Ring-Opening of σ-Thienyl and σ-Furyl Ligands at Ditungsten (M≡M) Centers

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Abstract: A series of compounds of formula 1,2-$M_2(\sigma\text{-Th})_2(NMe_2)_4$, **1**, has been prepared, where M = Mo and/or W and Th = 2-thienyl[2-Th], 3-thienyl[3-Th], 5-methyl-2-thienyl[2,5-MeTh], and 2-benzothienyl[2-BTh]. In hydrocarbon solvents these compounds exist as a mixture of anti and gauche rotamers having a central $CN_2M{\equiv}MN_2C$ core. Addition of ^{t}BuOH or CF_3Me_2COH to hydrocarbon solutions of **1**, where M = W, lead to ring-opened products, **2**, when the thienyl ligand is attached via the 2-carbon position. No ring-opening occurs for 3-thienyl derivatives. $W_2(OR)_5(\mu\text{-}CCH_2CHCHS)(\sigma\text{-2-Th})$, **2**, where one of the 2-thienyl rings has been opened, has been fully characterized and shown to be derived from a ring-opened μ-vinylidene intermediate $W_2(O^tBu)_4(\mu\text{-}CCHCHCHS)(\sigma\text{-2-Th})$. Rather interestingly, the compound $W_2(\sigma\text{-2-Th})(NMe_2)_5$ reacts with ^{t}BuOH to give only $W_2(2\text{-Th})(O^tBu)_5$ and $HNMe_2$. Reactions between **1** and the less sterically demanding alcohols ^{i}PrOH and ^{t}BuCH$_2$OH lead to $W_2(OR)_6$ compounds with liberation of $HNMe_2$ and the sulfur containing hydrocarbon. Compound **1** (M = W, 2-Th) reacts with CO_2 to give $W_2(NMe_2)_2(O_2CNMe_2)_2(\sigma\text{-2-Th})_2$, **3**, while with pivalic anhydride $W_2(O_2C^tBu)_4$ is formed via reductive elimination of the C−C coupled product 2,2′-bithiophene and ^{t}BuCONMe$_2$ (4 equiv). **1** (M = W, 2-Th) and CO yield a product formulated as $W_2(NMe_2)_4(\mu\text{-}CCHCHCHS)(\sigma\text{-2-Th})(CO)_3$ wherein one ring has opened to form a μ-vinylidene thiolate ligand. Attempts to prepare 1,2-$W_2L_2(NMe_2)_4$ compounds are described where L = an η^1-nitrogen containing heterocycle but only for L = 2-methylindolyl was a compound successfully characterized. Reactions of these compounds with ^{t}BuOH gave $W_2(O^tBu)_6$ and LH (2 equiv). The compound $W_2(\sigma\text{-2-Fu})_2(NMe_2)_4$ was prepared and characterized (2-Fu = 2-furyl) and shown to undergo ring-opening in its reaction with ^{t}BuOH to give $W_2(O^tBu)_5(\mu\text{-}CCH_2CHCHO)(\sigma\text{-2-Fu})$, **4**, in an analogous manner to the 2-Th complex. The complexes **1** (M = W, 2-Th), **2**, **3**, and **4** have been characterized by single crystal X-ray studies. The results described herein are compared to other ring-opening reactions of S, N, and O organic heterocyclic compounds as models for the activation of S, N, and O containing fossil fuels in hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) processes. The cleavage of the C−X bonds at the $(M{\equiv}M)^{6+}$ centers (M = Mo, W and X = S, N and O) is also compared with earlier cleavage reactions involving C≡O, RC≡N, $R_2C{=}O$, and $Ar_2C{=}S$ compounds.

Introduction

The removal of sulfur and nitrogen from fossil-fuel during the refining process, usually referred to as HDS (hydrodesulfurization) and HDN (hydrodenitrogenation), is extremely important for the reduction of SO_2 and NO_x emissions.[1] As petroleum and coal gas feedstocks are passed over a Co-Mo/Al_2O_3 catalyst under a H_2 atmosphere at roughly 400 °C,[2] sulfur and nitrogen are removed as hydrogen sulfide and ammonia from organosulfur and organonitrogen compounds, respectively, the composition of which may vary greatly depending on the source of feedstocks.[3] In addition to these processes, oxygen-containing organic compounds can undergo HDO (hydrodeoxygenation) to produce water. It is well documented that the presence of one heteroatom-containing organic compound can affect the removal of another.[1] Since these three classes of reactions (HDS, HDN, and HDO) occur simultaneously in hydroprocessing, all must be considered if the reactivity patterns of commercial fossil-fuels are to be understood. One approach to understanding how heteroatom-containing compounds undergo HDS, HDN, or HDO on transition-metal based heterogeneous catalysts is to look at model compounds in homogeneous systems, which can easily be studied using solution techniques. Both heterogeneous and homogeneous modeling studies of these processes have primarily focused upon reactions of less reactive aromatic heteroatom-containing compounds such as thiophene, thiophene derivatives, pyridine, indoles, furans, and furan derivatives.[1] Discussion has often focused on the initial binding mode of substrate to the catalyst surface and the accessibility of ring-opening routes.[4] Proposed mechanisms for heteroatom removal have been suggested for each process. For example, it is believed that HDS may proceed by two simultaneous but separate general pathways. Thiophene may lose sulfur through

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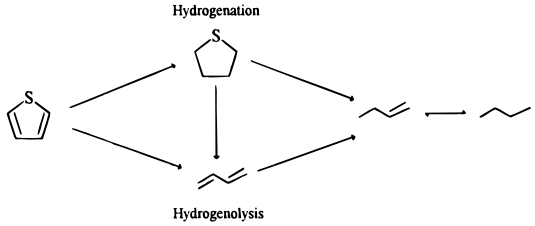
Scheme 1



hydrogenolysis *via* direct C−S bond cleavage or, alternatively, the carbon atoms of the ring may be fully or partially hydrogenated prior to C−S bond scission (Scheme 1).[5] In contrast, it is believed that hydrogenation of the heterocyclic ring is required to take place first in organonitrogen aromatics in order to reduce the energy of relatively strong C−N double bonds and, hence, permit facile carbon−nitrogen bond scission.[1,4d,e] Recent homogeneous studies on heterocyclic nitrogen compounds have suggested that substrates, such as quinoline and pyridine, may bind to the surface of a catalyst in an η^2-(N,C) (C = α-carbon) fashion.[6] Wigley *et al.*[6c,d] have demonstrated that this mode of coordination could disrupt the aromaticity of the nitrogen ring and subsequently facilitate hydrogenation of the heterocyclic ring or scission of the C−N bond. As compared to HDS and HDN, there are relatively few investigations of HDO reported in the literature, and, as a result, there is insufficient data to make any reliable conclusion about reaction pathways.

There have been several reported cases where heteroatom-containing aromatics have been activated initially *via* C−H activation.[7] For example, there is direct evidence for C−H activation in HDS; the cobalt−molybdenum−sulfide catalyst will selectively bring about C−H/D exchange of the 2 and 5 positions in thiophene at 200 °C (and to a lesser extent 3 and 4 positions). This is a temperature below which catalytic HDS proceeds.[8] A mechanism which accounts for C−H/D exchange of the 2 and 3 positions of benzothiophene was postulated, where, after initial adsorption onto the surface of the catalyst, C−H activation occurs forming either a σ-2-benzothienyl or a σ-3-benzothienyl moiety.[9a] These species may then incorporate deuterium from the surface to give deuterated benzothiophene. Similar examples of C−H/D exchange have been noted for nitrogen containing aromatics.[9b]

An example of C−H activation in homogeneous systems can be seen in the triosmium clusters $[Os_3(CO)_{12}]$ and $[Os_3(CO)_{10}(MeCN)_2]$, where both react with thiophene and furan to give the oxidative addition products $[Os_3(\mu\text{-}H)(\mu\text{-}C_4H_3E)(CO)_{10}]$ (*exo* and *endo* isomers, where E = O or S).[7a,b] Similarly, investigations by Laine,[7h,i] Deeming,[7j−l] and Merola[7m] have shown that these clusters readily activate both aliphatic and aromatic C−H bonds in heterocyclic amines.

Much of the mechanistic information known about the HDS of thiophene has been supplied by the homogeneous modeling studies of Angelici,[10] Jones,[11] Rauchfuss,[12] Bianchini,[13] Curtis,[14] and others.[15] A common aspect of their chemistry is the use of low valent, electron rich metal systems which are capable of undergoing oxidative addition reactions. In other words, many of these systems are known to activate C−H bonds.[16] For instance, Jones *et al*. have shown that the rhodium unsaturated fragment $[(C_5Me_5)Rh(PMe_3)]$ participates in C−H activation and C−S insertion processes with thiophene and a variety of its derivatives.[11a,c] The C−S and C−H activated products were formed in parallel reactions rather than in sequential reactions,

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where the C−H activated products were shown to slowly convert to the C−S insertion products. Therefore, it was concluded that C−H activation can be kinetically competitive with C−S bond cleavage, but the latter reaction is thermodynamically preferred. It is important to note that there is no evidence for a concerted process for the direct conversion of the C−H activated complexes into the C−S bond cleavage products in these systems.

The studies mentioned above have introduced new ways of viewing the reactivity of heteroatom-containing aromatics on hydroprocessing catalysts. Primarily, C−H activation has a very important role in reaction rates and mechanisms in HDS, HDN, and HDO and that α-metalated intermediates (such as the *σ*-2-thienyl moiety in the HDS of thiophene) may be involved in some of the important steps of C-E cleavage. Realizing that C−H activation may have significance in these processes, preparations of *σ*-thienyl, *σ*-indolyl, and *σ*-furyl ligands bound to ditungsten and dimolybdenum centers were undertaken, and studies of the activation of these ligands at these dinuclear centers are reported herein. These investigations were prompted by earlier work that revealed $M_2(OR)_6$ and $M_4(OR)_{12}$ compounds were capable of activating and cleaving C−O, C−S, and C−N multiple bonds.[17] However, these compounds failed to show any reactivity toward thiophene and furan, quite possibly because both are weak nucleophiles. Thus, the prior attachment to the M_2^{6+} via the η^1-C bond circumvented the problem of substrate binding.[18]

Results and Discussion

Synthesis. 1. *σ*-Thienyl Complexes. The reaction between 1,2-$W_2Cl_2(NMe_2)_4$ and 2 equiv of 2-lithiothiophene in toluene/THF at room temperature yields an orange solution containing 1,2-$W_2(\sigma\text{-2-Th})_2(NMe_2)_4$ according to eq 1.

$$1,2\text{-}W_2Cl_2(NMe_2)_4 + 2[2\text{-}LiC_4H_3S] \xrightarrow[\text{toluene/THF}]{22\ ^\circ C} 1,2\text{-}W_2(\sigma\text{-2-Th})_2(NMe_2)_4 + 2LiCl \quad (1)$$

A related reaction involving 1,2-$Mo_2Cl_2(NMe_2)_4$ yielded the molybdenum analogue **1**[Mo, *σ*-2-Th]. Compounds **1** [M = Mo and W, *σ*-2-Th] are orange, hydrocarbon-soluble, air-sensitive, crystalline solids that can also be prepared by metathesis reactions involving 1,2-$M_2Cl_2(NMe_2)_4$ and the copper reagent Li[CNCu(*σ*-2-Th)].

Related reactions involving 2-lithiobenzothiophene, 3-lithiothiophene, and 2-lithio-5-methylthiophene yielded orange crystalline complexes **1**[W, *σ*-2-BTh], **1**[W, *σ*-3-Th], and **1**[W, *σ*-2,5-MeTh]. Related molybdenum complexes were not made but most likely would be accessible from related reactions involving 1,2-$Mo_2Cl_2(NMe_2)_4$.

The reaction between $W_2I(NMe_2)_5$ and 1 equiv of 2-lithiothiophene (or Li[CNCu(*σ*-2-Th)] in toluene/THF at 0 °C gave the orange crystalline complex $W_2(\sigma\text{-2-Th})(NMe_2)_5$ in a similar manner.

The above compounds are thermally persistent at room temperature when stored under a purified N_2 or Ar atmosphere. **1**[M = Mo and W, *σ*-2-Th] sublime *in vacuo* (ca. 10^{-2} Torr) at 80 °C, while others showed considerable or total decomposition upon heating to 100 °C *in vacuo* with or without partial sublimation.

The addition of ^{t}BuOH or Me_2CF_3COH to hydrocarbon solutions of **1**[W, *σ*-2-Th; *σ*-2-BTh; *σ*-2,5-MeTh] gave ring-opened products, **2**, according to the type of reaction shown specifically for 1,2-$W_2(\sigma\text{-2-Th})_2(NMe_2)_4$ in eq **2**.

$$1,2\text{-}W_2(\sigma\text{-2-Th})_2(NMe_2)_4 + 5ROH \xrightarrow[\text{hexane}]{22\ ^\circ C} W_2(\mu\text{-}CCH_2CHCHS)(\sigma\text{-2-Th})(OR)_5 + 4HNMe_2 \quad (2)$$

The reaction between **1** (Mo, *σ*-2-Th) gave 1,2-$Mo_2(\sigma\text{-2-Th})_2(O^tBu)_4$. No ring opening was observed for molybdenum. Also for the tungsten compound **1**[W, 3-*σ*-Th] the product was $W_2(\sigma\text{-3-Th})_2(O^tBu)_4$. Reaction **2** requires sterically demanding *tert*-alcohols as neopentanol and 2-propanol yielded $W_2(OR)_6$ compounds with elimination of the thienyl ligand by C−H bond formation. Addition of neopentanol to $W_2(\mu\text{-}CCH_2CHCH)(\sigma\text{-2-Th})(O^tBu)_5$ in hydrocarbon solvents also yields $W_2(\mu\text{-}CCH_2CHCHS)(OCH_2{}^tBu)_6$ with protonolysis of the *σ*-2-Th ligand.

The compounds **2** are red-purple, hydrocarbon-soluble, air-sensitive crystalline solids that contain thiolato *μ*-alkylidyne metallacycles.

The addition of only 4 equiv of ROH (R = ^{t}Bu and Me_2CF_3C to **1**[W, *σ*-2-Th] gave a mixture of products including the ring opened product **2** shown in eq 2. Spectroscopic evidence will be presented later that reveals the key intermediate in the formation of **2** is a thiolato-*μ*-vinylidene metallocyclic compound $W_2(\mu\text{-}CCHCHCHS)(\sigma\text{-2-Th})(O^tBu)_4$.

The addition of ^{t}BuOH to $W_2(\sigma\text{-2-Th})(NMe_2)_5$ yielded only $W_2(\sigma\text{-2-Th})(O^tBu)_5$. No ring opened product was detected.

Addition of CO_2 to **1**[W, *σ*-2-Th] gave $W_2(\sigma\text{-2-Th})_2(NMe_2)_2(O_2CNMe_2)_2$ as a yellow-orange, hydrocarbon-soluble, air-sensitive crystalline material, eq 3. At room temperature this compound is resistant to further insertion of CO_2 into the remaining W-amide bonds. At temperatures above 60 °C further

$$W_2(\sigma\text{-2-Th})_2(NMe_2)_4 + \text{excess } CO_2 \xrightarrow[\text{toluene}]{22\ ^\circ C} W_2(\sigma\text{-2-Th})_2(NMe_2)_2(O_2CNMe_2)_2 \quad (3)$$

reaction with CO_2 was observed but the products were not fully characterized. Reactions of $W_2(\sigma\text{-2-Th})_2(NMe_2)_2(O_2CNMe_2)_2$ with ^{t}BuOH gave $W_2(O_2CNMe_2)_2(O^tBu)_4$ and thiophene.

Reaction with pivalic anhydride does displace all the NMe_2 ligands but the *σ*-2-thienyl ligands are eliminated by reductive carbon−carbon bond formation, eq 4.[19]

$$W_2(\sigma\text{-2-Th})_2(NMe_2)_4 + 4^tBuCOOCO^tBu \xrightarrow[\text{hexane}]{22\ ^\circ C} W_2(O_2C^tBu)_4 + 4^tBuCONMe_2 + 2,2'\text{-bithiophene} \quad (4)$$

Compound **1**[W, *σ*-2-Th] reacts with carbon monoxide (1 atm) in hydrocarbon solvents to give a ring-opened product having three carbonyl ligands according to eq 5. The carbonyl compound is red, insoluble in hexane, and only sparingly soluble in toluene and benzene. The compound is air-sensitive and thermally robust (70 °C, 12 h in toluene). It is worth mentioning that during the course of reaction **5** the carbonyl compound crystallizes as beautiful red needles on the walls of the glass.

An analogous reaction was observed for **1**[W, *σ*-2,5-MeTh] to give $W_2(\mu\text{-}CCHCHCMeS)(\sigma\text{-2,5-MeTh})(NMe_2)_4(CO)_3$.

(17) (a) For C≡O cleavage to give carbide and oxide: Chisholm, M. H.; Hammond, C. E.; Johnston, V. J.; Streib, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 7056. (b) Cleavage of RC≡N: Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291. (c) Cleavage of R_2C=O: Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 609. (d) Cleavage of ArC=S: Budzichowski, T. A.; Chisholm, M. H.; Streib, W. E. *Eur. J. Chem.* **1996**, *2*, 110.

(18) A preliminary account of one aspect of this work has appeared: Chisholm, M. H.; Haubrich, S. T.; Martin, J. D.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1994**, 683.

(19) For related reaction, see: Chisholm, M. H.; Clark, D. L.; Huffman, J. C.; Van Der Sluys, W. G.; Kober, E. M.; Lichtenberger, D. L.; Bursten, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 6796.

$$W_2(\sigma\text{-2-Th})_2(NMe_2)_4 + \text{excess CO} \xrightarrow[\text{toluene}]{22\ ^\circ\text{C}} W_2(\mu\text{-CCHCHCHS})(\sigma\text{-2-Th})(NMe_2)_4(CO)_3 \quad (5)$$

***σ*-C-Bonded Nitrogen-Containing Heterocycles.** Several problems were encountered in the attempted preparation of σ-C-bonded nitrogen-containing heterocycles according to the general reaction, eq 6, where L = the σ-C-nitrogen containing heterocycle. For example, the metathetic reaction does not proceed

$$1,2\text{-}W_2Cl_2(NMe_2)_4 + 2LiL \rightarrow 1,2\text{-}W_2(L)_2(NMe_2)_4 + 2LiCl \quad (6)$$

efficiently below 0 °C and above this temperature many of the organolithium compounds are unstable. Some react with ethers to form lithium alkoxides,[20] while others such as 2-lithiopyridine, prepared from the reaction between ^{n}BuLi and 2-bromopyridine, rearranged to give a mixture of 2-, 3-, and 4-lithiosubstituted pyridine.[21] 1-Methylpyrrole and alkyllithiums failed to react to give the desired 2-Li-1-methylpyrrole. However, the reaction between 1-methylindole and ^{n}BuLi in refluxing ether did give 2-lithio-1-methylindole in 78%[22] and thus afforded by reaction with $1,2\text{-}W_2Cl_2(NMe_2)_4$ the preparation of $1,2\text{-}W_2(\sigma\text{-2,1-MeInd})_2(NMe_2)_4$.

In a related reaction 2-lithio-1-methylimidazole was allowed to react with $1,2\text{-}W_2Cl_2(NMe_2)_4$ and a yellow crystalline product was obtained that was extremely air-sensitive and thermally unstable at room temperature under a N_2 atmosphere, decomposing with the liberation of 1-methylimidazole and the formation of an unidentified inorganic residue.

The reaction between $W_2(\sigma\text{-2,1-MeInd})_2(NMe_2)_4$ and ROH (R = ^{t}Bu, $CH_2{}^t$Bu) in hydrocarbon solutions gave $W_2(OR)_6$, $HNMe_2$, and 1-methylindole. No ring-opening was observed.

***σ*-2-Furyl Complexes.** The reaction between $1,2\text{-}W_2Cl_2(NMe_2)_4$ and 2 equiv of 2-lithiofuran in toluene/THF at room temperature yields the σ-2-furyl complex which was isolated as an orange, air-sensitive, crystalline solid, according to eq 7.

$$1,2\text{-}W_2Cl_2(NMe_2)_4 + 2[\text{Li-2-}C_4H_3O] \xrightarrow[\text{toluene/THF}]{22\ ^\circ\text{C}} 1,2\text{-}W_2(\sigma\text{-2-Fu})_2(NMe_2)_4 + 2LiCl \quad (7)$$

Treatment of a hydrocarbon solution of the latter with ^{t}BuOH gave the ring opened σ-2-furyl complex $W_2(\mu\text{-}CCH_2CHCHO)(\sigma\text{-2-Fu})(O^tBu)_5$, **4**, according to eq 8. Compound **4** is a red, air-sensitive, hydrocarbon-soluble, crystalline compound.

$$1,2\text{-}W_2(\sigma\text{-2-Fu})_2(NMe_2)_4 + 5{}^t\text{BuOH} \xrightarrow[\text{hexane}]{22\ ^\circ\text{C}} W_2(\mu\text{-}CCH_2CHCHO)(\sigma\text{-2-Fu})(O^tBu)_5 + 4HNMe_2 \quad (8)$$

Solid-State and Molecular Structures

$W_2(\sigma\text{-2-Th})_2(NMe_2)_4$. An ORTEP drawing of the structure of **1**[W, σ-2-Th] is given in Figure 1, and selected bond distances and angles are given in Table 1. In the solid state there is an anti-$CN_2W{\equiv}WN_2C$ core. All the bond distances and angles are unexceptional for a compound of the type $1,2\text{-}W_2R_2(NMe_2)_4$.[23] There is a disorder involving S(9) and C(12) of the 2-thienyl ligands. There is no evidence for W to S bonding in the ground state as the shortest W---S is ca. 3.3 Å.

$W_2(\mu\text{-}CCH_2CHCHS)(\sigma\text{-2-Th})(O^tBu)_5$. ORTEP drawings of the ring-opened thienyl compound viewed perpendicular to and down the W−W axis are given in Figure 2. Each W atom is in a pseudo trigonal bipyramidal environment sharing a common equatorial (μ-alkylidyne) carbon and an axial μ-OR group, O(28). The other axial ligand W(1) is the thiolate S(33) and at W(2) the σ-2-thienyl carbon, C(23). Selected bond distances and angles are given in Table 2.

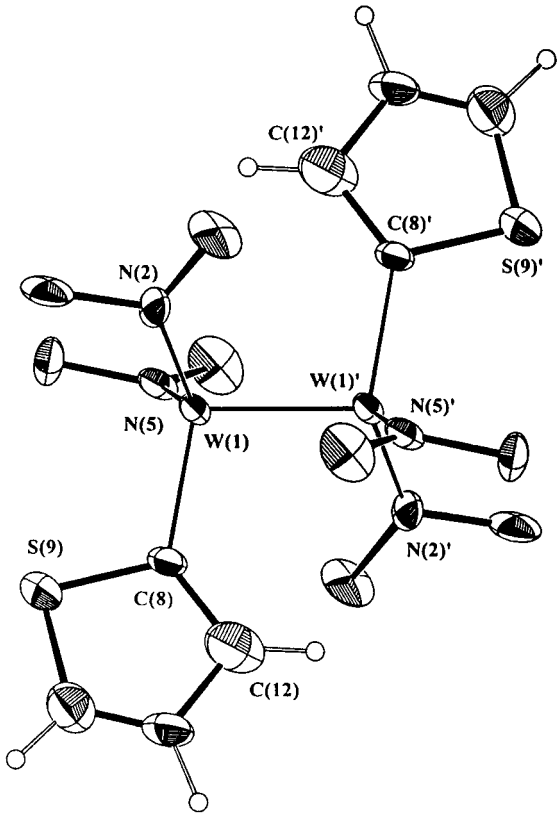


Figure 1. An ORTEP view of the centrosymmetric $W_2(\sigma\text{-2-Th})_2(NMe_2)_4$ molecule giving the atom number scheme. There is a disorder involving S(9) and C(12)—see text.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $1,2\text{-}W_2(\sigma\text{-2-Th})_2(NMe_2)_4$

A	B	distances
W(1)	W(1)′	2.2895(4)
W(1)	N(2)	1.966(1)
W(1)	N(5)	1.914(14)
W(1)	C(8)	2.138(15)
S(9)	C(8)	1.737(17)

A	B	C	angles
W(1)	W(1)	N(2)	104.3(4)
W(1)′	W(1)	C(8)	100.0(4)
W(1)	C(8)	S(9)	115.5(8)
N(5)	W(1)	N(2)	116.8(6)

The $(W{-}W)^{10+}$ distance of 2.66 Å, the W-μ-C distances 1.98(1) Å (av), and terminal and bridging W-O distances are comparable to those seen in related compounds such as $W_2(\mu\text{-}CCH_3)(OR)_7$.[24] The W−S distance, 2.43(1) Å and W−S−C angle, 108°, are both within a range expected for thiolate ligands.[25] There is a twist or puckering of both sulfur containing rings as can be seen from an inspection of Figure 2.

$W_2(\sigma\text{-2-Th})_2(NMe_2)_2(O_2CNMe_2)_2$. An ORTEP drawing of compound **3** is given in Figure 3, and a listing of selected bond

(20) Bates, R. D.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560.
(21) Gilman, H.; Spatz, S. M. *J. Org. Chem.* **1951**, *16*, 1485.
(22) Shirley, D. A.; Roussel, P. A. *J. Am. Chem. Soc.* **1953**, *75*, 375.
(23) (a) Chisholm, M. H.; Haitko, D. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 4046. (b) Chetcuti, M.; Chisholm, M. H.; Folting, K.; Haitko, D. A.; Huffman, J. C.; Janos, J. *J. Am. Chem. Soc.* **1983**, *105*, 1163.
(24) Chacon, S. T.; Chisholm, M. H.; Cook, C. M.; Hampden-Smith, M. J.; Streib, W. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 462.
(25) For thiolates bound to dimolybdenum and ditungsten centers see: Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5924; Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 754.

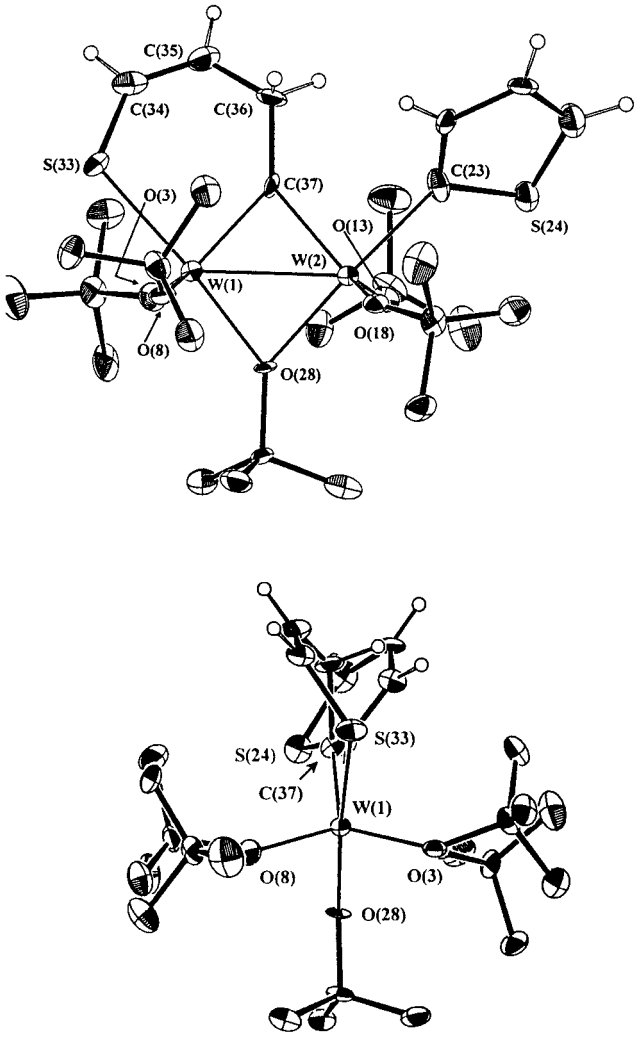


Figure 2. Two views of the $W_2(\mu\text{-}CCH_2CHCHS)(\sigma\text{-}2\text{-}Th)(O^tBu)_5$ molecule giving the atom number scheme.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $W_2(\mu\text{-}CCH_2CHCHS)(\sigma\text{-}2\text{-}Th)(O^tBu)_5$

A	B	distance
W(1)	W(2)	2.6633(6)
W(1)	C(37)	1.979(9)
C(37)	C(36)	1.485(13)
W(1)	O(28)	2.047(6)
W(1)	O(8)	1.858(6)
W(1)	S(33)	2.4314(6)
W(2)	C(37)	1.983(9)
W(2)	C(23)	2.175(10)
W(2)	O(28)	2.083(6)
W(2)	O(18)	1.875(7)

A	B	C	angle
W(1)	C(37)	W(2)	84.5(4)
S(33)	W(1)	C(37)	86.48(27)
W(1)	O(28)	W(2)	80.30(21)
S(33)	W(1)	O(28)	174.47(18)
W(2)	W(1)	S(33)	133.60(7)
C(37)	C(36)	C(35)	117.1(9)
W(1)	S(33)	C(34)	107.8(4)
O(13)	W(2)	O(18)	135.80(28)
O(3)	W(1)	O(8)	134.9(3)
C(23)	W(2)	O(28)	176.4(3)

distances and bond angles is given in Table 3. The molecule has a C_2 axis of symmetry bisecting the W−W bond. The two μ-carbamate ligands are cis and contain planar C_2NCO_2 units. The NC_2 planes of the W−NMe_2 ligands are aligned along the W−W axis to maximize Me_2N p_π-to-W d_π donation without competing for W−W π bonding d_π orbitals.[26] In order to accommodate this the two $WCNO_2$ units are significantly twisted from an eclipsed geometry. There is a disorder involving S(12) and C(15) (*i.e.*, the thienyl ring) as noted in the Experimental Section, but there is no evidence for S to W bonding as the shortest W−S distance is 3.4 Å.

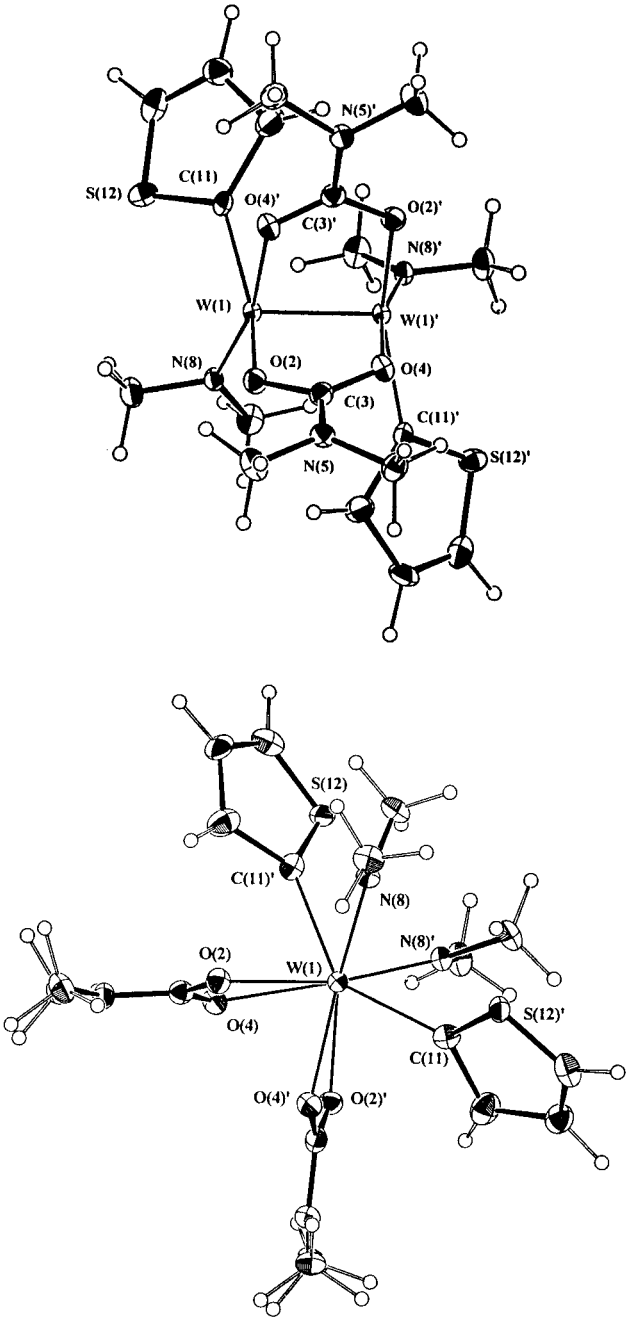


Figure 3. Two views of the $W_2(\sigma\text{-}2\text{-}Th)_2(NMe_2)_2(O_2CNMe_2)_2$ molecule giving the atom number scheme.

$W_2(\mu\text{-}CCH_2CHCHO)(\sigma\text{-}2\text{-}Fu)(O^tBu)_5$. ORTEP drawings of the molecular structure of compound **4** are shown in Figure 4, and selected bond distances and angles are given in Table 4. The compound is readily seen to be related to that of the ring-opened σ-2-thienyl compound, but the heteroatom rings are virtually planar when E = O. The W(1)−O(33) distance of 1.97(1) Å is typical for a terminal W−OR bond distance.[27] The W(1)−O(33)−C(34) angle of 131° is notably larger than the related W−S−C angle of 108° as perhaps might be expected for an alkoxide relative to a thiolate.

(26) For a discussion of the bonding in related compounds, see: Chisholm, M. H.; Haitko, D. A.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1981**, *20*, 2211.

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

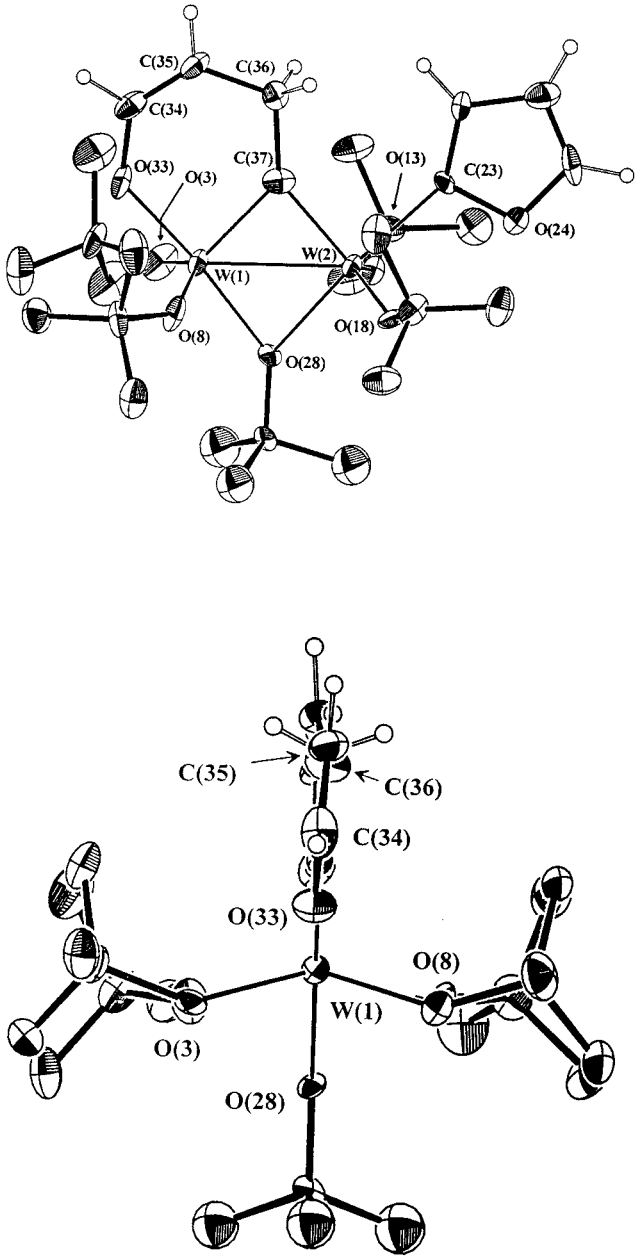


Figure 4. Two views of the $W_2(\mu\text{-}CCH_2CHCHO)(\sigma\text{-}2\text{-}Fu)(O^tBu)_5$ molecule giving the atom number scheme.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $1,2\text{-}W_2(\sigma\text{-}2\text{-}Th)_2(NMe_2)_2(O_2CNMe_2)_2$

A	B	distance
W(1)	W(1)′	2.2823(5)
W(1)	N(8)	1.948(5)
W(1)	O(2)	2.086(5)
W(1)	C(11)	2.182(7)
W(1)	O(4)′	2.173(5)

A	B	C	angle
W(1)′	W(1)	N(8)	105.85(15)
W(1)′	W(1)	C(11)	102.13(17)
W(1)	C(11)	S(12)	121.9(4)
O(2)	W(1)	O(4)′	77.48(18)
O(4)′	W(1)	N(8)	167.15(20)

Table 4. Selected Bond Distance (Å) and Angles (deg) for $W_2(\mu\text{-}CCH_2CHCHO)(\sigma\text{-}2\text{-}Fu)(O^tBu)_5$

A	B	distance
W(1)	W(2)	2.6488(13)
W(1)	C(37)	1.975(11)
C(37)	C(36)	1.491(15)
W(1)	O(28)	2.044(6)
W(1)	O(8)	1.875(7)
W(1)	O(33)	1.973(7)
W(2)	C(37)	1.971(10)
W(2)	C(23)	2.153(9)
W(2)	C(28)	2.085(6)
W(2)	O(18)	1.876(7)

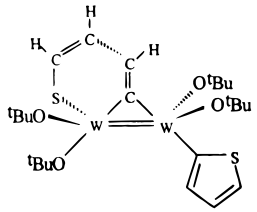
A	B	C	angle
W(1)	C(37)	W(2)	84.3(4)
O(33)	W(1)	C(37)	87.0(4)
W(1)	O(28)	W(2)	79.79(23)
O(33)	W(1)	O(28)	174.37(27)
W(2)	W(1)	O(33)	134.80(21)
C(37)	C(36)	C(35)	114.4(9)
W(1)	O(33)	C(34)	130.7(6)
O(13)	W(2)	O(18)	133.9(3)
O(3)	W(1)	O(8)	137.2(4)
C(23)	W(2)	O(28)	174.4(3)

Solution Behavior and Spectroscopic Characterizations

The NMR data for the new $1,2\text{-}W_2R_2(NMe_2)_4$ compounds, where R = a σ-carbon bonded (O, N, or S) heterocycle, are consistent with expectations based on an ethane-like $CN_2M{\equiv}MN_2C$ core with restricted rotations about the M≡M and M−N bonds on the NMR time scale. Typically, the compounds exist as a mixture of anti- and gauche-rotamers and rotation about the M−C bond when it can be inferred is rapid on the NMR time scale as was seen for $1,2\text{-}M_2(Ar)_2(NMe_2)_4$ compounds.[23b] The ^1H NMR data for $W_2(\sigma\text{-}2\text{-}Th)(NMe_2)_5$ were also consistent with expectations based on a staggered $CN_2W{\equiv}WN_3$ core with restricted rotation about the W≡W and W−N bonds.[28]

The ring-opened compounds of formula **2** and **4** showed five RO groups in the ratio 2:2:1 consistent with the solid-state structure. An assignment of the ^1H resonances arising from the ring opened compounds was possible by use of COSY ^1H coupled 2D NMR as shown in Figure 5 for the $W_2(\mu\text{-}CCH_2\text{-}CHCHS)(\sigma\text{-}2\text{-}Th)(O^tBu)_5$ compound. The carbon of the μ-alkylidyne ligand was found at δ ca. 307 with $J^{183}_{W-^{13}C} \sim 142$ Hz, $I = 22\%$ [^{183}W, $I = {}^1/_2$, 14.5% natural abundance]. These values for the $W_2(\mu\text{-}C\text{-alkylidyne})$ are almost identical to those seen for $W_2(\mu\text{-}CCH_2CH_2CH_2)(O^iPr)_6$ derived from the reaction of ethylene with $W_2(O^iPr)_6$.[29]

From ^1H and ^{13}C NMR studies of the reaction between $W_2(\sigma\text{-}2\text{-}Th)_2(NMe_2)_4$ and ^{t}BuOH in toluene-d_8 carried out in an NMR tube, the reactive intermediate in the formation of the μ-alkylidyne bridged compound **2** can reasonably be proposed to be the μ-vinylidene compound shown in **A** below. Of particular note is the detection of a $^{13}C\{^1H\}$ signal at δ 287 which is within



A

the region that we might well expect for a μ-alkylidene signal.[30] Reactions employing ^{t}BuOD reveal the formation of $W_2(\mu\text{-}CCHDCHCHS)(\sigma\text{-}2\text{-}Th)(O^tBu)_5$ supporting the view that the μ-alkylidyne complex is derived from the oxidative-addition of ^{t}BuOD to the intermediate **A**. Protonation of the vinylidene ligand in **A** would yield a μ-alkylidyne cationic complex which

(28) Schulz, H.; Folting, K.; Huffman, J. C.; Streib, W. E.; Chisholm, M. H. *Inorg. Chem.* **1993**, *32*, 6050.

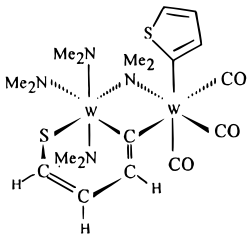
(29) Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284.

(30) (a) Reference 17. (b) Chisholm, M. H.; Klang, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2324.

would then add $^tBuO^-$. Of course, this is merely a formalism in terms of looking at the formation of $W_2(\mu\text{-}CCH_2CHCHS)(\sigma\text{-}2\text{-}Th)(O^tBu)_5$. When the reaction is followed by ^1H NMR, the formation of 1,2-$W_2(\sigma\text{-}2\text{-}Th)_2(O^tBu)_4$ can be seen at −20 °C. Ring-opening does not occur at this temperature and in the presence of an excess of ^{t}BuOH further alcoholysis occurs leading to $W_2(\sigma\text{-}2\text{-}Th)(O^tBu)_5$. However, at 0 °C in toluene-d_8 ring-opening to give $W_2(\mu\text{-}CCHCHCHS)(\sigma\text{-}2\text{-}Th)(O^tBu)_4$ is faster than alcoholysis so that compound **1** is formed preferentially.

The NMR spectra of $W_2(\sigma\text{-}R)_2(NMe_2)_2(O_2CNMe_2)_2$ compounds are quite straightforward. There are two NMe ^1H resonances separated by nearly 2 ppm assignable to the proximal and distal NMe groups.[31] Also the $O_2CN\mathit{Me}_2$ signals appear as two singlets of equal intensity because of restricted rotation about the central C−N bond of the carbamate ligands. One carbamate methyl is anti to a W−NMe_2 group, the other to the W σ-R group. When $^{13}CO_2$ is employed each of the $O_2{}^{13}CNMe_2$ signals appears as a doublet due to $^3J_{^{13}C-^1H} \sim 5$ Hz.

The structures of the ring-opened thienyl complexes formed upon the addition of CO to **1**[M = W, 2-Th and 2,5-MeTh] are proposed to be based on **B**. Evidence for the opening of one



B

of the rings comes from the two sets of C_3H_3 signals (six resonances of equal intensity). The COSY proton coupled 2D NMR spectra support the existence of two separate spin systems and show that one set has been shifted upfield relative to the other which is consistent with the disruption of aromatacity upon ring-opening. See Figure 6. There are four different NMe_2 groups at −60 °C, in toluene-d_8, 500 MHz, and eight inequivalent NMe signals of equal integral intensity are resolved.

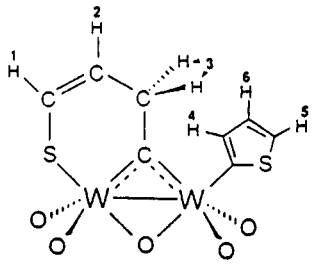
In the infrared spectrum there are three $\bar{\nu}$(CO) stretches: 1993, 1915, and 1852 cm^{-1}. These values are too high to be indicative of the formation of a carbamoyl ligand[32] and are consistent with three CO ligands occupying terminal positions on one W atom as shown in **B**. Furthermore, in the compound derived from reaction employing ^{13}CO the $^{13}C\{^1H\}$ NMR spectrum revealed three ^{13}C resonances assignable to W−^{13}CO ligands: δ 209, 203, and 202 ppm each flanked by satellites due to coupling to ^{183}W of intensity 14%. This clearly implies terminal rather than bridging CO ligands. The spectrum shown in Figure 7 reveals that each signal shows $^{13}C-^{13}C$ coupling being a doublet of doublets. The coupling between the CO ligand at δ 203.5 and 202 is 23 Hz, while that between the signals at 203/202 and 209 is ca. 3 Hz. This again is consistent with the notion that all three CO ligands are bonded to one W atom.

Because of the higher solubility in NMR solvents, the $^{13}C\{^1H\}$ NMR spectrum of the 5-methylthienyl derivative allowed detection of the μ-vinylidene carbon at δ 216.

The ^1H NMR spectra of $W_2(\mu\text{-}CCH_2CHCHS)(OCH_2{}^tBu)_6$ reveal dynamic behavior. At −70 °C in toluene-d_8 the compound is frozen out on the NMR time scale and can be assigned to the anticipated structure shown in **C** wherein a σ-2-Th ligand has merely been replaced by a neopentoxide.

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

(32) Ahmed, K. J.; Chisholm, M. H. *Organometallics* **1986**, *5*, 185.



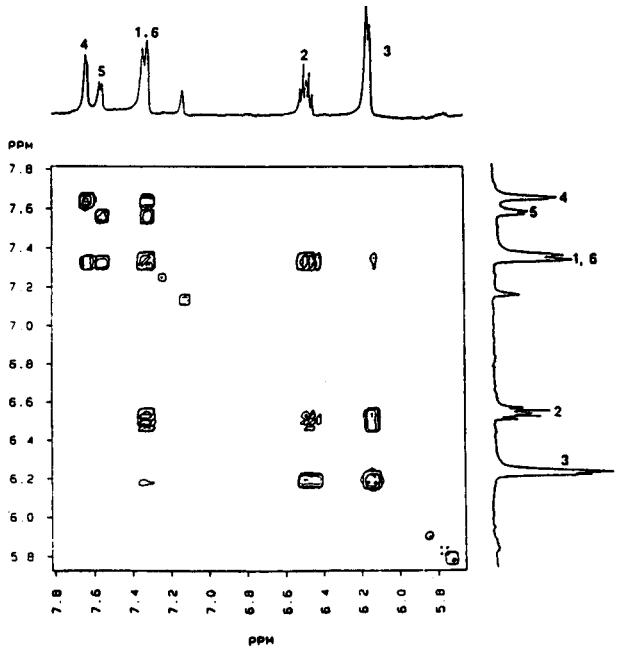
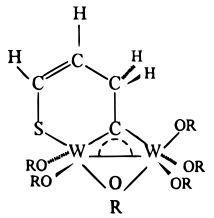


Figure 5. COSY proton coupled 2D NMR spectrum of the ring-opened and σ-2-Th region of $W_2(\mu\text{-}CCH_2CHCHS)(\sigma\text{-}2\text{-}Th)(O^tBu)_5$.

Specifically, the methylene protons exhibit six signals, two singlets and four doublets, and are in the ratio 1:1:1:1:1:1. This is consistent with two inequivalent RO ligands lying in a molecular mirror plane of symmetry and two pairs of inequivalent RO groups lying off this mirror plane. The ^{t}Bu signals appear as singlets in the ratio 1:1:2:2. Upon raising the temperature to +80 °C, the spectrum reveals only two types of



C

OR ligands in the ratio 2:4 with those of integral intensity two having diastereotopic methylene protons. The only simple explanation for this would seem to be that the bridging and one set of terminal alkoxides enter into a selective site exchange. This does not involve the two RO ligands bonded to the W atom that is also bonded to the thiolate sulfur. There is no obvious explanation why this should be so, but a similar dynamic behavior was observed for the related isopropoxide complex.

Comments on Ring-Opening

The lack of reactivity of $W_2(OR)_6$ compounds toward thiophene is understandable in terms of the weak nucleophic properties of the sulfur atom and the π-buffered weakly Lewis

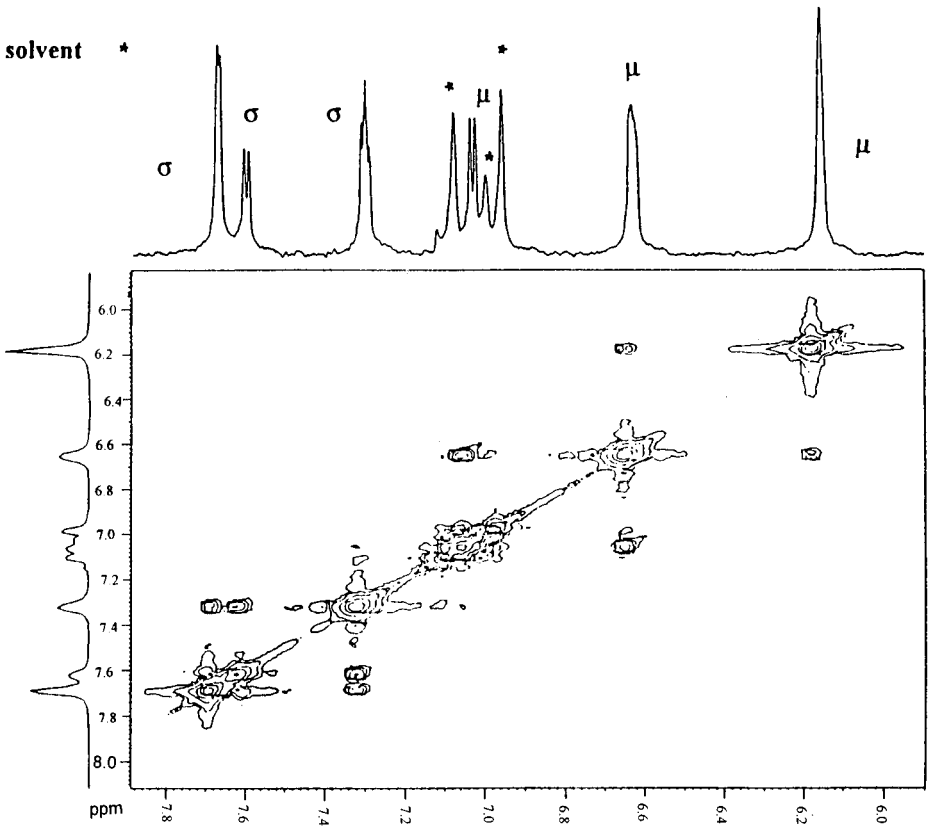


Figure 6. COSY proton coupled 2D NMR spectrum of the ring-opened and σ-2-Th region of $W_2(\mu\text{-CCHCHCHS})(\sigma\text{-2-Th})(NMe_2)_4(CO)_3$.

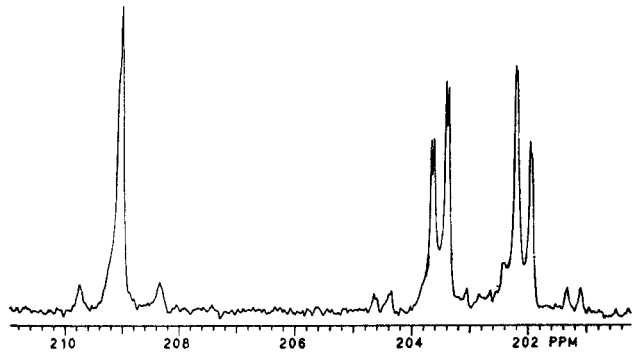


Figure 7. $^{13}C\{^1H\}$ spectrum of the carbonyl region of $W_2(\mu\text{-CCHCHCHS})(\sigma\text{-2-Th})(NMe_2)_4(^{13}CO)_3$.

acidic tungsten centers. In the presence of the strong π-donor ligands NMe_2 the new compounds of type 1,2-$W_2(\sigma\text{-R})_2(NMe_2)_4$ do not undergo ring-opening. However, replacement of NMe_2 by RO facilitates ring-opening presumably because the sulfur or oxygen is now within distance for W to E bond formation (where E = O or S). Similarly, addition of CO, which removes electron density from the $(W{\equiv}W)^{6+}$, is proposed to facilitate ring-opening for the same reason. Two points are worthy of mention at this point. 1. This ring-opening only occurs if the heteroatom can reasonably coordinate to the dimetal center. Thus σ-2-Th rings, but not σ-3-Th rings, are opened. Also no ring-opening is observed for the *N*-methylindolyl ligand where the nitrogen σ-lone pair is not accessible. 2. The ring-opening of 2-σ-Th ligands occurs for M = W and not for M = Mo. We attribute this to the greater propensity of the $(W{\equiv}W)^{6+}$ center to enter into oxidative-addition reactions relative to the $(Mo{\equiv}Mo)^{6+}$ center. This has previously manifest itself in the greater facility of $(W{\equiv}W)^{6+}$ centers to enter into reductive cleavage reactions with C−X multiple bonds.[33]

We can but speculate why $W_2(\sigma\text{-2-Th})(O^tBu)_5$ does not undergo ring-opening. Given that ring-opened products of the form $W_2(\mu\text{-CCH}_2\text{CHCHS})(OR)_6$ have been isolated from independent routes (R = ^{i}Pr and $CH_2{}^t$Bu) we feel the answer must lie in a kinetic phenomenon. Again it is possible that the π-buffered $W(O^tBu)_3$ center is insufficiently Lewis acidic to promote S-coordination across the W−W bond. In the reactions involving $W_2(\sigma\text{-2-Th})_2(NMe_2)_4$ and ^{t}BuOH only one ring is opened because ring-opening constitutes oxidative-addition. The facile conversion of the $(W{=}W)^{8+}$ center to $(W{-}W)^{10+}$ by reaction with ^{t}BuOH is consistent with earlier findings concerning the stability of alkylidyne bridged $(W{-}W)^{10+}$ centers.[34]

Concluding Remarks

The ring-opening reactions reported herein in many ways complement the modeling studies of earlier workers noted in the introduction. Namely, we have shown that substrate binding of thiophene and its derivatives to coordinatively unsaturated ditungsten centers can facilitate C−S bond cleavage. Sulfur to tungsten bonding is clearly implicated as being important since only when the metal center is sufficiently Lewis acidic does C−S bond cleavage occur. Also no ring-opening is observed in σ-3-thienyl complexes or for the methyl-indolyl derivative. The similarity of the ring-opening of the σ-2-furyl ligand is also noteworthy. Further studies of the reactivity of the ring-opened compounds, **2** and **4**, are underway. Also it will be of interest to see whether or not the addition of arylthiols facilitates similar ring-opening and in a compound of formula 1,2-$W_2(\sigma\text{-2-Th})(\sigma\text{-2-Fu})(NMe_2)_4$ which of the rings is more readily opened, *i.e.*, to compare C−O versus C−S bond cleavage.

Experimental Section

General Procedures. Standard Schlenk procedures and Vacuum Atmospheres Co. Dri-Lab Systems were used for all synthesis and sample manipulations. Solvents were distilled from sodium diphenyl

(33) See discussion in ref 17d.

(34) (a) Blau, R. J.; Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C.; Kramer, K. S.; Lobkovsky, E. B.; Streib, W. E. *Organometallics* **1995**, *14*, 1855. (b) Chisholm, M. H.; Cook. C. M.; Huffman, J. C.; Streib, W. E. Organometallics **1993**, *12*, 2677.

Table 5. Summary of Crystal Data

	I[c]	II[d]	III[e]	IV[f]
empirical formula	$C_{16}H_{30}N_4S_2W_2$	$C_{28}H_{52}O_5S_2W_2$	$C_{18}H_{30}N_4O_4S_2W_2$	$C_{28}H_{52}O_7W_2$
space group	*P*1	$P2_1/n$	*C*2/*c*	*P*1
T, °C	−170	−165	−170	−167
a, Å	16.405(4)	15.231(2)	12.912(2)	11.634(6)
b, Å	16.486(4)	12.733(2)	17.866(2)	13.024(6)
c, Å	8.757(2)	18.516(3)	10.491(2)	11.237(6)
α, deg	104.87(1)	90.0	90.0	100.14(2)
β, deg	103.90(1)	112.52(0)	98.31(1)	97.26(3)
γ, deg	88.79(1)	90.0	90.0	79.62(2)
Z	4	4	4	2
λ, Å	0.71069	0.71069	0.71069	0.71069
V, Å^3	2219.83	3317.33	2394.59	1640.71
calcd density, g/cm^{-3}	2.125	1.803	2.214	1.758
mol wt	710.26	900.54	798.28	868.41
μ (Mo Kα), cm^{-1}	15.87	15.87	15.87	15.87
$R(F)$[a]	0.0518	0.0366	0.0329	0.0414
$Rw(F)$[b]	0.0525	0.0351	0.0344	0.0400

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $Rw(F) = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2\}^{1/2}$ where $w = 1/\sigma^2(|F_o|)$. [c] I = 1,2-W_2(*σ*-2-Th)$_2$(NMe$_2$)$_4$. [d] II = W_2(*μ*-CCH$_2$CHCHS)(*σ*-2-Th)(O^{t}Bu)$_5$. [e] III = W_2(*σ*-2-Th)$_2$(NMe$_2$)$_2$(O$_2$CNMe$_2$)$_2$. [f] IV = W_2(*μ*-CCH$_2$CHCHO)(*σ*-2-Fu)(O^{t}Bu)$_5$.

ketyl under a N_2 flow and stored in solvent bottles over 4 Å molecular sieves and subjected to three freeze−thaw−degas cycles before use. *tert*-Butyl alcohol was distilled from CaH_2 as a 4.2 M benzene azeotrope and stored over 4 Å molecular sieves.

Physical Techniques. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded in dry and deoxygenated benzene-d_6, CD_2Cl_2, or toluene-d_8 on Varian XL300 (300 MHz and 75 MHz, respectively) and Bruker AM500 (500 MHz and 124 MHz, respectively) spectrometers. All ^{1}H NMR chemical shifts are reported relative to the CHD_2 quintet of toluene-d_8 set at δ 2.09 or the protio impurity in benzene-d_6 set at δ 7.15. The ^{13}C{^{1}H} NMR chemical shifts are reported relative to the ipso carbon of toluene-d_8 at δ 137.5, CD_2 (quintet) at δ 54.0, or against the central resonance of benzene-d_6 at δ 128.0. Infrared spectra were obtained from KBr pellets by using a Nicolet S510P FT-IR spectrophotometer.

Elemental analyses were performed by Desert Analytics, Tucson, AZ; ORS; Onedia Reseach Services, Inc., Whitesboro, NY, or Atlantic Microlab, Inc., Norcross, GA.

Chemicals. 1,2-$W_2Cl_2(NMe_2)_4$, 1,2-$Mo_2Cl_2(NMe_2)_4$, and $W_2I(NMe_2)_5$ were prepared by published methods.[35] *n*-Butyllithium/hexanes (2.5 M), 1-lithiothiophene (1.0 M in THF), Li[(CN)Cu(*σ*-2-thienyl)] (0.25 M in THF), and neopentanol were purchased from the Aldrich Chemical Company and used as received. Reagent grade 3-bromothiophene, benzothiophene, 1-methylthiophene, $HOCMe_2CF_3$, $HOSiMe_2{}^tBu$, isopropyl alcohol, cyclohexanol, and 1-methylindole, and furan were also purchased from the Aldrich Chemical Company and were degassed and stored over 4 Å molecular sieves.

Preparation of 1,2-W_2(*σ*-2-Th)$_2$(NMe$_2$)$_4$. A Schlenk flask was charged with 1.00 g of 1,2-$W_2Cl_2(NMe_2)_4$, (1.63 mmol), and the sample was dissolved in ≈15 mL of toluene. 2-Lithiothiophene (2.0 equiv, 3.25 mL, 3.25 mmol) was added. The reaction solution was stirred for 24 h and turned dark orange (appearance of a precipitate was apparent). The solvent was then removed *in vacuo*. The residue was extracted into hexane (4 × 10 mL) and filtered through a glass frit charged with Celite. The hexane was removed *in vacuo*, and the orange powder was dissolved in a minimal amount of toluene and crystallized at −20 °C. Orange-red, X-ray quality crystals were harvested by transferring the supernatant liquid to a separate flask and dried *in vacuo* (total crystalline yield 0.82 g, 71%). {Note: Li[(CN)Cu(*σ*-2-thienyl)] can be used instead of 2-lithiothiophene and usually allows for easier separation of salts if the reagent is fresh.}

Anal. Calcd for $W_2S_2N_4C_{16}H_{30}$: C, 27.10; H, 4.12; N, 7.89. Found: C, 27.52; H, 4.12; N, 7.64. ^{1}H NMR (toluene-d_8), −68 °C, 300 MHz: δ 7.75 (d, 2H, Th-gauche), 7.58 (d, 2H, Th-gauche), 7.28 (dd, 2H, Th-gauche), 4.16 (s, 6H, NMe proximal-gauche), 4.11 (s, 6H, NMe proximal-gauche), 2.52 (s, 6H, NMe distal-gauche), 2.45 (s, 6H, NMe distal-gauche), 7.71 (d, 2H, Th-anti), 7.38 (d, 2H, Th-anti), 7.32 (dd, 2H, Th-anti), 4.15 (s, 12H, NMe proximal-anti), 2.48 (s, 12H, NMe distal-anti). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 187 (s, *σ*-C), 184 (s, *σ*-C), 142 (s, Th), 140 (s, Th), 134 (s, Th), 133 (s, Th), two Th resonances are obscured by the solvent), 60 (s (br), proximal), 38 (s (br), distal). {Note: The ^{13}C{^{1}H} NMR data represent a mixture of anti- and gauche-rotamers.} IR data (KBr pellet) cm^{-1}: 2859 (s), 2815 (m), 2770 (s), 1447 (m), 1418 (w), 1383 (w), 1246 (s), 1198 (s), 1146 (s), 1125 (w), 1042 (w), 955 (s), 939 (s), 895 (m), 837 (m), 816 (w), 716 (s), 559 (m).

Preparation of 1,2-W_2(*σ*-2-BTh)$_2$(NMe$_2$)$_4$. A Schlenk flask was charged with 2.0 equiv of benzothiophene (1.14 mL, 9.80 mmol), and the sample was dissolved in ≈6 mL of diethyl ether. *n*-Butyllithium (2.0 equiv, 3.90 mL, 9.80 mmol) was slowly added at 0 °C. The solution was allowed to warm to room temperature and to stir for 1 h (at this point the flask contained 2-lithiobenzothiophene). Another Schlenk flask was charged with 1.0 equiv (3.00 g, 4.88 mmol) of 1,2-$W_2Cl_2(NMe_2)_4$, and the sample was dissolved in ≈25 mL of toluene. The 2-lithiobenzothiophene was added to the 1,2-$W_2Cl_2(NMe_2)_4$ solution, and the mixture was stirred for 24 h. The solution turned dark red-brown. The solvent was then removed *in vacuo*. The residue was washed with a small portion of hexane (5 mL) to remove any unreacted benzothiophene. The residue was extracted in benzene (5 × 10 mL) and filtered through a fine glass frit charged with Celite. The benzene was removed *in vacuo*, and the resulting yellow-orange powder was redissolved in toluene and crystallized at −20 °C. Orange-yellow crystals were harvested and dried *in vacuo* (total crystalline yield 2.10 g, 53%).

Anal. Calcd For $W_2S_2N_4C_{24}H_{36}$: C, 35.51; H, 4.47; N, 6.99. Found: C, 35.70; H, 4.31; N, 6.74. ^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 8.01 (d, BTh), 7.87 (dd, BTh), 7.72 (dd, BTh), 7.67 (d, BTh), 7.26 (m, BTh), 7.18 (m, BTh), 7.06 (m, BTh), 4.17 (s (br), NMe proximal), 2.57 (s (br), NMe distal). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 189 (s, *σ*-C), 187 (s, *σ*-C), 148 (s, BTh), 147 (s, BTh), 142 (s, BTh), 141 (s, BTh), 137 (s, BTh), 134 (s, BTh), 123.6 (s, BTh), 123 (s, BTh), 122 (s, BTh), 60.3 (s (br), NMe proximal), 39.0 (s (br), NMe distal). {Note: These spectra are representative of a mixture of anti- and gauche-rotamers.} IR data (KBr pellets) cm^{-1}: 2861 (s), 2816 (m), 2772 (s), 1447 (s), 1416 (w), 1397 (w), 1277 (w), 1244 (m), 1156 (w), 1143 (m), 1040 (w), 951 (s), 938 (s), 916 (w), 885 (w), 818 (m), 745 (s), 727 (s), 567 (m).

Preparation of 1,2-W_2(*σ*-3-Th)$_2$(NMe)$_4$. A Schlenk flask was charged with 2.0 equiv of 3-bromothiophene (0.290 mL, 3.07 mmol), and the sample was dissolved in diethyl ether and cooled to −75 °C. *n*-Butyllithium (2.0 equiv, 1.23 mL, 3.07 mmol) was then added. This solution was stirred for 30 min. Another Schlenk flask was charged with 1,2-$W_2Cl_2(NMe_2)_4$ (0.940 g, 1.53 mmol), and the sample was dissolved in ≈20 mL of toluene and cooled to −75 °C. The 3-lithiothiophene solution was then added to the 1,2-$W_2Cl_2(NMe_2)_4$ solution. The reaction mixture was allowed to warm to 0 °C. Upon

(35) (a) $M_2Cl_2(NMe_2)_4$: Akiyama, A.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407; (b) $W_2I(NMe_2)_5$: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Schultz, H. *Inorg. Chem.* **1993**, *32*, 6050.

(36) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

warming, the reaction solution turned darker red-brown. The solution was stirred at 0 °C for 2 h and then allowed to warm to room temperature. The solvent was then removed *in vacuo*. The residue was extracted in hexane (4 × 10 mL) and filtered through a fine glass frit charged with Celite. The hexane was removed *in vacuo*, and the resulting yellow-orange powder was redissolved in toluene and crystallized at −20 °C. Orange-yellow crystals were harvested and dried *in vacuo* (total crystalline yield 0.45 g, 42%).

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 7.62 (d, 1H, 3-Th), 7.60 (d, 1H, 3-Th), 7.51 (s (unresolved doublet), 1H, 3-Th), 7.43 (s (unresolved doublet), 1H, 3-Th), 7.36 (dd, 1H, 3-Th), 7.26 (dd, 1H, 3-Th), 4.20 (s (br), 12H, NMe proximal), 2.40 (s (br), 12H, NMe distal). {Note: This spectrum is representative of a mixture of anti- and gauche-rotamers.}

Preparation of 1,2-W_2(σ-2,5-MeTh)$_2$(NMe)$_4$. A Schlenk flask was charged with 2.1 equiv of 2-methylthiophene (0.331 mL, 3.42 mmol), and the sample dissolved in ≈6 mL of diethyl ether. *n*-Butyllithium in hexane (2.1 equiv, 1.37 mL, 3.42 mmol) was slowly added 23 °C. The solution was allowed to warm to room temperature, and it was stirred for 1 h (at this point the flask contained 2-lithio-5-methylthiophene). Another Schlenk flask was charged with 1.0 equiv (1.00 g, 1.63 mmol) of 1,2-$W_2Cl_2(NMe_2)_4$, and the sample was dissolved in ≈15 mL of toluene. The 2-lithio-5-methylthiophene was added to the 1,2-$W_2Cl_2(NMe_2)_4$ solution and was allowed to stir for 24 h. The solution turned dark orange-red, and the appearance of salt was observed. The solvent was then removed *in vacuo*. The residue was extracted in hexane (4 × 10 mL) and filtered through a fine glass frit charged with Celite. The hexane was removed *in vacuo*, and the resulting yellow-orange powder was redissolved in toluene and crystallized at −20 °C. Orange-yellow crystal were harvested and dried *in vacuo* (total crystalline yield 0.90 g, 75%).

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 7.67 (d, Me*Th*), 7.43 (d, Me*Th*), 7.04 (dd, Me*Th*), 6.99 (dd, Me*Th*), 4.20 (s (br), 12H, NMe proximal), 2.60 (s (br), 12H, NMe distal), 2.44 (s (unresolved doublet), *Me*Th), 2.34 (s (unresolved doublet), *Me*Th). {Note: This spectrum is representative of a mixture of anti- and gauche-rotamers.} IR data (KBr pellet) cm^{-1}: 2926 (m), 2857 (s), 2813 (s), 2770 (s), 1439 (s), 1416 (s), 1379 (m), 1242 (s), 1198 (s), 1146 (s), 1121 (w), 1042 (m), 951 (s), 939 (s), 893 (s), 835 (m), 812 (w), 714 (s), 700 (s) 565 (s).

Preparation of 1,2-Mo_2(σ-2-Th)$_2$(NMe$_2$)$_4$. A Schlenk flask was charged with 0.70 g of 1,2-$Mo_2Cl_2(NMe_2)_4$ (1.59 mmol) and the sample dissolved in ≈15 mL of toluene. 2-Lithiothiophene in THF (2.0 equiv, 3.20 mL, 3.19 mmol) was added. The reaction solution was stirred for 24 h and turned dark orange (appearance of a precipitate was apparent). The solvent was then removed *in vacuo*. The residue was extracted in hexane (4 × 10 mL) and filtered through a glass frit charged with Celite. The hexane was removed *in vacuo*, and the orange powder was redissolved in a minimal amount of toluene and crystallized at −20 °C. Yellow crystals were harvested, by transferring the supernatant liquid to a separate flask, and dried *in vacuo* (total crystalline yield 0.56 g, 66%). {Note: Li[(CN)Cu(σ-2-thienyl)] can be used instead of 2-lithiothiophene and usually allows for easier separation of salts if the reagent is fresh.}

Anal. Calcd For $Mo_2S_2N_4C_{24}H_{36}$: C, 35.96; H, 5.66; N, 10.48. Found: C, 34.44; H, 5.44; N, 9.86. {Note: This compound slowly decomposes at room temperature by loss of thiophene, which could explain why the E. A. is slightly low for carbon.} ^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 7.80 (d, 1H, Th), 7.75 (d, 1H, Th), 7.66 (d, 1H, Th), 7.57 (d, 1H, Th), 7.37 (dd, 1H, Th), 7.28 (dd, 1H, Th), 4.04 (s (br), 12H, NMe proximal), 2.62 (s (br), 12H, NMe distal). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 173 (s, σ-C), 172 (s, σ-C), 140 (s, Th), 137 (s, Th), 132.4 (s, Th), 131.8 (s, Th) (two Th resonances are obscured by the solvent), 59 (s (br), NMe proximal), 43 (s (br), NMe distal). {Note: These spectra are representative of a mixture of anti- and gauche-rotamers.} IR data (KBr pellet) cm^{-1}: 2926 (m), 2857 (s). 2813 (s), 2770 (s), 1429 (s), 1416 (s), 1379 (m), 1242 (s), 1198 (s), 1146 (s), 1146 (s), 1121 (w), 1042 (m), 951 (s), 939 (s), 893 (m), 835 (w), 812 (w), 713 (s), 700 (s), 565 (s).

Preparation of W_2(σ-Th)(NMe$_2$)$_5$. A Schlenk flask was charged with 1.00 g of $W_2I(NMe_2)_5$ (1.40 mmol), and the sample was dissolved in ≈15 mL of toluene −10 °C. Li[(CN)Cu(σ-2-thienyl)] in THF (1.0 equiv, 5.60 mL, 140 mmol) was added. The reaction solution was allowed to warm to 0 °C, stirred for 3 h, then warmed to room temperature, and stirred for an additional 3 h. The reaction solution turned dark orange (appearance of precipitate was apparent). The solvent was then removed *in vacuo*. The residue was extracted in hexane (5 × 10 mL) and filtered through a glass frit charged with Celite. The hexane was removed *in vacuo*, and the orange powder was redissolved in a minimal amount of toluene and crystallized at −20 °C. Orange crystals were harvested by transferring the supernatant to a separate flask and dried *in vacuo* (total crystalline yield 0.61 g, 65%). {Note: Because of the equilibrium: $2W_2I(NMe_2)_5 \rightleftharpoons W_2I_2(NMe_2)_6 +$ 1,2-$W_2(NMe_2)_4$ there always exists some 1,2-W_2(σ-2-Th)$_2$(NMe$_2$)$_4$ as an impurity ≈5−10% in the initial preparation.}

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 7.73 (d, 1H, Th), 7.70 (d, 1H, Th), 7.74 (dd, 1H, Th), 4.28 (s (br), 6H, W(N*Me*$_2$)$_2$(σ-2-Th) proximal), 3.39 (s (br), 6H, W(N*Me*$_2$)$_3$ anti-), 3.33 (s (br), 12H, W(N*Me*$_2$)$_3$ syn-), 2.51 (s (br), 6H, W(N*Me*$_2$)$_2$(σ-2-Th) distal). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 176 (s, σ-C), 140 (s, Th), 135 (s, Th) (signal is obscured by the solvent), 60 (s (br), N*Me geminal* to Th proximal), 41 (s (br), N*Me geminal* to Th distal), 51 (m (br), NMe *vicinal* to Th). IR data (KBr pellet) cm^{-1}: 2923 (s), 2855 (s), 2811 (s), 2766 (s), 1441 (s), 1425 (s), 1394 (m), 1383 (w), 1244 (s), 1200 (m), 1148 (s), 1125 (m), 1046 (m), 939 (s), 839 (2), 700 (m), 551 (s).

Preparation of W_2(O^{t}Bu)$_5$(μ-CCH$_2$CHCHS)(σ-2-Th). A Schlenk flask was charged with 0.200 g of 1,2-W_2(σ-2-Th)$_2$(NMe$_2$)$_4$ (0.282 mmol), and the sample was dissolved in 10 mL of toluene. *tert*-Butyl alcohol/benzene azeotrope (6.0 equiv, 0.402 mL, 1.69 mmol) was added, and the reaction was stirred for 5 h. Upon addition of the *tert*-butyl alcohol the solution slowly turned dark purple. The toluene was then removed *in vacuo*. The residue was extracted in hexane and filtered through a fine glass frit charged with Celite. The solvent volume was reduced, and the solution was placed at −20 °C. Red X-ray quality crystals were harvested by transferring the supernatant to a separate flask and dried *in vacuo* (total crystalline yield 0.215 g, 85%). {Note: When the alcoholysis is completed with 5.0 equiv of isopropyl alcohol, cyclohexanol, or neopentanol, and under the same conditions as mentioned above, the corresponding homoleptic alkoxides, $W_2(OR)_6$ (R = ^{i}Pr, *c*-hex or Np), were obtained.}

Anal. Calcd For $W_2S_2O_5C_{28}H_{52}$: C, 37.34; H, 5.82; N, 0.00. Found: C, 36.67; H, 5.87; N, 0.00. ^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 7.64 (d, 1H, σ-Th), 7.56 (d, 1H, σ-Th), 7.32 (d, 1H, σ-Th), 7.34 (d, 1H, μ-CCH$_2$CHCHS), 6.52 (dt, 1H, μ-CCH$_2$CHCHS), 6.21 (d, 2H, μ-CCH$_2$CHCHS), 1.76 (s, 9H, μ-O^{t}Bu), 1.40 (s, 18H, O^{t}Bu), 1.01 (s, 18H, O^{t}Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 23 °C, 75 MHz): δ 307 (s, μ-C_{37}, $^1J_{W-C}$ = 142 Hz, I = 22%), 187 (s, σ-C_{23}, $^1J_{W-C}$ = 134 Hz, I = 14%), 136 (s, σ-Th), 133 (s, σ-Th), 131 (s, σ-Th), 128 (s, μ-Th), 127 (s, μ-Th), 87 (s, O^{t}Bu, *tert*-carbon), 85 (s, μ-O^{t}Bu, *tert*-carbon) 54 (s, C_{36}), 31 (s, O^{t}Bu, methyl), 30.8 (s, μ-O^{t}Bu, methyl), 30.5 (s, O^{t}Bu, methyl). IR data (KBr pellet) cm^{-1}: 2970 (s), 2923 (s), 1389 (m), 1365 (s), 1259 (s), 1167 (s), 1132 (w), 1082 (m), 1031 (w), 943 (s), 913 (s), 791 (m), 723 (w), 562 (w), 490 (w).

Preparation of W_2(O^{t}Bu)$_4$(μ-CCHCHCHS)(σ-2-Th). A Schlenk flask was charged with 0.200 g of 1,2-W_2(σ-2-Th)$_2$(NMe$_2$)$_4$ (0.282 mmol), and the sample was dissolved in a minimal amount of toluene ≈5 mL and cooled to −78 °C. *tert*-Butyl alcohol/benzene azeotrope (4.2 equiv, 0.282 mL, 1.18 mmol) was dissolved in 2 mL of toluene, cooled to −78°, and then added to the solution of 1,2-W_2(σ-2-Th)$_2$-(NMe$_2$)$_4$. The solution was allowed to warm to room temperature, and it was stirred for 2 h. The solvent was then removed *in vacuo*. The resulting brown-purple solution was redissolved in hexane and filtered through a fine glass frit charged with Celite. Attempts to grow crystals were unsuccessful. This compound slowly decomposes.

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 8.65 (d, 1H, σ-Th), 8.19 (dd, 1H, σ-Th), 7.71 (d, 1H, σ-Th), 7.47 (dd, 1H, μ-CCHCHCHS), 7.01 (dd, 1H, μ-CCHCHCHS), 6.69 (dd, 1H, μ-CCHCHCHS), 2.11 (s, 9H, O^{t}Bu), 1.15 (s, 9H, O^{t}Bu), 0.90 (s, 9H, O^{t}Bu), 0.67 (s, 9H, O^{t}Bu). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 288 (s, μ-vinylidene carbon), 182 (s, σ-C), 149 (s, Th), 134 (s, Th), 132 (s, Th), 127 (s, Th), 124 (s, Th), 123 (s, Th), 86.5 (s, O^{t}Bu tert-carbon), 86.0 (s, O^{t}Bu tert-carbon), 84.7 (s, O^{t}Bu tert-carbon), 78 (s, O^{t}Bu tert-carbon), several resonances at 32−31 ppm for the Me carbons. (A HETCOR NMR was not undertaken to correlate the *C*H carbons with ring-opened *vs* σ-2-Th signals.)

Observance of 1,2-W_2(σ-2-Th)$_2$(O^{t}Bu)$_4$. A Schlenk flask was charged with 0.200 g of 1,2-W_2(σ-2-Th)$_2$(NMe$_2$)$_4$ (0.282 mmol), and

the sample was dissolved in a minimal amount of toluene ≈5 mL and cooled to −78 °C. *tert*-Butyl alcohol/benzene azeotrope (4.2 equiv, 0.282 mL, 1.18 mmol) was dissolved in 2 mL of toluene, cooled to −78 °C, and then added to the solution of 1,2-$W_2(\sigma$-2-Th$)_2(NMe_2)_4$. The solution was allowed to warm to ≈ −20 °C and allowed to react for 3−4 h. The solvent was then removed *in vacuo*. The resulting brown-purple solution was redissolved in hexane. The residue was extracted in hexane. The solvent volume was reduced, and the solution was placed at −20 °C. Crystals were obtained; however, the compound slowly decomposed.

^{1}H NMR of crystals (benzene-d_6, 23 °C, 300 MHz): δ 7.86 (d, 2H, σ-Th), 7.51 (d, 2H, σ-Th) (signal obscured by solvent-σ-Th 7.15 pm), 1.54 (s, 36H, O^{t}Bu).

Preparation of $W_2(\sigma$-2-Th$)(O^tBu)_5$. A Schlenk flask was charged with 1.0 equiv of $W_2(\sigma$-Th$)(NMe_2)_5$ (0.200 g, 0.298 mmol), and the sample was dissolved in ≈10 mL of hexane. Approximately 11 equiv of *tert*-butyl alcohol/benzene azeotrope (0.76 mL, 3.2 mmol) was added to this solution. The solution was stirred for 3 h at room temperature. The solution turned dark red. The solvent was removed *in vacuo*. The residue was redissolved in a minimal amount of toluene and crystals were obtained at −20 °C and dried *in vacuo* (total crystalline yield 0.210 g, 83%).

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 8.05 (d, 1H, Th) 7.59 (d, 1H, Th), 7.28 (dd, 1H, Th), 1.59 (s, 18H, O^{t}Bu *geminal* to Th), 1.54 (s, 27H, O^{t}Bu *vicinal* to Th). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): 170 (s, σ-C), 140 (s, Th), 129 (s, Th) (resonances obscured by solvent, Th 128 ppm), 81 (s, O^{t}Bu *tert*-carbon), 80 (s, O^{t}Bu *tert*-carbon), 33.3 (s, O^{t}Bu methyl), 33.1 (s, O^{t}Bu methyl).

Preparation of $W_2((\mu$-$SC_8H_6)(\sigma$-2-Th$)(O^tBu)_5$. This preparation is virtually the same as that for $W_2(\mu$-$CCH_2CHCHS)(\sigma$-2-Th$)(O^tBu)_5$. A Schlenk flask was charged with 1.00 g of 1,2-$W_2(\sigma$-2-BTh$)_2(NMe_2)_4$ (1.23 mol) and the sample was dissolved in ≈20 mL of toluene. *tert*-Butyl alcohol/benzene azeotrope (5.1 equiv, 1.50 mL, 6.30 mmol) was added, and the reaction mixture was stirred for 2 h at room temperature. Upon addition of *tert*-butyl alcohol the solution slowly turned dark purple. Toluene was then removed *in vacuo*. The residue was extracted in hexane and filtered through a fine glass frit charged with Celite. The solvent volume was reduced, and the solution was placed at −20 °C. Red-brown microscrystals were harvested by transferring the supernatant to a separate flask and dried *in vacuo* (total crystalline yield 0.88 g, 72%).

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 7.92 (m, 3H, BTh), 7.79 (d, 1H, BTh), 7.45 (d, 1H, BTh), 7.28 (dd, 1H, BTh), 7.15 (m, 2H, obscured by the solvent, BTh), 7.00 (dd, 1H, BTh), 7.59 (s, 2H, sp^3-carbon, benzothienyl), 1.73 (s, 9H, μ-O^{t}Bu), 1.31 (s, 18H, O^{t}Bu), 1.01 (s, 18H, O^{t}Bu). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 308 (s, μ-C), 191 (s, σ-C), 146 (s, BTh), 145.2 (s, BTh), 145.) (s, BTh), 143 (s, BTh), 134 (s, BTh), 131 (s, BTh) (two resonaces are obscured by the solvent 128 ppm), 127 (s, BTh), 126 (s, BTh), 125 (s, BTh), 124 (s, BTh), 123.2 (s, BTh), 122.9 (s, BTh), 122.0 (S, BTh), 87.2 (s, O^{t}Bu *tert*-carbon), 86.6 (s, O^{t}Bu *tert*-carbon), 86.5 (s, O^{t}Bu *tert*-carbon), 61.6 (s, CH_2 ring opened BTh), 32 (s, O^{t}Bu methyl), 31 (s, O^{t}Bu methyl), 30 (s, O^{t}Bu methyl).

Preparation of $W_2(\mu$-$SC_4H_3Me)(\sigma$-2,5-MeTh$)(O^tBu)_5$. A Schlenk flask was charged with 0.200 g of 1,2-$W_2(\sigma$-2,5-MeTh$)_2(NMe_2)_4$ (0.271 mmol), and the sample was dissolved in ≈10 mL of toluene. *tert*-Butyl alcohol/benzene azetrope (5.1 equiv, 0.330 mL, 1.38 mmol) was added, and the reaction was stirred for 5 h. Upon addition of *tert*-butyl alcohol the solution slowly turned dark red purple. The toluene was then removed *in vacuo*. The residue was extracted in hexane and filtered through a fine glass frit charged with Celite. The solvent volume was reduced, and the solution was placed at −20 °C. Red crystals were harvested by transferring the supernatant liquid to a separate flask and dried *in vacuo* (total crystalline yield 0.230 g, 91%).

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 4.47 (d, 1H, Th), 7.02 (d, 1H, Th), 6.36 (td, 1H, μ-C_4H_3MeS), 6.99 (d, 2H, μ-C_4H_3SMe), 2.58 (s, 3H, Me-Th), 2.40 (s, 3H, μ-C_4H_3S*Me*), 1.79 (2, 9H, μ-O^{t}Bu), 1.40 (s, 18H, O^{t}Bu), 1.06 (s, 18H, O^{t}Bu). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 306 (s, μ-C), 188 (s, σ-C), 142 (s, Th), 138 (s, Th), 137 (s, Th) (two resonances are obscured by the solvent 128 ppm), 85.7 (s, O^{t}Bu *tert*-carbon), 85.6 (s, O^{t}Bu *tert*-carbon), 85.5 (s, O^{t}Bu *tert*-carbon), 54.8 (s, CH_2 μ-C_4H_3MeS), 32 (s, O^{t}Bu methyl) 31 (s, O^{t}Bu methyl), 30 (s, O^{t}Bu methyl). IR data (KBr pellet) cm^{-1}: 2975 (s), 2923 (s), 1470 (w), 1451 (w), 1385 (m), 1362 (s), 1237 (m), 1163 (s) 955 (s), 895 (m), 788 (w), 554 (w).

Preparation of 1,2-$W_2(\sigma$-3-Th$)_2(O^tBu_4)$. A Schlenk flask was charged with 0.20 g of 1,2-$W_2(\sigma$-3-Th$)_2(NMe_2)_4$ (0.282 mmol), and the sample was dissolved in ≈10 mL of toluene. *tert*-Butyl alcohol/benzene azeotrope (6.0 equiv, 0.402 mL, 1.69 mmol) was added, and the reaction mixture was stirred for 5 h. Upon addition of *tert*-butyl alcohol the solution slowly turned dark purple-brown. The solvent was then removed *in vacuo*. A red microcrystalline residue resulted and was dried *in vacuo* (total yield 0.21 g, 90%).

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ7.63 (d, 1H, Th), 7.25 (dd, 1H, Th), 7.14 (d, 1H, Th, obscured by the solvent), 1.39 (s, 36H, O^{t}Bu).

Preparation of 1,2-$Mo_2(\sigma$-2-Th$)_2(O^tBu)_4$. A Schlenk flask was charged with 0.200 g of 1,2-$Mo_2(\sigma$-2-Th$)_2(NMe_2)_4$ (0.374 mmol), and the sample was dissolved in 10 mL of hexane and cooled to 0 °C. *tert*-Butyl alcohol/benzene azeotrope (4.2 equiv, 0.374 mL, 1.57 mmol) was added, and the reaction was allowed to warm to room temperature and stir for 12 h. Upon addition of *tert*-butyl alcohol the solution slowly turned red. The solvent was then removed *in vacuo*. A red microcrystalline residue resulted and was dried *in vacuo* (total yield of residue 0.22 g, 90%). The ^{1}H NMR of this residue showed a mixture of 1,2-$Mo_2(\sigma$-2-Th$)_2(O^tBu)_4$ and $Mo_2(\sigma$-2-Th$)(O^tBu)_5$. Further, 0.10 g of the residue was dissolved in ≈5 mL of toluene, an additional 4.5 equiv of *tert*-butyl alcohol/benzene azeotrope (0.200 mL, 0.84 mmol) was added, and the solution was stirred for 6 h. The solvent was removed *in vacuo*, and the ^{1}H NMR spectrum showed the residue to be the homoleptic alkoxide $Mo_2(O^tBu)_6$. {Note: It is very difficult to obtain pure 1,2-$Mo_2(\sigma$-2-Th$)_2(O^tBu)_4$ or $Mo_2(\sigma$-2-Th$)(O^tBu)_5$ because they usually crystallize together.}

^{1}H NMR of 1,2-$Mo_2(\sigma$-2-Th$)_2(O^tBu)_4$ (benzene-d_6, 23 °C, 300 MHz): δ 7.87 (d, 1H, Th), 7.51 (d, 1H, Th), 7.11 (dd, 1H, Th) 1.48 (s, 36H, O^{t}Bu).

^{1}H NMR of $Mo_2(\sigma$-2-Th$)(O^tBu)_5$ (benzene-d_6, 23 °C, 300 MHz): δ 8.02 (d, 1H, Th), 7.58 (d, 1H, Th) 7.11 (dd, 1H, Th), 1.57 (s, 18H, O^{t}Bu *gemimal* to Th), 1.49 (s, 27H, O^{t}Bu *vicinal* to Th). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 177 (s, σ-C), 138 (s, Th), 133 (s, Th) (resonance obscured by solvent, thienyl 128 ppm), 80 (s, O^{t}Bu *tert*-carbon), 79 (s, O^{t}Bu *tert*-carbon), 33 (s, O^{t}Bu methyl), 32 (s, O^{t}Bu methyl).

Preparation of $W_2(\mu$-$CCH_2CHCHS)(\sigma$-2-Th$)(OCMe_2CF_3)_4$. A Schlenk flask was charged with 0.300 g (0.422 mmol) of 1,2-$W_2(\sigma$-2-Th$)_2(NMe_2)_4$, and the sample was dissolved in 10 mL of toluene and cooled to 0 °C. CF_3Me_2COH (4.6 equiv) was then slowly added (0.200 mL, 1.98 mmol). The reaction solution was allowed to warm to room temperature and stirred for 24 h. The reaction solution slowly went from orange to dark red-brown. The solvent was then removed *in vacuo*. The residue was redissolved in hexane and filtered through a fine glass frit charged with Celite. The solvent volume was reduced, and the solution was placed at −20 °C. Red microcrystals were harvested by transferring the supernatant liquid to a separate flask and dried *in vacuo* (total crystalline yield 0.195 g). {^{1}H NMR spectrum shows a mixture of compounds; the resonances below are for the major product.}

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 8.45 (d, 1H, Th), 8.20 (dd, 1H, Th), 7.63 (d, 1H, Th), 7.33 (d, 1H, μ-CCH_2CHCHS), 5.38 (d, 1H, μ-CCH_2CHCHS), 2.50 (s, 3H, $OCMe_2CF_3$), 2.30 (s, 3H, $OCMe_2CF_3$), 2.05 (s, 3H, $OCMe_2CF_3$), 1.21 (s, 3H, $OCMe_2CF_3$), 1.05 (s, 3H, $OCMe_2CF_3$), 0.96 (s, 3H, $OCMe_2CF_3$), 0.78 (s, 3H, $OCMe_2CF_3$), 0.07 (s, 3H, $OCMe_3CF_3$). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 326 (s, μ-C), 184 (s, σ-C), 157 (s, Th), 149 (s, Th), 137 (s, Th), 133 (s, Th) (resonances are obscured by the solvent 128 ppm), 95 (s, $OCMe_2CF_3$), 80 (m, $OCMe_2CF_3$), 48 (s, $OCMe_2CF_3$), 40 (m, OCM_2CF_3), 27 (s, $OCMe_2CF_3$), 25 (s, $OCMe_2CF_3$), 23 (m, $OCMe_2CF_3$).

Preparation of 1,2-$W_2(\sigma$-2-Th$)_2(NMe_2)_2(O_2CNMe_2)_2$. A 15 mL Schlenk flask, equipped with a Kontes gas inlet tap, was charged with 0.080 g of 1,2-$W_2(\sigma$-2-Th$)_2(NMe_2)_4$ (0.117 mmol), and the sample was dissolved in 5 mL of toluene to give a clear orange solution. The solution was then subjected to three freeze−thaw−degas cycles. The flask was attached to a calibrated gas manifold, and 4.0 equiv (0.45 mmol, ≈1.2 atm) of CO_2 was added. The solution was allowed to react for 24 h, and occasionally the flask was vigorously shaken. The

solution slowly turned dark orange-brown. The solvent was then removed *in vacuo*. The residue was extracted with a minimal amount of toluene and placed at −20 °C. Yellow X-ray quality crystals were harvested by transferring the supernatant liquid to a separate flask and dried *in vacuo* (total crystalline yield 0.065 g, 72%). {Note: If this reaction is completed with >4 equiv at temperature above 60 °C, further insertion of CO_2 is evident. However, these reactions have not been fully investigated.}

Anal. Calcd For $W_2S_2N_4O_4C_{18}H_{30}$: C, 27.08; H, 3.79; N, 7.02. Found: C, 27.14; H, 3.87, N, 6.68. All NMR data are for 1,2-W_2(σ-2-Th)$_2$(NMe$_2$)$_2$(O$_2$^{13}CNMe$_2$)$_2$; ^{1}H NMR (toluene-d_8, 23 °C, 300 MHz): δ 7.62 (d, 2H, Th), 7.35 (dd, 2H, Th), 7.25 (d, 2H, Th), 3.96 (s, 6H, NMe proximal), 2.17 (s, 6H, NMe distal) 2.92 (d, 6H, carbamate methyl), 2.85 (d, 6H, carbamate methyl). ^{13}C{^{1}H} NMR (toluene-d_8, 23 °C, 75 MHz): δ 178.7 (s, bridging carbamate). IR data (KBr pellet) cm^{-1}: 2924 (s), 2853 (s), 1588 (m), 1570 (m), 1522 (s), 1481 (s), 1466 (s), 1441 (s), 1389 (s), 1350 (s), 1323 (s), 1229 (m), 1076 (w), 727 (s), 693 (m), 642 (m), 613 (w), 592 (s), 573 (s), 542 (m).

The preparation of the 5-methylthienyl derivative is similar to that described above. ^{1}H NMR for 1,2-W_2(σ-2,5-MeTh)$_2$(NMe$_2$)$_2$(O$_2$^{13}CNMe$_2$)$_2$ (benzene-d_6, 23 °C, 300 MHz): δ 7.18 (d, 2H Th), 7.09 (dd, 2H, Th), 4.13 (s, 6H, NMe promixal), 2.24 (s, 6H, NMe distal), 2.89 (d, 6H, carbamate methyl), 2.80 (d, 6H, carbamate methyl). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): δ 178.4 (s, bridging carbamate).

Preparation of $W_2(O_2CNMe_2)_2(O^tBu)_4$. A Schlenk flask was charged with 0.050 g of 1,2-W_2(σ-2-Th)$_2$(NMe$_2$)$_2$(O$_2$^{13}CNMe$_2$)$_2$ (0.060 mmol), and the sample was dissolved in 3 mL of toluene. Excess *tert*-butyl alcohol/benzene azeotrope (0.10 mL, 0.41 mmol) was added, and the reaction was stirred for 5 h. The solvent was then removed *in vacuo*. ^{1}H NMR spectrum of the resulting residue showed pure W_2(O$_2$CNMe$_2$)$_2$(O^{t}Bu)$_4$.

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): δ 2.63 (d, 12H, carbamate Me), 1.71 (s, 36H, O^{t}Bu).

Preparation of W_2(σ-2-Th)(μ-SC_4H_3)(μ-NMe$_2$)(NMe$_2$)$_3$(CO)$_3$. A 15 mL Schlenk flask, equipped with a Kontes gas inlet tap, was charged with 0.100 g of 1,2-W_2(σ-2-Th)$_2$(NMe$_2$)$_4$ (0.140 mmol), and the sample was dissolved in ≈5 mL of toluene (minimal solvent) to give a clear orange solution. The solution was then subjected to three freeze−thaw−degas cycles. The flask was attached to a calibrated gas manifold, and 4.0 equiv (0.56 mmol) of CO was added. The solution was allowed to react for 24 h, and occasionally the flask was vigorously shaken. The solution slowly turned dark red, and after 5 h red needles were apparent. The reaction solution was then filtered through a fine glass frit. Red crystalline needles were harvested and washed with hexane (2 × 5 mL). The crystals were then dried *in vacuo* (total crystalline yield 0.072 g, 64%). The preparation of the methylthienyl derivative, W_2(σ-2,5-MeTh)(μ-SC_4H_2Me)(μ-NMe$_2$)(NMe$_2$)$_3$(CO)$_3$, followed the same procedure. The elemental analysis was completed on the latter compound. Anal. Calcd for W_2(σ-2,5-MeTh)(μ-SC_4H_2Me)(μ-NMe$_2$)(NMe$_2$)$_3$(CO)$_3$ $W_2S_2N_4O_3C_{21}H_{34}$: C, 30.67; H, 4.17; N, 6.81. Found: C, 29.35; H, 4.03; N, 6.53. ^{1}H NMR (benzene-d_6, 23 °C, 300MHz) for W_2(σ-2-Th)(μ-SC_4H_3)(μ-NMe$_2$)(NMe$_2$)$_3$: δ 7.80 (dd, 1H, σ-Th), 7.69 (dd, 1H, σ-Th), 7.40 (dd, 1H, σ-Th), 7.06 (d, 1H, μ-C_4H_3S), 6.65 (dd, 1H, μ-C_4H_3S), 6.18 (d, 1H, μ-C_4H_3S), 3.54 (s (br), 3H, NMe), 3.25 (s, 3H, NMe), 3.19 (s (br), 3H, NMe), 2.96 (s, 9H, NMe), 2.75 (s (br), 3H, NMe), 1.98 (s (br), 3H, NMe). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz) for W_2(σ-2-Th)(μ-SC_4H_3)(μ-NMe$_2$)(NMe$_2$)$_3$(^{13}CO)$_3$: δ 209 (dd, $J^{183}_{W-^{13}C}$ = 107 Hz, I = 14%, $J^{13}_{C-^{13}C}$ = 2 Hz and 3 Hz), 203 (dd, $J^{183}_{W-^{13}C}$ = 120 Hz, I = 14%, $J^{13}_{C-^{13}C}$ = 23 Hz and 3 Hz), 202 (dd, $J^{183}_{W-^{13}C}$ = 120 Hz, I = 14%, $J^{13}_{C-^{13}C}$ = 23 Hz and 2 Hz). IR data (KBr pellet) cm^{-1}: ν(CO) {unlabeled} 1993 (s), 1915 (s) and 1852 (s). ^{1}H NMR (toluene-d_8, 23 °C, 300 MHz) for W_2(σ-2,5-MeTh)(μ-SC_4H_2Me)(μ-NMe$_2$)(NMe$_2$)$_3$(CO)$_3$: δ 7.33 (d, 1H, σ-Th), 6.80 (m, 1H, σ-Th), 6.23 (m, 1H, μ-Th), 6.06 (m, 1H, μ-SC_4H_2Me), 3.59 (s (br), 3H, NMe), 3.20 (s (br) 3H, NMe), 3.10 (s, 3H, NMe), 2.90 (s, 6H, NMe), 2.82 (s, 3H, NMe), 2.05 (s (br), 3H, NMe), 2.48 (d, 3H, methyl on Th), 1.92 (d, 3H, SC_4H_2Me), 1.97 (s (br), 3H, NMe). ^{13}C-{^{1}H} NMR (toluene-d_8, 23 °C, 75 MHz) {unlabeled}: δ 216 (s, μ-C, no ^{183}W satellites were resolved), 210 (s, CO), 204 (s, CO), 203 (s, CO), 154 (σ-C on Th), 147 (s, Th), 146 (s, Th), 139 (s, Th), 132 (s, Th) (two resonances were obscured by the solvent), 61 (s, NMe), 60.8 (s, two broad signals), 60 (s, NMe), 59 (s, NMe), 52 (s, NMe) 48 (s, two broad signals). IR data (KBr pellets) cm^{-1}: ν(CO) {unlabeled} 1995 (s), 1917 (s) and 1856 (s).

Preparation of W_2(μ-CCH_2CHCHS)(OCH_2^{t}Bu)$_6$. A Schlenk flask was charged with 0.100 g of W_2(μ-CCH_2CHCHS)(σ-2Th)(O^{t}Bu)$_5$ (0.111 mmol), and the sample was dissolved in 5 mL of toluene. In another flask 6.0 equiv of neopentanol (0.058 g, 0.666 mmol) was dissolved in 2 mL of hexane. The neopentanol solution was added to the solution of the former. The reaction was allowed to proceed for 6 h. The reaction mixture turned slightly more brown-red during the course of the reaction. The solvent was then removed *in vacuo*. The residue was redissolved in minimal hexane and placed at −20 °C. Red microcrystals were harvested by transferring the supernatant liquid to a separate flask and dried *in vacuo* (total crystalline yield 0.080 g, 78%).

^{1}H NMR (toluene-d_8, −70 °C, 300 MHz): δ 7.40 (d, 1H, μ-CCH_2-CHCHS), 6.45 (dt, 1H, μ-CCH_2CHCHS), δ 5.44 (d, 2H, μ-CCH_2-CHCHS), 4.82 and 4.55 (s, 2H, each, methylene proton of neopentoxides on the mirror plane), 4.07, 3.78, 3.53 and 3.30 (d, 2H each, methylene protons of neopentoxides not on the mirror plane), 1.39 and 1.27 (s, 9H each, *tert*-butyl for the neopentoxides on the mirror plane), 0.91 and 0.80 (s, 18H each, *tert*-butyl for the neopentoxides not on the mirror plane).

Preparation of 1,2-W_2(σ-2,5-MeInd)$_2$(NMe$_2$)$_4$. A Schlenk flask was charged with 2.2 equiv of 1-methylindole (0.23 mL, 1.8 mmol), and the sample was dissolved in approximately 10 mL of diethyl ether. *n*-Butyllithium (2.2 equiv, 0.72 mL, 1.8 mmol) was slowly added at room temperature (25 °C). The solution, after refluxing for 1 h, turned slightly yellow and was then allowed to cool to room temperature (at this point the flask contained ≈1.8 equiv of 2-lithio-1-methylindole). Another Schlenk flask was charged with 1.0 equiv (0.50 g, 0.81 mmol) of 1,2-W_2Cl_2(NMe$_2$)$_4$, and the sample was dissolved in ≈10 mL of toluene. The 2-lithio-1-methylindole solution was slowly added to the 1,2-W_2Cl_2(NMe$_2$)$_4$ solution (over 10 min) and was then stirred at room temperature for 24 h. The reaction mixture turned light yellow, and the appearance of a precipitate became evident. The solvent was then removed *in vacuo*. The resulting residue was oily due to unreacted 1-methylindole; therefore, the residue was washed with a small portion of hexane (5 mL). The residue was extracted into warm hexane (5 × 15 mL) and filtered through a fine glass frit charged with Celite. The hexane was removed *in vacuo*, the yellow powder was redissolved in a minimal amount of toluene, and the product crystallized at −20 °C. Yellow crystals were harvested by transferring the supernatant liquid to a separate flask and dried *in vacuo* (total crystalline yield 0.33 g, 51%).

Anal. Calcd for $W_2N_6C_{26}H_{40}$: C, 38.8; H, 5.0; N, 10.4. Found: C, 37.50; H, 4.93; N, 8.96. {Note: Separation of salts is sometimes very difficult and could explain why the E. A. is slightly low.} ^{1}H NMR (benzene-d_6, 70 °C, 300 MHz): δ 7.82 (m, 4H, Ind-phenyl ring), 7.32 (m, 4H, In-phenyl ring), 6.60 (d, 2H, on the β carbon), 3.25 (d (when resolved), 6H, CH_3-Ind), 3.35 (br s, 24 NMe). {Note: At room temperature there exists a mixture of anti- and gauche-rotamers; therefore, there are two sets of indolyl resonances, and the amide region show broad resonances at 4.2 ppm (proximal) and 2.3 ppm (distal).} ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz) of a mixture of anti- and gauche-rotamers: δ 193 (s, σ-C), 189 (s, σ-C), 146 (s, Ind), 142 (s, Ind) (several resonances are obscured by the solvent), 121 (s, Ind), 120 (s, Ind), 119 (s, Ind), 110 (s, Ind), 109 (s, Ind), 60 (br, NMe), 40 (s (br), NMe), 42 (s, CH_2 Ind), 34 (s, CH_3 Ind). IR data (KBr pellet) cm^{-1}: 2861 (s), 2772 (s), 1462 (m), 1368 (w), 1312 (w), 1281 (m), 1244 (w), 1144 (m), 1037 (s), 1038 (s), 951 (s), 938 (s), 774 (m), 750 (s).

Reaction of 1,2-W_2(σ-2,5-MeInd)$_2$(NMe$_2$)$_4$ with Alcohols. A Schlenk flask was charged with 0.050 g of the σ-2-MeInd tungsten complex (0.062 mmol), and the sample was dissolved in ≈5 mL of toluene. Another Schlenk flask was charged with 6.1 equiv of neopentanol (0.034 g, 0.38 mmol) or *tert*-butyl alcohol (0.090 mL, 0.38 mmol), respectively, in ≈2 mL of toluene. The alcohol solution was added to the solution containing the σ-2,5-MeInd tungsten complex. The reaction was stirred for 6 h, and then the solvent was removed *in vacuo*. The ^{1}H NMR spectrum of the resulting residue showed the production of the corresponding homoleptic alkoxide $W_2(OR)_6$ (R = ^{t}Bu, CH_2^{t}Bu) and free 1-methylindole.

Reaction of Lithiopyridine with 1,2-$W_2Cl_2(NMe_2)_4$. A Schlenk flask was charged with 2.0 equiv of 2-bromopyridine (0.080 mL, 0.82 mmol) in diethyl ether and cooled to −75 °C. *n*-Butyllithium in hexane (2.0 equiv, 0.32 mL, 0.81 mmol) was then added. This solution was stirred for 20 min. Another Schlenk flask was charged with 1,2-$W_2Cl_2(NMe_2)_4$ (0.25 g, 0.41 mmol) and dissolved in ≈120 mL of toluene and cooled to −75 °C. The lithiopyridine solution was then added to the 1,2-$W_2Cl_2(NMe_2)_4$ solution. The reaction mixture was allowed to warm to 0 °C. Upon warming, the reaction solution turned dark brown. The solution was allowed to stir at 0 °C for 3 h and then allowed to warm to room temperature. The solvent was then removed *in vacuo*. The residue was extracted into hexane (3 × 10 mL) and filtered through a fine glass frit charged with Celite. The hexane was removed *in vacuo*; the resulting orange residue was crystalline but slightly oily. The ^{1}H NMR data suggested a mixture of isomers: 1,2-$W_2(X)(Y)(NMe_2)_4$ (where X and Y = *σ*-2-pyridyl, *σ*-3-pyridyl, or *σ*-4-pyridyl). Attempts to recrystallize a pure product were unsuccessful. The ^{1}H NMR spectrum of the residue (benzene-d_6, 23 °C, 300 MHz) revealed several resonances in the aromatic region 9.0−6.0 ppm and broad resonances in the amide region 4.2 ppm (proximal) and 2.4 ppm (distal).

Reaction of 2-Lithio-1-methylimidazole with 1,2-$W_2Cl_2(NMe_2)_4$. A Schlenk flask was charged with 2.1 equiv of 1-methylimidizole (0.14 mL, 1.71 mmol) in diethyl ether. *n*-Butyllithium (2.0 equiv, 0.65 mL, 1.63 mmol) was slowly added at room temperature (25 °C). The solution was then refluxed for 30 min, during which time it turned slightly yellow. It was then allowed to cool to room temperature (at this point the flask contained 2-lithio-2-methylimidazole). Another Schlenk flask was charged with 1.0 equiv (0.50 g, 0.81 mmol) of 1,2-$W_2Cl_2(NMe_2)_4$, and the sample was dissolved in ≈10 mL of toluene. The 2-lithio-1-methylimidazole solution was slowly added to the 1,2-$W_2Cl_2(NMe_2)_4$ solution (over 10 min) and was then stirred at room temperature for 24 h. The reaction solution turned deeper yellow-orange. The solvent was then removed *in vacuo*. The residue was extracted into toluene and filtered through a fine glass frit charged with Celite. (The compound is only very sparingly soluble in hexanes.) The toluene was then removed *in vacuo*, the yellow crystalline material was redissolved in a minimal amount of toluene, and microcrystals were obtained at −20 °C. The yellow crystalline material slowly turned brown when stored at room temperature under nitrogen.

^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): *δ* 7.50 (dd, Im), 7.89 (dd, Im), 7.43 (dd, Im), 7.08 (dd, Im), 7.04 (dd, Im), 6.94 (dd, Im), 4.34 (s, NMe), 4.28 (s, NMe), 4.09 (s), 4.07 (s), 3.95 (s), 3.68 (s, Me-Im), 3.34 (br, NMe), 3.35 (s), 3.20 (br, NMe), 2.98 (s, NMe), 2.97 (s, NMe), 2.93 (s, NMe), 2.50 (s, NMe), 2.47 (s, NMe). ^{13}C {^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): *δ* 202.5 (s, *σ*-C), 202 (s, *σ*-C) (several resonances obscured by the solvent), 127.0 (s), 126.0 (s), 121.8 (s), 60.0 (s (br)), 59.5 (s), 59.0 (s), 58.8 (s (br)), 58.7 (s (br)), 49.0 (s), 41.0 (s), 40.6 (s (br)), 40.2 (s (br)), 39.3 (s (br)), 35.0 (s), 34.3 (s), 34.0 (s).

Preparation of 1,2-$W_2(\sigma\text{-2-Fu})_2(NMe_2)_4$. A Schlenk flask was charged with 2.1 equiv of furan (0.24 mL, 3.3 mmol) in approximately 6 mL of diethyl ether. *n*-Butyllithium in hexane (2.0 equiv, 1.30 mL, 3.25 mmol) was slowly added at room temperature (25 °C). The solution was then refluxed for 30 min during which time it turned slightly yellow. The solution was then allowed to cool to room temperature (at this point the flask contained ≈2.0 equiv of 2-lithiofuran). Another Schlenk flask was charged with 1.0 equiv (1.00 g, 1.63 mmol) of 1,2-$W_2Cl_2(NMe_2)_4$, and the sample was dissolved in ≈20 mL of toluene. The 2-lithiofuran solution was slowly added to the 1,2-$W_2Cl_2(NMe_2)_4$ solution (over a 10 min period) and was stirred at room temperature for 24 h. The reaction mixture turned slightly more yellow-orange, and the appearance of a precipitate was apparent. The solvent was then removed *in vacuo*. The residue was extracted into hexane (4 × 10 mL) and filtered through a fine glass frit charged with Celite. The hexane was removed *in vacuo*, and the orange powder was redissolved in a minimal amount of toluene and crystallized at −20 °C. Orange-yellow crystals were harvested by transferring the supernatant to a separate flask and dried *in vacuo* (total crystalline yield 0.70 g, 64%).

Anal. Calcd for $W_2O_2N_4C_{16}H_{30}$: C, 28.34; H, 4.45; N, 8.26. Found: C, 27.32: H, 4.45, N, 8.00. ^{1}H NMR (toluene-d_8, 23 °C, 300 MHz): *δ* 7.65 (d, 1H, Fu), 7.60 (d, 1H, Fu), 7.33 (d, 1H, Fu), 7.13 (d, 1H, Fu), 6.49 (dd, 1H, Fu), 6.45 (dd, 1H, Fu), 4.18 (s (br), 12H, NMe proximal), 2.64 (s (br), 12H, NMe distal). {Note: This spectrum is representative of a mixture of anti- and gauche-rotamers.} IR data (KBr pellet) cm^{-1}: 2859 (s), 2816 (s), 2772 (s), 1601 (m), 1447 (m), 1418 (m), 1246 (m), 1192 (w), 1148 (w), 1132 (w), 1078 (w), 1042 (w), 939 (s), 882 (w), 862 (w), 743 (m), 594 (w), 559 (w).

Preparation of $W_2(\mu\text{-CCH}_2\text{CHCHO})(\sigma\text{-2-Fu})(O^t\text{Bu})_5$. A Schlenk flask was charged with 0.200 g of 1,2-$W_2(\sigma\text{-2-Fu})(NMe_2)_4$ (0.290 mmol), and the sample was dissolved in ≈10 mL of toluene. *tert*-Butyl alcohol/benzene azeotrope (6.0 equiv, 0.421 mL, 1.77 mmol) was added, and the reaction stirred for 3 h. Upon addition of *tert*-butyl alcohol the solution immediately turned dark red-purple. The toluene was then removed *in vacuo*. The residue was extracted into hexane and filtered through a fine glass frit charged with Celite. The solvent volume was reduced, and the solution was placed at −20 °C. Red X-ray quality crystals were harvested, by transferring the supernatant liquid to a separate flask, and dried *in vacuo* (total crystalline yield 0.210 g, 82%).

Anal. Calcd for $W_2O_7C_{28}H_{52}$: C, 38.72; H, 6.,35; N, 0.00. Found: C, 38.60; H, 6.30; N, 0.19 (sample handled under nitrogen). ^{1}H NMR (benzene-d_6, 23 °C, 300 MHz): *δ* 7.83 (dt, 1H, *μ*-CCH_2CHCHO), 7.73 (d, 1H, Fu), 7.15 (d [obscured by the benzene-d_6, but is seen as a doublet in CCl_2D_2 and integrates to 1H], Fu), 6.10 (dd, 1H, Fu), 5.45 (dd, 2H, *μ*-CCH_2CHCHO), 5.17 (dt, 1H, *μ*-CCH_2CHCH), 1.86 (s, 9H, *μ*-O-^{t}Bu), 1.30 (s, 18H, O^{t}Bu), 0.94 (s, 18H, O^{t}Bu). ^{13}C{^{1}H} NMR (benzene-d_6, 23 °C, 75 MHz): *δ* 288 (s, *μ*-C_{37}), 207 (s, *σ*-C_{23}), 148 (s, Fu), 142 (s, Fu), 120 (s, Fu), 110 (s, *μ*-C_4H_4O), 106 (s, *μ*-C_4H_4O), 86 (s, *μ*-O^{t}Bu), C_{29}), 85 (s, O^{t}Bu, *tert*-carbon) 83 (s, O^{t}Bu, *tert*-carbon), 46 (s, C_{36}), 30 (3 singlets, Me's of O^{t}Bu). IR data (KBr pellet) cm^{-1}: 2974 (s), 2926 (s), 1634 (m), 1385 (m), 1360 (s), 1264 (m), 1167 (s), 1132 (w), 1076 (m), 1026 (w), 953 (s), 912 (s), 785 (m), 723 (m), 559 (w), 490 (w), 461 (w).

Single Crystal and Molecular Structure Determinations. General operating procedures and listings of programs have been previously given.[36] A summary of crystal data for the four structural determinations is given in Table 5.

1,2-$W_2(\sigma\text{-2-Th})_2(NMe_2)_4$. A crystal of suitable size was obtained by cleaving a large piece of the sample in a nitrogen atmosphere glove bag. The crystal was mounted using silicone grease and was transferred to a goniostat where it was cooled to −170 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed no symmetry among the observed intensities. An initial choice of space group $P\bar{1}$ was later proven correct by the successful solution of the structure. Following complete intensity data collection and correction for absorption, data processing gave a residual of 0.031 for the averaging of 2609 unique intensities which had been measured more than once. Four standards measured every 300 data showed no significant trends.

The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The positions of the tungsten atoms were determined from an E-map. The remaining non-hydrogen atoms were obtained from subsequent iterations of least-squares refinement and difference Fourier calculation. There is some disorder in the five-membered rings due to 2-fold rotation about the tungsten−carbon bonds. A refinement of the occupancies for positions that could be either carbon or sulfur gave preferred orientations with occupancies ranging from 74−86%. The labeling in the tables and figures is for the preferred orientations; however, it should be kept in mind that the distances and angles for the rings are distorted because of the disorder. Hydrogens were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the atom to which they were bonded.

In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters to a final $R(F) = 0.052$. The final difference map had tungsten residuals of 1.2−3.5 e/Å^3. All other residual peaks were less than 1.2 e/Å^3.

The asymmetric unit contains two half-molecules and one full molecule. In other words, the full unit cell contains two molecules at crystallographic centers of symmetry plus two molecules which are not.

$W_2(\mu\text{-CCH}_2\text{CHCHS})(\sigma\text{-2-Th})(O^t\text{Bu})_5$. A crystallite was separated from a cluster of crystallites, affixed to the end of a glass fiber with silicon grease, and transferred to the goniostat where it was cooled to −165 °C for characterization and data collection. Standard inert atmosphere techniques were employed.

A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited monoclinic symmetry. In addition to the primary crystallite, a secondary fragment of <5% of the principal crystallite was observed. The presence of all orders of *hkl* and the observed systematic extinctions for *h*01 of $h + 1 = 2n + 1$ and 0*k*0 $k = 2n + 1$ uniquely identified the space group as $P2_1/n$ (no. 14 from the international tables). Unit cell dimensions were determined from 48 reflections having $18° < 2\theta < 36°$. Data collection was undertaken as described in Table 5. A total of 7344 reflections was collected including space group extinctions and standard reflections. Standard reflections at 060, 600, 222, and 060 were measured every 300 reflections. An absorption correction was performed based on the crystal dimensions. Following the usual data reduction, absorption correction, and averaging of equivalent reflections a unique set of 4350 reflections was obtained. The *R* for averaging was 0.039 for 2536 redundant data.

The structure was solved using MULTAN and standard Fourier and least squares techniques. The two W atoms were located in the initial E-map. The remainder of the non-hydrogen atoms and 2/3 of the hydrogen atoms were located in successive difference Fouriers. All other hydrogen atoms were placed in calculated positions. All hydrogens were fixed in the final least squares refinement. The full matrix least-squares refinement was completed using anisotropic thermal parameters on all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The final *R* was 0.037 and *Rw*(*F*) 0.035.

The final difference map was essentially featureless except for several peaks located in the immediate vicinity of the tungsten atoms, the largest of which exhibited 1.57 e/Å^3.

$W_2(\sigma\text{-2-Th})_2(NMe_2)_2(O_2CNMe_2)_2$. A crystal of suitable size was mounted in a nitrogen atmosphere glove bag using silicone grease. The crystal was then transferred to a goniostat where it was cooled to −170 °C for characterization and data collection. The sample is thermochromic, the color going from orange to yellow on cooling. A preliminary search revealed a C-centered monoclinic cell. Following complete intensity data collection the additional condition $1 = 2n$ for *h*01 limited the space group to *Cc* or *C*2/*c*. The choice of *C*2/*c* was later proven correct by the successful solution of the structure. After correction for absorption, data processing produced a unique set of 2770 intensities and a residual of 0.043 for the averaging of redundant data (±*h*,*k*,±*1*). Four standards measured every 300 data showed no significant trends.

The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The position of the tungsten atom was obtained from an initial E-map. The positions of the other non-hydrogen atoms were obtained from subsequent iterations of a least-squares refinement followed by a difference Fourier calculation. The atoms labeled S(12) and C(15) are disordered (interchangeable), and both were refined as being 50% sulfur and 50% carbon. Hydrogens were included in fixed calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the carbon to which it was bonded. The hydrogens, H(15)A and H(15)B, associated with the above disorder were given 50% occupancy.

In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters to give a final $R(F) = 0.033$ for the 137 total variables using all of the observed data. Data having $F < 3*\sigma(F)$ were given zero weight. The largest peak in the final difference map was a tungsten residual of 2.5 e/Å^3 and the deepest hole was −1.7 e/Å.

The molecule lies on a crystallographic 2-fold axis. Symmetry related atoms are indicated with primes in the figures and tables.

The tungsten−sulfur nonbonded distances, not in the tables, are given below.

intramolecular	W(1)−S(12)	3.381(3)
	W(1)−C(15)	3.401(3)
	W(1)−C(15)′	3.899(3)
intermolecular	W(1)−S(12)″	3.417(3)

The intermolecular contacts, although weak, link the molecules into a chain.

$W_2(\mu\text{-}CCH_2CHCHO)(\sigma\text{-2-Fu})(O^tBu)_5$. A suitable red crystal was selected from the bulk sample and attached to a glass fiber with silicone grease. The crystal was transferred to the goniostat where it was cooled to −167 °C for characterization and data collection. A systematic search of selected ranges of reciprocal space yielded a set of reflections which exhibited no diffraction symmetry (other than 1bar). The choice of the centrosymmetric space group $P\bar{1}$ was confirmed by the solution and refinement of the structure. Unit cell dimensions were determined by a least-squares fit of the setting angles for 44 carefully centered reflections having 2θ values between 22° and 28°.

Data collection was undertaken as detailed in Table 5. A total of 8364 reflections, including standard reflections, was collected within the given range. Data processing gave a unique set of 4304 reflections and a residual of 0.056 for the averaging of 3940 reflections measured more than once. Plots of the four standard reflections (0 0 3, 0 5 0, 4 0 0, 3 3 2) measured every 300 reflections showed no significant trends. A correction for absorption was made.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The two unique W atoms were located in the initial solution, and the remaining non-hydrogen atoms were located in several iterations of least-squares refinement followed by difference Fourier calculations. Disorder is present in one of the ^{t}Bu groups (C(30), C(31), C(32) and C(38), C(39) and C(40)). The disorder is quite well defined, and the occupancies of the six atoms were refined and then fixed. The sum of the occupancies for the six atoms involved was 2.95. Following initial refinement many of the hydrogen atoms were evident in a difference Fourier. Hydrogen atoms were introduced in fixed idealized positions, except on the disordered atoms, with a C−H distance of 0.95 Å and individual isotropic thermal parameters equal to 1.0 plus the isotropic equivalent of the parent atom. The asymmetric unit contains one full molecule of the W_2 complex. The full matrix least-squares refinement was completed using anisotropic thermal parameters on all of the non-hydrogen atoms, except for the six disordered atoms, which were kept isotropic. The final *R*(*F*) was 0.041 using the full unique data set of 4304 reflections. The total number of parameters varied was 332, including the scale factor and an overall isotropic extinction parameter.

The final difference map contained several peaks of about 2.5 e/Å^3 in the immediate vicinity of the tungsten atoms. The deepest hole was −1.5 e/Å^3.

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Supporting Information Available: Atomic coordinates, anisotropic thermal parameters, complete listings of bond distances and bond angles, VERSORT, and stereodrawings (39 pages). See any current masthead for ordering and Internet access instructions.

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