium tetroxide.

Registry No. 1, 72282-40-7; 2, 87802-46-8; 3, 87802-47-9; 4, 91781-16-7; 5, 91781-17-8; $W(CO)_5(PMe_2Ph)$, 42565-94-6; W, 7440-33-7; Os, 7440-04-2.

Supplementary Material Available: Tables of structure factor amplitudes for the structural analyses of compounds 4 and 5 and tables of thermal parameters and hydrogen atom coordinates for each structure (34 pages). Ordering information is given on any current masthead page.

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A Molecule Containing the OWOWO Unit. Synthesis, Structure, and Spectroscopy of $W_2O_3(CH_2CMe_3)_6$

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Abstract: Addition of excess water to $W(CCMe_3)(CH_2CMe_3)_3$ yields pentane-soluble, water- and air-stable $W_2O_3(CH_2CMe_3)_6$ (1). Anhydrous HCl reacts with 1 in the presence of Me_3SiCl to produce $WONp_3Cl$ (2). $W_2O_3(CH_2CMe_3)_6$ crystallizes in the trigonal system, space group $R\bar{3}$, with a = 10.232 (2) Å, c = 61.446 (9) Å, V = 5571.1 Å^3, and Z = 6. The molecule, which has crystallographically imposed C_3 symmetry, contains a linear O=W—O—W=O unit in which three neopentyl groups are trigonally disposed about each tungsten atom. The W=O bond lengths are 1.726 (10) and 1.689 (13) Å, the W(μ-O) distances are 1.923 (10) and 1.977 (10) Å, and the independent W—C bond lengths are 2.141 (9) and 2.127 (14) Å. The two ends of the molecule are twisted by 31.9 (5)° with respect to one another. Spectroscopic examination of 1 (and [^{18}O]1) showed two IR active bands at 962 (905) (w) and 693 (668) (s) cm^{-1} and two Raman active bands at 942 (894) (s) and 205 (205) (m) cm^{-1} that we assign to the asymmetric W=O stretch, the asymmetric W—O—W stretch, the symmetric W=O stretch, and the symmetric W—O—W stretch, respectively. The calculated force constants are comparable to those reported for several rhenium(V) complexes containing a linear O=Re—O—Re=O backbone.

There is considerable evidence that, in many catalysts consisting of an early transition-metal deposited on silica or alumina, the catalytically active site contains the metal in its highest possible oxidation state (d^0).[1] In order to understand this chemistry better and to utilize spectroscopy to characterize such catalysts it is desirable to prepare and study homogeneous analogs of the catalytically active site. One such analogue is an oxo alkyl complex.[2]

Recently we reported that the addition of water to $W(CCMe_3)(CH_2CMe_3)_3$ and $W(CCMe_3)(OCMe_3)_3$ produced the air- and water-stable complexes $W_2O_3Np_6$ (**1**) ($Np = CH_2CMe_3$) and $[NEt_4][WO_3Np]$.[3] The infrared spectrum of **1** was unusual for its lack of strong bands in the 800–1000 cm^{-1} region where terminal metal–oxo stretching frequencies usually occur. It did have an intense broad band centered at 693 cm^{-1}, however. A preliminary X-ray structural study of **1**[3] revealed the relatively rare linear O═W—O—W═O fragment, the only one known for a d^0 complex. Since few vibrational analyses of related O═M—O—M═O species have been carried out,[4] we decided to investigate the infrared and Raman spectra of **1** and its ^{18}O-substituted analogue. Here we describe the results of this vibrational analysis, along with the preparation and some related chemistry of **1**, and a complete X-ray structural study of **1**.

Experimental Section

$W(CCMe_3)(CH_2CMe_3)_3$ was prepared by addition of $W(OMe)_3Cl_3$ to 6 equiv of NpMgCl and kept under nitrogen up to the hydrolysis step. $W_2O_3Np_6$ was handled in the air. $WONp_3Cl$ was handled under nitrogen to avoid hydrolysis to give $W_2O_3Np_6$. Isotopically substituted $[^{18}O]H_2O$ (99% pure) was purchased from Stohler Isotopes.

Preparation of $W_2O_3(CH_2CMe_3)_6$ (1). $W(CCMe_3)Np_3$ (4.0 g, 8.6 mmol) was dissolved in tetrahydrofuran (~30 mL) in a septum-stoppered 100-mL round-bottomed flask. A large excess of H_2O (~15 mL, ~833 mmol) was thoroughly degassed with nitrogen and then rapidly added via a syringe. A brownish orange color developed immediately but quickly lightened. A large amount of white crystalline precipitate was observed after ~20 min. After 1.5 h the white precipitate was filtered off and dried in vacuo to give 3.2 g (90%) of pure $W_2O_3Np_6$. This compound can be recrystallized from pentane at −30 °C to yield nicely formed colorless crystals: ^1H NMR (C_6D_6) δ 1.98 (s, 2, CH_2CMe_3), 1.31 (s, 9, CMe_3); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 91.89 (t, $J_{CW} = 93$ Hz, CH_2CMe_3), 35.42 (s, $J_{CW} = 48$ Hz, CMe_3), 32.90 (q, CMe_3); FD mass spectrum, M + 1 ion at *m/e* 843. Anal. Calcd for $W_2C_{30}H_{66}O_3$: C, 42.77; H, 7.90. Found: C, 42.76; H, 7.73.

Preparation of $WONp_3Cl$ (2). $W_2O_3Np_6$ (0.5 g, 0.59 mmol) was dissolved in pentane (~20 mL), and trimethylsilyl chloride (45 μL, 1.18 mmol) and an ethereal HCl solution (1.87 M, 0.63 mL, 1.18 mmol) were added. The reaction was stirred overnight at room temperature. Activated charcoal was added, and the mixture was filtered through Celite. The filtrate was concentrated and cooled to −30 °C to give 0.41 g (~77%) of colorless crystals: ^1H NMR (C_6D_6) δ 2.5 (s, 2, CH_2CMe_3), 1.14 (s, 9, CH_2CMe_3); ^{13}C NMR (C_6D_6) δ 101.1 (CH_2CMe_3), 36.8 (CH_2CMe_3), 32.5 (CH_2CMe_3); IR (Nujol) 972 cm^{-1} ($\nu_{W=O}$).

Preparation of $W_2O_3Np_6$ from $WONp_3Cl$. $WONp_3Cl$ (0.07 g, 0.16 mmol) was dissolved in a minimal amount of tetrahydrofuran (~2 mL). Excess water (0.85 mL, 48 mmol) was added rapidly. Immediately a white granular precipitate formed that was filtered off and dried in vacuo (0.025 g, 40%). The product was identified as $W_2O_3Np_6$ by its NMR spectrum.

Preparation of ^{18}O Labeled Compounds. The $[^{18}O]W_2O_3Np_6$ derivative was prepared as described above for the unlabeled compound from 0.2 g of $W(CCMe_3)Np_3$ in 5 mL of THF and 1 g of $[^{18}O]H_2O$. The yield was 0.115 g (65%). FAB mass spectroscopy showed it to be ~97% $[^{18}O]W_2O_3Np_6$.

$[^{18}O]WONp_3Cl$ was prepared as described for the unlabeled compound from 0.115 g of $[^{18}O]W_2O_3Np_6$ in 15 mL of pentane, Me_3SiCl (34.5 μL, 0.28 mmol), and an ethereal solution of HCl (2.5 M, 1.12 mL, 2.8 mmol): yield 51%.

Table I. Experimental Details of the X-ray Diffraction Study of $W_2O_3(CH_2CMe_3)_6$ (**1**)

(A) Crystal Parameters[a]

a, Å	10.232 (2)	*Z*	6
c, Å	61.446 (9)	ρ(calcd), g cm^{-3}	1.505
V, $Å^3$	5571.1	ρ(obsd),[b] g cm^{-3}	1.49 (1)
space group	$R\bar{3}$	mol wt	841.57

(B) Measurement and Treatment of Intensity Data[c]

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: MoKα ($\lambda_\alpha = 0.71073$ Å) graphite monochromatized
temp: 25 °C
standards, measd every 1 h:[d] $(\bar{1},\bar{1},\bar{1}\bar{2})$, $(\bar{4},0,\bar{1}\bar{6})$, $(\bar{1},\bar{1},\bar{1}\bar{8})$
no. of reflctns collected: 2373, 3° ≤ 2θ ≤ 30° ($-h,+k,\pm l$) and 30° ≤ 2θ ≤ 45° ($-h,+k,+l$)

(C) Treatment of Intensity Data[e]

linear abs coeff, cm^{-1}	59.3	no. of reflctns after averaging	1611
transmissn factors[f]	0.24–0.33	obsd unique data $[F_o > 6\sigma(F_o)]$	1290
average, R_{av}[c]	0.019		

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta \geq 25°$. [b] By flotation in an aqueous solution of KI. [c] See: Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 3379 for typical procedures. [d] Showed an average decay of 10.2% per 1000 reflections. [e] F_o and $\sigma(F_o)$ were corrected for background, attenuation, and Lorentz–polarization effects of X radiation as described in *c*. [f] Absorption corrections were performed with the Wehe–Busing–Levy ORABS program.

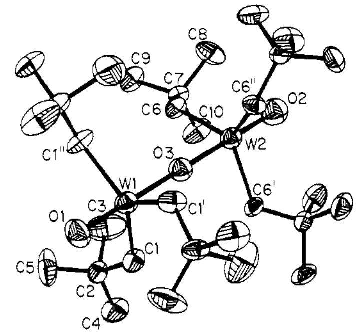

Figure 1. Structure of **1** showing the 40% probability thermal ellipsoids for the tungsten and oxygen atoms and the 25% probability ellipsoids for the carbon atoms.

Collection and Reduction of X-ray Data for 1. A colorless crystal was mounted on a glass fiber. It had approximate dimensions 0.22 mm × 0.27 mm × 0.30 mm, bounded by the faces (001), $(00\bar{1})$, (012), $(1\bar{1}\bar{2})$, $(\bar{1}02)$, $(10\bar{2})$, $(\bar{1}1\bar{2})$, $(1\bar{1}2)$. The quality of the crystal was examined by taking open counter ω scans of several intense low angle reflections and was found to be acceptable ($\Delta\bar{\omega}_{1/2} \approx 0.2°$). Intensity data and the unit cell parameters were measured with a single crystal diffractometer as described in Table I. The unit cell obtained was rhombohedral with the parameters $a = 21.317$ (2) Å and $\alpha = 27.773$ (3)°. Transformation to the obverse hexagonal setting yielded the following parameters: $a = 10.232$ (2) Å, $c = 61.446$ (9) Å. A preliminary study on the diffractometer was undertaken in order to verify the *R* centering, determine the Laue group, and examine the feasibility of collecting data with Mo Kα radiation (in view of the long *c* axis). The *R* centering was clearly evident from the systematic absences $-h + k + l \neq 3n$. Examination of the intensity data pointed to the Laue group $\bar{3}$ $[F(hkl) \neq F(khl)]$. With the *R* centering condition, no overlap between peaks was observed. Therefore, data were collected in the hexagonal setting with the condition $-h + k + l = 3n$ using Mo Kα radiation. The space group could be either *R*3 (C_3^4, No. 146) or $R\bar{3}$ (C_{3i}^2, No. 148).[5] Density measurements indicated that $Z = 6$ and pointed to the space group $R\bar{3}$. This choice was confirmed by statistical analysis of the data as well as by successful solution and refinement of the structure.

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(1) (a) Yermakov, Y. I. *Catal. Rev. Sci. Eng.* **1976**, *13*, 77. (b) Ballard, D. G. H. *Adv. Catal.* **1973**, *23*, 263. (c) Iwasawa, Y.; Hamamura, H. *J. Chem. Soc. Chem. Commun.* **1983**, 130.

(2) (a) d^0 Oxo alkyl complexes are rare. The list includes $[V(O)(CH_2SiMe_3)_3]$,[2b] $[ReO_2Me_3]$,[2c] $[ReO_3Me]$,[2d] $[MoO_3Me]^-$ (and analogues, observed in solution[2e]), and $[WO_3(CH_2CMe_3)]^-$ (isolated[3]). (b) Mowat, W.; Shortland, A.; Yagupsky, G.; Hill, N. J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 532. (c) Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488. (d) Beattie, I. R.; Jones, P. L. *Inorg. Chem.* **1979**, *18*, 2318. (e) Schrauzer, G. N.; Hughes, L.; Strumpach, N. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 380.

(3) Feinstein-Jaffe, I.; Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 7176.

(4) (a) Rowbottom, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972**, 826. (b) Cotton, F. A.; Robinson, W. R.; Walton, R. A. *Inorg. Chem.* **1967**, *6*, 223. (c) Howard-Lock, H. E.; Lock, C. J. L.; Turner, G. *Spectrochim. Acta, Part A* **1982**, *38A*, 1283. (d) Jezowska-Trzebiatowska, B.; Hanuza, J.; Baluka, M. *Spectrochim. Acta, Part A* **1971**, *27A*, 1753.

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Table II. Final Positional Parameters for $W_2O_3(CH_2CMe_3)_6$ (**1**)[a]

ATOM	X	Y	Z
W1	0.0000	0.0000	0.285520(10)
W2	0.0000	0.0000	0.222040(10)
O1	0.0000	0.0000	0.31362(17)
O2	0.0000	0.0000	0.1945(2)
O3	0.0000	0.0000	0.25334(17)
C1	0.1558(13)	0.2377(12)	0.2847(2)
C2	0.3162(12)	0.3103(12)	0.2921(2)
C3	0.391(2)	0.262(2)	0.2715(4)
C4	0.3996(15)	0.4811(14)	0.2879(3)
C5	0.3622(19)	0.2517(19)	0.3102(3)
C6	0.1776(11)	-0.0502(12)	0.22446(17)
C7	0.3042(11)	-0.0080(11)	0.20828(16)
C8	0.2360(16)	-0.1044(17)	0.1870(2)
C9	0.4147(14)	-0.0570(16)	0.2175(2)
C10	0.3846(14)	0.1575(14)	0.2019(3)

[a] Atoms are labeled as shown in Figures 1 and 2. Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter.

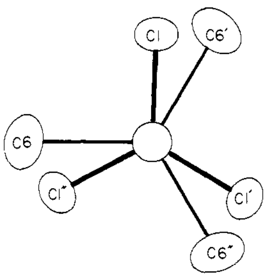

Figure 2. View of **1** looking down the threefold axis depicting the 31.9° staggering of the equatorial ligands.

Table III. Interatomic Distances (Å) and Angles (deg) for $W_2O_3(CH_2CMe_3)_6$ (1)[a]

Coordination Spheres			
W1 - O1	1.726(10)	W2 - O2	1.689(13)
W1 - O3	1.977(10)	W2 - O3	1.923(10)
W1 - C1	2.141(9)	W2 - C6	2.127(14)
O1 - W1 - O3	180	O2 - W2 - O3	180
O1 - W1 - C1	91.4(3)	O2 - W2 - C6	94.0(3)
O3 - W1 - C1	88.6(3)	O3 - W2 - C6	86.0(3)
C1 - W1 - C1'	119.94(3)	C6 - W2 - C6'	119.52(7)
Torsion (Dihedral) Angle			
C1 - W1 - W2 - C6'	31.9(5)		
Ligand Geometry[b]			
C1 - C2	1.49(2)	C6 - C7	1.51(2)
C2 - C3	1.67(3)	C7 - C8	1.58(2)
C2 - C4	1.54(2)	C7 - C9	1.56(2)
C2 - C5	1.45(2)	C7 - C10	1.52(2)
W1 - C1 - C2	124.5(8)	W2 - C6 - C7	126.7(7)
C1 - C2 - C3	100.0(11)	C6 - C7 - C8	108.5(5)
C1 - C2 - C4	111.3(12)	C6 - C7 - C9	108.9(9)
C1 - C2 - C5	122.0(10)	C6 - C7 - C10	113.3(12)
C3 - C2 - C4	97.8(10)	C8 - C7 - C9	105.5(12)
C3 - C2 - C5	99.7(15)	C8 - C7 - C10	108.0(10)
C4 - C2 - C5	119.1(11)	C9 - C7 - C10	112.2(9)

[a] See footnote *a* (Table II). Distances have not been corrected for thermal motion. [b] Atoms C3 and C5 were not well-behaved in the refinement and may be slightly disordered.

Solution and Refinement of the Structure. The tungsten atoms were located by using the direct methods program MULTAN.[6] All the remaining nonhydrogen atoms were located in subsequent difference maps. Neutral atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were obtained from ref 7. Anisotropic thermal parameters were used for all non-hydrogen atoms. The hydrogen atoms were not located in the difference Fourier maps nor were they placed in their calculated positions.

Using SHELX-76,[8] full-matrix, least-squares refinement was carried out on 106 variable parameters. The refinement converged at $R_1 = 0.0301$ and $R_2 = 0.0337$.[9] Unit weights were used. The maximum parameter shift in the final cycle of refinement was 0.005σ, and the largest peak on the final difference map (0.79 e Å^{-3}) was located at a distance of 1.94 Å from C2 and 1.97 Å from C5 (see labeling scheme, Figure 1). The remaining peaks were all less than 0.51 e Å^{-3}.

Final non-hydrogen atom positional parameters, together with their estimated standard deviations, appear in Table II. Interatomic distances and angles, with estimated standard deviations, are given in Table III. Listings of final observed and calculated structure factors and anisotropic thermal parameters are available in Tables S1 and S2, supplied as supplementary material. Figure 1 depicts the molecular geometry along with the atom labeling scheme, and Figure 2 shows a view down the threefold axis demonstrating the degree of staggering of the neopentyl ligands.

Spectroscopic Studies. Raman spectra were obtained on solid samples in spinning capillaries by using a back-scattering configuration. Laser excitation at 560 nm with 40 mW of power incident at the sample was provided by a Coherent Radiation Model CR-599 Dye laser using rhodamine 560 and a Model 591 utility module. The Dye laser was pumped with a Coherent Radiation Model 52 tunable argon ion laser set for all lines. Spectra were recorded by using a Spex double monochromator equipped with a cooled RCA 31034 photomultiplier tube and photon counting electronics. Slits were set to 200/250/200 μm. Spectra were recorded on a Linear Instruments Corp. chart recorder.

Infrared spectra were obtained by using a Nicolet 7199 Fourier transform spectrometer on samples prepared as KBr pellets.

Results and Discussion

Syntheses. White, pentane-soluble $W_2O_3Np_6$ (**1**) is prepared in high yield by adding a large excess of water to $W(CCMe_3)(CH_2CMe_3)_3$ dissolved in tetrahydrofuran. If only 1 or 2 equiv of water are added, **1** is obtained in poor yield and much starting material remains. Although in the initial stage of the hydrolysis a brown color develops, no intermediates were observed by NMR methods. $[^{18}O]W_2O_3Np_6$, which spectral analyses showed to be at least 97% pure, was prepared similarly. A plausible mechanism for the formation of **1** in this reaction can be found in the preliminary communication of these results.[3]

$W_2O_3Np_6$ reacts with 2 equiv of dry HCl in pentane in the presence of 2 equiv of Me_3SiCl to give white, volatile $WONp_3Cl$ (**2**) in high yield. In the absence of Me_3SiCl an equilibrium between **1** and **2** (plus H_2O) is established. $WONp_3Cl$ was identified by comparing its NMR spectrum with those previously reported[10a] and by elemental analysis.[10b] In contrast to the published mass spectral report,[10a] the highest mass ion we observed by conventional mass spectroscopy was the parent less a chloride. A reaction, similar to that described above, between $[^{18}O]W_2O_3Np_6$ and HCl yielded $[^{18}O]WONp_3Cl$ with isotopic purity of ~83%, according to its mass spectrum.

$WONp_3Cl$ reacts with H_2O in the presence of NEt_3 to give $W_2O_3Np_6$ in high yield. In the absence of NEt_3 a large excess (>300-fold) of water must be employed in order to drive the equilibrim toward **1**. When $[^{18}O]WONp_3Cl$ was treated with an excess of $[^{16}O]H_2O$ the product was exclusively $[^{16}O]W_2O_3Np_6$. But since ^{18}O in $[^{18}O]W_2O_3Np_6$ itself rapidly exchanges in the presence of excess $[^{16}O]H_2O$ to give $[^{16}O]W_2O_3Np_6$, we do not know whether $^{16}O/^{18}O$ exchange occurs during or exclusively after formation of $W_2O_3Np_6$. We suspect that $^{16}O/^{18}O$ exchange is rapid at all stages.

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(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(8) SHELX-76: Sheldrick, G. M. In "Computing in Crystallography"; Schenck, H.; Olthof-Hazekamp, R.; van Koningsveld, H., Bassi, G. C.; Eds.; Delft University Press: Delft, The Netherlands, 1978; pp 34–42.

(9) $R_1 = \sum w||F_o| - |F_c||/\sum|F_o|$; $R_2 = |\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$.

(10) (a) Kress, J. R. M.; Russell, J. H.; Wesolek, M. G.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 431. (b) Calcd for $WC_{15}H_{33}ClO$: C, 40.15; H, 7.41; Cl, 7.90. Found: C, 40.40; H, 7.34; Cl, 8.22.

Table IV. Geometric Comparison of O═M—O—M═O Moieties[a]

compd	M-O$_t$, Å	M-O$_b$, Å	M-O-M, deg	O-M-O, deg	staggering angle, deg	ref
$Re_2O_3(py)_4Cl_4$	1.764 (16) 1.715 (16)	1.903 (16) 1.943 (16)	174.5 (9)	165.5 (7) 172.8 (7)	~23	13
$Re_2O_3(S_2CNEt_2)_4$	1.723 (7) 1.721 (7)	1.917 (5) 1.903 (5)	175.5 (3)	177.9 (3) 173.8 (3)	~40	14
$[Pt(NH_3)_4]_2[Re_2O_3(CN)_8]$	1.698 (7)	1.9149 (4)	180	179.5 (8)	0	15
$Re_2O_3(en)_2Cl_4$	1.666 (47)	1.912 (5)	180	172.9 (16)	0	16
$W_2O_3(CH_2CMe_3)_6$	1.726 (10) 1.689 (13)	1.977 (10) 1.923 (10)	180	180	31.9 (5)	this work

[a] Numbers in parentheses are estimated standard deviations.

We were interested in the possibility that **1** might react with NpMgCl to give $W(CCMe_3)(CH_2CMe_3)_3$. Although addition of 6 equiv of NpMgCl to **1** in ether produces an orange solution from which an orange oil is obtained upon removal of all solvents, only traces of $W(CCMe_3)(CH_2CMe_3)_3$ could be sublimed out of the oil at 70 °C and 1 μm pressure. Also, the orange residue remaining after sublimation was no longer soluble in common solvents. Previously we had no success at preparing $W(CCMe_3)(CH_2CMe_3)_3$ from $WO(OCMe_3)_4$, $WOCl_4$, or WO_2Cl_2.[11a] The present results further imply that the presence of the oxo group is a significant problem. The mechanism of forming $W(CCMe_3)(CH_2CMe_3)_3$ from $W(OMe)_3Cl_3$ and 6 equiv of NpMgCl therefore almost certainly does not involve formation of a tungsten oxo complex. The proposal[11a] that the crucial intermediate is $W(OMe)_2Cl_2(CH_2CMe_3)_2$ still seems most plausible.

We briefly explored the possibility that α-hydrogen abstraction reactions of **1** might be induced by heat or light. Irradiation of **1** in C_6H_6 with a medium-pressure Hg lamp resulted only in extensive decomposition. Although neopentane was formed, no major organometallic products appeared in the ^1H NMR spectrum of the photolyzed sample. $W_2O_3Np_6$ is quite stable thermally, decomposing only at ~180 °C in the solid state at 1 atm to unidentifiable products. The failure to generate neopentylidene or neopentylidyne complexes from **1** by thermally or photochemically induced α-hydrogen abstraction reactions is not totally surprising in view of the sensitive balance of factors that encourage α-abstraction[11b] and the suspected retardation of such reactions by alkoxide or oxo ligands in place of chloride or alkyl ligands.[11a]

Molecular Structure of $W_2O_3(CH_2CMe_3)_6$ (1). Figure 1 displays the geometry of **1**; interatomic distances and angles are given in Table III. The molecule consists of two $WO(CH_2CMe_3)_3$ units joined by a μ-oxo group. The two tungsten and the three oxygen atoms lie on a crystallographic threefold axis and the entire O═W—O—W═O unit is therefore linear. The coordination geometry of each tungsten center is trigonal bipyramidal. The two W═O bond lengths are 1.726 (10) and 1.689 (13) Å, the W(μ-O) bond lengths are 1.923 (10) and 1.977 (10) Å, and the W–C bond lengths are 2.141 (9) Å for W(1)–C(1) and 2.127 (14) Å for W(2)–C(6). The two ends of the molecule are neither staggered nor eclipsed but are twisted with respect to one another, the C(1)–W(1)–W(2)–C(6′) torsion angle being 31.9 (5)° (Figure 2).

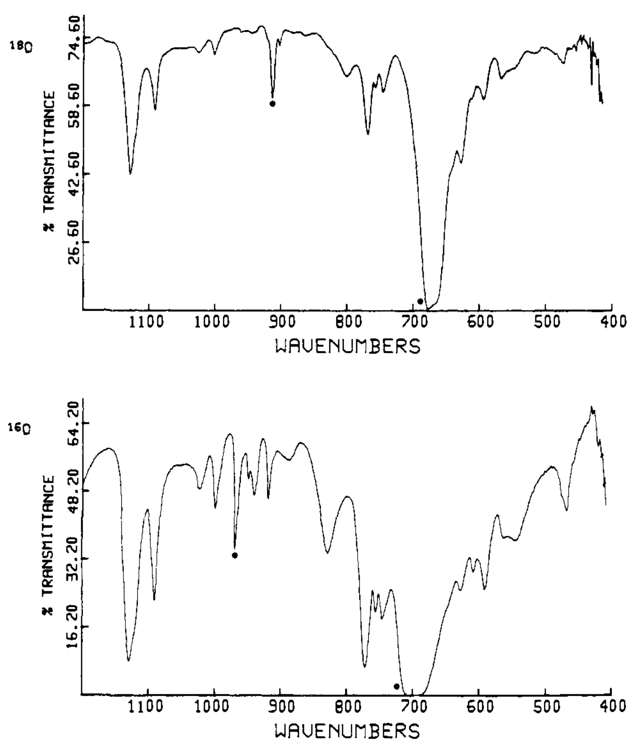

Figure 3. Low-frequency portions of the infrared spectra of (bottom) **1** and (top) [^{18}O]**1**. Asterisks denote the peaks that change upon isotopic substitution.

To our knowledge $W_2O_3Np_6$ is the only example of a molecule containing the linear O═M—O—M═O unit in whiich M has a d^0 configuration. Several d^2 rhenium complexes have been structurally characterized in which there are linear or nearly linear O═Re—O—Re═O units.[12-16] Selected structural parameters for these compounds are compared with those for **1** in Table IV. As can be seen from the table, both the bridging (M—O) and terminal (M═O) bond lengths in **1** compare favorably with the corresponding distances in the rhenium complexes. The short terminal bond distances, ~1.7 Å, reflect considerable O → M multiple-bond character involving donation of the p$_\pi$ electrons on oxygen into the empty π (xz, yz) orbitals on the metal centers.[17] The M–O bridge bond lengths of 1.90–1.98 Å are longer than those observed for $[W_2OCl_{10}]^{4-}$, 1.871 (1) Å, or $[W_4O_8Cl_8(H_2O)_4]^{2-}$, 1.856 (1) Å,[19] both of which have a linear Cl–W–O–W–Cl unit. This difference is due to the structural trans influence of the terminal W═O bonds[17,19,20] and would probably be even greater if the chloride complexes contained hexavalent tungsten rather than W(IV) or W(V).

The degree of overlap between the π-donor orbitals of the μ-oxo group and the d acceptor orbitals on tungsten (d_{xz} and d_{yz} if the O═M—O—M═O axis is taken to be the z axis) is independent of the twist angle between the two ends of the molecule. In the two compounds in which the μ-oxo ligand lies on a center of symmetry the twist angle is 0° while in the other two compunds the twist angles are 23° (in $Re_2O_3py_4Cl_4$) and 40° (in Re_2O_3-

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[11] (a) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645. (b) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.

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Table V. Comparison of Observed and Calculated Vibrational Frequencies (cm^{-1}) for **1** and [^{18}O]**1**

mode		^{16}O obsd	^{16}O calcd	^{18}O obsd	^{18}O calcd	force const, mdyn/Å
$M{=}O(\nu_s)$	Raman active	942	943	894	894	$k_r = 7.87$, $k_{rr} = -0.13$
$M{=}O(\nu_{as})$	IR active	962	959	905	909	
$MOM(\nu_s)$	Raman active	205	205	same as ^{16}O		$k_R = 3.38$, $k_{RR} = 1.17$
$MOM(\nu_{as})$	IR active	693	700	668	661	

$(S_2CNEt_2)_4)$. As expected, there is no obvious correlation between the bond lengths and twist angles.

Spectroscopic Studies. Since initially the infrared spectrum of **1** did not seem consistent with a linear O═W—O—W═O fragment, we undertook a simple vibrational analysis of **1**. A similar analysis was recently applied to the four structurally characterized complexes containing the analogous O═Re—O—Re═O units.[4c]

The vibrational analysis of **1** was simplified by making two basic assumptions. The first is that vibrations of the neopentyl group couple negligibly with those of the linear W_2O_3 unit. This postulate seems reasonable since (i) the metal-carbon bonds lie in a plane that is perpendicular to the O═W—O—W═O axis and (ii) the vibrations in the rest of a neopentyl group are both physically removed and likely to be quite different in frequency from the metal-oxygen vibrations. The second assumption is that the W═O and W—O—W vibrations are also not strongly coupled. Support for this assumption comes from the work on rhenium systems in which force constants for the Re═O stretches were found to be at least twice those for the Re—O stretches.[4c]

Four stretching vibrations are expected for the linear M_2O_3 system. With the above assumptions in mind, these can be described as symmetric and asymmetric terminal oxo stretches and symmetric and asymmetric $W_2(\mu\text{-oxo})$ stretches. Both symmetric vibrations transform as A_1 under the D_3 symmetry of **1**[21] and are therefore only Raman allowed. The two asymmetric stretches transform as A_2 under D_3 symmetry and are therefore only infrared allowed. The simplified secular equations for these four vibrations[22] are shown in eq[23] 2–4. An additional assumption

$$A_1\ M{=}O \quad \lambda_s = (\mu_M + \mu_O)(k_r + k_{rr}) \quad \text{Raman allowed} \tag{1}$$

$$A_2\ M{=}O \quad \lambda_{as} = (\mu_M + \mu_O)(k_r - k_{rr}) \quad \text{IR allowed} \tag{2}$$

$$A_1\ M\text{-}O\text{-}M \quad \lambda_s = (\mu_M)(k_R + k_{RR}) \quad \text{Raman allowed} \tag{3}$$

$$A_2\ M\text{-}O\text{-}M \quad \lambda_{as} = (\mu_M + 2\mu_O)(k_R - k_{RR}) \quad \text{IR allowed} \tag{4}$$

needed to derive these equations is that the interaction force constant k_{rR} between the W═O and $W_2(\mu\text{-}O)$ bond stretches is negligible. Studies of the analogous rhenium systems revealed that the derived force constants were insensitive to small deviations of k_{rR} from zero.[4c]

The infrared spectrum of **1** is shown in Figure 3a and that for [^{18}O]**1** in Figure 3b. The 962 cm^{-1} peak shifts to 905 cm^{-1} in the spectrum of [^{18}O]**1**, and the strong peak at 693 cm^{-1} shifts to 668 cm^{-1}. Since the 962 cm^{-1} peak is in the region where a W═O stretch would be expected, we assign it to the asymmetric W═O stretch. The much stronger 693 cm^{-1} peak is assigned to the asymmetric $W_2(\mu\text{-oxo})$ stretch. Although we have no good explanation for the fact that the 962 cm^{-1} peak is so weak, we can point to similar findings in other systems. For example, in the infrared spectrum of $Re_2O_3(en)_2Cl_4$ the Re═O stretch is much weaker than it is in $ReOCl_3(en)$.[4d] In the published spectrum of $Re_2O_3(py)_4Cl_4$ there is a relatively weak peak at 970 cm^{-1}, which was assigned as the asymmetric Re═O stretch.[4b] The spectra of the $M_2O_3(CN)_8^{6-}$ ions, M = Mo and W, also show weak IR bands at 940 cm^{-1} assigned to $\nu_{as}(M{=}O)$.[24] Finally, in complexes containing tetrapyrrole ligands and the O═M—O—M═O unit (M = Nb, Mo, W, Re) only peaks between 630 and 690 cm^{-1} were reported; evidently the terminal M═O stretches, if present in the IR spectra, were not recognized as such by the authors.[12]

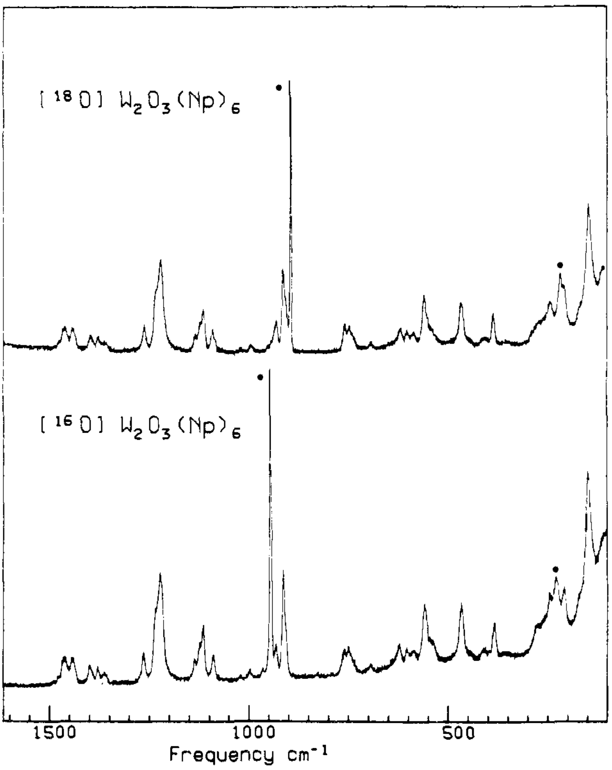

Figure 4. Raman spectra of (bottom) **1** and (top) [^{18}O]**1**. Asterisks denote the peaks that change upon isotopic substitution.

The Raman spectra of **1** and [^{18}O]**1** are shown in parts a and b, respectively, of Figure 4. As in the infrared spectra, there are two peaks that shift upon isotopic substitution. The large peak at 942 cm^{-1}, which shifts to 894 cm^{-1}, is clearly the symmetric W═O stretch. Since the symmetric $W_2(\mu\text{-oxo})$ stretch is not expected to shift with isotopic substitution (note the absence of the mass of oxygen in eq 3), the peak at 225 cm^{-1} that shifts to 217 cm^{-1} cannot be assigned to the stretch. It must be assigned as a bending mode of the O═W—O—W═O chain.

Equations 1 and 2 may be used to calculate the force constants for the terminal oxo stretches. Since four frequencies are available to calculate two force constants, the results using different data were averaged. The value of the frequencies of the symmetric and asymmetric terminal oxo stretches calculated from the constants are shown in Table V. Good agreement between calculated and observed values was obtained by using the average force constants k_r = 7.84 mdyn/Å and k_{rr} = −0.13 mdyn/Å. The stretching force constant compares well with those of the linear O═Re—O—Re═O systems in which k_r = 7.70–8.91 mdyn/Å.[4c] It is somewhat lower than the force constant (k_r = 8.29 mydn/Å)

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(21) The symmetry of **1** is D_3 in the crystal and all vibrational studies described herein were performed in the solid state.

(22) (a) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 867. (b) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955.

(23) $\lambda_i = 5.889 \times 10^{-7}\ \nu_i^2$ where ν_i is the frequency of the *i*th vibration in wavenumbers. μ_M and μ_O are the reciprocals of the masses of the metal and of the oxygen respectively. k_R is the metal-to-bridge oxygen bond stretching force constants, k_{RR} the metal-to-bridging oxygen bond stretching interaction force constant, k_r the metal-to-terminal oxygen bond stretching force constant, and k_{rr} the metal-to-terminal oxygen bond stretching interaction force constant. All force constants are in units of mdyn/Å.

(24) (a) Samotus, A.; Kanas, A.; Dudek, M. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1129. (b) Dudek, M.; Kanas, A.; Samotus, A. *Ibid.* **1979**, *41*, 1135.

we calculate for $WONp_3Cl$ (**2**), but in **1**, the oxo group is trans to a ligand with a larger "trans effect" than it is in **2**. Therefore the $W{=}O$ bond length is expected to be shorter in **2** and the force constant, as we find, larger. In the rhenium systems the interaction constant is small and positive.[4c] The difference in the sign of the constant in the W and Re systems is responsible for the finding that in the W system the Raman band is lower in energy than the infrared band; in the rhenium systems the opposite is true. The differences between the two systems are the coordination number and the number of valence electrons, but whether either of these differences is responsible for the change in sign of this interaction constant is not clear.

Equation 4 may be used to calculate the difference in force constants of the bridging oxygen stretches. This difference was calculated for both **1** and [^{18}O]**1**. The average of these two values was used to calculate the position of these asymmetric stretches. These results are shown in Table V. Reasonable agreement between calculated and observed values was obtained by using an average difference in the force constants ($k_R - k_{RR}$) = 2.2 mdyn/Å. Again, the difference compares well with those found for the rhenium systems, which range from 2.13 to 2.47 mdyn/Å.[4c] Equation 3, however, cannot be used to calculate the sum of these constants, and, therefore, their individual values until the symmetric stretch is assigned to a Raman band. As noted above, this band is not expected to shift upon isotopic substitution and is therefore less easy to identify. In the region of the Raman spectrum where a band ascribable to that stretch might be expected are four peaks (at 141, 205, 241, and 271 cm^{-1}) that do not shift upon isotopic substitution. There is no definitive way to choose among these possibilities with the data at hand. All of the force constants and sums and differences of force constants we have calculated for **1**, however, fall in the range of force constants and combinations thereof calculated for the rhenium systems. If force constants are calculated by assuming each of the peaks mentioned above is the symmetric M–O–M stretch, only those using the 205 cm^{-1} value fall into the ranges for analogous force constants in the linear Re_2O_3 complexes. The value calculated for k_R (3.38 mdyn/Å) falls in the range 3.25–3.73 mdyn/Å, while the value calculated for k_{RR} (1.17 mdyn/Å) falls in the range 1.04–1.29 mdyn/Å. We therefore tentatively assign the band at 205 cm^{-1} to the symmetric stretch of the bridging oxygen and accept the values of the force constants calculated above.

Acknowledgment. This work was supported by the National Science Foundation grants CHE 82-19587 (S.J.L.) and CHE 81-21282 (R.R.S.). I.F.-J. thanks the Bantrell Foundation for a postdoctoral fellowship, and D.G. is grateful to the National Institute of General Medical Sciences for a postdoctoral National Research Service Award GM 09253. Raman spectra were obtained at the MIT Regional Laser Center which is a National Science Foundation Regional Instrumentation Facility. Mass spectra were obtained at the Facility supported by NIH grant RR 00317 (Principal Investigator K. Biemann) from the Biotechnology Resources Branch, Division of Research Resources.

Registry No. 1, 87615-70-1; [^{18}O]**1**, 91841-53-1; **2**, 75846-05-8; [^{18}O]**2**, 91798-61-7; $W(CCMe_3)Np_3$, 68490-69-7; Me_3SiCl, 75-77-4.

Supplementary Material Available: Tables S1 and S2, listings of observed and calculated structure factors and anisotropic thermal parameters (7 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Equilibrium Studies of Group 6B Intramolecular Metalloesters: Crystal Structure of *trans*-(η^5-C_5H_4)$CH_2CH_2O_2CW(CO)_2PPh_3$

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Contribution No. 6984 from the Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91125. Received February 27, 1984

Abstract: Treatment of [(η^5-$C_5H_4CH_2CH_2OH$)$M(CO)_3PR_3$]$^+BF_4^-$ (**1a–d**, M = Mo, W; R = Ph, *p*-tolyl) with base affords solely the neutral intramolecular metalloester, *trans*-(η^5-C_5H_4)$CH_2CH_2O_2CM(CO)_2PR_3$ (**2**). The X-ray structure of **2b** (M = W; R = Ph) (space group $P2_1/n$, a = 8.127 Å, b = 16.823 Å, c = 17.623 Å, β = 101.980°, V = 2357 (1) Å^3, Z = 4) was solved by heavy-atom and Fourier methods and refined by full-matrix least squares to S (goodness-of-fit) = 1.27 and R = 0.043 (5728 reflections). The structural results indicate that there is little or no strain upon coordination of the Cp and ester groups when coupled with the ethylene bridge. Equilibrium studies indicate that $\Delta H°$ and $\Delta S°$ are −1.1 ± 0.6 kcal/mol and 3.2 ± 2.0 eu and −1.9 ± 0.2 kcal/mol and 4.5 ± 0.6 eu for **2c** (M = Mo; R = *p*-tolyl) and **2d** (M = W; R = *p*-tolyl), respectively, for the reaction with MeOH in benzene to form the methyl ester and regenerate the alcohol-substituted Cp. Treatment of the analogous compound (**1g**), in which the alcohol is connected to the Cp by CH_2, with methoxide yields an intramolecular metalloester (**3**) as well. Equilibrium data indicate that the intramolecular metalloester is more stable than the methyl ester, $K_{eq} \leq 3$ M^{-1}. The contrasting compounds with the $(CH_2)_3$ bridge (**1e** and **1f**) yield only the intermolecular methyl esters (**5e** and **5f**). The equilibrium constants are estimated to be ≥230 M^{-1} (**5e**) and ≥117 M^{-1} (**5f**).

New modes of activating small molecules by homogeneous systems have been a major theme in organometallic chemistry. Carbon monoxide has been the target of most recent interest due to scientific and economic developments. The work to be described involves the design of a bifunctional catalyst to accomplish this goal. Scheme I shows a plausible mechanism whereby carbon monoxide and hydrogen may react in the presence of a transition-metal complex and an external nucleophile to give organic products.[2]

The overall thermodynamics should in all probability be favorable (e.g., for the formation of methanol, $\Delta G_f° = -6.0$ kcal/mol), and even the unfavorable formation of formaldehyde

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