O14 to O12 and O13 (3.25 and 3.44 Å, respectively), the two carbonyls C12–O12 and C13–O13 are significantly displaced from idealized positions by carbonyl C14–O14. In triangle (O51, O52, O53) and triangle (O21, O22, O23), there are also longer oxygen–oxygen distances associated with the oxygen(s) that are close to O14. Collectively there are five relatively short oxygen–oxygen distances involving O14, and these are taken to indicate the significant interligand repulsions associated with carbonyl C14–O14. In contrast, the triangle (O31, O32, O33), formed by oxygens of carbonyls that are not in close proximity to carbonyl C14–O14, is almost an equilateral triangle.

Solution Stereodynamics of $[PPN]_2[Re_6C(CO)_{19}]$. The infrared spectra (ν_{CO}) determined for $[PPN]_2[Re_6C(CO)_{19}]$ are very similar in solution and in the solid state. In particular, a band at 1815 cm^{-1} (CH_2Cl_2) or 1810 cm^{-1} (KBr) can be attributed to a bridging carbonyl in each case. This compares well with an analogous band observed for $[PPN][Re_7C(CO)_{22}]$ at 1843 cm^{-1} (CH_2Cl_2), when the effect of the unit change in charge is taken into account. However, it is not clear whether both structural forms observed for $[PPN]_2[Re_6C(CO)_{19}]$ in the solid state are present also in solution, since no structure-limiting information was obtained from the ^{13}C NMR spectrum even at −85 °C (see Figure 4d). The high degree of fluxionality displayed by $[PPN]_2[Re_6C(CO)_{19}]$ in solution could result from the facile interconversion of two alternative orientations of the octahedral metal core within the carbonyl ligand ensemble, as seen in the solid-state structure.[23,24] However, $[Re_7C(CO)_{22}]^-$ also shows rapid and complete scrambling of the carbonyl ligands at room temperature,[25] and no disorder was mentioned in the reported crystallographic study.[7] Furthermore, other derivatives of the "$Re_6C(CO)_{18}$" core, e.g., $[Re_7C(CO)_{21}]^{3-}$,[2] $[Re_8C(CO)_{24}]^{2-}$,[10] and $[Re_7C(CO)_{21}ML_n]^{2-}$,[26] none of which has more than three carbonyls per metal atom, show no evidence for rapid carbonyl migration on the metal framework. Thus, the steric repulsions resulting from an "excess" number of carbonyl ligands, with the attendant reduction in strongly directional bonding, are probably responsible for the fluxionality displayed by both $[Re_6C(CO)_{19}]^{2-}$ and $[Re_7C(CO)_{22}]^-$.

Photoinduced Substitution Reaction of $[PPN]_2[Re_6C(CO)_{19}]$ with Dihydrogen. In spite of the obvious steric interactions in the structure of $[PPN]_2[Re_6C(CO)_{19}]$, the compound does not dissociate a carbonyl ligand under mild thermal conditions. In particular, it does not react with H_2 to give the known derivative $[PPN]_2[H_2Re_6C(CO)_{18}]$[3,5] before it begins to decompose at ca. 150 °C. However, photoinduced hydrogenation of $[PPN]_2[Re_6C(CO)_{19}]$ to $[PPN]_2[H_2Re_6C(CO)_{18}]$ does occur cleanly at room temperature with just sunlamp irradiation. This is especially remarkable in that most large metal carbonyl clusters have appeared to be inert to photoinduced carbonyl ligand substitution,[27-29] even though they are often intensely colored. We assume that this unusual reaction proceeds through an unsaturated cluster intermediate of the formula $[Re_6C(CO)_{18}]^{2-}$ and that the expected high symmetry and low steric repulsions of such a species may be important elements in its facile formation. Efforts to characterize such an intermediate by additional reactions are ongoing.

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Supplementary Material Available: A description of the crystallographic details and tables of equivalent positions, atomic positional parameters, thermal parameters, and bond distances and angles (22 pages); a stable of final observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
University of Calgary, Calgary, Alberta, Canada T2N 1N4

C–S Bond Cleavage in Tris(μ-thioether)ditungsten(III) Complexes in Reactions with Anionic Nucleophiles, Including Hydride: Synthesis and Structure of $[PPh_4][Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4Cl)WCl_3]$ and $Na[Cl_3W(\mu\text{-}SEt_2)_2(\mu\text{-}SEt)WCl_3]\cdot 3THF$

P. Michael Boorman,* Xiaoliang Gao, James F. Fait, and Masood Parvez

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The bridging thioether ligands in the complexes $Cl_3W(\mu\text{-}Et_2S)_3WCl_3$ (**1**) and $Cl_3W(\mu\text{-}THT)_3WCl_3$ (**2**) (THT = tetrahydrothiophene) are highly susceptible to nucleophilic attack by the anions X^- ($X = SR^-, SeR^-, Cl^-, Br^-, H^-$), resulting in the cleavage of a C–S bond. Attack on **1** yields complexes containing the deethylated anion $[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]^-$, and the byproducts EtX. Nucleophilic attack on the THT in **2** results in ring opening to give functionalized μ-thiolate anions of general formula $[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4X)WCl_3]^-$. The yields of these derivatives are essentially quantitative. Crystal structures of two representative derivatives are reported. $Na[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]\cdot 3THF$ (**3a**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.306$ (1) Å, $b = 12.750$ (1) Å, $c = 14.936$ (1) Å, $\alpha = 91.990$ (9)°, $\beta = 105.180$ (8)°, $\gamma = 114.530$ (8)°, $V = 1865.0$ (4) Å^3, $Z = 2$, $d_c = 1.890$ g/cm^3, $\mu(\text{Mo K}\alpha) = 69.24$ cm^{-1}, $R = 0.061$, and $R_w = 0.079$ for 274 parameters and 6229 unique data having $F > 4.0\sigma(F)$. $[PPh_4][Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4Cl)WCl_3]$ (**4**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.952$ (3), $b = 18.136$ (5), $c = 26.525$ (5) Å, $\beta = 94.43$ (2)°, $V = 4293.56$ Å^3, $Z = 4$, $d_c = 1.887$ g/cm^3, $\mu(\text{Mo K}\alpha) = 58.5$ cm^{-1}, $R = 0.040$, and $R_w = 0.045$ for 433 parameters and 5956 unique data having $I > 3\sigma(I)$. The anions in both **3a** and **4** have a confacial bioctahedral framework in which one of the μ-thioether ligands in the precursor complexes has been converted to a μ-thiolate. The reaction between hydride and **1** or **2** is a possible model for hydrodesulfurization.

Introduction

The activation of C–S bonds in coordinated organosulfur ligands is of interest in connection with the modeling of catalytic hydrodesulfurization (HDS) reactions. We report here on a rare example of a stoichiometric, facile C–S bond cleavage in a μ-thioether ligand that may provide a mechanism by which thioethers

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Table I. Crystal Data for (THF)$_3$NaCl$_3$W(μ-SEt)(μ-SEt$_2$)$_2$WCl$_3$ (**3a**)

formula	$C_{22}H_{49}Cl_6NaO_3S_3W_2$	V, Å^3	1865.0
MW	1061.18	Z	2
cryst size, mm	0.15 × 0.3 × 0.4	d_c, g cm^{-3}	1.890
cryst syst	triclinic	μ(Mo Kα), cm^{-1}	69.2
space group	$P\bar{1}$	T, K	295
a, Å	11.306 (1)	R	0.061
b, Å	12.750 (1)	R_w	0.079
c, Å	14.936 (1)	no. of variables	274
α, deg	91.990 (9)	no. of observns	6229
β, deg	105.180 (8)	($F > 4.0\sigma(F)$)	
γ, deg	114.530 (8)		

Table II. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for **3a**

	x	y	z	U(eq)^a
W(1)	0.53891 (5)	0.32320 (4)	0.26830 (3)	0.0274 (2)
W(2)	0.36846 (6)	0.11841 (4)	0.25173 (3)	0.0321 (2)
S(1)	0.3079 (3)	0.2598 (3)	0.1774 (2)	0.035 (1)
S(2)	0.4902 (4)	0.2402 (3)	0.4028 (2)	0.037 (1)
S(3)	0.5790 (4)	0.1631 (3)	0.2131 (2)	0.039 (1)
Cl(11)	0.7798 (4)	0.4092 (3)	0.3570 (2)	0.048 (1)
Cl(12)	0.6042 (4)	0.4206 (3)	0.1406 (2)	0.041 (1)
Cl(13)	0.5337 (4)	0.4998 (3)	0.3347 (2)	0.047 (2)
Cl(21)	0.4124 (5)	−0.0317 (3)	0.3264 (3)	0.056 (2)
Cl(22)	0.1615 (4)	0.0564 (4)	0.2977 (3)	0.058 (2)
Cl(23)	0.2426 (4)	−0.0088 (3)	0.1040 (2)	0.053 (2)
Na(1)	0.7962 (6)	−0.3818 (5)	0.2854 (4)	0.050 (3)
C(11)	0.259 (2)	0.254 (1)	0.0511 (9)	0.050 (7)
C(12)	0.197 (2)	0.313 (1)	0.214 (1)	0.056 (8)
C(13)	0.263 (2)	0.370 (2)	0.022 (1)	0.078 (10)
C(14)	0.046 (2)	0.240 (2)	0.158 (1)	0.079 (10)
C(21)	0.620 (2)	0.215 (1)	0.487 (1)	0.060 (8)
C(22)	0.405 (2)	0.287 (2)	0.474 (1)	0.063 (9)
C(23)	0.710 (2)	0.320 (2)	0.566 (1)	0.085 (12)
C(24)	0.356 (2)	0.199 (2)	0.539 (1)	0.070 (10)
C(31)	0.552 (1)	0.141 (1)	0.0863 (9)	0.045 (6)
C(33)	0.690 (2)	0.188 (2)	0.0672 (1)	0.069 (9)
O(4)	0.966 (1)	−0.368 (1)	0.220 (1)	0.078 (7)
C(41)	1.061 (2)	−0.264 (2)	0.195 (1)	0.077 (5)
C(42)	1.1275 (28)	−0.3135 (26)	0.1354 (18)	0.107 (8)
C(43)	1.090 (3)	−0.4305 (27)	0.1497 (20)	0.118 (9)
C(44)	0.9771 (29)	−0.4716 (25)	0.1881 (19)	0.110 (8)
O(5)	0.7130 (14)	−0.2573 (12)	0.2071 (10)	0.083 (7)
C(51)	0.7991 (28)	−0.1333 (25)	0.2174 (18)	0.106 (8)
C(52)	0.709 (4)	−0.079 (3)	0.185 (2)	0.141 (1)
C(53)	0.571 (3)	−0.165 (2)	0.180 (2)	0.111 (8)
C(54)	0.572 (2)	−0.283 (2)	0.167 (1)	0.081 (6)
O(6)	0.928 (1)	−0.270 (1)	0.4344 (8)	0.076 (7)
C(61)	0.931 (2)	−0.321 (2)	0.516 (1)	0.073 (5)
C(62)	1.019 (2)	−0.219 (2)	0.595 (1)	0.087 (6)
C(63)	1.094 (2)	−0.115 (2)	0.555 (2)	0.094 (7)
C(64)	1.047 (3)	−0.159 (2)	0.454 (2)	0.101 (7)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for **3a**

(a) Bond Lengths

W(1)–W(2)	2.474 (1)	W(1)–S(1)	2.373 (3)
W(1)–S(2)	2.388 (3)	W(1)–S(3)	2.429 (5)
W(1)–Cl(11)	2.430 (3)	W(1)–Cl(12)	2.422 (4)
W(1)–Cl(13)	2.458 (4)	W(1)–Na(1A)	3.624 (5)
W(2)–S(1)	2.391 (4)	W(2)–S(2)	2.399 (3)
W(2)–S(3)	2.437 (4)	W(2)–Cl(21)	2.409 (5)
W(2)–Cl(22)	2.433 (5)	W(2)–Cl(23)	2.391 (3)
S(1)–C(11)	1.811 (13)	S(1)–C(12)	1.833 (23)
S(2)–C(21)	1.820 (20)	S(2)–C(22)	1.831 (25)
S(3)–C(31)	1.830 (14)	Cl(11)–Na(1A)	2.858 (8)
Cl(12)–Na(1A)	2.891 (6)	Cl(13)–Na(1A)	3.021 (8)
Na(1)–O(4)	2.326 (19)	Na(1)–O(5)	2.359 (19)
Na(1)–O(6)	2.343 (12)	Na(1)–W(1A)	3.624 (5)
Na(1)–Cl(1A)	2.858 (8)	Na(1)–Cl(1B)	2.891 (6)
Na(1)–Cl(1C)	3.021 (8)	C(11)–C(13)	1.535 (30)
		C(21)–C(23)	1.538 (23)
		C(31)–C(33)	1.528 (26)

(b) Bond Angles

W(2)–W(1)–S(1)	59.1 (1)	W(2)–W(1)–S(2)	59.1 (1)
S(1)–W(1)–S(2)	95.9 (1)	W(2)–W(1)–S(3)	59.6 (1)
S(1)–W(1)–S(3)	100.0 (1)	S(2)–W(1)–S(3)	92.6 (1)
W(2)–W(1)–Cl(11)	127.2 (1)	S(1)–W(1)–Cl(11)	173.7 (1)
S(2)–W(1)–Cl(11)	88.2 (1)	S(3)–W(1)–Cl(11)	84.5 (1)
W(2)–W(1)–Cl(12)	125.5 (1)	S(1)–W(1)–Cl(12)	87.9 (1)
S(2)–W(1)–Cl(12)	175.3 (1)	S(3)–W(1)–Cl(12)	89.5 (1)
Cl(11)–W(1)–Cl(12)	87.8 (1)	W(2)–W(1)–Cl(13)	127.1 (1)
S(1)–W(1)–Cl(13)	88.0 (1)	S(2)–W(1)–Cl(13)	88.2 (1)
S(3)–W(1)–Cl(13)	171.8 (1)	Cl(11)–W(1)–Cl(13)	87.3 (1)
Cl(12)–W(1)–Cl(13)	89.1 (1)	W(2)–W(1)–Na(1A)	177.2 (1)
S(1)–W(1)–Na(1A)	121.9 (1)	S(2)–W(1)–Na(1A)	122.7 (1)
S(3)–W(1)–Na(1A)	117.7 (2)	Cl(11)–W(1)–Na(1A)	51.9 (1)
Cl(12)–W(1)–Na(1A)	52.7 (1)	Cl(13)–W(1)–Na(1A)	55.7 (2)
W(1)–W(2)–S(1)	58.4 (1)	W(1)–W(2)–S(2)	58.7 (1)
S(1)–W(2)–S(2)	95.2 (1)	W(1)–W(2)–S(3)	59.3 (1)
S(1)–W(2)–S(3)	99.2 (1)	S(2)–W(2)–S(3)	92.1 (1)
W(1)–W(2)–Cl(21)	125.4 (1)	S(1)–W(2)–Cl(21)	175.8 (1)
S(2)–W(2)–Cl(21)	86.1 (1)	S(3)–W(2)–Cl(21)	84.7 (2)
W(1)–W(2)–Cl(22)	125.4 (1)	S(1)–W(2)–Cl(22)	86.9 (2)
S(2)–W(2)–Cl(22)	87.8 (1)	S(3)–W(2)–Cl(22)	173.8 (2)
Cl(21)–W(2)–Cl(22)	89.1 (2)	W(1)–W(2)–Cl(23)	123.5 (1)
S(1)–W(2)–Cl(23)	86.3 (1)	S(2)–W(2)–Cl(23)	177.8 (1)
S(3)–W(2)–Cl(23)	89.3 (1)	Cl(21)–W(2)–Cl(23)	92.4 (1)
Cl(22)–W(2)–Cl(23)	90.6 (1)	W(1)–S(1)–W(2)	62.6 (1)
W(1)–S(1)–C(11)	121.8 (6)	W(2)–S(1)–C(11)	123.1 (7)
W(1)–S(1)–C(12)	121.4 (5)	W(2)–S(1)–C(12)	122.2 (6)
C(11)–S(1)–C(12)	103.0 (9)	W(1)–S(2)–W(2)	62.2 (1)
W(1)–S(2)–C(21)	119.0 (6)	W(2)–S(2)–C(21)	120.7 (6)
W(1)–S(2)–C(22)	123.2 (6)	W(2)–S(2)–C(22)	122.3 (5)
C(21)–S(2)–C(22)	105.3 (9)	W(1)–S(3)–W(2)	61.1 (1)
W(1)–S(3)–C(31)	114.0 (6)	W(2)–S(3)–C(31)	112.8 (5)

could be dealkylated by hydride in HDS reactions. It also offers some interesting potential synthetic applications.

The observation of the series of reactions reported herein was the result of a different synthetic objective. We recently prepared two binuclear W(III) complexes that possess three bridging thioether ligands, namely Cl$_3$W(μ-Et$_2$S)$_3$WCl$_3$ (**1**) and Cl$_3$W(μ-THT)$_3$WCl$_3$ (**2**) (THT = tetrahydrothiophene).[1] The structure of **1** displayed the well-established short M–S bond lengths associated with μ-thioether complexes of the early transition elements.[2] It was thus of interest to explore reactions that might replace the terminal Cl ligands by sulfur donors. It was anticipated that this might provide a route to binuclear W(III) complexes completely ligated by sulfur, should the W(μ-thioether)$_3$W unit be resistant to chemical degradation during the displacement of Cl.

Results

(a) Reactions of Cl$_3$W(μ-R$_2$S)$_3$WCl$_3$ with Thiolate and Selenolate Anions. Following some earlier studies in our laboratory,[3] which used soluble quaternary thiolate salts, solutions of **1** and **2** were reacted with these reagents or alternatively with solid sodium thiolates in heterogeneous reactions. The reaction shown in eq 1 has been conclusively proven by spectroscopic and crystallographic characterization of the products.

$$\underset{\mathbf{1}}{\mathrm{Cl_3W(\mu\text{-}SEt_2)_3WCl_3{\cdot}MeCN}} + \mathrm{NaS}(p\text{-tol}) \xrightarrow{\mathrm{MeCN}} \mathrm{EtS}(p\text{-tol}) + \underset{\mathbf{3}}{\mathrm{Na[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]}} \quad (1)$$

After recrystallization from THF, **3** was subjected to an X-ray crystal structure determination as the THF solvate, **3a**, Na-

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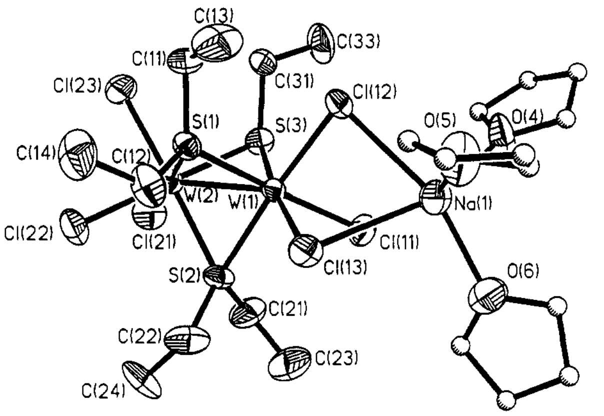
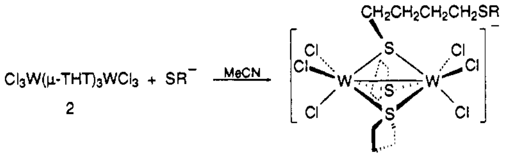


Figure 1. ORTEP plot of **3a**, $(THF)_3NaCl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3$.

$[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]\cdot 3THF$. The relevant data are presented in Tables I–III, and as shown in Figure 1, the key feature of the structure is the loss of an ethyl group from one of the three bridging SEt_2 moieties in **1**, giving this unprecedented combination of bridging sulfur donor ligands. The average W–S bond lengths are slightly longer in the case of S(3) (the thiolate sulfur) than for S(2) and S(3). The W–W distance has been shortened from 2.499 (1) Å in **1** to 2.474 (1) Å in **3a**; the geometry and relative dimensions of **3a** are very similar to those observed in the anion $[Cl_3W(\mu\text{-}SMe_2)_2(\mu\text{-}Cl)WCl_3]^-$, which was previously studied in our laboratory.[1,4]

Analogous reactions between **1** and other thiolate anions, SR^- (R = Ph, ^{t}Bu, 2,4,6-trimethylphenyl (Mes), C_6H_2-2,4,6-^{i}Pr$_3$ (tipp)), were shown to occur, and each yielded **3** and the appropriate thioether.

Although **2** is much less soluble than **1** in MeCN and THF, reactions with thiolate anions proceed as shown in eq 2.



(2)

The selenolate anion is known to be a strong nucleophile and was therefore expected to display the same reactivity toward **1** and **2**. The reaction of $Na^+[SePh]^-$ with **2** was carried out (see Experimental Section) with MeCN as solvent. The complex $Na^+[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4SePh)WCl_3]^-$ was prepared and characterized and could be converted to the more convenient PPh_4^+ derivative by metathesis with PPh_4Cl. The PPh_4^+ complex can also be prepared by direct reaction of $PPh_4[SePh]$ with **2**. The ^{77}Se NMR spectrum possessed one resonance (δ 289 ppm) which is at a frequency very similar to the literature value (288 ppm)[5] for ^{n}BuSePh.

Full details on the characterization of the complexes containing $[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4ER)WCl_3]^-$ (E = S, Se) anions are given in the Experimental Section. All attempts to grow X-ray quality crystals of any of these compounds proved unsuccessful, and hence reactions with other nucleophiles were examined, in part, to address this problem.

Table IV. Crystal Data for $PPh_4[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4Cl)WCl_3]$ (**4**)

formula	$C_{36}H_{44}Cl_7PS_3W_2$	V, Å^3	4293.56
MW	1219.79	Z	4
cryst size, mm	0.15 × 0.18 × 0.4	d_c, g cm^{-3}	1.887
cryst syst	monoclinic	μ(Mo Kα), cm^{-1}	58.5
space group	$P2_1/n$	T, K	293
a, Å	8.952 (3)	R	0.040
b, Å	18.136 (5)	R_w	0.045
c, Å	26.525 (5)	no. of variables	433
		no. of observns ($I > 3.0\ \sigma(I)$)	4385
β, deg	94.43 (2)		

Table V. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for **4**[a]

	x	y	z	u
W(1)	0.13521 (5)	0.62083 (3)	0.85551 (2)	0.0460 (3)
W(2)	0.28907 (5)	0.70663 (3)	0.91104 (2)	0.0444 (3)
Cl(1)	0.0557 (4)	0.4978 (2)	0.8803 (1)	0.062 (2)
Cl(2)	−0.1154 (3)	0.6436 (2)	0.8190 (1)	0.067 (2)
Cl(3)	0.2027 (4)	0.5716 (2)	0.7766 (1)	0.072 (2)
Cl(4)	0.2070 (4)	0.8251 (2)	0.9407 (1)	0.063 (2)
Cl(5)	0.3900 (4)	0.6801 (2)	0.9967 (1)	0.066 (2)
Cl(6)	0.5246 (3)	0.7585 (2)	0.8924 (1)	0.064 (2)
Cl(7)	0.582 (1)	0.6980 (6)	0.1290 (4)	0.154 (4)
Cl(7′)	0.713 (2)	0.7116 (8)	0.1161 (6)	0.127 (5)
S(1)	0.1915 (4)	0.7453 (2)	0.8270 (1)	0.057 (2)
S(2)	0.0543 (3)	0.6619 (2)	0.9341 (1)	0.045 (2)
S(3)	0.3809 (3)	0.5898 (2)	0.8874 (1)	0.049 (2)
C(1)	0.660 (2)	0.2541 (9)	0.2176 (7)	0.085 (5)
C(2)	0.762 (4)	0.740 (2)	0.230 (2)	0.128 (13)
C(2′)	0.675 (6)	0.201 (3)	0.256 (2)	0.106 (15)
C(3)	0.730 (4)	0.665 (2)	0.226 (1)	0.100 (9)
C(3′)	0.814 (9)	0.699 (5)	0.195 (3)	0.198 (26)
C(4)	0.732 (3)	0.644 (2)	0.163 (1)	0.107 (10)
C(4′)	0.642 (7)	0.717 (4)	0.195 (3)	0.176 (26)
C(5)	−0.109 (1)	0.7198 (7)	0.9417 (5)	0.057 (8)
C(6)	−0.176 (2)	0.6909 (11)	0.9873 (7)	0.11 (1)
C(7)	−0.101 (2)	0.6322 (13)	1.0117 (7)	0.13 (2)
C(8)	0.029 (1)	0.6007 (8)	0.9884 (5)	0.064 (9)
C(9)	0.536 (1)	0.5776 (8)	0.8484 (6)	0.07 (1)
C(10)	0.606 (2)	0.5039 (11)	0.8637 (8)	0.11 (1)
C(11)	0.584 (2)	0.4898 (10)	0.9161 (10)	0.12 (2)
C(12)	0.428 (2)	0.5126 (7)	0.9297 (6)	0.08 (1)
P	0.6171 (3)	1.0010 (2)	0.8702 (1)	0.047 (2)
C(13)	0.706 (1)	1.0894 (7)	0.8675 (5)	0.051 (8)
C(14)	0.736 (1)	1.1282 (8)	0.9130 (6)	0.07 (1)
C(15)	0.800 (2)	1.1988 (8)	0.9138 (7)	0.08 (1)
C(16)	0.841 (2)	1.2282 (8)	0.8668 (7)	0.08 (1)
C(17)	0.806 (2)	1.1893 (9)	0.8231 (6)	0.08 (1)
C(18)	0.740 (1)	1.1188 (7)	0.8208 (5)	0.063 (9)
C(19)	0.675 (1)	0.9449 (7)	0.8210 (5)	0.045 (7)
C(20)	0.616 (1)	0.9607 (8)	0.7713 (5)	0.060 (9)
C(21)	0.665 (1)	0.9209 (8)	0.7298 (6)	0.07 (1)
C(22)	0.771 (2)	0.8630 (8)	0.7396 (6)	0.07 (1)
C(23)	0.820 (1)	0.8466 (8)	0.7910 (7)	0.07 (1)
C(24)	0.774 (1)	0.8864 (7)	0.8304 (5)	0.055 (8)
C(25)	0.417 (1)	1.0119 (7)	0.8598 (4)	0.048 (8)
C(26)	0.353 (1)	1.0836 (8)	0.8613 (5)	0.065 (9)
C(27)	0.196 (1)	1.0887 (9)	0.8498 (5)	0.07 (1)
C(28)	0.114 (1)	1.0236 (10)	0.8410 (6)	0.07 (1)
C(29)	0.178 (1)	0.9542 (9)	0.8408 (6)	0.07 (1)
C(30)	0.330 (1)	0.9477 (8)	0.8506 (5)	0.064 (9)
C(31)	0.674 (1)	0.9583 (7)	0.9305 (4)	0.050 (8)
C(32)	0.570 (1)	0.9223 (8)	0.9581 (5)	0.063 (9)
C(33)	0.623 (2)	0.8841 (8)	1.0023 (5)	0.08 (1)
C(34)	0.779 (2)	0.8846 (9)	1.0171 (6)	0.08 (1)
C(35)	0.877 (2)	0.9204 (9)	0.9905 (6)	0.07 (1)
C(36)	0.829 (1)	0.9577 (7)	0.9465 (5)	0.061 (9)

[a] C(2)–C(4) and Cl(7) atoms were disordered over two sites with primed atoms representing 0.40 sof.

(b) Reactions of $Cl_3W(\mu\text{-}R_2S)_3WCl_3$ with Halide Ions. The generality of the reactions of **1** and **2** with nucleophiles was examined by carrying out reactions between these complexes and PPh_4Cl, PPh_4Br, and PPh_4I in MeCN solution. In the cases of Cl^- and Br^- and, for **1**, I^-, these reactions were shown to follow the same pathway as with thiolate anion and resulted in cleavage of the S–C bond in a bridging thioether ligand. Thus **1** gave the complex $[PPh_4]^+[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]^-$ and either EtCl, EtBr, or EtI in almost quantitative yield, while **2** underwent ring opening to give the corresponding μ-(4-halobutanethiolato) complexes of general formula $[PPh_4]^+[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4X)WCl_3]^-$ (X = Cl^- and Br^- but not I^-). The characterization of this series of complexes was based on analytical and

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Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for 4[a]

(a) Bond Lengths

W(1)–W(2)	2.4846 (8)	W(2)–Cl(4)	2.422 (3)
W(1)–S(1)	2.446 (4)	W(2)–Cl(5)	2.428 (3)
W(1)–S(2)	2.379 (3)	W(2)–Cl(6)	2.394 (3)
W(1)–S(3)	2.363 (3)	S(1)–C(1)	1.85 (2)
W(1)–Cl(1)	2.448 (4)	S(2)–C(5)	1.83 (1)
W(1)–Cl(2)	2.409 (3)	S(2)–C(8)	1.85 (1)
W(1)–Cl(3)	2.395 (4)	S(3)–C(9)	1.81 (1)
W(2)–S(1)	2.434 (4)	S(3)–C(12)	1.82 (1)
W(2)–S(2)	2.377 (3)	Cl(7)–C(4′)	1.83 (7)
W(2)–S(3)	2.373 (3)	Cl(7′)–C(4)	1.74 (4)

(b) Bond Angles

S(3)–W(1)–S(2)	95.6 (1)	S(2)–W(2)–Cl(4)	85.6 (1)
S(3)–W(1)–Cl(3)	86.2 (1)	S(2)–W(2)–Cl(5)	87.9 (1)
S(3)–W(1)–Cl(2)	175.5 (1)	S(2)–W(2)–S(1)	94.2 (1)
S(3)–W(1)–S(1)	97.0 (1)	Cl(6)–W(2)–Cl(4)	90.7 (1)
S(3)–W(1)–Cl(1)	88.2 (1)	Cl(6)–W(2)–Cl(5)	90.1 (1)
S(2)–W(1)–Cl(3)	175.4 (1)	Cl(6)–W(2)–S(1)	87.6 (1)
S(2)–W(1)–Cl(2)	87.8 (1)	Cl(4)–W(2)–Cl(5)	88.4 (1)
S(2)–W(1)–S(1)	93.8 (1)	Cl(4)–W(2)–S(1)	86.9 (1)
S(2)–W(1)–Cl(1)	86.3 (1)	Cl(5)–W(2)–S(1)	174.7 (1)
Cl(3)–W(1)–Cl(2)	90.2 (1)	C(1)–S(1)–W(2)	111.3 (5)
Cl(3)–W(1)–S(1)	90.1 (1)	C(1)–S(1)–W(1)	112.3 (6)
Cl(3)–W(1)–Cl(1)	89.6 (1)	C(5)–S(2)–C(8)	96.4 (6)
Cl(2)–W(1)–S(1)	85.7 (1)	C(5)–S(2)–W(2)	124.4 (4)
Cl(2)–W(1)–Cl(1)	89.0 (1)	C(5)–S(2)–W(1)	125.3 (5)
S(1)–W(1)–Cl(1)	174.7 (1)	C(8)–S(2)–W(2)	124.8 (4)
S(3)–W(2)–S(2)	95.4 (1)	C(8)–S(2)–W(1)	124.0 (5)
S(3)–W(2)–Cl(6)	88.1 (1)	C(9)–S(3)–C(12)	96.0 (7)
S(3)–W(2)–Cl(4)	175.9 (1)	C(9)–S(3)–W(1)	124.0 (5)
S(3)–W(2)–Cl(5)	87.6 (1)	C(9)–S(3)–W(2)	123.9 (5)
S(3)–W(2)–S(1)	97.1 (1)	C(12)–S(3)–W(1)	124.7 (5)
S(2)–W(2)–Cl(6)	175.8 (1)	C(12)–S(3)–W(2)	126.4 (5)

[a] C(1), C(2), C(3′), C(4), Cl(7′) and C(1), C(2′), C(3), C(4′), Cl(7) represent the two disordered halves of the ^{n}BuCl chain.

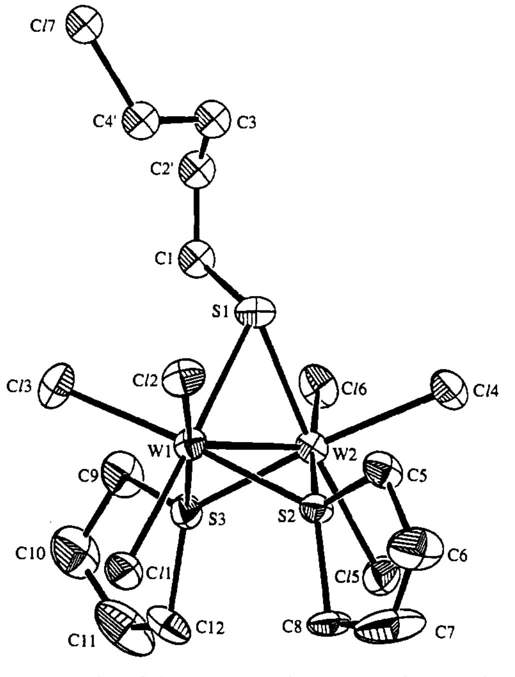
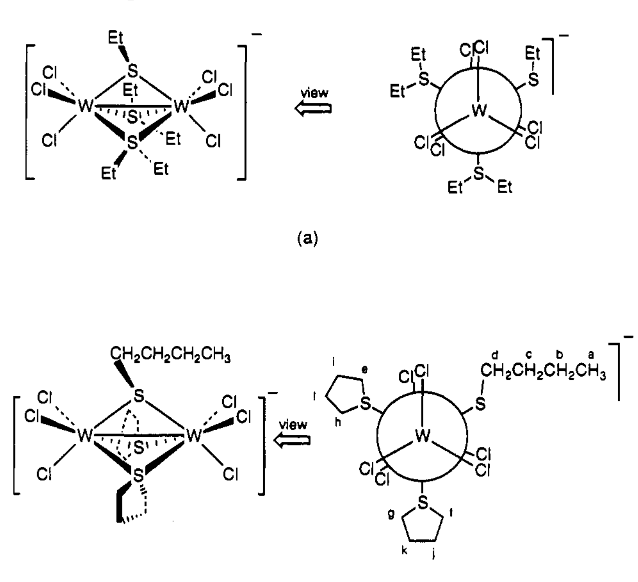


Figure 2. ORTEP plot of the structure of the anion of 4, $Ph_4P[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4Cl)WCl_3]$, showing the labeling scheme employed.

spectroscopic data and an X-ray crystal structure of the complex $[PPh_4]^+[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_4Cl)WCl_3]^-$ (**4**) (Tables IV–VI). The structure of **4** (Figure 2) confirms that the proposed ring opening reaction occurred and that the basic geometry of the ditungsten core is the same as in **3a**. The W–W bond distance and the relative lengths of the $W\text{–}S_{thiolate}$ and $W\text{–}S_{thioether}$ bonds are similar to those in **3a**. The $-(CH_2)_4Cl$ side chain shows some disorder in the positions of the C(2), C(3), C(4), and Cl(7) atoms, but this was successfully modeled on the basis of partial occupancy of two sites for each of these atoms.



(a)

(b)

Figure 3. Views of (a) the anion $[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]^-$, showing the inequivalence of the ethyl groups, and (b) the anion $[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_3CH_3)WCl_3]^-$ indicating the labeling scheme for hydrogen atoms used in Figure 4.

(c) Reactions of $Cl_3W(\mu\text{-}R_2S)_3WCl_3$ with Hydride Ions: Possible Models for Hydrodesulfurization. The successful cleavage of C–S bonds in the $\mu\text{-}SR_2$ ligands of **1** and **2** posed the question as to whether this reactivity would be exhibited with hydride as the nucleophile, since considerable attention has been paid in our laboratory[6,7] and in many others[8–11] to the possible mechanisms for hydrodesulfurization. The labilization of the C–S bond by coordination of the sulfur to a metal has been assumed to be a key step in such processes. The reactions described above clearly demonstrate that such is the case in the tris(μ-thioether)ditungsten(III) complexes. The retention of the nucleophile in the complexes produced in reactions of **2**, in contrast to the volatility of the C_2H_6 which would be the expected product in reactions with **1**, directed our attention to the THT complex, **2**. When a finely ground sample of **2** was stirred under nitrogen with $Li[BEt_3H]$ with THF as solvent, a reaction occurred, resulting in a clear orange solution. The impure product, shown to be $Li[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_3CH_3)WCl_3]$, was converted to the PPh_4^+ derivative, **5a**, which proved to be analytically and spectroscopically pure. A discussion of the ^1H NMR spectrum of **5a** is presented below. This reaction was repeated with the deuterated reagent $Li[BEt_3D]$, and the product, after conversion to the PPh_4^+ derivative, was shown by its ^1H NMR spectrum to be $PPh_4^+[Cl_3W(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)_3CH_2D)WCl_3]^-$ (**5b**).

(d) ^1H NMR Studies of the Anions $[Cl_3W(\mu\text{-}SEt)(\mu\text{-}SEt_2)_2WCl_3]^-$ and $[Cl_3(\mu\text{-}THT)_2(\mu\text{-}S(CH_2)X)WCl_3]^-$ (X = H, D). It can be seen from Figure 3a that the pyramidal structure of the μ-SEt sulfur will render the five ethyl groups inequivalent. The ^1H NMR spectrum at room temperature confirms this, and within the thermal stability range of the complex (decomposition was observed at 113 °C), we did not observe rapid pyramidal inversion to reduce the number of unique ethyl groups to three.

The ^1H NMR spectra of **5a**, with and without selective decoupling, are shown in Figure 4. A Newman projection of the

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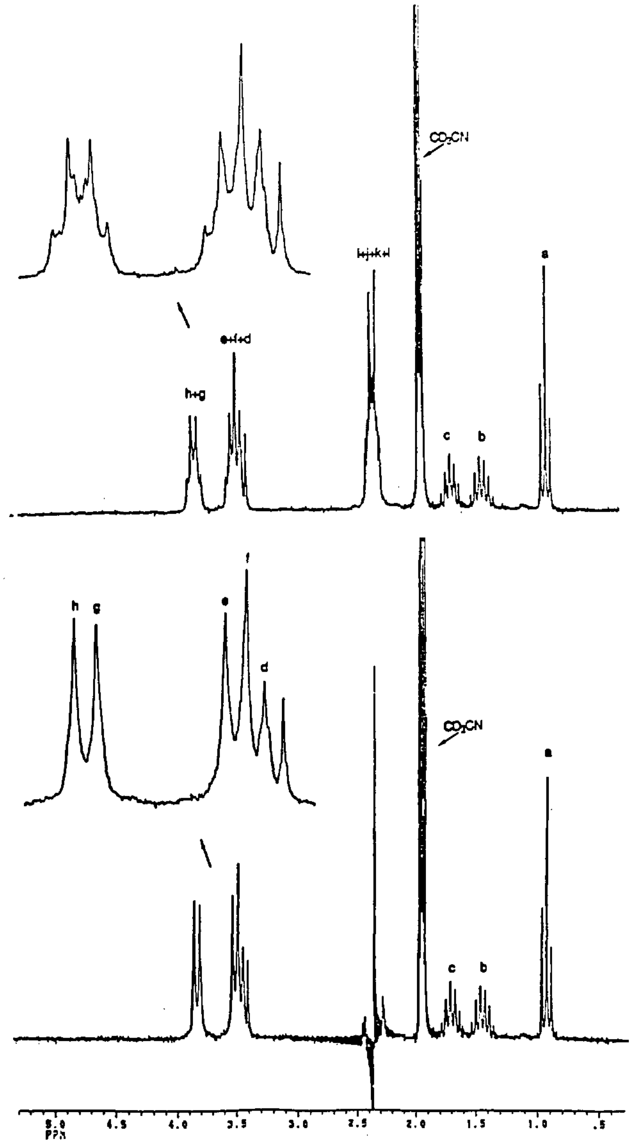

Figure 4. ^{1}H NMR spectra of $Ph_4P[Cl_3W(\mu\text{-THT})_2(\mu\text{-S(CH}_2)_3CH_3)WCl_3]$ in CD_3CN solution: (a) no decoupling; (b) Selective decoupling by irradiation of the β-CH_2 protons (i, j, k, and l) of the THT rings. See Figure 3b for the H atom-labeling scheme.

ion, to indicate the labeling scheme, is shown in Figure 3b. The assignments imply that there is again no inversion at the μ-S_{thiolate} atom, which would have made the g and h pairs of protons equivalent with the e and f pairs of protons. The spectra also confirm that the THT ring has been opened by the hydride to give a butyl-substituted μ-thiolate.

Discussion

The reactions reported above demonstrate that bridging thioethers in the tightly coupled ditungsten(III) complexes are activated toward nucleophilic displacement of sulfur from an α-carbon atom. In reactions of halide ions or thiolate anions with terminally bound thioethers, in complexes such as $WCl_4(R_2S)_2$, there has been no evidence for C–S bond cleavage at ambient temperature. The displacement of either Cl or R_2S from the metal center is invariably observed as the first step, as had been anticipated in the present case. Indeed, it at first seemed probable that reaction of **1** or **2** with thiolate was a stepwise process, in which displacement of a terminal chloride by the incoming nucleophile would be followed by an intramolecular transfer of an ethyl group to give the observed mixed thioethers and an intermediate $[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_2(\text{solv})]$. The displaced Cl^- would then be likely to displace the solvent in the complex to complete the coordination sphere. To test this possibility, the reaction between **1** and $Ph_4P[S(p\text{-tol})]$ was carried out in the presence of an excess of Ph_4PBr, on the assumption that the bromide would preferentially displace solvent from the structure. No bromide incorporation was observed, and the final product was $(Ph_4P)[Cl_3W(\mu\text{-Et}_2S)_2(\mu\text{-SEt})WCl_3]$. Hence, the most likely explanation for the products in reaction 1 is that direct nucleophilic attack of the thiolate anion at an α-C of a μ-Et_2S occurs.

The reactions described here are not unprecedented in the coordination chemistry of thioethers; earlier work by Roundhill[12,13] showed that the displacement of alkyl groups from complexes of Pd(II) and Pt(II) with the ligand o-$Ph_2PC_6H_4SR$ can be accomplished with amines. The proposed mechanism involved a nucleophilic substitution at the electrophilic α-carbon of the thioalkyl group, which is promoted by coordination of the sulfur to the metal. Frequently in systems of this sort it is found that the metal center is as electrophilic as the carbon atom, so that ligand displacement from the metal center is a competing reaction. The chemistry of bridging thioether ligands has, to our knowledge, received much less attention, and the reactions described here are of interest in this regard. The activation of the thioether in **1** and **2** may be the result of the acute (ca. 62.5°) angles subtended at the bridging sulfur atoms in **1**. These are a consequence of the very short W–W bonds in this complex.[14] The abnormally short metal–sulfur bonds in μ-thioether complexes may contribute to the instability of the carbon–sulfur bonds, but these bond lengths are not detectably longer in the complex than in free thioethers.

The stability of the WS_3W core during the reactions described is a notable feature and clearly lends itself to exploitation in the functionalization of the ring-opened THT ligands. This is currently under further investigation, as are reactions involving an excess of nucleophile.

The reactions are of particular interest in the context of HDS modeling, since the reactivity of μ-thioethers toward hydride may represent a mode of C–S bond activation that is feasible on the catalyst surface. Recent work has been more concentrated on thiophene[10] or thiolates[6-8] as the organosulfur ligands, but there has been little attention to thioethers except as possible intermediates in the HDS of thiophene. We intend to extend the study of hydride reactions with coordinated thioethers to explore the generality of these initial observations.

Experimental Section

General Procedures and Techniques. All manipulations were carried out by using standard glovebox and double-manifold vacuum line techniques. Acetonitrile, diethyl ether, dichloromethane, and hexanes were dried over calcium hydride and distilled under nitrogen prior to use. Tetrahydrofuran was dried and distilled over sodium and benzophenone. 2,4,6-Trimethylbenzenethiol and 2,4,6-triisopropylbenzenethiol were obtained by reduction of the corresponding sulfonyl chloride with lithium aluminium hydride in ether.[15] Sodium benzeneselenolate was made by reduction of diphenyl diselenide with sodium in THF.[16] Sodium thiolates were prepared by reacting the corresponding thiols with sodium methoxide in methanol. Tetraphenylphosphonium thiolates were prepared by refluxing a mixture of tetraphenylphosphonium chloride and an excess of the corresponding sodium thiolate in acetonitrile. The crude products were recrystallized from acetonitrile. Elemental analyses were performed by the Microanalytical and Spectroscopy Laboratory, Department of Chemistry, University of Calgary. ^{1}H and ^{2}H NMR spectra were obtained by using either a Bruker ACE-200 or ACE-400 NMR spectrometer. Infrared spectra were recorded as Nujol mulls between CsI plates on a Mattson 4030 Galaxy Series FT-IR spectrometer and UV–vis spectra were obtained by using a Varian 219 spectrophotometer in the range 800–250 nm.

(a) Preparation of $Na[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$. This synthetic procedure will be described in detail and is typical of that used. Subsequent descriptions will be limited to the details unique to that preparation. $Cl_3W(\mu\text{-SEt}_2)_3WCl_3\cdot CH_3CN$ (2.00 g, 2.24 mmol) and $NaS(p\text{-tol})$ (0.328 g, 2.24 mmol) were weighed into a Schlenk tube, which was

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then evacuated and refilled with dry nitrogen. The pump and fill procedure was repeated three times to ensure complete absence of oxygen and moisture. To this mixture was introduced dry deoxygenated acetonitrile (50 mL) under nitrogen. Under vigorous stirring conditions, the insoluble sodium thiolate disappeared in 2–3 min, and a dark orange solution was produced. The solution was stirred for 3 h and then filtered. The filtrate was pumped to dryness to give a slightly tarry product, which was extracted with ether or hexanes (3 × 20 mL) and CH_2Cl_2 (1 × 30 mL) in an ultrasonic bath, and the residual solid was then dried in vacuum. Yield of $Na[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$: 1.75 g, 92%. Anal. Calcd for $C_{10}H_{25}Cl_6NaS_3W_2$: C, 14.21; H, 2.98. Found: C, 14.17; H, 2.95. ^1H NMR data (200 MHz, CD_3CN; δ (ppm), J (Hz)): 3.78 (q, 7.34, 2 H), 3.65 (q, 7.34, 2 H), 3.55 (q, 7.34, 2 H), 3.49 (q, 7.34, 2 H), 3.47 (q, 7.60, 2 H), 1.76 (t, 7.34, 3 H), 1.74 (t, 7.34, 3 H), 1.71 (t, 7.34, 3 H), 1.70 (t, 7.34, 3 H), 1.40 (t, 7.60, 3 H). IR data (cm^{-1}; Nujol mull, CsI plates): 1402 (s), 1307 (w), 1267 (ms), 1246 (ms), 1168 (w), 1159 (w), 1064 (s), 1045 (ms), 1018 (w), 968 (ms), 771 (s), 740 (ms), 428 (w), 389 (vw), 289 (vs), 281 (vs), 246 (w). UV–vis data (MeCN solution, nm (ϵ)): 507 (300); 382 (6540); 306 (5010). All the analogous complexes described below have electronic spectra very similar to this and will therefore not be reported individually.

The combined ether or hexanes extractant solutions were pumped to dryness and a colorless oil of $CH_3CH_2SC_6H_4CH_3$ was obtained. The identity of this oil was confirmed by a mass spectrum, M^+ = 152, and ^1H NMR data. ^1H NMR (CD_3CN; δ (ppm), J (Hz)): 7.27–7.10 (m, 4 H, C_6H_4), 2.91 (q, 7.33, 2 H, CH_2), 2.30 (s, 3 H, $C_6H_4CH_3$), 1.24 (t, 7.34, 3 H, CH_3).

(b) Reaction of $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$ and NaSR (R = Ph, 2,4,6-Triisopropylphenyl (tipp), and ^{i}Bu). By the use of the procedures described above and the appropriate reagents (on an approximately 2 mmol scale), $Na[Cl_3W(\mu\text{-SEt}_2)_2(\mu\text{-SEt})WCl_3]$ and CH_3CH_2SR were isolated. The yield of $Na[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$ was always more than 90%. In the case of $NaSBu^i$, CD_3CN was used as the solvent, which allows the separation of the volatile product $CH_3CH_2SBu^i$, together with CD_3CN, by condensation in a cold trap.

CH_3CH_2Stipp. M^+ = 264. ^1H NMR (CD_3CN; δ (ppm), J (Hz)): 7.10 (s, 2 H, C_6H_2), 3.95 (hept, 6.89, 2 H, *o*-$CH(CH_3)_2$), 2.90 (hept, 6.98, 1 H, *p*-$CH(CH_3)_2$), 2.63 (q, 7.34, 2 H, CH_2CH_3), 1.23 (d, 6.75, 6 H, *p*-$CH(CH_3)_2$), 1.21 (d, 6.75, 12 H, *o*-$CH(CH_3)_2$), 1.17 (t, 7.34, 3 H, CH_2CH_3).

$CH_3CH_2S^i$Bu. M^+ = 118. ^1H NMR (CD_3CN, δ (ppm), J (Hz)): 2.51 (q, 7.34, 2 H, CH_3CH_2), 2.40 (d, 6.88, 2 H, SCH_2), 1.77 (m, 1 H, SCH_2CH), 1.21 (t, 7.34, 3 H, CH_3CH_2), 0.97 (d, 6.64, 6 H, $SCH_2CH(CH_3)_2$).

CH_3CH_2SPh. M^+ = 138. ^1H NMR (CD_3CN, δ (ppm), J (Hz)): 7.30–7.35 (m, 5 H, C_6H_5), 2.97 (q, 7.34, 2 H, CH_3CH_2), 1.28 (t, 7.34, 3 H, CH_3CH_2).

(c) Preparation of $Ph_4P[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$. To a slurry of $Na[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$ (0.364 g, 0.431 mmol) in CH_2Cl_2 (20 mL) was added Ph_4PCl (0.170 g, 0.453 mmol) in 10 mL of CH_2Cl_2. The slurry immediately became a clear orange solution, which was stirred for 1 h and then filtered. The filtrate was pumped to dryness, and the resultant solid was extracted with 2-PrOH (2 × 10 mL) and ether (3 × 20 mL) in an ultrasonic bath and then dried in vacuum. Yield of $Ph_4P[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$: 0.419 g, 98%. Anal. Calcd for $C_{34}H_{45}Cl_6PS_3W_2$: C, 35.16; H, 3.90. Found: C, 35.07; H, 3.84. The ^1H NMR spectrum is the same as that of $Na[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$ except for the resonance due to the protons in Ph_4P^+.

Alternative method: $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$ (1.403g, 1.648 mmol) and Ph_4PS(*p*-tol) (0.762 g, 1.648 mmol) were weighed into a Schlenk tube. Dry, deoxygenated acetonitrile (25 mL) was introduced. The mixture was stirred for 1 h and filtered. To the filtrate was added ether (20 mL) to precipitate any unreacted $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$. The solution was cooled to 4 °C for 5 h and then filtered and pumped to dryness. The solid was extracted with 2-PrOH (2 × 20 mL) and ether (3 × 20 mL) and dried in vacuum. Yield of $Ph_4P[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$: 1.72 g, 90%. The product was proven by ^1H NMR and chemical analysis to be the same as that obtained by the first method.

(d) Reaction of $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$ with Ph_4PCl. $Cl_3W(\mu\text{-SEt}_2)_3WCl_3\cdot MeCN$ (0.446 g, 0.5 mmol) and dry Ph_4PCl (0.187 g, 0.5 mmol) were loaded into a Schlenk tube, and dry CH_3CN (30 mL) was introduced. The mixture was stirred and maintained at 50–60 °C for 5 h. The resulting orange solution was filtered, and the filtrate was pumped to dryness. The solid was extracted with 2-PrOH (20 mL), washed with ether, and dried in vacuum. Yield of $Ph_4P[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$: 0.54 g, 93%. ^1H NMR spectrum is the same as that for the product from reaction c.

The synthesis was repeated in a modified form to identify the volatile byproduct C_2H_5Cl. $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$ (89 mg, 0.1 mmol) and Ph_4PCl (37 mg, 0.1 mmol) were loaded into a 30-mL pressure bottle, and dry CD_3CN (3 mL) was added. The bottle was closed, stirred, and maintained at 50–60 °C for 5 h. After cooling, the volatile product and solvent were condensed into a cold trap, and the ^1H NMR spectrum was taken, which confirmed the identity of the volatile product as CH_3CH_2Cl. ^1H NMR (δ (ppm), J (Hz): 3.62 (q, 7.20, 2 H, CH_3CH_2); 1.45 (t, 7.20, 3 H, CH_3CH_2).

Similarly, the reaction between Ph_4PX (X = Br, I) and $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$ gave CH_3CH_2X and $Ph_4P[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3$. ^1H NMR of CH_3CH_2Br (CD_3CN; δ (ppm), J (Hz)): 3.49 (q, 7.33, 2 H, CH_3CH_2), 1.64 (t, 7.33, 3 H, CH_3CH_2). ^1H NMR of CH_3CH_2I (CD_3CN; δ (ppm), J (Hz)): 3.25 (q, 7.48, 2 H, CH_3CH_2), 1.81 (t, 7.48, 3 H, CH_3CH_2).

(e) Reaction of $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$ with $Ph_4P[S(p\text{-tol})]$ and Ph_4PBr. $Cl_3W(\mu\text{-SEt}_2)_3WCl_3\cdot CH_3CN$ (8.9 mg, 0.01 mmol), $Ph_4P[S(p\text{-tol})]$ (4.7 mg, 0.01 mmol), and Ph_4PBr (8.4 mg, 0.02 mmol) were loaded into an NMR tube, and 1 mL of dry CD_3CN was added under nitrogen. The reaction was monitored immediately after the reactants were mixed, and spectra were acquired every 1 min for the first 10 min. The production of $Ph_4P[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]$ was completed in the first 7 min. During this time, only the consumption of $Cl_3W(\mu\text{-SEt}_2)_3WCl_3$ and the production of $[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_3]^-$ and EtS-*p*-tol was observed. There was no evidence for the formation of EtBr or the Br^-substituted product $[Cl_3W(\mu\text{-SEt})(\mu\text{-SEt}_2)_2WCl_2Br]^-$ in the system.

(f) Preparation of $Na[Cl_3W(\mu\text{-THT})_2(\mu\text{-S}(CH_2)_4ER)WCl_3]$ (E = S, Se; R = Alkyl, Aryl). General Procedures. Finely ground $Cl_3W(\mu\text{-THT})_3WCl_3$ (usually ca. 1–2 mmol) and an equimolar amount of NaER were weighed into a Schlenk tube, and CH_3CN was introduced. The slurry was vigorously stirred, and within 3–5 min a clear orange solution was obtained. After a 4 h reaction time, the solution was filtered, and the filtrate was pumped to dryness. The resultant solid was extracted with CH_2Cl_2 (3 × 20 mL) in an ultrasonic bath and dried in vacuum. The yield of $Na[Cl_3W(\mu\text{-THT})_2(\mu\text{-S}(CH_2)_4ER)WCl_3]$ was always greater than 90%.

$Na[Cl_3W(\mu\text{-THT})(\mu\text{-S}(CH_2)_4SPh)WCl_3]$. Anal. Calcd for $C_{18}H_{29}Cl_6NaS_4W_2$: C, 22.13; H, 2.99. Found: C, 22.40; H, 2.87. ^1H NMR (CD_3CN; δ (ppm)): 7.45–7.11 (m, 5 H, C_6H_5), 3.90–3.72 (m, 4 H, α-CH_2 of THT's), 3.59–3.37 (m + t, 4 H + 2 H, α-CH_2 of THT's and $SCH_2(CH_2)_3SPh$), 2.96 (t, 2 H, $S(CH_2)_3CH_2SPh$), 2.48–2.23 (m, 8 H, β-CH_2 of THT's), 1.92–1.64 (m, 4 H, $SCH_2CH_2CH_2CH_2SPh$). IR (cm^{-1}; Nujol mull, CsI): 1580 (w); 1305 (w), 1257 (vw), 1246 (vw), 1192 (vw), 1168 (vw), 1155 (vw), 1128 (ms), 1089 (w), 1035 (w), 1016 (w), 960 (w, br), 939 (vw), 916 (vw), 879 (w), 800 (ms), 723 (ms), 509 (ms), 495 (ms, sh), 322 (w, sh), 297 (vs), 281 (vs).

$Na[Cl_3W(\mu\text{-THT})_2(\mu\text{-S}(CH_2)_4S(p\text{-tol}))WCl_3]$. Anal. Calcd for $C_{19}H_{31}Cl_6NaS_4W_2$: C, 23.02; H, 3.15. Found: C, 22.78; H, 3.15. ^1H NMR ($(CD_3)_2CO$; δ (ppm)): 7.30–7.10 (m, 4 H, C_6H_4), 3.93–3.71 (m, 4 H, α-CH_2 of THT's), 3.60–3.39 (m + t, 4 H + 2 H, α-CH_2 of THT's and $SCH_2(CH_2)_3S(p\text{-tol})$), 2.96 (t, 2 H, $S(CH_2)_3CH_2S(p\text{-tol})$), 2.51–2.25 (m, 8 H, β-CH_2 of THT's), 2.28 (s, 3 H, Ph–CH_3); 2.00–1.66 (m, 4 H, $SCH_2CH_2CH_2S(p\text{-tol})$). IR ($cm^{-1}$; Nujol mull, CsI): 1606 (ms), 1305 (ms), 1275 (vw), 1248 (w), 1194 (w), 1128 (ms), 1089 (w), 1033 (w), 1014 (w), 958 (w), 879 (w), 802 (s), 723 (ms), 509 (ms), 493 (ms), 289 (vs), 279 (vs), 239 (ms).

$Na[Cl_3W(\mu\text{-THT})_2(\mu\text{-S}(CH_2)_4S^iBu)WCl_3]$. Anal. Calcd for $C_{16}H_{34}Cl_6NaS_4W_2$: C, 20.06; H, 3.57. Found: C, 20.09; H, 3.56. ^1H NMR ($(CD_3)_2CO$; δ (ppm)): 3.92–3.78 (m, 4 H, α-CH_2 of THT's), 3.56–3.41 (m + t, 4 H + 2 H, α-CH_2 of THT's + $SCH_2(CH_2)_3S^iBu$), 2.53 (t, 2 H, $S(CH_2)_3CH_2S^iBu$), 2.48–2.30 (m, 8 H, β-CH_2 of THT's), 2.40 (d, 2 H, $SCH_2CH(CH_3)_2$), 1.96–1.63 (m, 5 H, $SCH_2CH_2CH_2CH_2SCH_2CH(CH_3)_2$); 0.98 (d, 6 H, $SCH_2CH(CH_3)_2$). IR (cm^{-1}; Nujol mull, CsI): 1415 (w), 1305 (w), 1277 (vw), 1248 (w), 1232 (w, sh), 1194 (w), 1167 (w), 1128 (ms), 1074 (w), 1033 (w), 958 (ms), 920 (vw), 879 (ms), 796 (ms), 723 (ms), 509 (ms), 322 (ms, sh), 295 (vs), 287 (vs), 275 (vs), 246 (w).

$Na[Cl_3W(\mu\text{-THT})_2(\mu\text{-S}(CH_2)_4SMes)WCl_3]$ (Mes = 2,4,6-Trimethylphenyl). Anal. Calcd for $C_{21}H_{35}Cl_6NaS_4W_2$: C, 24.75; H, 3.46. Found: C, 25.00; H, 3.34. ^1H NMR ($(CD_3)_2CO$; δ (ppm)): 6.92 (s, 2 H, C_6H_2), 3.89–3.74 (m, 4 H, α-CH_2 of THT's), 3.57–3.38 (m + t, 4 H + 2 H, α-CH_2 of THT's and $SCH_2(CH_2)_3SMes$), 2.68 (t, 2 H, $S(CH_2)_3CH_2SMes$), 2.49 (s, 6 H, *o*-CH_3), 2.46–2.30 (m, 8 H, β-CH_2 of THT's), 2.21 (s, 3 H, *p*-CH_3), 1.94–1.76 (m, 2 H, $SCH_2CH_2(CH_2)_2SMes$), 1.75–1.55 (m, 2 H, $S(CH_2)_2CH_2CH_2SMes$). IR (cm^{-1}; Nujol mull, CsI): 1599 (ms), 1305 (ms), 1275 (vw), 1248 (w), 1186 (ms, br), 1127 (ms), 1091 (w), 1057 (vw), 1031 (ms, br), 958 (w), 881 (w), 850 (ms), 798 (w), 723 (ms), 690 (w), 623 (vw), 578 (vw), 557 (w), 509 (ms), 293 (vs), 287 (vs), 246 (w).

$Na[Cl_3W(\mu\text{-THT})_2(\mu\text{-S}(CH_2)_4Stipp)WCl_3]$. Anal. Calcd for $C_{27}H_{47}Cl_6NaS_4W_2$: C, 29.39; H, 4.29. Found: C, 29.64; H, 4.17. ^1H NMR (CD_3CN; δ (ppm)): 7.09 (s, 2 H, C_6H_2), 3.95 (hept, 2 H, *o*-$CHMe_2$), 3.91–3.75 (m, 4 H, α-CH_2 of THT's), 3.59–3.37 (m + t, 4 H

+ 2 H, α-CH_2 of THT's and SCH_2(CH$_2$)$_3$Stipp), 2.90 (hept, 1 H, *p*-CHMe$_2$), 2.64 (t, 2 H, S(CH$_2$)$_3$CH_2Stipp), 2.48–2.27 (m, 8 H, β-CH$_2$ of THT's), 1.92–1.76 (m, 2 H, SCH$_2$CH_2(CH$_2$)$_2$Stipp), 1.76–1.59 (m, 2 H, S(CH$_2$)$_2$CH_2Stipp); 1.23 (d, 6 H, *o*-CH(CH_3)$_2$, 1.22 (d, 12 H, *o*-CH(CH_3)$_2$). IR (cm^{-1}; Nujol mull, CsI): 1599 (ms), 1560 (w), 1307 (ms), 1271 (vw), 1249 (w), 1195 (w), 1167 (w), 1155 (vw), 1130 (ms), 1101 (w), 1068 (w), 1060 (w), 1035 (w), 1014 (w), 937 (w), 920 (vw), 877 (ms), 841 (vw), 800 (w), 756 (vw), 651 (w), 509 (ms), 295 (vs), 287 (vs), 275 (vs), 241 (w).

Na[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$SePh)WCl$_3$]. Anal. Calcd for C$_{18}$H$_{29}$Cl$_6$NaS$_3$SeW$_2$: C, 21.11; H, 2.85. Found: C, 20.86; H, 2.84. ^{1}H NMR (CD$_3$CN; δ (ppm)): 7.56–7.18 (m, 5 H, C$_6H_5$), 3.92–3.73 (m, 4 H, α-CH_2 of THT's), 3.60–3.36 (m + t, 4 H + 2 H, α-CH_2 of THT's and SCH_2(CH$_2$)$_3$Se), 3.01 (t, 2 H, S(CH$_2$)$_3$CH_2Se), 2.48–2.27 (m, 8 H, β-CH_2 of THT's), 1.93–1.75 (m, 4 H, SCH$_2$CH_2CH_2CH$_2$Se). ^{77}Se NMR (CH$_3$CN/D$_2$O insert, reference to Me$_2$Se at 0 ppm): 289 ppm (s), $W_{1/2}$ = 30.5 Hz; broad-band ^{1}H decoupling, 289 ppm (s), $W_{1/2}$ = 10 Hz; literature value (δ(^{77}Se) in ^{n}BuSePh), 288 ppm.[5] IR (cm^{-1}; Nujol mull, CsI): 1574 (ms), 1417 (ms, sh), 1327 (vw), 1303 (ms), 1255 (w, sh), 1248 (w), 1221 (vw), 1195 (w), 1175 (vw), 1155 (vw), 1128 (ms), 1068 (w), 1033 (vw), 1020 (w), 999 (vw), 958 (ms), 920 (vw), 879 (w), 846 (vw), 796 (ms), 736 (vs), 690 (s), 669 (w), 509 (ms), 472 (w, sh), 464 (w), 322 (ms, sh), 300 (vs), 293 (vs), 279 (vs), 246 (w).

(g) General Procedures for Preparation of Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$ER)WCl$_3$. The procedures are the same as those described in part c; i.e., the compounds were prepared either by metathesis reactions between Ph$_4$PCl and the sodium salt of [Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$ER)WCl$_3$]$^-$ in dichloromethane or by the reactions between Ph$_4$PER and Cl$_3$W(μ-THT)$_3$WCl$_3$ in acetonitrile. The ^{1}H NMR spectra of the compounds Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$ER)WCl$_3$] are the same as those of the corresponding sodium salts except for the resonances due to the protons in Ph$_4$P$^+$.

Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$SPh)WCl$_3$]. Anal. Calcd for C$_{42}$H$_{49}$Cl$_6$PS$_4$W$_2$: C, 39.00; H, 3.82. Found: C, 39.36; H, 3.76. IR (cm^{-1}; Nujol mull, CsI): 1581 (ms), 1338 (w), 1273 (vw), 1246 (vw), 1186 (w), 1163 (w), 1128 (w), 1105 (vs), 1072 (ms, sh), 1024 (w), 995 (ms), 960 (w), 879 (w), 848 (vw), 798 (w), 750 (s), 721 (vs), 688 (vs), 615 (vw), 526 (vs), 298 (vs), 283 (vs).

Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$S(*p*-tol))WCl$_3$]. Anal. Calcd for C$_{43}$H$_{51}$Cl$_6$PS$_4$W$_2$: C, 39.50; H, 3.93. Found: C, 39.60; H, 3.92. IR (cm^{-1}; Nujol mull, CsI): 1583 (ms), 1338 (w), 1305 (ms), 1273 (vw), 1246 (vw), 1188 (ms), 1163 (w), 1130 (ms), 1107 (vs), 1072 (w, sh), 1033 (vw), 1014 (vw), 995 (s), 960 (w), 881 (w), 846 (vw), 802 (s), 754 (s), 723 (vs), 688 (vs), 615 (vw), 524 (vs), 509 (ms, sh), 297 (vs), 287 (vs), 275 (vs).

Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$S^{t}Bu)WCl$_3$]. Anal. Calcd for C$_{40}$H$_{53}$Cl$_6$PS$_4$W$_2$: C, 37.72; H, 4.19. Found: C, 37.71; H, 4.06. IR (cm^{-1}; Nujol mull, CsI): 1585 (w), 1342 (ms), 1273 (vw), 1246 (vw), 1188 (w), 1165 (w), 1128 (ms), 1107 (vs), 1072 (vw), 1030 (vw), 997 (ms), 960 (w), 885 (vw), 846 (vw), 796 (w), 750 (ms), 721 (vs), 690 (s), 528 (vs), 509 (ms, sh), 297 (vs), 285 (vs).

Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$Stipp)WCl$_3$]. Anal. Calcd for C$_{51}$H$_{67}$Cl$_6$PS$_4$W$_2$: C, 43.14; H, 4.75. Found: C, 43.18; H, 4.59. IR (cm^{-1}; Nujol mull, CsI): 1595 (w), 1585 (w), 1558 (vw), 1340 (w), 1305 (ms), 1246 (vw), 1188 (w), 1165 (w), 1130 (w), 1107 (vs), 1070 (w), 1058 (w), 1035 (vw), 1028 (vw), 995 (ms), 960 (vw), 935 (vw), 977 (w), 733 (vw), 798 (w), 754 (ms), 723 (vs), 688 (s), 526 (vs), 300 (vs), 289 (vs), 275 (vs), 246 (w).

Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$SePh)WCl$_3$]. Anal. Calcd for C$_{42}$H$_{49}$Cl$_6$PS$_3$SeW$_2$: C, 37.63; H, 3.68. Found: C, 37.62; H, 3.70. IR (cm^{-1}; Nujol mull, CsI): 1584 (ms), 1576 (ms), 1560 (w), 1336 (w), 1342 (w), 1320 (vw), 1370 (w), 1278 (vw), 1257 (vw), 1249 (w), 1231 (vw), 1219 (w), 1196 (w, sh), 1188 (w), 1164 (w), 1130 (w), 1109 (vs), 1068 (w), 998 (ms), 963 (w), 800 (w), 767 (ms), 757 (ms), 754 (ms), 738 (s), 726 (vs), 701 (w, sh), 689 (s), 670 (w), 615 (vw), 528 (vs), 509 (w), 462 (w), 298 (vs), 286 (vs).

(h) Preparation of Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_3$CH$_2$Y)WCl$_3$] (Y = H, D). Finely ground Cl$_3$W(μ-THT)$_3$WCl$_3$ (0.868 g, 1.027 mmol) was weighed into a Schlenk tube, to which THF (60 mL) was introduced. The slurry was stirred, and 1.2 mL of a 1 M THF solution of Li[BEt$_3$H] was slowly added. The mixture was stirred overnight, and a dark orange solution formed. The solution was filtered, and the filtrate was pumped to give a tarry product. This product was then extracted with hexanes in an ultrasonic bath, and 0.53 g (60%) of dry, crystalline material was obtained. The material was formulated as Li[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_3$CH$_3$)WCl$_3$]. However, elemental analysis (Calcd: C, 16.90; H, 2.95. Found: C, 18.62; H, 3.36) and the ^{1}H NMR spectrum showed that it contains unknown impurities. It was therefore converted to the Ph$_4$P$^+$ salt. The impure lithium salt (0.5 g, ca. 0.58 mmol) and Ph$_4$PCl (0.22 g, 0.58 mmol) were weighed into a Schlenk tube, and dichloromethane (15 mL) was introduced. The solid instantly dissolved, and an orange solution formed. The solution was stirred for 2 h and was filtered. The filtrate was pumped to dryness and then extracted with 2-PrOH (2 × 20 mL) and with ether (3 × 20 mL) in an ultrasonic bath. Yield of Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_3$CH$_3$WCl$_3$]: 0.578 g, 81%. Anal. Calcd for C$_{36}$H$_{45}$Cl$_6$PS$_3$W$_2$: C, 36.47; H, 3.83. Found: C, 36.60; H, 3.75. ^{1}H NMR (CD$_3$CN; δ (ppm)): 8.02–7.10 (m, 20 H, C$_6H_5$), 3.92–3.73 (m, 4 H, α-CH_2 of THT's), 3.60–3.37 (m + t, 4 H + 2 H, α-CH_2 of THT's and SCH_2(CH$_2$)$_2$CH$_3$), 2.47–2.24 (m, 8 H, β-CH_2 of THT's), 1.83–1.60 (m, 2 H, SCH$_2$CH_2CH$_2$CH$_3$), 1.58–1.32 (m, 2 H, S(CH$_2$)$_2$CH_2CH$_3$), 0.92 (t, 3 H, S(CH$_2$)$_3$CH_3). IR (cm^{-1}; Nujol mull, CsI): 1587 (ms), 1340 (ms), 1315 (ms), 1246 (w), 1190 (ms), 1161 (w), 1130 (s), 1107 (vs), 1074 (w), 1030 (w), 997 (ms), 960 (w), 931 (vw), 902 (vw), 881 (w), 856 (vw), 842 (vw), 798 (ms), 756 (s, sh), 748 (s), 723 (vs), 692 (vs), 615 (vw), 528 (vs), 509 (ms), 455 (w), 432 (vw), 324 (ms), 304 (vs), 291 (vs), 274 (vs), 237 (w).

The analogous deuterium compound Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_3$CH$_2$D)WCl$_3$] was made by a similar procedure in about 60% yield (which depends on the quality of Li[BEt$_3$D]). Anal. Calcd for C$_{36}$H$_{44}$DCl$_6$PS$_3$W$_2$: C, 36.44; H, 3.91. Found: C, 36.18; H, 3.77. ^{1}H NMR (CD$_3$CN; δ (ppm)): 8.02–7.10 (m, 20 H, C$_6H_5$), 3.92–3.73 (m, 4 H, α-CH_2 of THT's), 3.60–3.37 (m + t, 4 H + 2 H, α-CH$_2$ of THT's and SCH_2(CH$_2$)$_2$CH$_2$D, 2.47–2.24 (m, 8 H, β-CH_2 of THT's), 1.83–1.60 (m, 2 H, SCH$_2$CH_2CH$_2$CH$_2$D), 1.59–1.31 (m, 2 H, S(CH$_2$)$_2$CH_2CH$_2$D), 0.92 (m, 2 H, –CH_2D). ^{2}H NMR (CH$_3$CN, referenced to natural abundance CH$_2$DCN, δ = 1.95 ppm): 0.92 ppm, (t, $^2J_{HD}$ = 1.83 Hz) with selective decoupling of –CH_2CH$_2$D).

(i) Preparation of Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$X)WCl$_3$] (X = Cl, Br). Finely ground Cl$_3$W(μ-THT)$_3$WCl$_3$ (0.423 g, 0.500 mmol) and Ph$_4$PCl (0.280 g, 0.75 mmol) were loaded into a Schlenk tube, and CH$_3$CN (60 mL) was introduced. The mixture was stirred and heated to 75–80 °C. The slurry became a dark orange solution within 20 min, and the reaction was allowed to continue for another 15 min. The solution was cooled, filtered, and pumped to dryness. The solid was then extracted with 2-PrOH (2 × 20 mL) and ether (3 × 20 mL) to remove the excess Ph$_4$PCl and was again pumped to dryness. Yield: 0.59 g (96%) of Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$Cl)WCl$_3$]. Anal. Calcd for C$_{36}$H$_{44}$Cl$_7$PS$_3$W$_2$: C, 35.45; H, 3.63. Found; C, 35.54; H, 3.46. ^{1}H NMR (CDCl$_3$; δ (ppm)): 8.10–7.50 (m, 20 H, C$_6H_5$), 4.00–3.78 (m, 4 H, α-CH_2 of THT's), 3.68–3.47 (m, 6 H, α-CH_2 of THT's and SCH$_2$(CH$_2$)$_2$CH_2Cl), 3.45 (m, 2 H, SCH_2(CH$_2$)$_3$Cl, 2.52–2.23 (m, 8 H, β-CH_2 of THT's), 1.83 (m, 4 H, SCH$_2$CH_2CH_2CH$_2$Cl). IR (cm^{-1}; Nujol mull, CsI): 1585 (w), 1338 (ms), 1305 (ms), 1280 (vw), 1246 (w), 1188 (w), 1161 (w), 1128 (ms), 1107 (vs), 1072 (w, sh), 1026 (vw), 995 (ms), 960 (w), 931 (vw), 879 (w), 848 (vw), 896 (w), 750 (s), 723 (vs), 690 (vs), 648 (w), 615 (vw), 526 (s, sh), 468 (vw), 457 (vw), 304 (vs), 287 (vs), 275 (vs), 248 (w).

The bromide analogue, Ph$_4$P[Cl$_3$W(μ-THT)$_2$(μ-S(CH$_2$)$_4$Br)WCl$_3$], was made similarly by refluxing a mixture of Ph$_4$PBr and Cl$_3$W(μ-THT)$_3$WCl$_3$ in acetonitrile for 24 h in 30% yield after recrystallization from acetone. Anal. Calcd for C$_{36}$H$_{44}$BrPCl$_6$S$_3$W$_2$: C, 34.20; H, 3.51. Found: C, 34.49; H, 3.52. ^{1}H NMR (CDCl$_3$; δ (ppm)): 8.01–7.55 (m, 20 H, C$_6H_5$), 4.02–3.85 (m, 4 H, α-CH_2 of THT's), 3.70–3.57 (m, 4 H, α-CH_2 of THT's), 3.53 (m, 2 H, S(CH$_2$)$_3$CH_2Br), 3.45 (m, 2 H, SCH_2(CH$_2$)$_3$Br), 2.54–2.29 (m, 8 H, β-CH_2 of THT's), 1.85 (m, 4 H, SCH$_2$CH_2CH_2CH$_2$Br). IR (cm^{-1}; Nujol, CsI): 1585 (ms), 1342 (w), 1307 (ms), 1279 (vw, sh), 1247 (w), 1218 (vw), 1189 (ms), 1165 (w), 1129 (ms), 1107 (vs), 1073 (w), 1037 (w), 1027 (w), 996 (s), 978 (vw), 960 (w), 881 (w), 852 (vw), 815 (w, sh), 798 (ms), 754 (s), 723 (vs), 691 (vs), 649 (w), 618 (w), 528 (vs), 509 (ms, sh), 457 (w), 304 (vs), 287 (vs), 275 (vs), 246 (w).

No reaction occurred between Ph$_4$PI and Cl$_3$W(μ-THT)$_3$WCl$_3$, even if the reaction mixture was allowed to reflux for 3 days.

X-ray Crystallography. Na[Cl$_3$W(μ-SEt$_2$)$_2$(μ-SEt)WCl$_3$]·3THF. A single crystal of **3a** was slowly grown from a THF solution of **3** to which diethyl ether was added. Dark orange crystals of **3a** were obtained after 24 h. An approximate trigonal prism was mounted on a glass fiber and protected with epoxy resin and then mounted on a Nicolet R3m/E diffractometer. The unit cell parameters were derived from the setting angles of 25 automatically centered reflections. The intensity data were collected in the 2θ–θ scan mode, with crystal and instrumental instability being monitored through the measurement of three standard reflections every 100. Other details are given in Table I. The structure was solved by locating the W atoms in an E map, with phases derived from symbolic addition.[17] The remaining non-hydrogen atoms were located in difference maps after refining scale and thermal parameters. Neutral-atom

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(17) Schenk, H.; Hall, S. R. SIMPEL. In *XTAL2.6 User's Manual*; Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1989.

scattering factors were used, with anomalous dispersion corrections applied.[18] No corrections for extinction were made. The data were corrected for absorption by using an empirical ψ scan method ($T_{max} = 1$; $T_{min} = 0.208$). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were not included in the model. The model converged at $R = 0.061$. The final values of the refined positional parameters are presented in Table II. All other supporting data are available as supplementary material. The final full-matrix least-squares refinement cycles used a weighting scheme of $w = 1/(\sigma^2(F) + 0.0031F^2)$. All calculations were carried out at Montana State University (by J.F.F.) using the program package XTAL2.6,[19] on a micro Vax cluster.

$[PPh_4][Cl_3W(\mu\text{-THT})_2(\mu\text{-S}(CH_2)_4Cl)WCl_3]$. Well-formed, needle-shaped crystals were grown from a saturated acetone solution of **4** by slow evaporation of the solvent. A portion of one of these needles was cut and mounted on a glass fiber. Accurate cell dimensions and a crystal orientation matrix were determined on an Enraf-Nonius CAD4 diffractometer, by a least-squares refinement of the setting angles of 25 reflections in the θ range, 10–15°. Data were collected in the ω–2θ scan mode. Three reflections were monitored every 2 h of exposure time, and a linear loss of intensity (1.8%) was corrected for by appropriate scaling. Data were corrected for absorption effects (DIFABS[20]); correction factors were in the range 0.688–1.237. All other pertinent data are given in Tables IV and SIII. The structure was solved by direct methods. It was refined by full-matrix least-squares calculations, initially with isotropic and finally with anisotropic temperature factors for the non-hydrogen atoms, except for the chlorobutyl group. This was disordered over two sites with site occupancy factors of 0.4 and 0.6. The C(1)–C(4) and Cl(7) atoms were allowed to refine with isotropic temperature factors. Refinement converged with $R = 0.040$ and $R_w = 0.045$. Scattering factors were taken from Cromer and Mann,[21] and allowance was made for anomalous dispersion.[22] A difference map calculated at the end of the refinement showed maxima at positions expected for hydrogen atoms, but these were not included in the model. There were no other chemically significant features. All the crystallographic calculations (by M.P.) were carried out by using XTAL2.6;[19] Figure 2 was plotted by using ORTEP II.[23]

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Supplementary Material Available: Tables SI–SVI, listing complete crystallographic data, thermal parameters, and additional bond lengths and angles for **3** and **4** (13 pages); tables of observed and calculated structure factors (81 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry, National Tsing Hua University,
Hsinchu, Taiwan, ROC, and National Taiwan University, Taipei, Taiwan, ROC

Stereochemical Nonrigidity in Six-Coordinate Monochelate Complexes via Polytopal Rearrangement

C. Y. Lee,[*,†] Y. Wang,[‡] and C. S. Liu[*,†]

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Analysis of the ^{19}F, ^{13}C, and ^{31}P NMR data for $F_2\overline{SiC(t\text{-Bu}){=}CHSiF_2Fe}(CO)_3$(phosphine) (phosphine = PMe_3, PPh_2Me, PPh_3, and PEt_3, for compounds **3–6**, respectively) over a temperature range covering slow and fast exchange characterizes those complexes as stereochemically nonrigid on the NMR time scale. The activation parameters for the rearrangement process are $\Delta G^* = 16.8$, 15.0, 12.5, and 13.2 kcal/mol for complexes **3–6**, respectively. The crystal and molecular structures of **3b** and **5a** were determined. The molecular structures are best described as distorted octahedra. The space group of both **3b** and **5a** is $Pca2_1$: $a = 15.617$ (3) Å, $b = 8.161$ (3) Å, $c = 29.858$ (4) Å, and $Z = 8$ for **3b**; $a = 17.409$ (8) Å, $b = 9.439$ (2) Å, $c = 17.332$ (5) Å, and $Z = 4$ for **5a**. The intramolecular ligand permutations are interpreted in terms of the "trigonal-twist" mechanism.

It is generally accepted that six-coordinate complexes in solution may undergo permutation of ligand positions via either a bond-breaking process or an intramolecular polytopal rearrangement.[1,2] The established cases of polytopal rearrangement of octahedral complexes are rare in the literature and sometimes inconclusive. Most of these cases involve tris-chelate and bis-chelate derivatives where the trigonal-twist mechanism was considered to be the most likely mechanism for the isomerization.[3-8]

The nonchelate metal complexes $M(CO)_4(ER_3)_2$ (M = Fe, Ru, Os; E = Si, Ge, Sn, Pb) have been known for their fluxional behavior in solutions.[9] The study of the ^{13}C NMR spectral pattern of coalescence in cis–trans mixtures strongly suggests that axial–equatorial averaging proceeds via a cis-to-trans-to-cis isomerization process. This mechanism is further supported by the observation that monochelate complexes $Me_2\overline{SiCH_2CH_2SiMe_2Fe}(CO)_4$ do not show fluxional behavior in solutions, since the chelate ring would not allow a trans configuration.[10]

On the other hand, if a six-coordinate complex adopts the geometry of a highly distorted octahedron, other pathways of intramolecular rearrangement are possible. For example in the case of highly twisted octahedral complex $H_2Fe(PPh_3)_4$, the permutation mechanism was proposed to be a "tetrahedral jump".[11]

In the case of monochelate octahedral complexes, the stereochemical nonrigidity has been much less understood. One fluxional

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[†] National Tsing Hua University.

[‡] National Taiwan University.

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