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Dinuclear (d^3−d^3) Diolate Complexes of Molybdenum and Tungsten. 1. Preparation and Characterization of Complexes Derived from 2,5-Dimethylhexane-2,5-diol

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Reaction of $M_2(O^tBu)_6$ (M = Mo, W) with 3 equiv of 2,5-dimethylhexane-2,5-diol (LH_2) in hexane/THF produces orange crystals of $M_2(\mu\text{-}L_3)_2$, **Ia** (M = Mo), **Ib** (M = W), in high yield (80%). Treatment of $M_2(NMe_2)_6$ with excess (>8 fold) LH_2 in THF/hexane solution at −20 °C produces exclusively green crystals of $M_2(\mu\text{-}L)(\eta^2\text{-}L)_2(HNMe_2)_2$, **IIa** (M = Mo), **IIb** (M = W), in high yield (75%). Dissolving **IIa** and **IIb** in toluene at room temperature slowly produces **Ia** and **Ib**, respectively, the process being accelerated by heat ($t_{1/2}$ = 10 min at 60 °C). Compounds **Ia**, **Ib**, **IIa**, and **IIb** were characterized by ^1H NMR, IR, melting point, and microanalysis, and **Ib** and **IIb** were also characterized by X-ray crystallography. Addition of excess $HNMe_2$ to a solution of **Ia** or **Ib** at −50 °C does not produce any **IIa** or **IIb** after 2 months, but at +25 °C, 40% **IIa** and **IIb** are produced with $HNMe_2$ after 2 days. Crystal data for **Ib**: $W_2(\mu\text{-}L)_3$ at −171 °C, a = 12.568(2) Å, b = 12.568(3) Å, c = 37.075(8) Å, Z = 8, d_{calcd} = 1.822 g/cm³, space group $I4_1/a$. The molecule **Ib** adopts an "ethane-like" staggered conformation with three eight-membered diolate rings spanning the W−W triple bond: W≡W = 2.3628(11) Å; W−O = 1.87 Å (average). Crystal data for compound **IIb**: $W_2(\mu\text{-}L)(\eta^2\text{-}L)_2(HNMe_2)_2$ at −170 °C, a = b = 20.198(3) Å, c = 17.819(3) Å, Z = 8, d_{calcd} = 1.629 g/cm³, space group $P4/ncc$. **IIb** has two essentially square planar WO_3N units connected by a W−W triple bond, W≡W = 2.3196(12) Å, W−O = 1.95 Å (average), and W−N = 2.294(11) Å, and one bridging eight-membered diolate ring. The other two diolate ligands chelate at opposite ends of the molecule forming two seven-membered rings.

Introduction

Chelating ligands have played a remarkable role in the development of mechanistic inorganic chemistry of mononuclear systems.[1] Chelates offer kinetic and thermodynamic control of reaction pathways and have given insightful information about rates and modes of ligand substitution. A large number of dimetallic compounds containing single, double, triple, and even quadruple bonds are known for the transition elements.[2] The use of chelating ligands in this chemistry has been important but limited and primarily involves the use of either carboxylate, formamidine, 2-hydroxypyridinate and related anionic ligands or chelating phosphines that form five- or six-membered rings.[2] For metal−metal triply bonded complexes, few examples of anionic bidentate ligands have been used.[3] The reaction of $W_2(NMe_2)_6$ with pinacol produces $W_2(O_2C_2Me_4)_3$ in which the ligands span the metal−metal bond to form an eclipsed W_2O_6 structure.[3b] Despite the uses of these ligands little information about intramolecular rearrangements or ligand substitution has accrued at the M≡M center.

Here we describe the reactions of 2,5-hexane-2,5-diol with $M_2(OBu^t)_6$ and $M_2(NMe_2)_6$ (M = Mo, W) to ascertain information about ligand substitution and intra- and intermolecular rearrangements at the metal−metal triply bonded core.[4]

Results and Discussion

Synthesis. Reaction of $M_2(OBu^t)_6$ (M = Mo, W) with 2,5-dimethylhexane-2,5-diol (LH_2) in THF/toluene or diethyl ether/hexane at room temperature for 3 days produces $M_2(\mu\text{-}L)_3$, **Ia** and **Ib**, in quantitative yield, eq 1, (**Ia**, M = Mo; **Ib**, M = W).

$$M_2(OBu)_6 + 3HOCMe_2CH_2CH_2CMe_2OH \xrightarrow{RT} 6HOBu^t + M_2(\mu\text{-}L)_3 \quad (1)$$

The products **Ia** and **Ib** are orange in color and partially precipitate from the reaction solution. Removal of all the solvent in vacuo leaves pure **Ia** and **Ib** after 3 days at room temperature or 3 h at +65 °C. The reaction was monitored by ^1H NMR spectroscopy. However, no intermediate $M_2(OBu^t)_{6-2n}L_n$ (n = 1,2) species was detected, only LH_2, ^tBuOH, $M_2(OBu^t)_6$, and **Ia** and **Ib**.

Reaction of $M_2(NMe_2)_6$ (M = Mo, W) with LH_2 at −20 °C in hexane/THF produces a green solution from which crystals of $M_2(\mu\text{-}L)(\eta^2\text{-}L)_2(HNMe_2)_2$, **IIa** (M = Mo) and **IIb** (M = W), are precipitated in 80% yield, eq 2.

$$M_2(NMe_2)_6 + 3LH_2 \xrightarrow{-20\ °C} M_2(\mu\text{-}L)(\eta^2\text{-}L)_2(HNMe_2)_2 + 4HNMe_2 \quad (2)$$

$$5M_2(NMe_2)_6 + 15LH_2 \xrightarrow{+65\ °C/1\ h} 4M_2(\mu\text{-}L)(\eta^2\text{-}L)_2(HNMe_2)_2 + M_2(\mu\text{-}L)_3 + 22HNMe_2$$

If the reaction is performed at room temperature crystals of **IIa** and **IIb** and a small

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(1) (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*, 2nd ed.; J. Wiley and Sons: New York, 1968. (b) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes,* 2nd ed.; VCH: Weinheim, Germany, 1991.

(2) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Oxford University Press: Oxford, England, 1993.

(3) (a) $M_2(MeNCH_2CH_2NMe)_3$: Blatchford, T. P.; Chisholm, M. L.; Huffman, J. C. *Inorg. Chem.* **1987**, *26*, 1920. (b) $M_2(OCMe_2Me_2CO)_3$: Chisholm, M. H.; Folting, K.; Hampden-Smith, M. J.; Smith, C. A. *Polyhedron* **1987**, *6*, 1747. (c) $M_2(\mu\text{-}CH_2CH_2CH_2CH_2)(NMe_2)_4$: Chetcuti, M. J.; Chisholm, M. H.; Chiu, H. T.; Huffman, J. C. *Polyhedron* **1985**, *4*, 1213.

(4) A preliminary communication of one aspect of ths work has been published: Chisholm, M. H.; Folting, K.; Lobkovsky, E; Parkin, I. P.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1673.

amount (~5%) of orange crystals of **Ia** and **Ib** are coprecipitated. As the temperature of the reaction is raised to +65 °C in a closed system for 1 h and then lowered to −20 °C, 80% of the crystalline product is **IIa** or **IIb** and 20% is **Ia** or **Ib**. Furthermore if the reaction is carried out at +65 °C with a flow of dry dinitrogen passed over the solution the ratio of **IIa/IIb** to **Ia/Ib** is changed with time such that no **IIa/IIb** is present after a few hours. The interconversion of **Ia/Ib** to **IIa/IIb** is discussed below.

Physical Characterization. $M_2(\mu\text{-}L)_3$, **Ia/Ib**, decompose upon heating at 140−143 °C (M = W) and 135 °C (M = Mo) but **Ib** (M = W) does give a parent molecular ion peak at 800 amu with the associated isotopic distribution expected for two tungsten atoms. Other fragmentation peaks include M^+-L and M^+-2L. **Ia** and **Ib** are relatively air-stable as solids, only slowly decomposing over 2 weeks at room temperature. However, they are air-sensitive and hydrolytically sensitive in solution, precipitating a brown intractable solid on exposure to air for 2−3 h. They are soluble in aromatic hydrocarbon solvents and THF but insoluble in hexane and pentane.

The IR spectra of **Ia** and **Ib** as a KBr disk showed only the expected resonances for the alkoxide ligands, slightly shifted from the free alcohol.

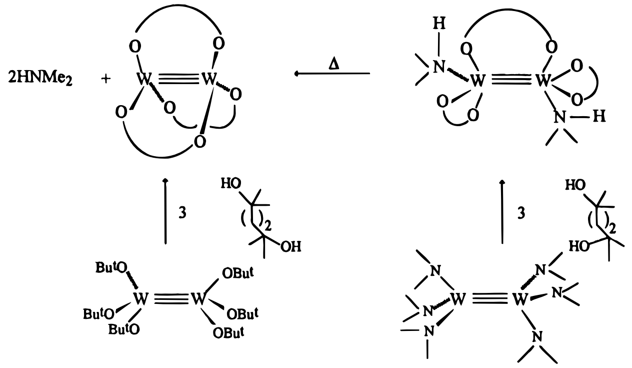
The ^{1}H NMR spectra of **Ia** and **Ib** are essentially identical and are invariant over the temperature range −90 to +150 °C in $C_6D_5CD_3$ and independent of field as measured at 300 and 500 MHz on Varian XL300 and Bruker 500 spectrometers. The spectra show two equal intensity methylene proton resonances at $\delta = 2.78$ and $\delta = 1.92$ ppm as approximately 1:2:3:3:2:1 sextets and two methyl resonances at $\delta = 1.62$ and $\delta = 1.23$ ppm of equal intensity. The temperature invariance and shape of the spectra for **Ia** and **Ib** suggest that in solution all three of L ligands span the M−M multiple bond.

The ^{1}H NMR spectra in the methyl region suggest that there are two environments of the methyl groups. The methyl groups on any one carbon atom are diastereotopic, with one being proximal and the other distal with respect to the metal−metal bond. These methyl groups are related by three C_2 axes running through the center of each diolate group and the M−M multiple bond, and a pseudo C_3 axis along the M−M vector. Thus two methyl resonances are observed.

In the methylene region AA′MM′ spectra are observed, with two sets of inequivalent protons. The difference in chemical shift between the sets is attributable to the shielding/deshielding induced by the metal−metal triple bond[5] (one group points toward and the other away from the bond). These protons are magnetically inequivalent which leads to the complex multiplet pattern observed; this is evidenced by the same coupling pattern at varying magnetic field strengths. From the above we can infer that rotation about the M_2O_6 moiety, wherein one staggered conformation is interconverted with the other by way of an eclipsed W_2O_6 moiety, is slow on the NMR time scale.

Compounds **IIa** and **IIb** decompose upon heating above 100 °C with loss of the Lewis base dimethylamine. No parent ion peak was observed for **IIb** (M = W) in the electron impact mass spectrum, with the highest peak occurring at 800 amu corresponding to $W_2(\mu\text{-}L)_3$. Compounds **IIa** and **IIb** crystallize as large (50−200 mg) green crystals which are air sensitive (and somewhat thermally sensitive) in solution, but decompose only slowly in the solid state over a few days. Compounds **IIa** and **IIb** are much more soluble than **Ia** and **Ib** in aromatic and aliphatic hydrocarbon solvents. The IR spectra of **IIa** and **IIb** measured as powdered KBr disks, although more complicated than **Ia** and **Ib,** do show L skeletal vibrations with the additional adsorptions due to $HNMe_2$. Notable is the ν(N−H) stretch at 3140 cm^{-1} and a δ(N−H) deformation at 1440 cm^{-1} due to the coordinated dimethylamine.

Scheme 1



The ^{1}H NMR spectra of $W_2(\mu\text{-}O_2C_8H_{16})(\eta^2\text{-}O_2C_8H_{16})_2(HNMe_2)_2$ is temperature invariant from +25 to −55 °C, with only a slight broadening of the resonances being observed at −55 °C. The spectrum is quite complex but the amine protons (NH) are seen at δ 5.2, and a sextet at $\delta = 3.6$ of integral intensity 2 is likely due to one set of diastereotopic methylene protons on the diolate bridging the metal−metal core. The other sextet due to the bridging group, along with the methylene protons on the terminally bound chelating rings cannot be assigned with certainty at 300 MHz due to overlapping resonances. At least three groups of methyl resonances centered at $\delta = 1.70$, 1.45, and 0.97 ppm are observed; again these cannot be unambiguously assigned.

Interconversion of Ia/Ib and IIa/IIb. Heating a solution of **IIa** or **IIb** to 65 °C in C_6D_6 for 15 min produces **Ia** and **Ib**, respectively, in greater than 90% yield, as assessed by ^{1}H NMR spectroscopy. If the reaction of $W_2(NMe_2)_6$ with 2,5-dimethylhexane-2,5-diol is heated to reflux for $^1/_2$ h under a continuous nitrogen flow, **Ib** is produced in greater than 95% in benzene. When **IIa** and **IIb** are heated in solution, the dimethylamine Lewis base ligands are liberated as dimethylamine gas, and a rearrangement occurs concomitantly with the two terminal chelating rings opening up and closing to bridge the dimetallic center, thereby forming **Ia** and **Ib**. We propose that the loss of dimethylamine and formation of the bridging eight-membered rings occur in a rapid sequential fashion. The presence of hydrogen bonds between the terminal diolate oxygens and the coordinated dimethylamine[6] may play a role in this transformation. Another factor which may be important is release of steric strain in the transformation of the terminal seven-membered rings, to the eight-membered rings that span the M−M bond.

Addition of a 100-fold excess of dimethylamine gas to a solution of **Ia** or **Ib** at room temperature does, as deduced by ^{1}H NMR spectroscopy, produce a significant amount of **IIa** and **IIb** (>40%) along with untransformed **Ia** and **Ib**. These processes can be described by Scheme 1.

Cooling to −20°C immediately after mixing a reaction solution of $W_2(NMe_2)_6$ and 2,5-dimethylhexane-2,5-diol gives 100% **IIb** by crystallization. Leaving a solution of **IIb** in an NMR tube for 5 days under nitrogen at room temperature produces >60% **Ib** and free $HNMe_2$. Thus **IIb** is the kinetic product from the reaction between $W_2(NMe_2)_6$ and LH_2 and only rearranges at temperatures above 0 °C to **Ib** with liberation of amine.

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(5) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477.

(6) Similar Me_2NH---OR bonding across the W≡W bond was seen in the structure of $W_2(O^iPr)_6(HNMe_2)_2$: Chetcuti, M. J.; Chisholm, M. H.; Huffman, J. C.; Leonelli, J. *J. Am. Chem. Soc.* **1983**, *105*, 292.

Interestingly keeping a solution of **Ib** at −50 °C for 2 months with a 100-fold excess of HNMe$_2$ does not give any **IIb** as evidenced by ^{1}H NMR spectroscopy. At low temperatures, formation of the Lewis base adduct **IIb** should be thermodynamically favored.[7] The fact that the interconversion of **Ib** to **IIb** is slow in the presence of excess dimethylamine and that it occurs only at a measurable rate at room temperature indicates a significant kinetic barrier to the uptake of HNMe$_2$ and diolate rearrangement.

Reaction of W$_2$(OBu^t)$_6$ with 2,5-dimethylhexane-2,5-diol does give a green solution if the reaction solution is cooled after initial mixing; however, only **Ib** is precipitated. No analogous W$_2$(O$_2$C$_8$H$_{16}$)$_3$(HOBu^t)$_2$ compound has been obtained.

Compounds **Ia** and **Ib** do not react with carbon monoxide, acetylene, ethene or acetonitrile at room temperature or +65 °C in toluene, even after a period of weeks. This lack of reactivity is noteworthy in contrast to that seen for W$_2$(OR)$_6$ compounds.[8] Quite probably the presence of three chelating ligands imposes a kinetic barrier to substrate uptake and activation. Certainly the reluctance of **Ib** to bind HNMe$_2$ in the formation of **IIb** supports this fact.

W$_2$(μ-O$_2$C$_8$H$_{16}$)$_3$. Crystals suitable for X-ray diffraction were obtained by slowly cooling a saturated toluene solution of **Ib** from +65 °C to room temperature in a 5 mm NMR tube. **Ib** crystallized as bright orange cubic crystals in the space group $I4_1/a$ with an included disordered THF on the 4-fold axis. ORTEP diagrams looking parallel and perpendicular to the M−M vector are shown in Figure 1. Selected bond lengths and angles for **Ib** are shown in Table 1 and crystallographic data collection parameters are given in Table 3.

The structure of **Ib** reveals a staggered ethane-like geometry with the diolate groups spanning the metal−metal bond making three eight-membered rings. This structure represents an example of an inorganic [6,6,6] propellane, where the metal−metal bond is supported by three bridging groups spanning the central bond. The molecule has three local C_2 axes running between the center of the methylene units and the middle of the multiple bond and a C_3 axis down the M−M vector. The molecule is chiral and an equal number of enantiomers is found in the unit cell.

The W−W bond length of 2.3628(11) Å is the longest metal−metal triple bond distance so far recorded (2.29−2.32 Å average) for an ethane-like X$_3$W≡WX$_3$ molecule.[9] This lengthening is likely due to the easing of steric transannular strain in the three eight membered rings. All the W−O bond lengths are identical within the 3σ criteria at 1.872(8), 1.870(9) and 1.879(7) Å, while the W−W−O angles are all identical at 110.16 ± 0.6°. These bond lengths and angles are consistent with significant O(pπ)−W(dπ) interactions.

Ib is the first example of a dimetallic compound supported by three eight membered rings. The angles and lengths at the carbon atoms within the ring are normal. The long M−M and short C−O bond lengths compared to C−C bond lengths minimize transannular strain compared to that in a cyclooctane.

The space-filling diagram of **Ib** indicates that the metal−metal core is accessible only along the W−W vector, with the ligands forming an effective steric shield for the approach of ligands perpendicular to the metal−metal bond.

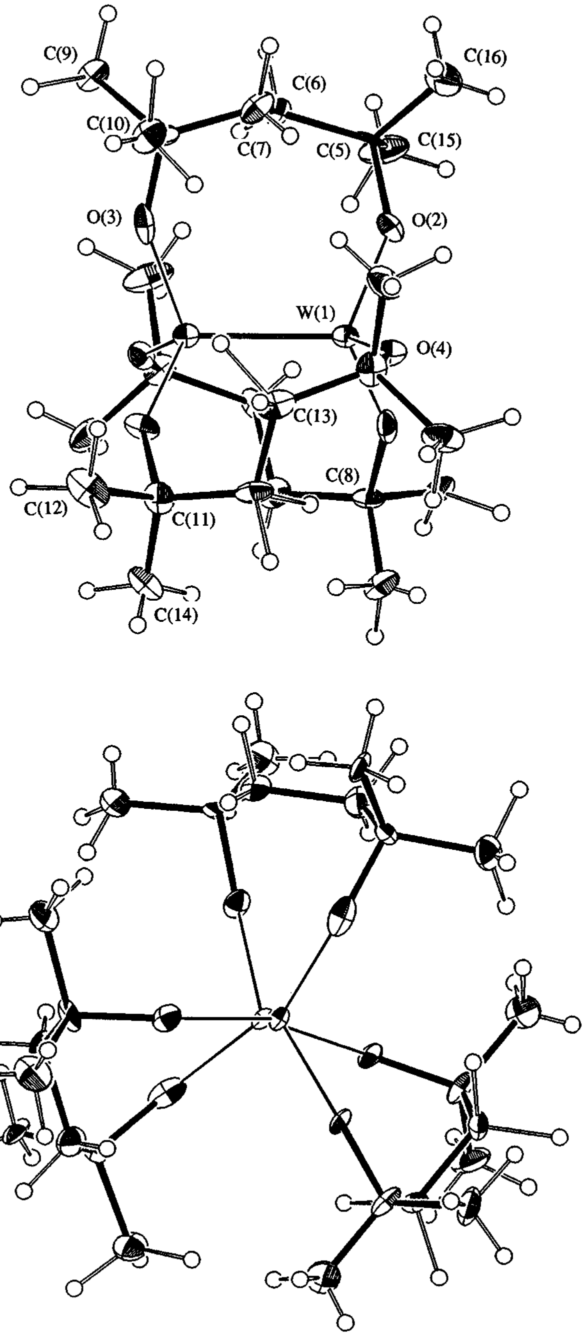

Figure 1. ORTEP drawing of **Ib** showing the atom number scheme (top) and a view of the molecule down the W−W axis (bottom).

W$_2$(μ-O$_2$C$_8$H$_{16}$)(O$_2$C$_8$H$_{16}$)$_2$(HNMe$_2$)$_2$, IIb. Crystals suitable for X-ray diffraction were obtained by cooling a THF/diethyl ether/hexane reaction solution of W$_2$(NMe$_2$)$_6$ and 2,5-dimethylhexane-2,5-diol to −20 °C for 10 h. The material crystallized with a disordered solvent molecule on a four fold axis. This was included in the refinement, although the absolute nature of the solvent cannot be rigorously defined but probably it is THF. A ball-and-stick diagram is shown parallel to the metal−metal vector in Figure 2. Crystallographic data collection parameters are given in Table 3 and selected bond distances and angles in Table 2.

The molecule of **IIb** adopts essentially two staggered square planar ends supporting a metal−metal multiple bond. The diolate ligands form one seven-membered ring to each tungsten atom and one eight-membered ring incorporating the metal−metal multiple bond. The two dimethylamine Lewis base ligands are anti to one another about the metal−metal multiple bond. The compound has a C_2 axis bisecting the M−M multiple bond and C(14)−C(14)′.

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(7) Cf. The reaction W$_2$(OCH$_2{}^t$Bu)$_6$ + P^{n}Bu$_3$ $\rightleftharpoons$ W$_2$(OCH$_2{}^t$Bu)$_6$(P^{n}Bu$_3$): Budzichowski, T. A.; Chisholm, M. H.; Folting, K. *Chem.—Eur. J.* **1996**, *2*, 110.

(8) Chisholm, M. H. *J. Chem. Soc., Dalton Trans.***1996**, 1781.

(9) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681.

Table 1. Selected Bond Distances (Å) and Angles (deg) in **Ib**

Bond Distances			
W(1)−W(1′)	2.363(1)	C(5)−C(16)	1.53(2)
W(1)−O(2)	1.872(8)	C(6)−C(7)	1.56(2)
W(1)−O(3)	1.870(9)	C(7)−C(8)	1.50(2)
W(1)−O(4)	1.879(7)	C(8)−C(9)	1.52(2)
O(2)−C(5)	1.45(1)	C(8)−C(10)	1.54(2)
O(3)−C(8)	1.44(1)	C(11)−C(12)	1.54(2)
O(4)−C(11)	1.43(1)	C(11)−C(13)	1.53(2)
C(5)−C(6)	1.49(2)	C(11)−C(14)	1.49(2)
C(5)−C(15)	1.55(2)	C(13)−C(13′)	1.55(2)
Bond Angles			
W(1)−W(1′)−O(2)	110.7(2)	C(5)−C(6)−C(7)	114(1)
W(1)−W(1′)−O(3)	109.4(2)	C(6)−C(7)−C(8)	113(1)
W(1)−W(1′)−O(4)	110.2(3)	O(3)−C(8)−C(7)	111.3(9)
O(2)−W(1)−O(3)	108.0(3)	O(3)−C(7)−C(9)	106.2(9)
O(2)−W(1)−O(4)	107.7(3)	O(3)−C(8)−C(10)	106.2(9)
O(3)−W(1)−O(4)	110.8(3)	C(7)−C(8)−C(9)	112(1)
W(1)−O(2)−C(5)	148.3(7)	C(7)−C(8)−(C10)	110(1)
W(1)−O(3)−C(8)	149.8(7)	C(9)−C(8)−C(10)	110(1)
W(1)−O(4)−C(11)	149.5(8)	O(4)−C(11)−C(12)	106(1)
O(2)−C(5)−C(6)	110.3(9)	O(4)−C(11)−C(13)	111(1)
O(2)−C(5)−C(15)	105.2(9)	O(4)−C(11)−C(14)	108(1)
O(2)−C(5)−C(16)	106(1)	C(12)−C(11)−C(13)	111(1)
C(6)−C(5)−C(15)	111(1)	C(12)−C(11)−C(14)	110(1)
C(6)−C(5)−C(16)	113(1)	C(13)−C(11)−C(14)	111(1)
C(15)−C(5)−C(16)	111(1)	C(11)−C(13)−C(13′)	115(1)

Table 2. Selected Bond Distances (Å) and Angles (deg) for **IIb**

Bond Distances			
W(1)−W(1)′	2.320(1)	O(7)−C(6)	1.42(2)
W(1)−O(2)	1.976(9)	O(12)−C(13)	1.44(2)
W(1)−O(7)	1.961(9)	N(17)−C(18)	1.49(2)
W(1)−O(12)	1.925(8)	N(17)−C(19)	1.46(2)
W(1)−N(17)	2.29(1)	N(17)−H(25)	0.79(5)
O(2)−C(3)	1.44(2)	H(25)−O(2)′	2.24(5)
Bond Angles			
W(1)′−W(1)−O(2)	97.4(3)	W(1)−N(17)−C(19)	114.5(9)
W(1)′−W(1)−O(7)	101.9(2)	C(18)−N(17)−C(19)	109(1)
W(1)′−W(1)−O(12)	106.6(3)	O(2)−C(3)−C(4)	111(1)
W(1)′−W(1)−N(17)	92.1(3)	O(2)−C(3)−C(8)	108(1)
O(2)−W(1)−O(7)	91.6(3)	O(2)−C(3)−C(9)	106(1)
O(2)−W(1)−O(12)	98.5(3)	O(7)−C(6)−C(5)	111(1)
O(2)−W(1)−N(17)	170.0(4)	O(7)−C(6)−C(10)	112(1)
O(7)−W(1)−O(12)	148.2(4)	O(7)−C(6)−C(11)	105(1)
O(7)−W(1)−N(17)	83.3(4)	O(12)−C(13)−C(14)	111(1)
O(12)−W(1)−N(17)	81.7(4)	O(12)−C(13)−C(15)	110(1)
W(1)−−O(2)C(3)	126.7(8)	O(12)−C(13)−C(16)	106(1)
W(1)−O(7)−C(6)	133.1(8)	C(14)−C(13)−C(15)	109(1)
W(1)−O(12)−C(13)	148.8(9)	N(17)−H(25)−O(2)′	168(3)
W(1)−N(17)−C(18)	116.5(9)		

Table 3. Summary of Crystallographic Data

	Ib	IIb
empirical formula	$C_{24}H_{48}O_6W_2$	$C_{28}H_{62}N_2O_6W_2$
space group	$I4_1/a$	$P4/ncc$
cell dimens		
T (°C)	−171	−170
a (Å)	12.568(3)	20.188(3)
b (Å)	12.568(3)	
c (Å)	37.075(8)	17.819(3)
Z	8	8
V (Å^3)	5856.41	7261.98
d_{calcd} (g cm^{-3})	1.822	1.629
MW	800.00	890.51
λ (Å)	0.710 69	0.710 69
$R(F)^a$	0.0384	0.0439
$R_w(F)^b$	0.0372	0.0421

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = \{\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$ where $w = 1/\sigma^2(|F_o|)$.

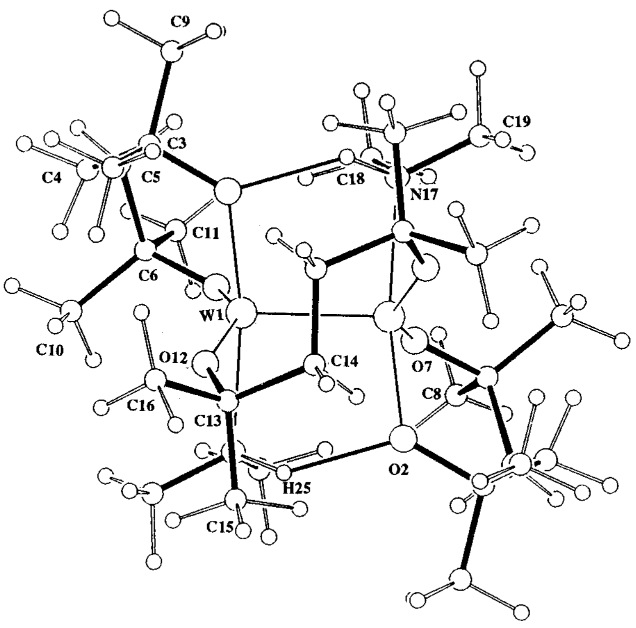

Figure 2. Ball-and-stick representation of **IIb** looking perpendicular to the metal−metal vector.

The W−W distances of 2.320(1) Å and the W−O distances of 1.976(9), 1.961(9) and 1.925(8) Å are typical of those observed in other $M_2(OR)_6L_2$ complexes.[9] These M−O bond distances are indicative of some $M(d\pi)-O(p\pi)$ interactions with the oxygen acting as π bases. Notably, the eight-membered diolate ring has the shorter M−O distance of 1.925(8) Å, possibly as a consequence of less ring strain in a metal−metal-containing eight-membered ring relative to that of a seven-membered ring. The W−N distances of 2.29(1) Å are not exceptional and are identical to the W−N distances found in $W_2(OPr^i)_6(py)_2$ and $W_2(OPr^i)_6(HNMe_2)_2$.[9]

The W−W−O angles are 97.4(3) and 101.9(3)° for the seven-membered rings and 106.6(3)° for the eight-membered rings. The W−W−N angle is smaller than the M−M−O angles at 92.1(3) Å.

The hydrogen atoms were refined isotropically in the analysis, and this together with the N(17)−O(2)′ distance of 2.923(2) Å suggests that a hydrogen bond is present between N(17)/O(2)′ and N(17)′/O(2). This nonbonded distance involving N−H···O has been seen in two similar structures, $W_2(OPr^i)_6(HNMe_2)_2$[6] and $W_2(OBu^t)_4(HNPh)_2(H_2NPh)_2$.[10]

IIb is the first structural example of a dinuclear complex containing an eight membered (M−M) ring and two seven-membered rings. In hydrocarbon rings the angle strain induced by placing a triple bond (180° angle preferred) into the ring can only be accommodated in rings with nine or more atoms. The formation of an eight-membered ring containing a W−W triple bond is facilitated by the smaller angles obtainable at the metal (as a result of more MOs available). The ring is sufficiently flexible to allow the presumably energetically preferred staggered conformation of the O(12)−W(1)−W(1)′−O(12)′ frame (dihedral angle >30°), rather than the eclipsed configuration observed in $W_2(O_2C_2Me_4)_3$[3b] which has the M≡M incorporated in three six-membered rings. It seems likely that a propellane-like structure with the three diolate rings spanning the W≡W moiety would not be able to accommodate attendant Lewis bases perpendicular to the W−W vector because of steric crowding afforded by the methyl groups on L.

Concluding Remarks

The formation of the compounds **Ia** and **Ib** provide rare examples of inorganic (6,6,6) propellanes. The central W_2O_6

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(10) Chisholm, M. H.; Folting, K.; Parkin, I. P., Streib, W. E. *Polyhedron* **1991**, *10*, 237.

core is distorted little from that seen in other $W_2(OR)_6$ structures. Rotation about the $M\equiv M$ bond is restricted on the NMR time scale. The formation of the kinetic product **IIb**, W_2(diolate)$_3$-$(HNMe_2)_2$, in the reaction involving $W_2(NMe_2)_6$ and the diol is most interesting as is the reluctance of **Ib** to react with excess $HNMe_2$ to form **IIb** at low temperatures. The latter finding might lead one to think that the conversion of **IIb** to **Ib** involves initial loss of $HNMe_2$ followed by the η^2-diolate → μ-diolate conversion. By the law of microscopic reversibility, compounds **Ia** and **Ib** would not directly react with $HNMe_2$ to give **IIa** and **IIb** but rather **Ia** and **IIb** must undergo an isomerization to $M_2(\mu\text{-L})(\eta^2\text{-L})_2$. This matter will be given further attention in the following paper. The lack of reactivity of the $M_2(\mu\text{-L})_3$ complexes with CO, ethyne, ethene, and $MeC\equiv N$ is also noteworthy with respect to the facility of reactions involving related $M_2(OR)_6$ complexes. This presumably reflects the higher barrier to substrate uptake and activation imposed by the introduction of the three bridging diolate ligands. This was seen previously for the pinacolate complex $W_2(O_2C_2Me_4)_3$.[3b]

Experimental Section

All reactions were performed under dry nitrogen atmospheres by standard Schlenk techniques. Solvents were dried and deoxygenated by standard methods. ^{1}H and ^{13}C NMR were recorded on a Varian XL300 spectrometer in C_6D_6 or $C_6D_5CD_3$ and referenced to residual protio and ^{13}C peaks of the solvents. Higher field ^{1}H NMR measurements were obtained on a Brucker Model 500 instrument at 500 MHz in C_6D_6. Variable-temperature ^{1}H NMR were obtained at 300 MHz and referenced to an external methanol standard. Infrared spectra were obtained as pressed KBr disks on a Perkin-Elmer Model 283 spectrophotometer. $M_2(OBu^t)_6$ and $M_2(NMe_2)_6$ (M = Mo, W) were prepared by literature procedures and recrystallized from hot hexane prior to use. 2,5-Dimethylhexane 2,5-diol, LH_2, was purchased from Aldrich Chemical Co. and used a supplied. Microanalyses were furnished by Oneida Research Services, Whiteboro, NY.

Preparation of $W_2(\mu\text{-L})_3$, Ib. Ditungsten hexakis(*tert*-butoxide) (1.80 g, 2.20 mmol) was dissolved in hexane (10 mL) at room temperature and LH_2 (0.96 g, 0.066 mmol) was added in THF (15 mL)/toluene (15 mL) dropwise over 5 min. The mixture was stirred at room temperature for 2 days, during which time the solution lightened from dark red to bright orange and produced a fine orange precipitate. The solvent was removed *in vacuo* to leave an orange powder which was washed with cold diethyl ether (10 mL at 0 °C). The solid was redissolved in toluene (15 mL) at +60 °C and allowed to cool to −20 °C in a refrigerator overnight. This produced orange cubic crystals of **Ib**. The solvent was removed by filtration and the crystals washed with hexane (10 ml) yielding $W_2(\mu\text{-L})_3$ (1.21 g, 1.50 mmol, 70%). Anal. Calcd: C, 36.10; H, 6.00; N, 0.0. Found: C, 36.36; H, 6.19; N, 0.0. Mp: 130 °C dec. Mass spectrometry: parent ion M^+ at 800 amu with correct isotopic correlation. IR (cm^{-1}): 2950 vs, 2900 vs, 2860 sh, 1460 m, 1440 m, 1415 m, 1370 s, 1355 vs, 1305 m, 1260 s, 1210 s, 1185 s, 1160 s, 1140 vs, 1095 vs, 1050 w, 1010 s, 970 vvs, 930 s, 915 s, 910 m, 830 s, 790 s, 590 s, 570 vs, 530 s, 465 m, 400 m, 340 m. ^{1}H NMR in C_6D_6 at 25 °C: $\delta = 2.78$ (m, 6H), 1.92 (m, 6H), 1.62 (s, 18H), 1.23 (m, 18H) ppm (temperature and field invariant −90 to +105 °C in $C_6D_5CD_3$).

The crystals grown from toluene of **Ib** were suitable for X-ray crystallography.

The reaction of $Mo_2(OBu^t)_6$ and LH_2 was performed under the same scale and conditions as outlined for tungsten above, yielding $Mo_2(\mu\text{-L})_3$, **Ia**, (1.00 g, 1.60 mmol, 72%). Mp: 135 °C dec. IR (cm^{-1}): 2955 vs, 2900 vs, 2860 sh, 1465 m, 1440 m, 1415 m, 1370 s, 1355 vs, 1305 m, 1260 s, 1210 s, 1185 s, 1165 s, 1145 vs, 1100 vs, 1055 w, 1010 s, 975 vvs, 930 m, 915 s, 915 m, 835 m, 790 s, 590 s, 575 vs, 520 s, 465 m, 400 m, 340 m. ^{1}H NMR in C_6D_6 at 25 °C: $\delta = 2.82$ (m, 6H), 1.88 (m, 6H), 1.60 (s, 18H), 1.22 (s, 18H), ppm (temperature invariant +25 to +80 °C in C_6D_6).

Preparation of $W_2(\mu\text{-L})(\eta^2\text{-L})_2(HNMe_2)$, IIb. $W_2(NMe_2)_6$ (0.750 g, 1.18 mmol) was dissolved in hexane (10 mL) and toluene (5 mL) at room temperature. This solution was cooled to −10 °C and LH_2 (0.54 g, 3.54 mmol) added in THF (10 mL)/diethyl ether (10 mL) causing a darkening in color of the solution to dark red and after 25 min with stirring to a dark green. The solution was stirred at −10 °C for 4 h by use of a magnetic follower, then reduced to one-third volume *in vacuo* and cooled to −20 °C in the refrigerator. After 12 h at −20 °C a number of very large (30−250 mg each) parallelepiped green crystals were deposited. The solvent was removed by decanting, and the crystals were washed with cold hexane (2 × 10 mL) (0 °C), yielding **IIb** (0.795 g, 0.89 mmol, 75%). Anal. Calcd: C, 37.88; H, 6.98; N, 3.15. Found for $W_2(\mu\text{-}O_2C_8H_{16})(\eta^2\text{-}O_2C_8H_{16})_2(HNMe_2)_2$: C, 37.62; H, 7.12; N, 3.03. Mp: 101 °C dec. IR (cm^{-1}): 3140 m, 2940 vs, 2900 vs, 1460 vs, 1410 m, 1370 vs, 1300 w, 1280 s, 1255 m, 1240 s, 1195 s, 1140 vs, 1090 vs, 1040 w, 1015 m, 960 s, 920 s, 895 vs, 8960 m, 815 s, 780 m, 640 s, 580 s, 550 m, 500 m, 470 m, 405 m, 360 m, 340 m. ^{1}H NMR (C_6D_6 at 25 °C): $\delta = 5.21$, (s, 2H), 3.62 (s, 2H), 3.10 (m, 4H), 2.21 (m, 4H), 1.79 (m, 4H), 1.70 (d, 12H), 1.45 (m, 18H), 1.23 (s, 3H), 0.97 (s, 3H) ppm. ^{1}H VT NMR of **IIb** showed little variation from −95 to +25 °C ($C_6D_5CD_3$); above 35 °C **IIb** converts to **Ib** quite rapidly ($t_{1/2} \sim 10$ min at 65 °C). Mass spectrometry: no M^+, highest $M = M^+ - 2HNMe_2$, 800 amu, with correct isotopic correlation. If the reaction of $W_2(NMe_2)_6$ with LH_2 is performed at room temperature or above, significant amounts of **Ib** are formed (up to 20%) along with **IIb**. The crystals of **IIb** can be easily manually separated in this case because of their size. If the reaction to form **IIb** is performed at +65 °C for 5 h under a flowing nitrogen atmosphere, then almost exclusively **Ib** is obtained.

The reaction to form $Mo_2(\mu\text{-L})(\eta^2\text{-L})_2(HNMe_2)_2$, **Ia**, proceeds analogously to the tungsten case. Yield: 0.475 g, 0.80 mmol, 68%. ^{1}H NMR in C_6D_6 at 25 °C: $\delta = 5.18$ (s, 2H), 3.65 (s, 2H), 3.05 (m, 4H), 2.20 (m, 4H), 1.80 (m, 4H), 1.70 (d, 12H), 1.47 (m, 18H), 1.25 (s, 3H), 0.98 (s, 3H) ppm. IR (KBr disk): 3140 m, 2945 vs, 2895 vs, 1460 vs, 1410 m, 1375 vs, 1300 w, 1280 s, 1255 m, 1240 s, 1195 s, 1140 vs, 1085 vs, 1035 vs, 1020 m, 970 s, 920 s, 895 vs, 860 w, 815 s, 769 m, 640 s, 585 m, 555 m, 505 m, 475 m, 415 m, 360 m, 340 m. Mp: 100.3 °C dec.

Thermolysis Studies of IIb. **IIb** (0.015 g) was dissolved in C_6D_6 in a 5 mm NMR tube. The solution was warmed to 65 °C for 1 h and the ^{1}H NMR obtained every 10 min. This showed the formation of **IIa** and $HNMe_2$. The half-life of **IIa** at +65 °C was 10 min; after 1 h >90% **Ib** was produced. The formation of **Ib** was also confirmed by allowing the NMR solvent to evaporate at RT under N_2 to produce orange crystals of **Ib** which had the same IR, mp, and ^{1}H NMR as those obtained above for **Ib**.

An NMR tube containing **IIb** dissolved in C_6D_6 was sealed under vacuum and kept at room temperature. After 2 days, only **Ib** and $HNMe_2$ could be detected by ^{1}H NMR spectroscopy.

A sample (0.100 g) of solid **IIb** was powdered and heated to 85 °C under dynamic vacuum for 2 h. The ^{1}H NMR in C_6D_6 of the resultant solid showed only unreacted **IIb.** A sample of solid **IIb** was heated under dynamic vacuum to above its melting point (120 °C), for 5 min; the green solid turned orange after this time. The IR and ^{1}H NMR spectra of the resulting powder revealed the conversion to **Ib**, by comparison with standard spectra. Similar results were obtained for **IIa**.

Reactions of Ia with $HNMe_2$. $W_2(\mu\text{-L})_3$ **Ia** (0.100 g, 0.086 mmol), was dissolved in toluene (3 mL, $C_6D_5CD_3$) at room temperature. The solution was freeze−thaw degassed twice and a 100-fold excess of $HNMe_2$(g) was condensed onto the frozen solution at −170 °C on a calibrated gas line. The solution was allowed to warm to room temperature and left for 10 h. After this time the solution had changed color from orange to dark green. After 3 days, 0.5 mL of the resulting solution was withdrawn and the ^{1}H NMR spectrum recorded, and excess (10-fold excess) dimethylamine was added to the mother solution. The ^{1}H NMR spectrum showed in addition to $HNMe_2$, >50% $W_2(\mu\text{-L})(\eta^2\text{-L})_2(HNMe_2)_2$, 30% $W_2(\mu\text{-L})_3$, and a trace of other unidentified products. Over successive days further aliquots of solution were taken and the ^{1}H NMR spectra were recorded. These showed no change in the equilibrium distribution as outlined above.

NMR tube solutions of **Ib** in toluene-d_8 were frozen at −171 °C and a >100-fold excess of $HNMe_2$ was added. The frozen solutions were allowed to warm to −70 and −50 °C respectively and held at these temperatures for 2 months with the ^{1}H NMR spectra of the solutions being recorded every 2 weeks. Both solutions showed only the presence of **Ib** and $HNMe_2$ throughout the time period of the experiment.

Crystallographic Determinations. General operating procedures and listings of programs have been reported.[11]

$W_2(\mu$-L$)_3$, Ib. A crystal of suitable size was mounted using silicone grease and was transferred to a goniostat where it was cooled to −171 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed symmetry and systematic absences corresponding to the tetragonal space group $I4_1/a$.

The structure was solved by a standard combination of direct methods (SHELXS) and Fourier techniques. The W atom position was obtained from an initial *E*-map, and the remainder of the non-hydrogen atoms were found in subsequent iterations of least-squares refinement and difference Fourier calculations. After partial refinement of the non-hydrogen atoms, a difference Fourier revealed many of the hydrogen atoms. The remaining hydrogen atoms were placed in idealized locations based on the positions of the located atoms, and all were refined in the final cycles. Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms, isotropically to a final *R* factor of 3.8%.

$W_2(\mu$-L$)(\eta^2$-L$)_2(HNMe_2)_2$, IIb. The air-sensitive sample was handled in a dry nitrogen glovebag. A small fragment was cleaved from a larger crystal, and it was affixed to the glass fiber and transferred to the goniostat where it was cooled to −170 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited 4/*mmm* diffraction symmetry. The systematic extinctions of $hk0$ for $h + k = 2n + 1$, of $hh1$ for $1 - 2n+1$, and of $0k1$ for $1 - 2n+1$, uniquely identified the space group as $P4/ncc$. This choice was confirmed by the successful solution and refinement of the structure. Data collection was undertaken as detailed in Table 3. Within the given range a total of 6941 reflections (including space group extinctions and standard reflections) were collected. Plots of the four standard reflections monitored every 400 reflections showed no systematic trends. Following the usual data reduction and averaging of redundant data a unique set of 2394 reflections was obtained. An absorption correction was carried out. The *R* for the averaging was 0.078 for 2315 reflections observed more than once.

The structure was solved by using the usual combination of direct methods and Fourier techniques. The unique W atom was located in the initial *E*-map from MULTAN78. The remainder of the non-hydrogen atoms were located in successive difference Fouriers. Following initial refinement almost all of the hydrogen atoms (at least one on each methyl-group) were located. The asymmetric unit contains one half-molecule of the W_2-complex, as well as a very disordered, unidentified (possibly THF) solvent molecule. The W_2 complex is located on a crystallographic 2-fold axis (f), while the solvent molecule is disordered around a 4-fold axis (c). The final cycles of full-matrix least squares refinement was carried out by using anisotropic thermal parameters on the non-hydrogen atoms in the W_2 complex and isotropic thermal parameters on the hydrogen atoms and the solvent atoms (C(20) through C(23)). The final *R* was 0.044; $R_w(F)$ was 0.042. The total number of variables was 308, giving a ratio of observations to variables of 5.80.

The final difference Fourier was essentially featureless. In spite of the absorption correction there was a residual of about 3 e/Å^3 in the immediate vicinity of the W atom. Several 1 e/Å^3 peaks were located in the area of the solvent.

Since the solvent was not identified with certainty, it has not been included in the calculation of the density.

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Supporting Information Available: Tables of isotropic thermal parameters, anisotropic thermal parameters, complete listings of bond distances and bond angles, and full details of the data collection and VERSORT and stereodrawings (19 pages). Ordering information is given on any current masthead page.

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