

Hybrid Metal Carbonyl–Oxide Clusters: Synthesis and Structure of $[\text{Et}_4\text{N}]_2[(\text{OC})_5\text{WSbW}_3(\text{CO})_9(\mu_3\text{-OMe})_2(\mu_3\text{-O})\text{WO}_2(\text{OR})]$ ($\text{R} = \text{Me}, \text{H}$)

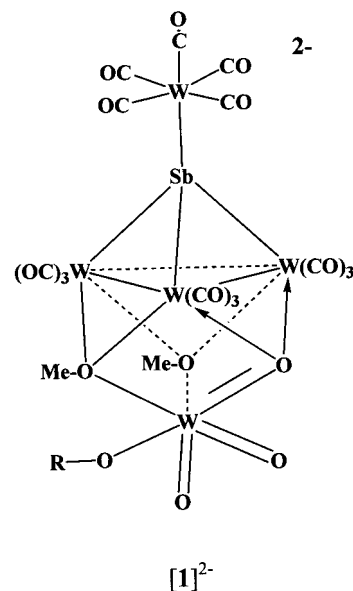
Li Xu and Kenton H. Whitmire*

Department of Chemistry, Rice University, 6100 Main Street, Houston, Texas 77005

Received February 19, 2002

Summary: The novel hybrid metal carbonyl–oxide cluster $[\text{Et}_4\text{N}]_2[(\text{OC})_5\text{WSbW}_3(\text{CO})_9(\mu_3\text{-OMe})_2(\mu_3\text{-O})\text{WO}_2(\text{OR})]$ produced from $\text{W}(\text{CO})_6$ and NaSbO_3 contains a SbW_3 tetrahedron that is triply bridged by the tungsten trioxide $[\text{WO}_3(\text{OMe})_3]^{3-}$. The terminal methoxide is loosely coordinated and can be hydrolyzed to produce the hydroxide derivatives.

Transition-metal oxides and metal carbonyl cluster compounds have both been studied as models for catalytic processes or as catalysts themselves, but it is rare that both high and low valence states are found in the same molecule. Some metal carbonyl cluster compounds that contain bridging oxide ligands have been reported;^{1–9} the systems studied to date are all homometallic clusters constituted solely of transition metals. Although main-group–transition-metal carbonyl clusters have been well documented¹⁰ and heterometallic clusters have received attention for attachment to support materials such as silica and alumina,¹⁰ no studies have yet appeared on supported metal clusters that also contain the heavy main-group elements. In this paper, we report the reaction of tungsten hexacarbonyl with sodium antimonate in methanol that leads to unusual metal cluster complexes containing tungsten in its highest oxidation state coupled to a low-valent tungsten carbonyl unit. These compounds are $[\text{Et}_4\text{N}]_2[(\text{OC})_5\text{WSbW}_3(\text{CO})_9(\mu_3\text{-OMe})_2(\mu_3\text{-O})\text{WO}_2(\text{OR})]$, which have been isolated for $\text{R} = \text{Me}$ ($[\text{Et}_4\text{N}]_2[\mathbf{1a}]$) and $\text{R} = \text{H}$ ($[\text{Et}_4\text{N}]_2[\mathbf{1b}]$). To our knowledge, they represent the first examples that have the metal trioxide moiety MO_3 incorporated into metal carbonyl cluster units.



Heating NaSbO_3 and $\text{W}(\text{CO})_6$ in boiling methanol under an atmosphere of nitrogen after 3 days leads to a brown-black solution from which $[\text{Et}_4\text{N}]_2[\mathbf{1a}]$ was obtained upon cooling and addition of $[\text{Et}_4\text{N}]\text{BF}_4$.¹¹ According to the infrared spectrum of the reaction solution, in the absence of NaSbO_3 , about half of the $\text{W}(\text{CO})_6$ ($1980 \text{ (s)} \text{ cm}^{-1}$) reacts in 3 days to produce a compound with bands at 1926 (s) and $1881 \text{ (m)} \text{ cm}^{-1}$. This compound is believed to be $\text{W}(\text{CO})_5(\text{HOME})$. For comparison, the known anionic compound $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5-$

(11) $[\text{Et}_4\text{N}]_2[\mathbf{1a}]$: Using standard air-free techniques, a Schlenk flask was charged with 1.0 mmol of NaSbO_3 (0.19 g) and 5.0 mmol of $\text{W}(\text{CO})_6$ (1.8 g). To this were added 60 mL of methanol and 5 mL of *n*-heptane. The mixture was further degassed with dry nitrogen for 30 min and then refluxed for 5 days. The black crude reaction solution was cooled to room temperature, at which point solid $[\text{Et}_4\text{N}]\text{BF}_4$ (2.2 g, 10 mmol) was added. The resulting solution was evacuated under vacuum. The resulting black solid was purified by extracting the cluster into THF and allowing diethyl ether to diffuse slowly into the thf solution to give $[\text{Et}_4\text{N}]_2[\mathbf{1a}]$ (0.54 g, 30%). IR (thf; cm^{-1}): 2070 (m), 1957 (s), 1916 (ms), 1874 (mw), 1850 (mw), 896 (s). $^1\text{H NMR}$ (CD_3CN ; ppm): 4.47 (t-OCH₃, 3H), 4.07 (b-OCH₃, 6H), 3.18 ($[\text{Et}_4\text{N}]^+$, q), 1.22 ($[\text{Et}_4\text{N}]^+$, t). Anal. Calcd for $\text{C}_{33}\text{H}_{49}\text{N}_2\text{O}_{20}\text{SbW}_5$: C, 21.59; H, 2.67; N, 1.53. Found: C, 21.05; H, 2.56; N, 1.54. $[\text{Et}_4\text{N}]_2[\mathbf{1b}]$: $[\text{Et}_4\text{N}]_2[\mathbf{1a}]$ (0.36 g, 0.2 mmol) was dissolved in a mixture of acetonitrile (20 mL) and acetic acid (1 mL). The resulting brown-black solution was refluxed under an atmosphere of nitrogen for 10 h. The reaction solution was concentrated in vacuo to half its volume. $[\text{Et}_4\text{N}]_2[\mathbf{1b}]$ was obtained as needlelike crystals from slow diffusion of diethyl ether into the CH_3CN solution. Yield: 0.20 g, ca. 60%. IR (thf; cm^{-1}): 2071 (m), 1957, 1918 (ms), 1876 (w), 1848, 896 (s). $^1\text{H NMR}$ (CD_3CN ; ppm): 4.11 (OCH₃, 6H), 6.11 (t-OH, 1H), 3.18 ($[\text{Et}_4\text{N}]^+$, q), 1.22 ($[\text{Et}_4\text{N}]^+$). Anal. Calcd for $\text{C}_{32}\text{H}_{47}\text{N}_2\text{O}_{20}\text{SbW}_5$: C, 21.10; H, 2.58; N, 1.54. Found: C, 20.88; H, 2.59; N, 1.61.

(1) Gong, J.-H.; Hwang, D.-K.; Tsay, C.-W.; Chi, Y.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1994**, *13*, 1720–1727.

(2) Churchill, M. R.; Bueno, C.; Park, J. T.; Shapley, J. R. *Inorg. Chem.* **1984**, *23*, 1017–1021.

(3) (a) Chi, Y.; Hwang, L.; Lee, G.-H.; Peng, S.-M. *J. Chem. Soc., Chem. Commun.* **1988**, 1456–1457. (b) Chi, Y.; Shapley, J. R.; Ziller, J.; Churchill, M. R. *Organometallics* **1987**, *6*, 301–307.

(4) Goudsmit, R. J.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1983**, 246–247.

(5) Lavigne, G.; Lugan, N.; Bonnet, J.-J. *Nouv. J. Chim.* **1981**, *5*, 423–425.

(6) Ceriotti, A.; Resconi, L.; Demartin, F.; Longoni, G.; Mansserso, M.; Sansoni, M. *J. Organomet. Chem.* **1983**, *249*, C35–C37.

(7) Schauer, C. K.; Harris, S.; Sabat, M.; Voss, E. J.; Shriver, D. F. *Inorg. Chem.* **1995**, *34*, 5017–5028.

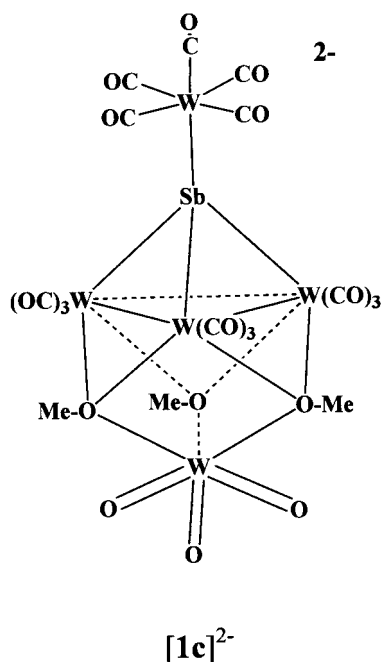
(8) Puga, J.; Fehlner, T. P.; Gates, B. C.; Braga, D.; Grepioni, F. *Inorg. Chem.* **1990**, *29*, 2376.

(9) Liu, J.; Wilson, S. R.; Shapley, J. R.; Feher, F. J. *Inorg. Chem.* **1990**, *29*, 5138.

(10) (a) Whitmire, K. H. *Adv. Organomet. Chem.* **1998**, *42*, 1–145. (b) *J. Coord. Chem.* **1988**, *17*, 95–204.

(OMe)] exhibits bands at 1901 (s) and 1847 (m) cm^{-1} .¹² Similar shifts in CO stretching frequencies are exhibited by $\text{W}(\text{CO})_4(\text{HOMe})_2$ (1864 (s), 1804 (m), 1790 (m) cm^{-1}) when converted to $(\text{Et}_4\text{N})_2[\text{W}(\text{CO})_4(\text{OMe})_2]$ (1851 (s), 1808 (m), 1774 (m)).¹² Boiling longer than 3 days did not increase the amount of the hypothetical $\text{W}(\text{CO})_5(\text{HOMe})$ present in solution. In boiling phenol, we found that $\text{W}(\text{CO})_6$ is quantitatively oxidized to the known compound $\text{W}(\text{OPh})_6$, which has previously been prepared by the phenolysis of WOCl_4 or the reaction of $\text{W}(\text{OCH}_2\text{CH}_2\text{O})_3$ with PhOAc .¹³ Workup of the reaction mixture using $(\text{Et}_4\text{N})\text{Br}$ instead of $(\text{Et}_4\text{N})\text{BF}_4$ leads to the formation of $(\text{Et}_4\text{N})[(\text{CO})_5\text{WBr}]$ in addition to $(\text{Et}_4\text{N})_2[\mathbf{1a}]$. Presumably this byproduct arises from the reaction of bromide ion with $\text{W}(\text{CO})_5(\text{HOMe})$. It is difficult to separate from $(\text{Et}_4\text{N})_2[\mathbf{1a}]$; therefore, the use of the BF_4^- salt is preferred.

When $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ is treated with acetic acid in MeCN, no change is observed after 1 h, but the cluster is completely hydrolyzed to form $(\text{Et}_4\text{N})_2[\mathbf{1b}]$ after 18 h. $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ shows two types of methoxy ^1H NMR signals at 4.47 and 4.07 ppm in a ratio of 1:2 attributable to the terminal and bridging methoxide ligands. The bridging MeO^- and terminal OH^- groups in $(\text{Et}_4\text{N})_2[\mathbf{1b}]$ display proton signals at 4.11 and 6.12 ppm, respectively. It is interesting that an additional MeO^- proton signal at 4.25 ppm was observed in the reaction solution containing $(\text{Et}_4\text{N})_2[\mathbf{1a}]$. We believe this signal to arise from the symmetric isomer $(\text{Et}_4\text{N})_2[(\text{OC})_5\text{WSbW}_3(\text{CO})_9(\mu_3\text{-OMe})_3\text{WO}_3]$ ($(\text{Et}_4\text{N})_2[\mathbf{1c}]$) with the methoxide ligands



in the bridging positions based upon the chemical shift of the ^1H NMR signal. The signal disappears in the presence of phenol or acetic acid. It appears that this compound is much less stable than $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ under acidic conditions. It has eluded isolation to this point. The compounds $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ and $(\text{Et}_4\text{N})_2[\mathbf{1b}]$ exhibit

nearly identical CO absorption patterns in their infrared spectra (2070 (w), 1956 (s), 1916 (ms), 1876 (w), 1848 (w) cm^{-1}). A strong band at 896 cm^{-1} is attributable to $\nu(\text{W}=\text{O})$.

The compound $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ is an air-stable crystalline solid. It is soluble in polar organic solvents such as tetrahydrofuran, acetone, acetonitrile, and dichloromethane. The solution is stable under an inert atmosphere, but the compound is converted into $(\text{Et}_4\text{N})_2[\text{W}_6\text{O}_{19}]$ when its solutions are exposed to air. In contrast, $(\text{Et}_4\text{N})_2[\mathbf{1b}]$ remains unchanged in solution even after several days in air. The reaction of $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ with $(^t\text{Bu}_4\text{N})_2\text{Mo}_2\text{O}_7$ in refluxing acetonitrile, which was designed to replace the WO_3 unit with polyoxomolybdate, leads to the formation of $(^t\text{Bu}_4\text{N})_3[\text{Mo}_3\text{W}_3\text{O}_{19}]$.¹⁴ The related heterometallic compound $(^t\text{Bu}_4\text{N})_3[\text{MoW}_5\text{O}_{19}]$ was obtained from electrochemical reduction of the corresponding dianion prepared from WO_3 and Na_2MoO_4 .¹⁵ Attempts to prepare derivatives from replacement of the methoxide ligands in $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ with phenolate or benzoate groups failed even under refluxing conditions. In both cases the observed product was $(\text{Et}_4\text{N})_2[\mathbf{1b}]$.

Both $(\text{Et}_4\text{N})_2[\mathbf{1a}]$ and $(\text{Et}_4\text{N})_2[\mathbf{1b}]$ crystallize as isomorphous, black, needle-shaped crystals from THF/hexane.¹⁶ Figure 1 shows the structure of the cluster dianion $(\text{OC})_5\text{WSbW}_3(\text{CO})_9(\mu_3\text{-OMe})_2(\mu_3\text{-O})\text{WO}_2(\text{OMe})^{2-}[\mathbf{1a}]^{2-}$. The core structures of $(\mathbf{1a})^{2-}$ and $(\mathbf{1b})^{2-}$ differ only in that the former has the terminal MeO^- ligand, while the latter possesses a OH^- ligand. The core structure is characteristic of the SbW_3 tetrahedron, similar to those in the related clusters $(\text{Et}_4\text{N})_2[(\text{OC})_5\text{MoAsMo}_3(\text{CO})_9(\mu_3\text{-OMe})_3\text{Mo}(\text{CO})_3]$ ¹⁷ and $(\text{Et}_4\text{N})_2[\text{BiMo}_3(\text{CO})_9(\mu_3\text{-OMe})_3\text{Mo}(\text{CO})_3]$.¹⁸ The Sb atom donates its external lone pair of electrons to a $\text{W}(\text{CO})_5$ fragment, showing more basic character of the lone pair of electrons than the Bi atom.¹⁰ Like $(\text{OC})_5\text{MoAsMo}_3(\text{CO})_9(\mu_3\text{-OMe})_3\text{Mo}(\text{CO})_3$,¹⁷ $(\mathbf{1a})^{2-}$ and $(\mathbf{1b})^{2-}$ have 50 cluster electrons with one more pair of electrons than the typical count. This counting scheme considers the complex to be composed of $[\text{WO}_3(\text{OMe})_3]^{3-}$ or $[\text{WO}_3(\text{OMe})_2(\text{OH})]^{3-}$ groups attached to a $[\text{SbW}_3(\text{CO})_9]^+$ cluster core. The $[\text{WO}_3(\text{OMe})_3]^{3-}$ and $[\text{WO}_3(\text{OMe})_2(\text{OH})]^{3-}$ units donate 12 electrons (4 electrons for each bridging methoxide and oxo ligand).

An interesting structural feature is the asymmetry in the positions of the methoxide and oxide ligands. Instead of having all oxide ligands in bridging or terminal modes, two oxide ligands are terminal and one is bridging. As a consequence, one of the three methoxy

(14) Xu, L.; Whitmire, K. H. Unpublished results. Crystal data: $a = 30.301(3)$ Å, $b = 18.390(2)$ Å, $c = 27.411(2)$ Å, $\beta = 112.258(1)^\circ$, $V = 14136(2)$ Å³, $Z = 8$, $R1/wR2 = 0.048/0.14$ for 7115 observed reflections ($I = 2\sigma(I)$), $\text{GOF} = 1.17$.

(15) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3194.

(16) Crystal data for $(\text{Et}_4\text{N})_2[\mathbf{1a}]$: crystal size $0.72 \times 0.17 \times 0.07$ mm, monoclinic, space group $C2/c$, $a = 38.606(8)$ Å, $b = 11.595(2)$ Å, $c = 24.166(5)$ Å, $\beta = 112.11(3)^\circ$, $V = 10\,022(3)$ Å³, $Z = 8$, $\mu = 12.03$ cm^{-1} , $d_{\text{calcd}} = 2.432$ g/cm^3 , $R1/wR2 = 0.031/0.074$ for 5916 observed reflections ($I = 2\sigma(I)$), $\text{GOF} = 0.8$. Crystal data for $(\text{Et}_4\text{N})_2[\mathbf{1b}]$: crystal size $0.52 \times 0.20 \times 0.18$ mm, monoclinic, space group $P2_1/c$, $a = 11.352(2)$ Å, $b = 44.091(9)$ Å, $c = 19.876(4)$ Å, $\beta = 104.11(3)^\circ$, $V = 9648(3)$ Å³, $Z = 4$, $\mu = 12.50$ cm^{-1} , $d_{\text{calcd}} = 2.507$ g/cm^3 , $R1/wR2 = 0.072/0.168$ for 7441 observed reflections ($I = 2\sigma(I)$), $\text{GOF} = 0.89$.

(17) Van Hal, J. W.; Whitmire, K. H.; Zouhoune, B.; Halet, J.-F.; Saillard, J.-Y. *Inorg. Chem.* **1995**, *34*, 5455–5460.

(18) Shieh, M.; Mia, F.-D.; Peng, S.-M.; Lee, G.-H. *Inorg. Chem.* **1993**, *32*, 2785.

(12) Darenbourg, D. J.; Klausmeyer, K. K.; Draper, J. D.; Chojnacki, J. A.; Reibenspies, J. H. R. *Inorg. Chim. Acta* **1998**, *270*, 405.

(13) (a) Mortimer, P. I.; Strong, M. A. *Aust. J. Chem.* **1965**, *18*, 1579. (b) Lehtonen, A.; Sillanp, R. *Polyhedron* **1999**, *18*, 175.

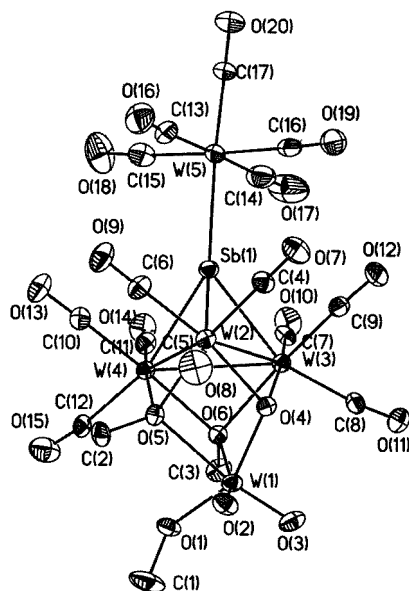


Figure 1. ORTEP drawing of $[1a]^{2-}$ with 30% probability thermal ellipsoids. Selected bond lengths (Å): Sb(1)–W(1), 2.7338(8); Sb(1)–W(2), 2.732(1); Sb(1)–W(3), 2.7124(7); Sb(1)–W(4), 2.7390(8); W(2)–W(3), 3.0805(7); W(2)–W(4), 3.0327(10); W(3)–W(4), 3.0942(7); W(2)–O(51), 2.187(5); W(2)–O(53), 2.148(5); W(3)–O(52), 2.207(5); W(3)–O(53), 2.149(5); W(4)–O(51), 2.191(5); W(4)–O(52), 2.213(5); W(5)–O(51), 2.190(5); W(5)–O(52), 2.213(5); W(5)–O(53), 1.928(5); W(5)–O(54), 1.901(6); W(5)–O(55), 1.713(6); W(5)–O(56), 1.718(6). The corresponding values (Å) for one of the molecules in the asymmetric unit of $[1b]^{2-}$ are as follows: Sb(1a)–W(1a), 2.732(2); Sb(1a)–W(2a), 2.731(2); Sb(1a)–W(3a), 2.706(2); Sb(1a)–W(4a), 2.730(2); W(2a)–W(3a), 3.051(2); W(2a)–W(4a), 3.040(2); W(3a)–W(4a), 3.071(2); W(2a)–O(51a), 2.19(1); W(2a)–O(53a), 2.21(1); W(3a)–O(52a), 2.20(1); W(3a)–O(53a), 2.08(1); W(4a)–O(51a), 2.19(2); W(4a)–O(52a), 2.22(1); W(5a)–O(51a), 2.18(1); W(5a)–O(52a), 2.27(2); W(5a)–O(53a), 1.86(1); W(5a)–O(54a), 1.94(1); W(5a)–O(55a), 1.74(2); W(5a)–O(56a), 1.63(2).

ligands in $[1a]^{2-}$ becomes terminal, and it is this methoxide ligand that is replaced by hydroxide ion. It is not clear whether selection of this asymmetric structure is determined by kinetics or thermodynamics, but the trianionic $[WO_3(\mu_3\text{-OMe})_3]^{3-}$ unit in the symmetric isomer may be highly reactive because of the strong basicity of the terminal oxo ligands as observed in Cp^*WO_3 .¹⁹ While the proton attached to the hydroxide ligands could not be located with certainty in the X-ray structure determination, it is clear from the asymmetry in the W–O bond distances that this ligand occupies the same coordination site as the methoxide group. The W–O bond length assigned to the OH^- ligand in $[1b]^{2-}$ (1.94(2) Å) is similar to the Mo–OMe bond in $[1a]^{2-}$

(1.901(6) Å), whereas the other terminal W–O distances are considerably shorter, being within the range observed for W=O double bonds: $[1a]^{2-}$ (W(5)–O(55) = 1.713(6) Å, W(5)–O(56) = 1.718(6) Å); $[1b]^{2-}$ (1.63(2)–1.74(2) Å, average 1.67(2) Å). The W(5)– μ_3 -O bond lengths (1.931(6) Å in $[1a]^{2-}$, 1.87(1) Å in $[1b]^{2-}$) are considerably shorter than the $[W_3]-\mu_3\text{-O}$ bonds in the carbonyl cluster unit (average 2.146(6) Å in $[1a]^{2-}$, 2.15(1) Å in $[1b]^{2-}$). This may be explained by the W=(μ_3 -O)– W_2 bonding mode as shown in the line drawing. Such a bonding mode is not observed in related organometallic molybdenum oxide clusters, such as $Cp^*Mo_5O_{11}$ (Mo– μ_3 -O = 2.060(7) Å)²⁰ and $Cp^*_6Mo_8O_{16}$ (Mo– μ_3 -O = 2.144(2) Å),²¹ although the W=(μ -O)–Os system has been discussed previously.³ The W(5)–(μ_3 -OMe) bonds (average 2.314(6) Å in $[1a]^{2-}$ and 2.29(2) Å in $[1b]^{2-}$) are longer than the $[W_3]-\mu_3\text{-OMe}$ bonds (average 2.210(6) Å in $[1a]^{2-}$ and 2.21(2) Å in $[1b]^{2-}$) due to the trans influence of the terminal oxo atoms. The dative σ -bonds between the Sb atoms and W(1) are slightly shorter than those found in $Ph_3SbW(CO)_5$ (2.753(0) Å).²² Unlike the case of the As cluster $[2]^{2-}$, the Sb–W bonds are longer than in the open Sb–W compound $W_2(CO)_{10}Sb\{CH(SiMe_3)_2\}$ (2.687(1) Å)²³ but considerably shorter than those found in closed species such as $\{W_2(CO)_{10}\}\{W(CO)_5\}Sb^tBu$ (2.825(5) Å),²⁴ $(F_3C)_2\text{-}SbW(CO)_3MeCp$ (2.8058(7) Å),²⁵ and $CpW(CO)_3Sb(N^t\text{-}Bu)_2SiMe_2$ (3.010(1) Å).²⁶ The W–W distances in the W_3 triangle (average 3.069(1) Å) are within the range of formal W–W single bonds, as found in $[W_3(CO)_9(\mu\text{-}OC_2H_5)(\mu_3\text{-}OC_2H_5)_2]$ (2.939(2), 2.966(2) Å),²⁷ $[CpW(CO)_3]_2$ (3.222(1) Å),²⁸ and $[(\mu\text{-}Et_2P)W(CO)_4]_2$ (3.05(1) Å).²⁹

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE9983352) and the Robert A. Welch Foundation.

Supporting Information Available: Tables of crystal data, atomic coordination and isotopic parameters, and bond lengths and angles for $[Et_4N]_2[1]$ and $[Et_4N]_2[2]$ and an ORTEP drawing of $[1b]^{2-}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM020129C

(20) Bottomley, F.; Chen, J.; Preston, K. F.; Thompson, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 7989–7995.

(21) Harper, J. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 4037.

(22) Willims, G. A.; Whyte, T. *Aust. J. Chem.* **1995**, *48*, 1045.

(23) Arif, A. M.; Cowley, A. H.; Norman, N. C.; Pakulski, M. *Inorg. Chem.* **1986**, *25*, 4836.

(24) Weber, U.; Hutter, G.; Scheidsteger, O.; Zsolnai, L. *J. Organomet. Chem.* **1985**, *289*, 357.

(25) Grob, J.; Golla, W.; Van, D. L.; Krebs, B.; Lage, M. *Organometallics* **1998**, *17*, 5717.

(26) Caminade, A. M.; Veith, M.; Huch, V.; Malisch, W. *Organometallics* **1990**, *9*, 1798.

(27) Ellis, J. E.; Rochfort, G. L. *Organometallics* **1982**, *1*, 682–689.

(28) Cotton, F. A.; Adams, R. D.; Collins, D. M. *Inorg. Chem.* **1974**, *13*, 1086.

(29) Linck, M. H. *Cryst. Struct. Commun.* **1973**, *2*, 379.

(19) Rau, M. S.; Kretz, C. M.; Mecando, L. A.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *31*, 1112.