Organometallics 1994, 13, 1624-1634

New Heterobimetallic μ-Oxo Complexes Formed via Halide Displacement Reactions Using the Trioxo Anions $[Cp^*Mo(O)_3]^-$ and $[Cp^*W(O)_3]^-$

Melinda S. Rau, Christine M. Kretz, and Gregory L. Geoffroy*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Arnold L. Rheingold and Brian S. Haggerty

Department of Chemistry, The University of Delaware, Newark, Delaware 19716

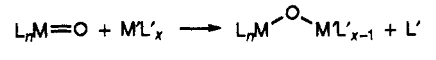
Received November 22, 1993⊗

The trioxo anions $[Cp^*W(O)_3]^-$ and $[Cp^*Mo(O)_3]^-$ have been shown to be useful reagents for the formation of μ-oxo complexes via halide displacement reactions. For example, they react with $Cp^*M(O)_2Cl$ (M = Mo, W) to form the known homometallic μ-oxo complexes $Cp^*(O)_2M{-}O{-}M(O)_2Cp^*$ along with the heterometallic complex $Cp^*(O)_2Mo{-}O{-}W(O)_2Cp^*$. This latter species was also observed to form via a metal exchange process upon mixing the homometallic complexes $Cp^*(O)_2Mo{-}O{-}Mo(O)_2Cp^*$ and $Cp^*(O)_2W{-}O{-}W(O)_2Cp^*$. Reaction of the trioxo anions with $Cp_2M'Cl_2$ led to the new heterobimetallic complexes $Cp_2M'(Cl){-}O{-}M(O)_2Cp^*$ (M' = Ti, Zr, M = Mo, W; M' = V, M = W). The corresponding trinuclear complexes $Cp^*(O)_2W{-}O{-}M'(Cp)_2{-}O{-}W(O)_2Cp^*$ were formed via addition of 2 equiv of $[Cp^*W(O)_3]^-$ to $Cp_2M'Cl_2$ (M' = Ti, Zr). Addition of Et_2O to $Cp_2V(Cl){-}O{-}W(O)_2Cp^*$ gave the solvated complex $[Cp_2V(Et_2O){-}O{-}W(O)_2Cp^*]Cl$, and the tetrametallic complex $[(Cp_2Ti)_2(Cp^*W(O)_2)_2(\mu\text{-}O)_4][BPh_4]_2$ was produced via halide abstraction from $Cp_2Ti(Cl){-}O{-}W(O)_2Cp^*$ with $Na[BPh_4]$ followed by dimerization of the resulting monocations. The trioxo anion $[Cp^*W(O)_3]^-$ also displaced halides from $BrCPh_3$, chlorosilanes, and chlorogermanes to give the corresponding alkoxy ($Cp^*W(O)_2{-}O{-}CPh_3$), siloxy ($Cp^*W(O)_2{-}O{-}SiR_2R'$: R, R' = CH_2Ph; R = Bu^t, R' = H; R = Me, R' = Bu^t; R, R' = Me), and germoxy ($Cp^*W(O)_2{-}O{-}GeR_3$; R = Me, Ph) complexes. The complex $Cp^*W(O)_2{-}O{-}SiMe_3$ was better prepared via reaction of $[Cp^*W(O)_3]^-$ with $CF_3C({=}NSiMe_3)OSiMe_3$. However, reaction of $[Cp^*W(O)_3]^-$ with the tin analogue $ClSnMe_3$ did not give the corresponding bimetallic complex but instead produced $[(Me_3Sn)_4(Cp^*W(O))_4(\mu\text{-}O)_8]$ with a 16-membered ring which is formally a $[{-}O{-}WCp^*(O){-}O{-}SnMe_3{-}]_4$ tetramer. A variable-temperature ^{17}O NMR study showed that this species undergoes a fluxional process which exchanges the bridging and terminal oxo ligands. Crystal structures are reported for $Cp^*(O)_2W{-}O{-}Zr(Cp)_2{-}O{-}W(O)_2Cp^*$, $Cp^*W(O)_2{-}O{-}Si(CH_2Ph)_3$, $Cp^*W(O)_2{-}O{-}Si(Bu^t)_2H$, and $(Me_3Sn)_4(Cp^*W(O))_4(\mu\text{-}O)_8$.

Introduction

Complexes which contain two or more different metal atoms are interesting because of their potential utility as polyfunctional catalysts, precursors for the preparation of bi- and polymetallic heterogeneous catalysts, and reagents for the development of a more fundamental understanding of how ligands on one metal may interact with an adjacent metal and its ligands.[1] Of the very large number of heterometallic complexes that have been prepared, relatively few have oxo ligands bridging between the different metals.[2,3] Such compounds are important because of the variety of mixed-metal oxides that have found catalytic applications in numerous reactions, including several of commercial importance.[1c,4]

The "bridge-assisted" synthetic method has proven to be one of the most flexible routes to heterometallic complexes with bridging ligands of all sorts.[1b] For oxo complexes, this method involves the addition of a complex with a nucleophilic M=O functional group to a second complex having an open coordination site for the oxo ligand to bind or having another ligand that can be easily displaced by the oxo group (eq 1). Several heterometallic



$$L_nM{=}O + M'L'_x \longrightarrow L_nM\overset{O}{\frown}M'L'_{x-1} + L' \qquad (1)$$

μ_2-oxo complexes have been prepared by this method,[3] as illustrated in eq 2 by a family of complexes prepared in these laboratories.[3g]

We have previously described the preparation of the anionic trioxo complexes $[Cp^*W(O)_3]^-$ (1) and $[Cp^*Mo(O)_3]^-$ (2) and have shown that the oxo ligands of these complexes are highly nucleophilic and readily add to a variety of organic substrates.[5] The anionic nature of these complexes should also render them sufficiently nucleophilic to displace halides and neutral ligands from other metal centers to form heterometallic oxo-bridged complexes. This is indeed the case, and herein we describe the synthesis and reactivity properties of a number of new heterometallic oxo-bridged complexes that are derived

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⊗ Abstract published in *Advance ACS Abstracts*, March 15, 1994.

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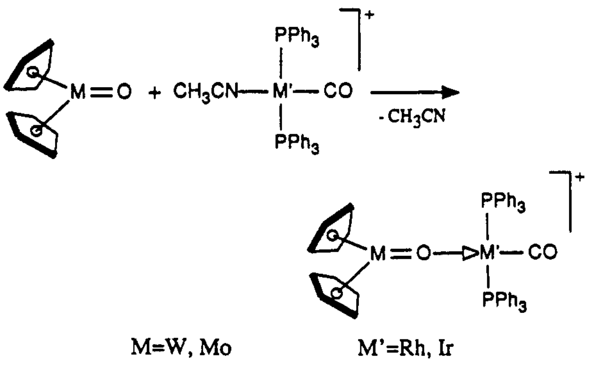
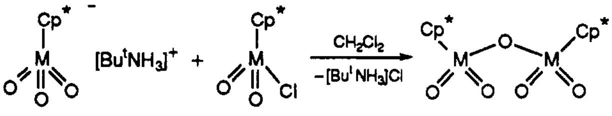


(2)

from 1 and 2. Part of this work has been previously communicated.[5a]

Results and Discussion

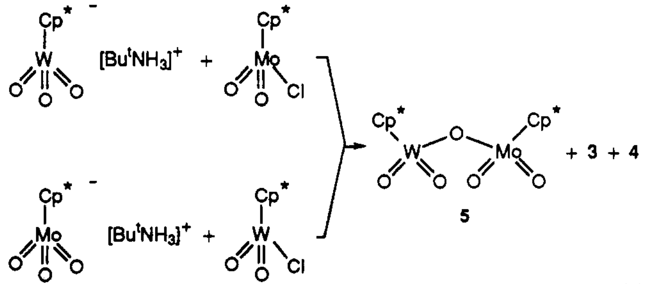
Reaction of $[Cp^*W(O)_3]^-$ and $[Cp^*Mo(O)_3]^-$ with $Cp^*M(O)_2Cl$ (M = Mo, W) and Cp_2MCl_2 (M = V, Ti, Zr). It was initially found that the known *homo*metallic binuclear complexes 3 and 4 could be formed in excellent yields by displacement of the chloride ligand from $Cp^*M(O)_2Cl$[6] by an oxo ligand of the nucleophilic anion $[Cp^*M(O)_3]^-$ (eq 3). Complex 3 has been previously prepared by a variety of means,[6,7] but the ditungsten complex 4 has only been reported to form in low yield (14%) by stirring $[Cp^*W(CO)_2]_2$ in air for 18 h.[6] Both complexes 3 and 4 were obtained as microcrystalline solids, and their spectroscopic data matched those previously reported. These compounds were further characterized by ^{17}O NMR analysis, and each exhibited resonances assigned to the terminal oxo (3, δ 843.8; 4, δ 678.0) and bridging oxo (3, δ 277.9; 4, δ 193.4) ligands.



(3)

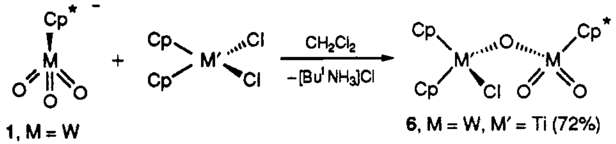
3, M = Mo (66%)
4, M = W (89%)

It was also observed that the heterobimetallic complex $Cp^*(O)_2W–O–Mo(O)_2Cp^*$ (5) readily formed upon treatment of $[Cp^*W(O)_3]^-$ with $Cp^*Mo(O)_2Cl$ and with the reverse combination of $[Cp^*Mo(O)_3]^-$ with $Cp^*W(O)_2Cl$ (eq 4). However, ^1H and ^{17}O NMR analysis of both reactions indicated that the homometallic complexes 3 and 4 were also produced. Integration of the NMR spectra showed their formation in an identical 1:2.5:1 (3/5/4) ratio from each reaction, suggesting that these complexes may be in equilibrium. This is indeed the case, since ^1H NMR analysis showed that an equimolar mixture of 3 and 4 in CD_2Cl_2 gave a 1:2.7:1 mixture of 3/5/4 on standing at room temperature in an NMR tube for 15 min. The heterometallic compound 5 could thus not be separated from 3 and 4, but its presence was clearly indicated by spectroscopic analysis of the 3/5/4 product mixture. A strong parent ion at *m/z* 631 was observed for 5 in the mass spectrum of this mixture, in addition to the parent ions of 3 and 4. Likewise, the ^1H NMR spectrum showed Cp* resonances for 3 (δ 1.99), 4 (δ 2.13), and 5 (δ 2.02, 2.10), and the ^{17}O NMR spectrum of this mixture also showed resonances for all three species (5: W(*O*)$_2$, δ 666.4; Mo(*O*)$_2$, δ 869.6; W–*O*–Mo, δ 230.2). Note that the μ-oxo resonance of 5 is midway between the corresponding μ-oxo resonances of 3 (δ 277.9) and 4 (δ 193.4).



(4)

Addition of 1 equiv of $[Cp^*W(O)_3]^-$ or $[Cp^*Mo(O)_3]^-$ to the complexes Cp_2MCl_2 (M = Ti, Zr, V) led to displacement of one chloride ligand and formation of the new heterobimetallic μ-oxo compounds 6–10 (eq 5). Evidence was also obtained for a similar reaction between $[Cp^*Mo(O)_3]^-$ and Cp_2VCl_2, but the $Cp^*(O)_2Mo–O–VCp_2Cl$ product (11) was unstable and could not be obtained in sufficient purity



(5)

1, M = W
2, M = Mo

6, M = W, M' = Ti (72%)
7, M = W, M' = Zr (69%)
8, M = W, M' = V (66%)
9, M = Mo, M' = Ti (57%)
10, M = Mo, M' = Zr (47%)

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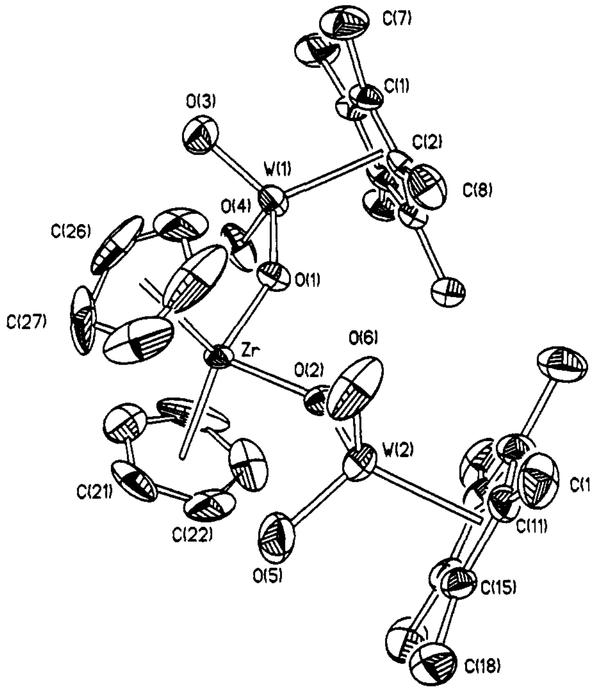
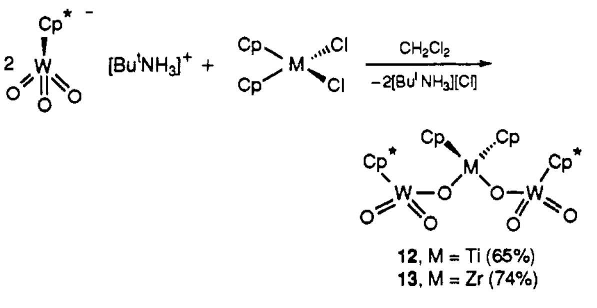


Figure 1. ORTEP drawing for $[Cp_2Zr](\mu\text{-}O)_2[Cp^*W(O)_2]_2$ (**13**).

to characterize. Complexes **6**–**10** were isolated as spectroscopically characterized microcrystalline solids. Each gave satisfactory C,H analyses, parent ions in their mass spectra, IR bands characteristic of a MO_2 fragment (*e.g.*, **6**: $\nu_{W=O}$ 923 (s), 875 (m) cm^{-1}; ν_{W-O-Ti} 776 (br)), and ^1H NMR resonances characteristic of the Cp* and Cp ligands for each of the metal fragments. For **8**, the Cp* resonance was sharp, but the resonances for the Cp ligands attached to the paramagnetic V(IV) center were quite broad. The presence of both bridging and terminal oxo ligands was also indicated by ^{17}O NMR data, which showed downfield resonances for the terminal oxo ligands (**6**, δ 632.6; **7**, δ 639.8; **9**, δ 802.2; **10**, δ 809.5) and upfield resonances for the μ-oxo ligand (**6**, δ 449.5; **7**, δ 350.5; **9**, δ 527.1; **10**, δ 407.4). These data also illustrate the characteristic downfield shift of the resonances for oxo ligands bound to molybdenum as compared to tungsten.

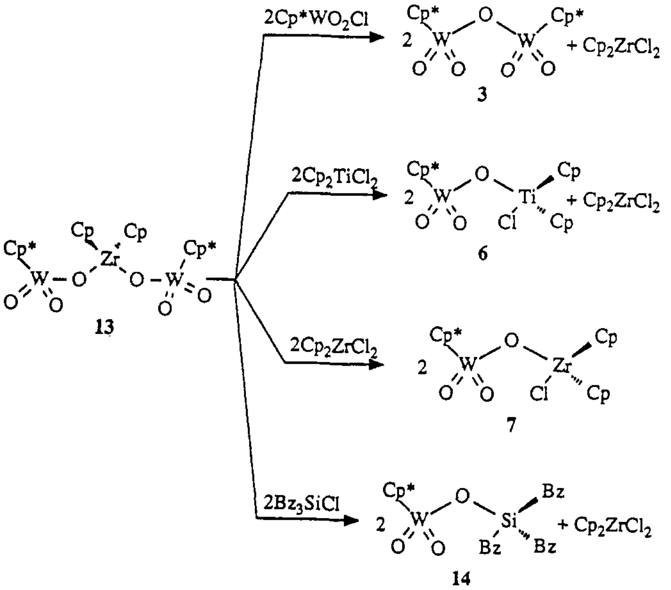
The reactions of Cp_2TiCl_2 and Cp_2ZrCl_2 with 2 equiv of $[Cp^*W(O)_3]^-$ were also investigated and found to give in good yield the trimetallic complexes **12** and **13** (eq 6) by displacement of both chloride ligands. Both complexes were isolated as microcrystalline solids, and complex **13** was characterized by an X-ray diffraction study (see Figure 1 and below). Both compounds gave satisfactory C,H analyses, showed parent ions in their mass spectra, exhibited Cp and Cp* resonances in the expected 1:3 intensity ratio in their ^1H NMR spectra, and gave typical dioxo and μ-oxo patterns in their IR spectra. Each also showed ^{17}O NMR resonances for the terminal (**12**, δ 632.4; **13**, δ 635.4) and bridging (**12**, δ 449.3; **13**, δ 332.1) oxo ligands. In each case, these resonances were shifted only slightly from those of the bimetallic complexes **6** and **7**.



(6)

12, M = Ti (65%)
13, M = Zr (74%)

Scheme 1



Complex **13** was observed to undergo a series of redistribution reactions (Scheme 1) when it was treated with 2 equiv of $Cp^*W(O)_2Cl$, Cp_2TiCl_2, and Cp_2ZrCl_2. A similar displacement of Cp_2ZrCl_2 occurred when **13** was treated with $(PhCH_2)_3SiCl$ to give $Cp^*W(O)_2(OSiBz_3)$ (**14**), whose independent and more direct preparation is described below. ^1H NMR analysis indicated that each of the reactions shown in Scheme 1 was nearly quantitative.

Crystal and Molecular Structure of $[Cp^*W(O)_2(\mu\text{-}O)]_2ZrCp_2$ (13). An ORTEP drawing of complex **13** is shown in Figure 1, and the important crystallographic data are presented in Tables 1 and 2. The Zr center in the molecule has the usual pseudotetrahedral arrangement of the two Cp and two μ-oxo ligands, and the O–Zr–O bond angle of 98.9(3)° compares well to the O–Zr–Cl angle of 97.3(9)° found in the related compound $Cp(CO)_3W\text{–}O\text{–}Zr(Cl)Cp_2$.[3k] The W–O–Zr bonds are clearly bent (W–O–Zr: 153.5(3) and 142.5(3)°), and the rotational disposition of the $Cp^*W(O)_2(\mu\text{-}O)$ units about the Zr center shows no decipherable pattern and appears to be dictated by steric constraints. The terminal W=O bond lengths average 1.719 Å (range 1.716–1.723 Å), close to the average terminal tungsten–oxo bond distance of 1.692 Å found in previously reported compounds.[8] The W–(μ-O) bond lengths of 1.860(7) and 1.850(6) Å are slightly shorter than the mean W–(μ-O) bond distance of 1.916 Å found in data tabulated by Orpen *et al.*,[8] whereas the Zr–O bond lengths of 2.003(7) and 2.026(6) Å are slightly longer than the mean Zr–(μ-O) bond distance of 1.957 Å found in the same tabulation.[8] However, the Zr–O bond lengths of **13** are significantly longer than the 1.871(3)-Å Zr–O bond distance reported for $Cp(CO)_3W\text{–}O\text{–}Zr(Cl)Cp_2$,[3k] whereas the W–($\mu$-O) bond distances for **13** are significantly shorter than the corresponding distance found in this reference compound (2.065(3) Å). This disparity is likely a consequence of the greatly different tungsten oxidation states in **13** (W(VI)) and this reference compound (W(II)). In **13**, this leads to enhanced π-donation from oxygen to tungsten and a

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Table 1. Crystallographic Parameters for $[Cp^*W(O)_2(\mu\text{-}O)]_2Zr(Cp)_2$ (13), $Cp^*W(O)_2\text{-}O\text{-}SiBz_3$ (14), $Cp^*W(O)_2\text{-}O\text{-}Si(Bu^t)_2H$ (20), and $(Me_3Sn)_4(Cp^*W(O))_4(\mu\text{-}O)_8$ (26)[a]

	13	14	20	26
Crystal Parameters				
formula	$C_{30}H_{40}O_6W_2Zr$	$C_{31}H_{36}O_3SiW$	$C_{18}H_{34}O_3SiW$	$C_{52}H_{96}O_{12}Sn_4W_4$
fw	955.56	668.56	510.4	2123.5
cryst syst	triclinic	orthorhombic	orthorhombic	triclinic
space group	$P\bar{1}$	*Pbca*	*Pnma*	$P\bar{1}$
a, Å	11.9085(18)	15.866(1)	8.622(3)	14.403(3)
b, Å	12.1147(22)	12.382(1)	14.712(5)	15.051(4)
c, Å	12.3074(23)	28.937(3)	17.514(5)	16.084
α, deg	105.245(15)			86.18(3)
β, deg	107.031(13)		79.27(3)	
γ, deg	102.721(13)			86.88(3)
V, Å^3	1550.6(5)	5685(1)	2221.6(9)	3415(3)
Z	2	8	4	2
D(calc), g cm^{-3}	2.047	1.562	1.526	2.065
μ(Mo Kα), cm^{-1}	77.70	41.35	52.64	81.92
temp, K	298	298	298	296
Data Collection				
diffractometer	Siemens P4	Siemens R3m/V	Siemens P4	Siemens P4
monochromator	graphite			
radiation	Mo Kα (λ = 0.710 73 Å)			
2θ scan rnge, deg	4–52	4–55	4–60	4–45
data (*hkl*)	±13, ±14, ±15	+20, +14, +37	+12, +20, +24	±15, ±16, ±17
no. of rflns collected	6387	5958	3355	9125
no. of indpt rflns	6088	5458	3355	8925
no. of reflns, $F_o \geq 4\sigma(F_o)$	4827	2889	2155	6133
std reflns	3 std/197			
Refinement				
R(*F*), %	3.89	5.32	5.91	5.17
R(w*F*), %	4.98	5.53	6.91	8.18
Δ/σ(max)	0.653	0.077	0.091	0.005
Δ(ρ), e Å^{-3}	2.96	1.07	2.64	1.23
GOF	1.15	1.05	1.04	1.18

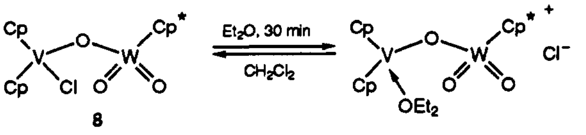
[a] $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R(wF) = \Sigma(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$; GOF $= [\Sigma w||F_o| - |F_c||/N_o - N_v]^{1/2}$.

Table 2. Selected Bond Distances and Angles for $[Cp^*W(O)_2(\mu\text{-}O)]_2Zr(Cp)_2$ (13)

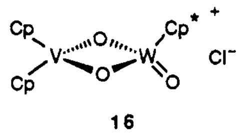
(a) Bond Distances (Å)			
W(1)–O(1)	1.860(7)	W(2)–O(2)	1.850(6)
W(1)–O(4)	1.720(9)	W(2)–O(6)	1.723(8)
W(1)–O(3)	1.716(6)	W(2)–O(5)	1.716(12)
Zr–O(1)	2.003(7)	Zr–O(2)	2.026(6)
(b) Bond Angles (deg)			
O(1)–W(1)–O(3)	105.4(4)	O(2)–W(2)–O(6)	105.0(3)
O(3)–W(1)–O(4)	105.6(4)	O(5)–W(2)–O(6)	105.2(5)
O(1)–W(1)–O(4)	104.6(4)	O(2)–W(2)–O(5)	104.0(4)
W(1)–O(1)–Zr	153.5(3)	W(2)–O(2)–Zr	142.5(3)
O(1)–Zr–O(2)	98.9(3)		

corresponding shortening of W–O distances and lengthening of the Zr–O bonds.

Solvation of $Cp^*W(O)_2\text{-}O\text{-}V(Cl)Cp_2$ (8). It was observed that when complex 8 was dissolved in Et_2O, a color change from green to yellow occurred over a period of minutes and a yellow precipitate was deposited. Dissolution of this precipitate in CH_2Cl_2, THF, acetone, or CH_3CN resulted in an immediate color change back to green and re-formation of 8, as confirmed by IR. The yellow precipitate is proposed to be the salt 15 (eq 7) formed by Et_2O displacement of chloride from 8. The IR (KBr) spectrum of 15 showed two terminal W=O vibrations (911, 868 cm^{-1}), which are shifted slightly from those of 8 (904, 849 cm^{-1}), and a μ-oxo band at 783 cm^{-1} (8: 726 cm^{-1}). The presence of a typical $W(O)_2$ IR pattern argues against a formulation such as 16 with a single W=O unit. The C,H analysis of 15 is consistent with the presence of 1 equiv of Et_2O, although the highest mass ion observed in the FAB(+) mass spectrum of 15 corresponded to the ion $[Cp_2V\text{-}O\text{-}WCp^*(O)_2]^+$ without the coordinated Et_2O, which is presumed lost during the vaporization process. It should be noted that we only see evidence for the formation of 15 in the solid state, and the lattice energy associated with its crystallization must be an important factor in its formation.

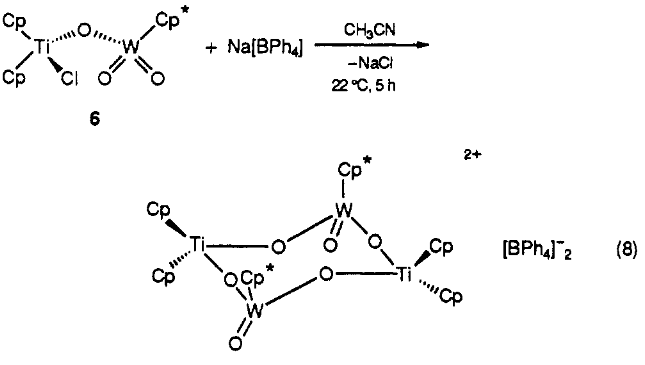


8 15 (58%) (7)

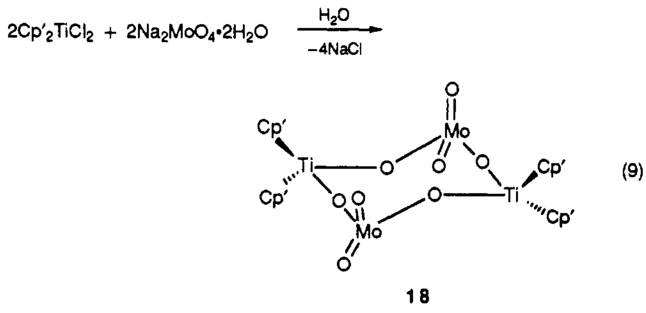


16

Abstraction of Chloride from $Cp_2(Cl)Ti\text{-}O\text{-}WCp^*(O)_2$ (6) To Form the Tetrametallic Complex $[\{Cp_2Ti\}_2\{Cp^*W(O)\}_2(\mu\text{-}O)_4]^{2+}$. Treatment of complex 6 with $Na[BPh_4]$ induced loss of chloride and formation of complex 17 (eq 8), which was isolated as an orange-red microcrystalline solid in high yield. Spectroscopic data for 17 are consistent with the proposed tetrametallic structure, which is similar to that of complex 18, characterized earlier by Floriani and co-workers (eq 9).[3x] Compound 17 was insoluble in common nonpolar and polar organic solvents, except for CH_3NO_2, in which it was sparingly soluble. Its IR spectrum showed a single W=O stretch (938 cm^{-1}), and both bridging (δ 442.2) and terminal (δ 714.0) oxo resonances were observed in its ^{17}O NMR spectrum. Its ^{1}H NMR spectrum showed the presence of the BPh_4^- counterion and the Cp* (δ 2.44) and Cp (δ 6.64, 6.75) ligands with the resonances integrated to the ratios



17 (81%)

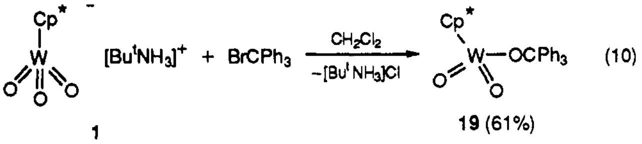


18

$Cp' = \eta^5\text{-}MeC_5H_4$

corresponding to 17. The inequivalence of the Cp ligands suggests the structure drawn in eq 8 with the Cp* ligands attached to the tungsten atoms on the same side of the eight-membered ring.

Reaction of $[Cp^*W(O)_3]^-$ with $BrCPh_3$, Chlorosilanes, and Chlorogermanes to Form Alkoxy, Siloxy, and Germoxy Complexes. Complex 1 was also found to react with main-group-element halides. Thus, when treated with Ph_3CBr, the alkoxide complex $Cp^*W(O)_2\text{–}O\text{–}CPh_3$ (19) was formed (eq 10). This species was isolated in modest yield as a light yellow microcrystalline solid and was spectroscopically characterized (see Experimental Section).



19 (61%)

Table 3. Selected Bond Distances and Angles for $Cp^*W(O)_2\text{–}O\text{–}SiBz_3$ (14)

(a) Bond Distances (Å)

W–O(1)	1.894(7)	W–O(2)	1.722(8)
W–O(3)	1.720(8)	Si–O(1)	1.633(8)
Si–C(11)	1.858(13)	Si–C(12)	1.869(12)
Si–C(13)	1.881(13)		

(b) Bond Angles (deg)

O(1)–W–O(2)	103.8(4)	O(1)–W–O(3)	105.4(4)
O(2)–W–O(3)	105.3(4)	O(1)–Si–C(11)	111.4(6)
O(1)–Si–C(12)	109.1(5)	C(11)–Si–C(12)	110.9(6)
O(1)–Si–C(13)	107.6(5)	C(11)–Si–C(13)	108.4(6)
C(12)–Si–C(13)	109.4(6)	W–O(1)–Si	141.5(5)

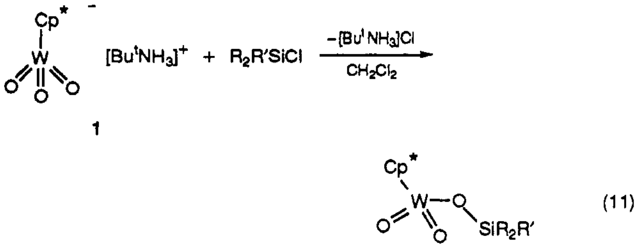
Table 4. Selected Bond Distances and Angles for $Cp^*W(O)_2\text{–}O\text{–}Si(Bu^t)_2H$ (20)

(a) Bond Distances (Å)

W–O(1)	1.834(10)	W–O(2)	1.718(9)
Si–O(1)	1.677(10)	Si–C(7)	1.899(10)

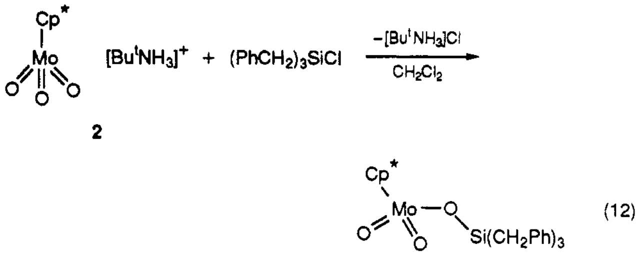
(b) Bond Angles (deg)

O(1)–W–O(2)	105.2(4)	O(2)–W–O(2A)	106.0(6)
O(1)–Si–C(7)	108.6(4)	C(7)–Si–C(7A)	119.7(7)
W–O(1)–Si	161.1(6)		



14, R,R′ = $PhCH_2$ (33%)
20, R = Bu^t, R′ = H (52%)
21, R = Me, R′ = Bu^t (64%)
22, R, R′ = Me

The anion $[Cp^*W(O)_3]^-$ has also been found to readily undergo silylation with $(PhCH_2)_3SiCl$, $(Bu^t)_2HSiCl$, $Bu^t(Me)_2SiCl$, and Me_3SiCl (1 equiv) to give the siloxy complexes 14 and 20–22 (eq 11). The use of *excess* Me_3SiCl in this reaction gave formation of $Me_3Si\text{–}O\text{–}SiMe_3$ and $Cp^*W(O)_2Cl$, but no $Cp^*W(O)_2Cl$ formed with the bulkier silanes, even when they were added in excess. Complex 22 was also prepared by treating the anion $[Cp^*W(O)_3]^-$ with the known silylating agent $CF_3C(=NSiMe_3)OSiMe_3$,[9] a reaction which minimized the formation of $Cp^*W(O)_2Cl$. The molybdenum complex $[Cp^*Mo(O)_3]^-$ (2) was also found to react with $(PhCH_2)_3SiCl$ to form $Cp^*(O)_2Mo\text{–}O\text{–}SiBz_3$ (23) (eq 12).



23 (73%)

With the exception of 22, which was obtained as a colorless oil, the remainder of the complexes given in eqs 11 and 12 were isolated as microcrystalline solids. Complex 22 proved to be very moisture sensitive and readily formed $Cp^*(O)_2W\text{–}O\text{–}W(O)_2Cp^*$ upon exposure to air, but the remainder of the complexes were air stable. Complexes 14, 20, and 21 and showed parent ions in their mass spectra, exhibited ^1H NMR resonances consistent with the presence of both Cp* and SiR_2R groups, and showed a typical $M(O)_2$ band pattern in the $\nu(M{=}O)$ IR region. ^{17}O NMR analysis of the complexes showed the presence of the $W(O)_2$ unit (δ 655–670) and the siloxy ligand (δ 103–131) (see Experimental Section).

Complexes 14 and 20 were also crystallographically characterized. ORTEP drawings are shown in Figures 2 and 3, and important crystallographic data are given in Tables 1, 3, and 4. The compounds are similar, and both have a typical three-legged piano-stool structure. The terminal oxo–tungsten bond lengths average 1.721 Å for 14 and 1.718 Å for 20 and are similar to the 1.719-Å average given earlier for 13 and the 1.692-Å average W=O bond distances tabulated by Orpen *et al.*[8] The tungsten–oxygen bond lengths to the siloxy ligands (14, 1.894(7) Å; 20, 1.834-

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(9) Klebe, J. F.; Finkbeiner, H.; White, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 3390.

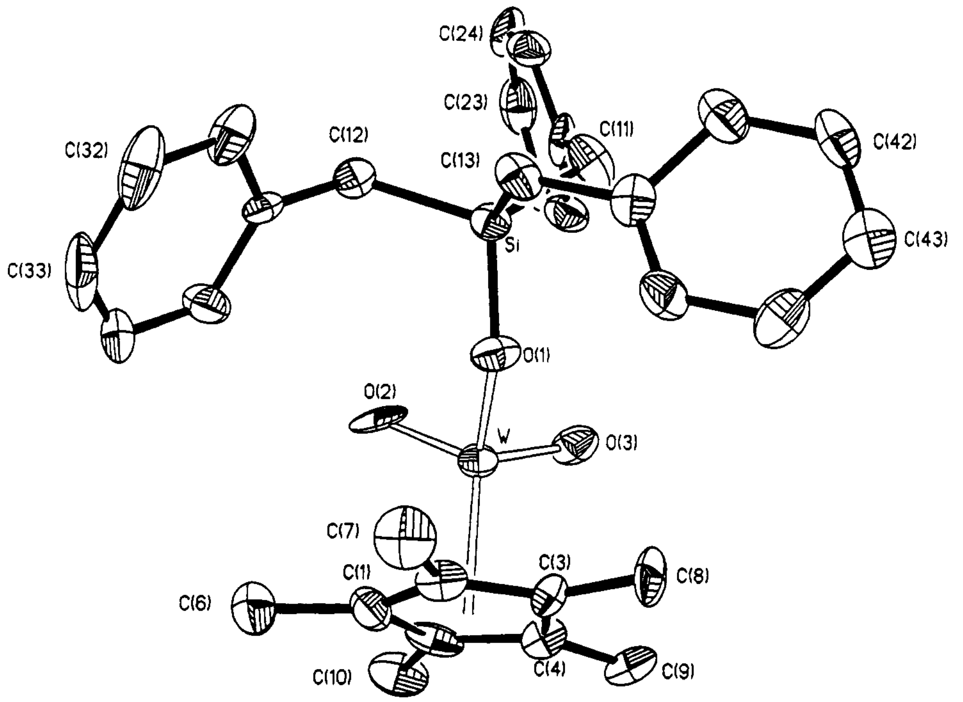


Figure 2. ORTEP drawing for $Cp^*W(O)_2$–O–$Si(CH_2Ph)_3$ (**14**).

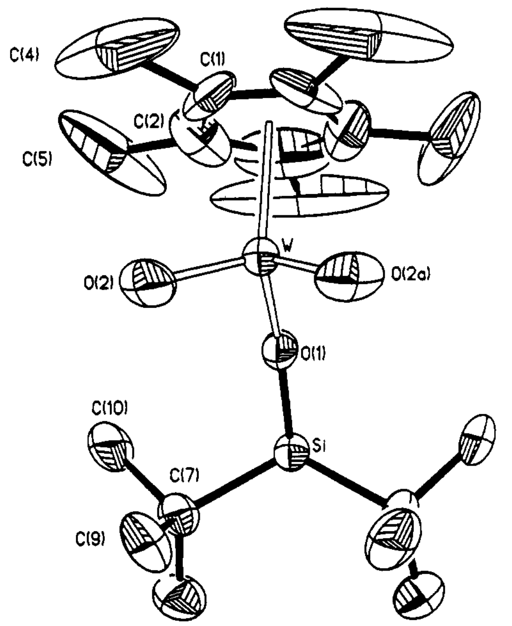
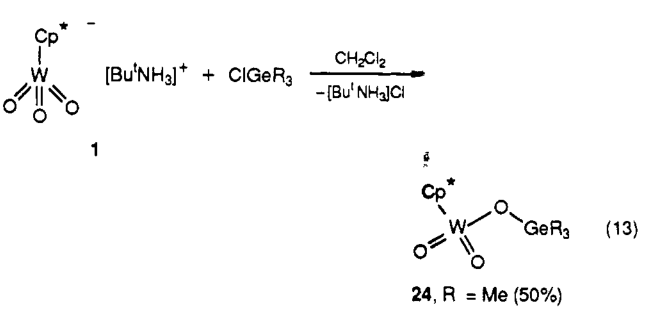


Figure 3. ORTEP drawing for $Cp^*W(O)_2$–O–$Si(Bu^t)_2H$ (**20**).

(10) Å) are similar to the mean W—O distance of 1.900 Å found in W–alkoxy complexes.[8]

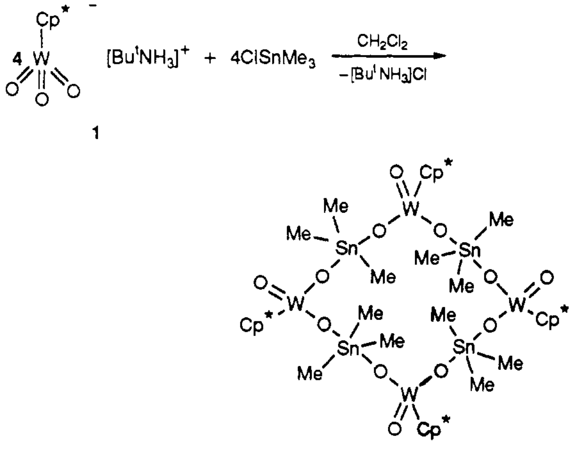
The trioxo anion $[Cp^*W(O)_3]^-$ also readily reacts with the chlorogermanes $ClGeR_3$ (R = Me, Ph) to form the new complexes **24** and **25** (eq 13). The clean reaction with $ClGeMe_3$ differs substantially from the failure of complex **1** to react with $ClCMe_3$ and the sensitivity of its reaction with $ClSiMe_3$ to the reaction conditions. Both complexes **24** and **25** were isolated as air-stable microcrystalline solids and were spectroscopically characterized (see Experimental Section). The IR and ^{17}O NMR spectral data associated with the $W(O)_2$ fragment are nearly identical for the two compounds, although the data for the W–O–Ge linkage differ significantly (ν_{W-O-Ge} 786 (**24**) vs 738 (**25**) cm^{-1}; ^{17}O NMR δ 160.7 (**24**) vs 132.3 (**25**)), illustrating an important effect of the substituents attached to the germanium atom.



(13)

24, R = Me (50%)
25, R = Ph (55%)

Reaction of $[Cp^*W(O)_3]^-$ with $ClSnMe_3$ To Form a Complex with a 16-Membered $[-O-Sn-O-W]_4$ Ring. The above-described reactions of $[Cp^*W(O)_3]^-$ with $ClCPh_3$, $ClSiR_3$, and $ClGeR_3$ all led to products having a simple $Cp^*(O)_2W-O-ER_3$ structure. However, a different reaction occurred for the heavier group IV element tin. Thus, when $ClSnMe_3$ and $[Cp^*W(O)_3]^-$ were allowed to react, the product which formed was **26** (eq 14). This species was isolated as a microcrystalline solid and was spectroscopically and crystallographically characterized (see Figure 4 and below). The molecule has a sixteen-



(14)

26 (49%)

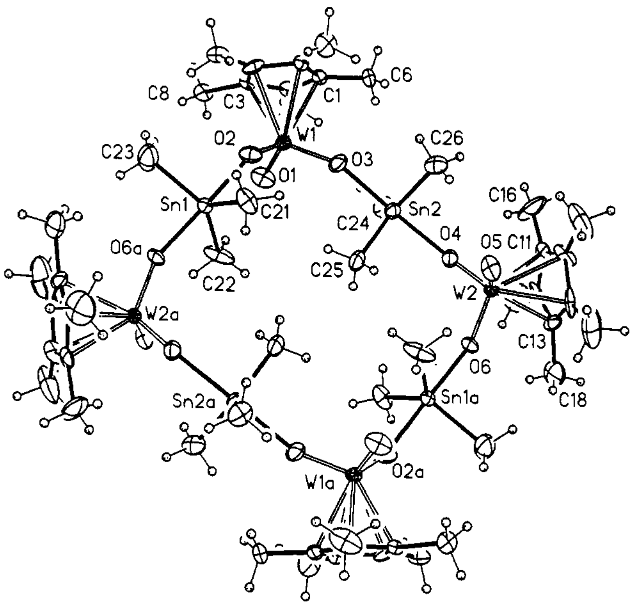
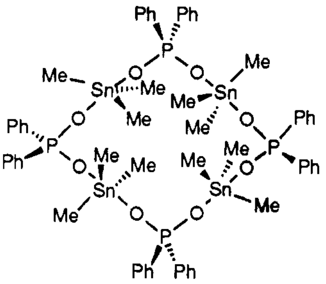
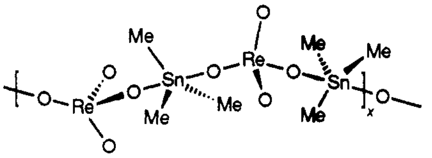


Figure 4. ORTEP drawing for $(Me_3Sn)_4(Cp^*W(O))_4(\mu\text{-}O)_8$ (**26**), showing one of the two chemically similar but symmetry independent molecules.

membered [-O-Sn-O-W]$_4$ ring and is formally a [-O-WCp*(O)-O-Sn(Me)$_3$]$_4$ tetramer. The molecule is related to the trimethyltin phosphinate complex $[Me_3SnO_2PPh_2]_4$ (**27**)[10a] and to the polymeric complex $[Me_3Sn\text{-}O\text{-}ReO_3]_x$ (**28**) recently reported by Herrmann *et al.*[10b] The spectroscopic data for **26** are consistent with its determined structure. For example, the KBr IR spectrum showed a single $\nu_{W=O}$ band at 921 cm^{-1} and two bands at 856 and 733 cm^{-1} which are assigned to the symmetric and asymmetric vibrations of the -O-W-O- unit. The ^{119}Sn NMR spectrum of **26** showed a single resonance at δ -7.3, which is significantly upfield of the resonances of the related tetrahedral complexes Me_3SnOH (δ 118) and $(Me_3Sn)_2O$ (δ 117).[11] These data indicate that **26** does not likely dissociate in solution to form $Cp^*(O)_2W\text{-}O\text{-}SnMe_3$, since if it did, its ^{119}Sn NMR resonance would be expected to be found near those of the above two complexes and near the δ 91.8 resonance reported for $(O)_3Re\text{-}O\text{-}SnMe_3$.[2e] Also consistent with maintenance of the tetrameric structure in CH_2Cl_2 solution is the measured molecular weight[12] of 1800 ± 50, which compares to the calculated value of 2122 for the tetrameric structure.



27



28

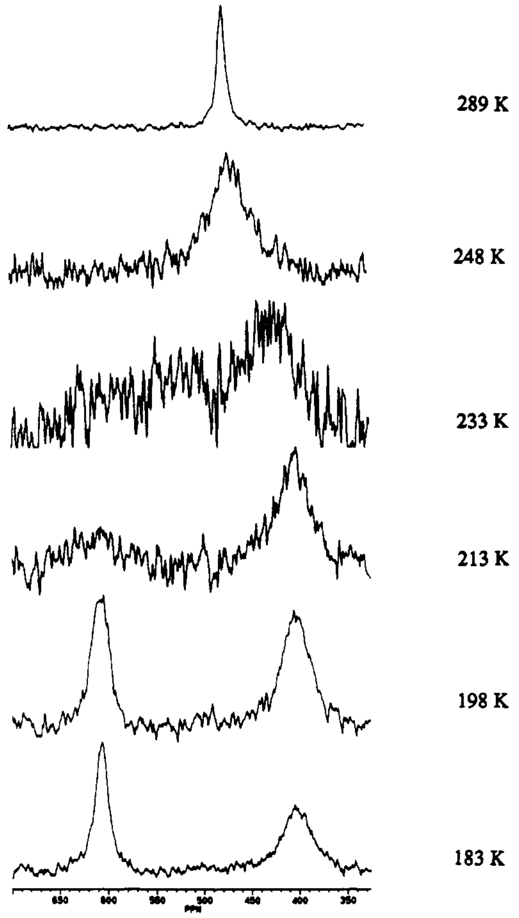


Figure 5. Variable-temperature ^{17}O NMR study of $(Me_3Sn)_4(Cp^*W(O))_4(\mu\text{-}O)_8$ (**26**) in CH_2Cl_2 solution.

A priori, it was expected that the ^{17}O NMR spectrum of **26** should show separate resonances for the terminal and bridging oxo ligands, as seen in the many other complexes reported herein. However, at room temperature, only a single resonance was observed at δ 474.1 (Figure 5). This is, of course, not consistent with the determined structure and is also in an unusual position. All of the other $Cp^*(O)_2W{-}O{-}ML_n$ complexes described above show the terminal oxo resonances for the $W(O)_2$ unit in the narrow range δ 632–679. This analysis prompted a variable-temperature ^{17}O NMR study (Figure 5) which showed a broadening of the resonance upon cooling, coalescence around 233 K, and then sharpening into two separate resonances at 183 K. The downfield resonance at δ 605.6 is just outside the δ 632–679 range noted above for the terminal oxo resonances and is thus logically assigned to the W=O unit of **26**. The upfield resonance at δ 404.4 may then be attributed to the μ-oxo ligand in the W—O—Sn linkage. It is significant that the δ 474.1 resonance observed at room temperature is very close to the δ 471 weighted average of the low-temperature resonances assuming one W=O unit and two W—O—Sn

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[10] (a) Newton, M. G.; Haiduc, I.; King, R. B.; Silvestru, C. *J. Chem. Soc., Chem. Commun.* **1993**, 1229. (b) Herdtweck, E.; Kiprof, P.; Herrmann, W. A.; Kuchler, J. G.; Degnan, I. *Z. Naturforsch.* **1990**, *45B*, 937.

[11] (a) Kennedy, J. D.; McFarlane, W. *J. Organomet. Chem.* **1975**, *94*, 7. (b) ^{119}Sn NMR resonances are known to be solvent and concentration dependent. The values reported in ref 11a were determined as follows: Me_3SnOH (δ 118 ± 1 ppm, saturated in CD_2Cl_2); $(Me_3Sn)_2O$ (δ 113.1 ppm; average of δ 109.5 (neat liquid) and δ 117.1 (50% in CD_2Cl_2)).

[12] Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 94-96.

Table 5. Selected Bond Distances and Angles for $(Me_3Sn)(Cp^*W(O))_4(\mu\text{-}O)_8$ (26)

(a) Bond Distances (Å)

W(1)–O(1)	1.709(15)	W(1′)–O(1′)	1.731(13)
W(1)–O(2)	1.762(11)	W(1′)–O(2′)	1.799(12)
W(1)–O(3)	1.777(15)	W(1′)–O(3′)	1.796(12)
W(2)–O(4)	1.784(12)	W(2′)–O(4′)	1.782(11)
W(2)–O(5)	1.735(12)	W(2′)–O(5′)	1.738(14)
W(2)–O(6)	1.768(12)	W(2′)–O(6′)	1.752(15)
Sn(1)–O(2)	2.229(12)	Sn(1′)–O(2′)	2.225(12)
Sn(1)–O(6)	2.274(12)	Sn(1′)–O(6′)	2.236(14)
Sn(2)–O(4)	2.268(12)	Sn(2′)–O(4′)	2.223(11)
Sn(2)–O(3)	2.209(15)	Sn(2′)–O(3′)	2.231(13)

(b) Bond Angles (deg)

O(1)–W(1)–O(2)	105.0(6)	O(1′)–W(1′)–O(2′)	105.5(7)
O(1)–W(1)–O(3)	104.7(7)	O(1′)–W(1′)–O(3′)	105.5(6)
O(2)–W(1)–O(3)	106.5(6)	O(2′)–W(1′)–O(3′)	105.1(6)
O(4)–W(2)–O(5)	105.5(6)	O(4′)–W(2′)–O(5′)	103.6(6)
O(4)–W(2)–O(6)	105.7(6)	O(4′)–W(2′)–O(6′)	104.3(7)
O(5)–W(2)–O(6)	105.6(6)	O(5′)–W(2′)–O(6′)	104.3(7)
O(2)–Sn(1)–O(6A)	177.8(4)	O(2′)–Sn(1′)–O(6′A)	178.2(5)
O(3)–Sn(2)–O(4)	178.6(5)	O(3′)–Sn(2′)–O(4′)	177.5(4)
W(1)–O(2)–Sn(1)	146.6(7)	W(1′)–O(2′)–Sn(1′)	150.2(6)
W(2)–O(4)–Sn(2)	139.7(7)	W(2′)–O(4′)–Sn(2′)	146.7(6)
W(1)–O(3)–Sn(2)	155.4(9)	W(1′)–O(3′)–Sn(2′)	142.9(7)
W(2)–O(6)–Sn(1A)	147.3(7)	W(2′)–O(4′)–Sn(2′)	146.7(6)

units, as crystallographically observed. This lends further support to the suggestion made above that **26** maintains its cyclic structure in solution.

The variable-temperature ^{17}O NMR data clearly imply that some sort of exchange process is occurring that makes the terminal and bridging oxo ligands equivalent, so as to give an averaged resonance at room temperature. We do not know the nature of this exchange process, but it may involve a 3-fold rotation of the Cp^*WO_3 unit within the cyclic structure, or it may be due to reversible dissociation/association of the Sn–O linkages. It should be noted that a single ^{17}O NMR resonance was also observed for $Me_3Sn\text{–}O\text{–}ReO_3$, instead of the expected two, but no interpretation of this observation was given.[2e] We note that a variable-temperature ^1H NMR study of **26** did not reveal any splitting of the Cp* or methyl resonances upon cooling, although some broadening of the latter was observed. Similarly, the ^{119}Sn NMR spectrum at 198 K showed a single resonance at δ −19.5.

Crystal and Molecular Structure of $(Me_3Sn)_4(Cp^*W(O))_4(\mu\text{-}O)_8$ (26). An ORTEP drawing of **26** is given in Figure 4, and the relevant crystallographic data are set out in Tables 1 and 5. There are two structurally similar but symmetry independent molecules (unprimed and primed) in the unit cell, and each has a crystallographically imposed center of symmetry located in the middle of the 16-membered ring. In each molecule, the tin and tungsten atoms form crystallographically required homoatomic planes. The interplanar angle between the Sn_4 and the W_4 planes in the unprimed molecule is 11° and in the primed molecule is 14°. Each tin atom has a trigonal-bipyramidal coordination geometry, whereas each tungsten atom has the typical three-legged piano-stool geometry. The O–Sn–O angles average 178.0°, and the Me–Sn–Me angles average 120.0° in the two molecules. The average Sn–O bond distance of 2.235 Å is similar to the 2.238-Å value reported for the polymeric complex $[\text{–O–Re(O)}_2\text{–O–Sn(Me)}_3\text{–}]_x$.[10b] The trigonal-bipyramidal geometry about the tin atom is similar to that found in other pentacoordinate triphenyl- and trimethyltin(IV) complexes.[13] The terminal W═O distances average 1.728 Å in the two molecules, similar to the average value of 1.719 Å given above for complexes **13**, **14**, and **20**. The bridging W—O bond lengths in the two molecules average 1.778 Å, which is 0.08 Å longer than the 1.860-Å average bridging W—O distance found in complexes **13**, **14**, and **20**, suggesting that the W—(μ-O) bonds in **26** have more π-bond character than found in these reference compounds. This conclusion is also consistent with the ^{17}O NMR data, which show the resonance for the μ-oxo ligand of **26** (δ 404.4) to be considerably downfield of the μ-oxo resonances of these reference compounds (δ 332.1, 111.5, 103.8) and closer to the region typical of W═O resonances (see Figure 6). ^{17}O NMR chemical shifts are known to be extremely sensitive to π-bonding environment in metal oxo complexes.[14] The average value for the O–W–O bond angles is 105.3°.

Concluding Remarks

The reactions reported herein show that $[Cp^*W(O)_3]^-$ (**1**) and $[Cp^*Mo(O)_3]^-$ (**2**) are versatile reagents for the preparation of bi- and multimetallic μ-oxo compounds via the displacement of a halide ion from one metal center by a nucleophilic oxygen of the trioxo anion. The reactions worked best for early-transition-metal halides (M′ = Ti, Zr, V, Mo, W) and the group IV main-group-metal halides (M′ = Si, Ge, Sn) because of the strength of the M′–O bond. In contrast, similar reactions with late-transition-metal halides (M′ = Fe, Ru, Ir, Rh, Ni, Pd, Pt) either failed to react or did not produce stable products.[15] The various complexes described herein have been characterized by ^{17}O NMR, and for future reference Figure 6 summarizes the data obtained. For the tungsten complexes, all the terminal W═O resonances appeared in the δ 606–714 range and all the μ-O resonances appeared upfield of δ 450, but with a significant dependence on the attached M′ atom. Similarly, for the molybdenum complexes, the terminal Mo═O resonances appeared in the narrow range δ 802–870 with the μ-oxo resonances all upfield of δ 527.

Experimental Section

The compounds $[Bu^tNH_3][Cp^*M(O)_3]$, $Cp^*M(O)_2Cl$, and $Cp^*M(O)_2\text{–O–}MCp^*(O)_2$ (M = W, Mo) were prepared as described in ref 5b. All ^{17}O-labeled compounds were prepared using ^{17}O-enriched $[Bu^tNH_3][Cp^*M(O)_3]$ that was in turn prepared from ^{17}O-enriched water, Bu^tNH_2, and Cp^*WCl_4 or $Cp^*M(O)_2Cl$. The reagents Cp_2TiCl_2, Cp_2ZrCl_2, Cp_2VCl_2, Me_3SiCl, $CF_3C(\text{=NSiMe}_3)OSiMe_3$, Bz_3SiCl, $(Bu^t)_2HSiCl$, Bu^tMe_2SiCl, Ag_2O, and $Na[BPh_4]$ (Aldrich Chemical, Inc.), Ph_3GeCl, Me_3GeCl, Ph_3SnCl, and Me_3SnCl (Strem Chemical Co.), and Ph_3CBr (Pfaltz and Bauer) were purchased and used as received. All manipulations were performed with standard Schlenk techniques under an N_2 atmosphere unless indicated otherwise. Solvents were dried by refluxing over Na/benzophenone ketyl (tetrahydrofuran (THF),

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(15) No reaction occurred between $[Bu^tNH_3][Cp^*WO_3]$ (1) and $Cp(CO)_2FeCl$, $Cp(CO)_2FeI$, *trans*-$IrCl(CO)(PPh_3)_2$, $[Cp^*RuCl_2]_2$, $Cp^*Ru(CO)_2I$, $(PPh_3)_2NiCl_2$, or $(PEt_3)_2PtCl_2$. IR analysis indicated that reactions occurred when 1 was combined with $Rh_2(CO)_4(\mu\text{-}Cl)_2$ and $(COD)PdCl_2$, but stable bimetallic products could not be isolated. The only identifiable products were $Cp^*W(O)_2Cl$ from both reactions and $[Cp^*W(O)_2]_2(\mu\text{-}O)$ from the reaction with $Rh_2(CO)_4(\mu\text{-}Cl)_2$.

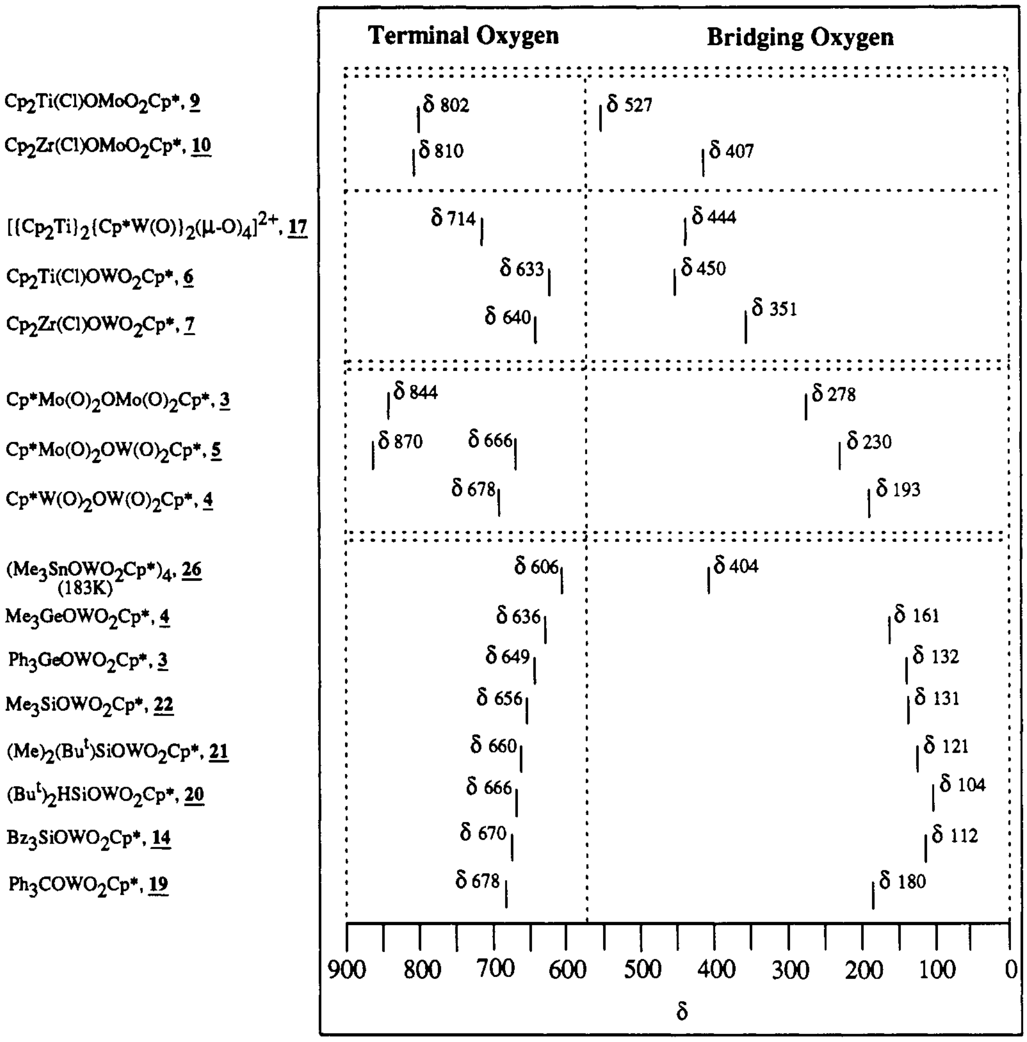

Figure 6. ^{17}O NMR chemical shifts for the terminal and bridging oxygen atoms of the compounds examined in this work.

Et_2O), CaH_2 (CH_2Cl_2, pentane, acetonitrile, hexane), or $MgSO_4$ (CH_3NO_2). IR spectra were recorded on an IBM FTIR-32 spectrometer operating in the absorbance mode. NMR spectra were obtained with a Bruker AM-300 FT NMR spectrometer and referenced to the residual solvent peak for ^1H, to $H_2(^{17}O)$ for ^{17}O, and to Me_4Sn for ^{119}Sn spectra. The variable-temperature ^{17}O NMR spectra were obtained with a Bruker AM-500 FT NMR. Mass spectra were recorded on AEI-MS9 (EI) and AFAB-MS9 (FAB) mass spectrometers. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY, and Galbraith Laboratories, Inc., Knoxville, TN.

Reaction of [Cp*Mo(O)$_3$]$^-$ with Cp*Mo(O)$_2$Cl To Form [Cp*Mo(O)$_2$]$_2$(μ-O) (3). The salt $[Bu^tNH_3][Cp^*Mo(O)_3]$ (2; 0.098 g, 0.28 mmol) and $Cp^*Mo(O)_2Cl$ (0.075 g, 0.25 mmol) were placed in a Schlenk flask to which was added CH_2Cl_2 (20 mL). The resulting solution was stirred at room temperature for 1 h, and then it was filtered through Celite to remove the precipitated $[Bu^tNH_3]Cl$. The solution volume was reduced to 2 mL under reduced pressure, and hexane (10 mL) was added to induce precipitation of the known compound 3 as a bright yellow solid, which was washed (3 × 5 mL) with hexane and dried under vacuum (0.090 g, 0.17 mmol, 66%). ^{17}O-enriched $Cp^*Mo(O)_2Cl$ was prepared by bubbling HCl(g) through a solution of ^{17}O-enriched 2, and this was then used with the latter compound to prepare ^{17}O-enriched 3.

3: IR (KBr) $\nu_{Mo=O}$ 906 (s), 876 (s), $\nu_{Mo-O-Mo}$ 754 (br) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.99 (Cp*); ^{17}O NMR (CD_2Cl_2) δ 843.8 (Mo*O*$_2$), 277.9 (Mo–*O*–Mo); MS (EI) *m/z* 542 (M$^+$) (lit.:[6] IR (CS_2) $\nu_{Mo=O}$ 912 (s), 882 (s), $\nu_{Mo-O-Mo}$ 771 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (Cp*)).

Reaction of [Cp*W(O)$_3$]$^-$ with Cp*W(O)$_2$Cl To Form [Cp*W(O)$_2$]$_2$(μ-O) (4). Complex 4 was prepared similarly to 3 using $[Bu^tNH_3][Cp^*W(O)_3]$ (0.063 g, 0.14 mmol) and $Cp^*W(O)_2Cl$ (0.050 g, 0.13 mmol) and was isolated in 89% yield (0.083 g, 0.12 mmol).

4: IR (KBr) $\nu_{W=O}$ 939 (s), 890 (s), ν_{W-O-W} 810 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.13 (Cp*); ^{17}O NMR (CD_2Cl_2) δ 678.0 (W*O*$_2$), 193.4 (W–*O*–W); MS (EI) *m/z* 718 (M$^+$) (lit.:[6] IR (CS_2) $\nu_{W=O}$ 942 (s), 896 (s), ν_{W-O-W} 820 (broad); ^1H NMR ($CDCl_3$) δ 2.16 (Cp*)).

Reaction of [Cp*M(O)$_3$]$^-$ with Cp*M′(O)$_2$Cl To Form Cp*(O)$_2$Mo–O–WCp*(O)$_2$ (5). The complexes $Cp^*Mo(O)_2Cl$ (0.090 g, 0.302 mmol) and $[Bu^tNH_3][Cp^*W(O)_3]$ (0.160 g, 0.363 mmol) were placed in a Schlenk flask to which was added CH_2Cl_2 (30 mL). The resulting bright yellow solution was stirred overnight, during which time it became cloudy and deposited a white precipitate. The solution was filtered through a pad of Celite, the solvent was reduced to ~2 mL, and hexane (10 mL) was added to force the precipitation of a bright yellow solid. The solvent was removed by cannula, and the resulting yellow solid was washed with hexane (3 × 10 mL) and dried under vacuum. ^1H NMR analysis showed the product to be a ~1:2.5:1 mixture of 3, 5, and 4. A similar mixture of products was obtained from reaction of $Cp^*W(O)_2Cl$ with $[Bu^tNH_3][Cp^*Mo(O)_3]$.

5: ^1H NMR (CD_2Cl_2) δ 2.02 (Cp*), 2.10 (Cp*); ^{17}O NMR (CD_2Cl_2) δ 869.6 (Mo*O*$_2$), 666.4 (W*O*$_2$), 230.2 (Mo–*O*–W); MS (FAB+) *m/z* 631 (M$^+$).

Reaction of [Cp*W(O)$_3$]$^-$ and [Cp*Mo(O)$_3$]$^-$ with Cp$_2$MCl$_2$ To Form Complexes 6–10. In a typical reaction, Cp_2TiCl_2 (0.200 g, 0.262 mmol) and $[Bu^tNH_3][Cp^*W(O)_3]$ (0.116 g, 0.262 mmol) were placed in a Schlenk flask in a glovebox to which CH_2Cl_2 (30 mL) was added. This reaction mixture was stirred overnight (10 h), and the resulting cloudy orange solution was filtered through Celite to remove the precipitated $[Bu^tNH_3]Cl$. The solution volume was concentrated to 3 mL under reduced pressure, and hexane (20 mL) was added to induce precipitation of $Cp_2(Cl)Ti–O–WCp^*(O)_2$ (**6**) as a bright orange solid which was washed with hexane (3 × 15 mL) and dried under vacuum (0.190 g, 0.328 mmol, 72%). Compounds $Cp_2(Cl)Zr–O–WCp^*(O)_2$ (**7**; 69%, white solid), $Cp_2(Cl)V–O–WCp^*(O)_2$ (**8**; 66%, green solid), $Cp_2(Cl)Ti–O–MoCp^*(O)_2$ (**9**; 57%, orange solid), and $Cp_2(Cl)Zr–O–MoCp^*(O)_2$ (**10**; 47%, white solid) were similarly prepared from $[Bu^tNH_3][Cp^*W(O)_3]$ or $[Bu^tNH_3][Cp^*Mo(O)_3]$ and the appropriate Cp_2MCl_2 reagent and were isolated in the indicated yields.

6: IR (KBr) $\nu_{W=O}$ 923 (s), 875 (m), $\nu_{W–O–Ti}$ 776 (s, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (s, 15H, Cp*), 6.42 (s, 10H, Cp); ^{17}O NMR (CD_2Cl_2) δ 632.6 (WO_2), 449.5 (W–*O*–Ti); MS (FAB$^-$) *m/z* 580 (M$^-$). Anal. Calcd for $C_{20}H_{25}ClO_3TiW$: C, 41.37; H, 4.34. Found: C, 41.16; H, 4.51.

7: IR (KBr) $\nu_{W=O}$ 924 (s), 881 (s), $\nu_{W–O–Zr}$ 784 (s, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.14 (s, 15H, Cp*), 6.38 (s, 10H, Cp); ^{17}O NMR (CD_2Cl_2) δ 639.8 (WO_2), 350.5 (W–*O*–Zr); MS (FAB+) *m/z* 623 (M$^+$). Anal. Calcd for $C_{20}H_{25}ClO_3WZr$: C, 38.50; H, 4.04. Found: C, 38.28; H, 4.19.

8: IR (KBr) $\nu_{W=O}$ 904 (s), 849 (s), $\nu_{W–O–V}$ 793 (vs) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.11 (br s, Cp*), 4.7 (br, Cp). Anal. Calcd for $C_{20}H_{25}ClO_3VW$: C, 41.16; H, 4.32. Found: C, 41.66; H, 4.65.

9: IR (KBr) $\nu_{Mo=O}$ 892 (s), 866 (m), $\nu_{Mo–O–Ti}$ 755 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (s, 15H, Cp*), 6.35 (s, 10H, Cp); ^{17}O NMR (CD_2Cl_2) δ 802.2 (Mo*O*$_2$), 527.1 (Mo–*O*–Ti); MS (FAB+) *m/z* 494 (M$^+$). Anal. Calcd for $C_{20}H_{25}ClMoO_3Ti$: C, 48.75; H, 5.11. Found: C, 48.78; H, 5.08.

10: IR (KBr) $\nu_{Mo=O}$ 897 (s), 871 (m), $\nu_{Mo–O–Zr}$ 761 (vs, br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.02 (s, 15H, Cp*), 6.33 (s, 10H, Cp); ^{17}O NMR (CD_2Cl_2) δ 809.5 (MoO_2), 407.4 (Mo–*O*–Zr); MS (EI) *m/z* 537 (M$^+$). Anal. Calcd for $C_{20}H_{25}ClMoO_3Zr$: C, 44.81; H, 4.70. Found: C, 44.52; H, 4.83.

Reaction of 2 Equiv of $[Cp^*W(O)_3]^-$ with Cp_2MCl_2 (M = Ti, Zr) To Form 12 and 13. A 2-fold excess of $[Bu^tNH_3][Cp^*W(O)_3]$ (0.300 g, 0.680 mmol) was added to solid Cp_2ZrCl_2 (0.100 g, 0.342 mmol) in a Schlenk flask to which CH_2Cl_2 (50 mL) was added. The solution was stirred for 24 h and then filtered through Celite followed by reduction of the solvent volume to a minimum under reduced pressure. Hexane was then added to induce precipitation of $[Cp^*W(O)_2(\mu\text{-}O)]_2ZrCp_2$ (**13**) as a white solid, which was washed with hexane (3 × 15 mL) and dried under vacuum (0.240 g, 0.251 mmol, 74%). Complex **12** was similarly prepared from Cp_2TiCl_2 and obtained as a pale orange, microcrystalline solid in 65% yield.

12: IR (KBr) $\nu_{W=O}$ 920 (s), 877 (s), $\nu_{W–O–V}$ 774 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.12 (s, 30H, Cp*), 6.39 (s, 10H, Cp); ^{17}O NMR (CD_2Cl_2 δ 632.4 (WO_2) δ 449.3 (W–*O*–Ti); MS (FAB+) *m/z* 913 (M$^+$). Anal. Calcd for $C_{30}H_{40}O_6TiW_2$: C, 39.50; H, 4.42. Found: C, 39.88; H, 4.27.

13: IR (KBr) $\nu_{W=O}$ 927 (s), $\nu_{W–O–Zr}$ 728 (vs) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.12 (s, 30H, Cp*), 6.30 (s, 10H, Cp); ^{17}O NMR (CD_2Cl_2) δ 635.4 (WO_2), 332.1 (W–*O*–Zr); MS (FAB+) *m/z* 955 (M$^+$). Anal. Calcd for $C_{30}H_{40}O_6W_2Zr$: C, 37.71; H, 4.22. Found: C, 37.85; H, 4.42.

Reaction of $[Cp^*W(O)_2(\mu\text{-}O)]_2ZrCp_2$ (13) with Cp_2MCl_2 (M = Ti, Zr), $Cp^*W(O)_2Cl$, and $(PhCH_2)_3SiCl$. One equivalent of complex **13** and 2 equiv of Cp_2MCl_2 (M = Ti, Zr), $Cp^*W(O)_2Cl$, or $(PhCH_2)_3SiCl$ were stirred in CH_2Cl_2 at room temperature overnight. The solvent volume was then reduced to approximately 3 mL, and hexane was added to induce precipitation. The resultant solids were then washed several times with hexanes and dried under vacuum. Infrared and ^1H NMR analysis showed the formation of **3**, **6**, **7**, and **14** and Cp_2ZrCl_2, as appropriate for the particular reaction (see Scheme 1).

Solvation of $Cp_2(Cl)V–O–WCp^*(O)_2$ (8) To Form $[Cp_2(Et_2O)V–O–WCp^*(O)_2]Cl$ (15). Compound **8** (0.260 g, 0.446 mmol) was added to Et_2O (100 mL) in a beaker in air, and the solution was stirred vigorously for ~30 min, during which time the color changed from green to bright yellow and a yellow precipitate formed. The solvent was reduced to ~10 mL, and the bright yellow solid was collected by filtration and dried under vacuum to give **15** in 58% yield (0.170 g, 0.259 mmol).

15: IR (KBr) $\nu_{W=O}$ 911 (s), 868 (s), $\nu_{W–O–V}$ 783 cm^{-1}; MS (FAB+) *m/z* 548 (M$^+$ – Et_2O). Anal. Calcd for $C_{24}H_{35}ClO_4VW$: C, 43.82; H, 5.36. Found: C, 43.85; H, 5.14.

Reaction of $Cp_2(Cl)Ti–O–WCp^*(O)_2$ (6) with $Na[BPh_4]$ To Form $[\{Cp_2Ti\}_2(Cp^*W(O))_2(\mu\text{-}O)_4][BPh_4]_2$ (17). An excess of $Na[BPh_4]$ (0.088 g, 0.258 mmol) was added to complex **6** (0.100 g, 0.172 mmol) in CH_3CN (20 mL), and the solution was stirred for 5 h to yield a cloudy, bright orange solution. The solvent was removed under reduced pressure, CH_2Cl_2 was added to the residue, and this suspension was stirred for several minutes. Filtration left an orange-red solid consisting of NaCl, excess $Na[BPh_4]$, and **17**. This solid was washed with CH_2Cl_2 (3 × 10 mL), THF (3 × 10 mL), and Et_2O (3 × 10 mL) to leave **17** as a red-orange microcrystalline powder in 81% yield (0.120 g, 0.139 mmol).

17: IR (KBr) $\nu_{W=O}$ 938 cm^{-1}, $\nu_{W–O–Ti}$ 852 cm^{-1}; ^1H NMR (CH_3NO_2) δ 2.44 (s, 15H, Cp*), 6.64 (s, 5H, Cp), 6.75 (s, 5H, Cp), 6.82–7.37 (m, 20H, Ph); ^{17}O NMR (CH_3NO_2) δ 714.0 (WO), 442.2 (W–O–Ti); MS (FAB+) *m/z* 545. Anal. Calcd for $C_{88}H_{90}B_2O_6Ti_2W_2$: C, 61.14; H, 5.21. Found: C, 60.81; H, 5.21.

Reaction of Ph_3CBr with $[Cp^*W(O)_3]^-$ To Form $Cp^*W(O)_2–O–CPh_3$ (19). To a mixture of Ph_3CBr (0.145 g, 0.449 mmol) and $[Bu^tNH_3][Cp^*WO_3]$ (0.198 g, 0.449 mmol) was added CH_2Cl_2 (15 mL) in a Schlenk flask. The light yellow solution was stirred for 5 h, filtered through Celite, and concentrated to dryness. This residue was then dissolved in a 1:5 mixture of THF/Et_2O (24 mL), and this solution was filtered and concentrated to approximately 10 mL. Hexane (25 mL) was added to this solution to precipitate **19** as a very light yellow solid (0.168 g, 61%).

19: IR (KBr) $\nu_{W=O}$ 926 (m), 914 (m); $\nu_{W–O–C}$ 763 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.29 (m, 15H, Ph), 2.07 (s, 15H, Cp*); ^{17}O NMR (CD_2Cl_2) δ 678.2 (WO_2), 180.0 (W–*O*–C); MS (EI) *m/z* 610 (M$^+$). Anal. Calcd for $C_{29}H_{30}O_3W$: C, 57.06; H, 4.92. Found: C, 56.60; H, 4.70.

Reaction of $[Cp^*W(O)_3]^-$ with Chlorosilanes To Form $Cp^*W(O)_2–O–SiR_2R'$ Complexes. In a typical reaction, equimolar amounts of $(PhCH_2)_3SiCl$ (0.076 g, 0.226 mmol) and $[Bu^tNH_3][Cp^*WO_3]$ (0.100 g, 0.226 mmol) were dissolved in CH_2Cl_2 (25 mL) in a Schlenk flask. The solution was stirred overnight and then filtered through Celite followed by evaporation of the solvent under vacuum. The residue was dissolved in hexane (5 mL), and the resultant solution was cooled in a –78 °C bath to induce precipitation of $Cp^*W(O)_2OSi(PhCH_2)_3$ (**14**) as a white solid, which was then dried under reduced pressure (0.050 g, 0.0747 mmol, 33%). The complexes $Cp^*W(O)_2OSi(Bu^t)_2H$ (**20**; 0.060 g, 0.118 mmol, 52%) and $Cp^*W(O)_2OSi(Bu^t)Me_2$ (**21**; 0.141 g, 0.293 mmol, 64%) were similarly prepared from $(Bu^t)_2HSiCl$ and Bu^tMe_2SiCl and were isolated as white solids in the indicated yields.

14: IR (KBr) $\nu_{W=O}$ 947 (s), 877 (s), $\nu_{W–O–Si}$ 779 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.99 (s, 15H, Cp*), 2.19 (s, 6H, C*H*$_2$Ph), 6.98–7.23 (m, 15H, Ph); ^{13}C NMR (CD_2Cl_2) δ 10.7 ($C_5(CH_3)_5$), 24.1 (CH_2Ph), 119.9 ($C_5(CH_3)_5$), 124.9–138.3 (Ph); ^{17}O NMR (CD_2Cl_2) δ 669.6 (WO_2), 111.5 (W–*O*–Si); MS (EI) *m/z* 668 (M$^+$). Anal. Calcd for $C_{31}H_{36}O_3SiW$: C, 55.69; H, 5.43. Found: C, 55.88; H, 5.50.

20: IR (KBr) $\nu_{W=O}$ 918 (s), 895 (s), $\nu_{W–O–Si}$ 822 (s), $\nu_{Si–H}$ 2091 (m), $\delta_{R–Si–H}$ 970 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.97 (s, 18H, Bu^t), 2.13 (s, 15H, Cp*), 4.40 (s, 1H, Si–H); ^{13}C NMR (CD_2Cl_2) δ 10.8 ($C_5(CH_3)_5$), 21.8 ($C(CH_3)_3$), 27.2 ($C(CH_3)_3$), 119.7 ($C_5(CH_3)_5$); ^{17}O NMR (CD_2Cl_2) δ 666.1 (WO_2), 103.8 (W–*O*–Si); MS (EI) *m/z* 511 (M$^+$). Anal. Calcd for $C_{18}H_{34}O_3SiW$: C, 42.36; H, 6.71. Found: C, 42.02; H, 6.58.

21: IR (KBr) $\nu_{W=O}$ 913 (m), 890 (s), $\nu_{W–O–Si}$ 834 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6H, SiC*H*$_3$), 0.89 (s, 9H, Bu^t), 2.12 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ –3.6 (Si–CH$_3$), 10.6 ($C_5(CH_3)_5$), 19.7 ($C(CH_3)_3$), 25.8 ($C(CH_3)_3$), 119.1 ($C_5(CH_3)_5$); ^{17}O NMR (CD_2Cl_2) δ 660.1 (WO_2), 120.7 (W–*O*–Si); MS (FAB+) *m/z* 483 (M$^+$). Anal. Calcd for $C_{16}H_{30}O_3SiW$: C, 39.84; H, 6.27. Found: C, 39.76; H, 5.99.

Reaction of $[Cp^*W(O)_3]^-$ with $CF_3C(=NSiMe_3)OSiMe_3$ To Form $Cp^*(O)_2W–O–SiMe_3$ (22). Equimolar amounts of

$CF_3C({=}NSiMe_3)OSiMe_3$ (0.141 mL, 0.531 mmol) and $[Bu^tNH_3][Cp^*W(O)_3]$ (0.213 g, 0.483 mmol) were dissolved in CH_2Cl_2 (20 mL) in a Schlenk flask at room temperature. The resulting solution was stirred for 1 h, filtered through Celite, and the solvent was removed under reduced pressure to leave $Cp^*W(O)_2OSiMe_3$ (**22**) as a colorless oil. When the reaction was performed in an NMR tube, ^1H NMR monitoring indicated a near-quantitative reaction, but the moisture sensitivity of **22** prevented the determination of an accurate isolated yield and a satisfactory C,H analysis.

22: IR (KBr) $\nu_{W=O}$ 897 (s), 891 (s), ν_{W-O-Si} 846 (s), ν_{Si-Me} 949 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.14 (s, 9H, $SiMe_3$), 2.11 (s, 15H, Cp*); ^{13}C NMR ($CDCl_3$) δ 0.98 ($Si(\mathit{C}H_3)_3$), 10.5 ($C_5(\mathit{C}H_3)_5$), 119.3 ($\mathit{C}_5(CH_3)_5$); ^{17}O NMR (CD_2Cl_2) δ 655.8 ($W\mathit{O}_2$), 130.8 (W–*O*–Si); MS (EI) *m/z* 440 (M^+).

Reaction of $[Cp^*W(O)_3]^-$ with Me_3SiCl to Form 22. Compound 1 (0.023 g, 0.052 mmol) and Me_3SiCl (0.005 mL, 0.039 mmol) were mixed in an NMR tube at room temperature in CD_2Cl_2 solvent with careful exclusion of air. Formation of **22** was observed along with unreacted **1**. The use of more than 1 equiv of Me_3SiCl gave no **22**; $Cp^*W(O)_2Cl$ and $Me_3Si{-}O{-}SiMe_3$ were formed instead.

Reaction of $[Cp^*Mo(O)_3]^-$ with $(PhCH_2)_3SiCl$ To Form $Cp^*Mo(O)_2{-}O{-}Si(CH_2Ph)_3$ (23). Equimolar amounts of **2** (0.150 g, 0.425 mmol) and $(PhCH_2)_3SiCl$ (0.143 g, 0.425 mmol) were stirred at room temperature in CH_2Cl_2 under N_2 overnight. The resulting cloudy yellow solution was filtered to remove $[Bu^tNH_3]Cl$ and concentrated under reduced pressure, and Et_2O was added to precipitate **23** as a pale yellow solid. The precipitate was extracted with Et_2O (3 × 10 mL) to remove $Cp^*Mo(O)_2Cl$ that formed during the course of the reaction. The yellow solid was dried under vacuum to give **23** in 73% yield (0.180 g, 0.310 mmol).

23: IR (KBr) $\nu_{Mo=O}$ 923 (s), 871 (s), $\nu_{Mo-O-Si}$ 779; ^1H NMR (CD_2Cl_2) δ 1.89 (s, 15H, Cp*), 2.18 (s, 6H, $C\mathit{H}_2Ph$), 7.00–7.25 (m, 15H, Ph); ^{13}C NMR (CD_2Cl_2) δ 10.8 ($C_5(\mathit{C}H_3)_5$), 24.4 ($\mathit{C}H_2Ph$), 121.6 ($\mathit{C}_5(CH_3)_5$), 124.7–138.7 (Ph); ^{17}O NMR (CD_2Cl_2) δ 842.6 ($Mo\mathit{O}_2$), 128.9 (Mo–*O*–Ti); MS (FAB+) *m/z* 583. Anal. Calcd for $C_{31}H_{36}MoO_3Si$: C, 64.13; H, 6.21. Found: C, 63.87; H, 6.34.

Reaction of $[Cp^*W(O)_3]^-$ with Chlorogermanes To Form $Cp^*W(O)_2{-}O{-}GeMe_3$ (24) and $Cp^*W(O)_2{-}O{-}GePh_3$ (25). Equimolar amounts of Ph_3GeCl (0.046 g, 0.136 mmol) and $[Bu^tNH_3][Cp^*WO_3]$ (0.060 g, 0.136 mmol) were dissolved in CH_2Cl_2 (15 mL) in a Schlenk flask. The pale yellow solution was stirred for about 4 h (until an abundant amount of precipitate had formed, indicating formation of $[Bu^tNH_3]Cl$), filtered through Celite, and concentrated to dryness. The residue was then washed with pentane (2 × 5 mL) and dried under vacuum to give **25** as a cream-colored solid (0.050 g, 0.075 mmol, 55% yield). Complex **24** was similarly prepared from reaction of $[Cp^*WO_3]^-$ with Me_3GeCl and was isolated as a cream-colored solid in 50% yield.

24: IR (KBr) $\nu_{W=O}$ 932 (s), 890 (s), ν_{W-O-Ge} 786 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.47 (s, 9H, Me), 2.06 (s, 15H, Cp*); ^{17}O NMR (CD_2Cl_2) δ 635.5 (WO_2), 160.7 (W–O–Ge); MS (EI) *m/z* 484 (M+). Anal. Calcd for $C_{13}H_{24}GeO_3W$: C, 32.20; H, 4.95. Found: C, 32.62; H, 5.08.

25: IR (KBr) $\nu_{W=O}$ 935 (s), 887 (s), ν_{W-O-Ge} 738 (w-m) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.00 (s, 15H, Cp*), 7.40–7.65 (m, 15H, Ph); ^{17}O NMR (CD_2Cl_2) δ 648.7 ($W\mathit{O}_2$), 132.3 (W–*O*–Ge); MS (FAB+) *m/z* 671 (M + 1). Anal. Calcd for $C_{28}H_{30}GeO_3W$: C, 50.12; H, 4.47. Found: C, 50.02; H, 4.59.

Reaction of $[Cp^*W(O)_3]^-$ with Me_3SnCl To Form $(Me_3Sn)_4(Cp^*W(O))_4(\mu{-}O)_8$ (26). To $[Bu^tNH_3][Cp^*WO_3]$ (0.208 g, 0.472 mmol) in CH_2Cl_2 (30 mL) was added Me_3SnCl (0.094 g, 0.472 mmol) to give a pale yellow solution that was stirred for 8 h, after which the reaction mixture was filtered through Celite and concentrated to dryness. The resulting residue was dissolved in THF (30 mL), and the solution was filtered and concentrated to 5 mL. Hexane (25 mL) was then added to precipitate a white solid, which was washed with pentane (10 mL) and dried under vacuum to give **26** in 49% yield (0.123 g, 0.231 mmol).

26: IR (KBr) $\nu_{W=O}$ 921 (s), 856 (m-s), ν_{W-O-Sn} 733 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 0.47 (s, 15H, Cp*), 2.00 (s, 9H, Me); ^{17}O NMR (CD_2Cl_2, 298 K) δ 474.1; ^{17}O NMR (CD_2Cl_2, 183 K) δ 605.6 (W(*O*)), 404.4 (W–*O*–Sn); ^{119}Sn NMR (CD_2Cl_2, 298 K) δ −7.28; ^{119}Sn NMR (CD_2Cl_2, 198 K) δ −19.47 (*Sn*Me_3); MS (FAB+) *m/z* 531 (M + 1). Anal. Calcd for $C_{13}H_{24}O_3SnW$: C, 29.40; H, 4.52. Found: C, 29.85; H, 4.65.

Molecular Weight Determination of Complex 26. The standard PhN=NPh (0.0122 g, 0.067 mmol) and complex **26** (0.041 g, 0.019 mmol) were carefully weighed and transferred to separate, but connected, reservoirs using an apparatus and procedure similar to that described by Burger *et al.*[12] To each reservoir was added CH_2Cl_2 (0.500 ± 0.003 mL to the PhN=NPh reservoir; 0.698 ± 0.003 mL to the reservoir with **26**), and the solutions were then cooled to −78 °C. The system was evacuated and then allowed to equilibrate at room temperature. The volumes of each reservoir were measured daily until the volumes remained constant. The final volume of the system was 1.139 ± 0.003 mL, which is slightly less than the amount of solvent initially added due to a small amount of solvent evaporation. A molecular weight value of 1800 ± 50 was calculated for complex **26**.

Crystal and Molecular Structures of 13, 14, 20, and 26. Crystallographic data are collected in Table 1. All samples were affixed to glass fibers with epoxy cement and photographically characterized. Complexes **13** and **26** showed $\bar{1}$ Laue symmetry and **14** and **20** *mmm* symmetry. The choice of the centrosymmetric alternative for both triclinic samples was supported by the chemically sensible results of refinement. For **14**, the choice of space group is unambiguous, and for **20** the centrosymmetric choice is consistent with the presence of a molecular mirror plane perpendicular to the *b* direction. All data sets were corrected for absorption; for **13**, **14**, and **20** empirical ψ-scan methods were used, and for **26** an empirical absorption tensor was generated by an expression relating F_o and F_c.

The locations of the metal atoms were determined by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were idealized. Rotational disorder is evident in the C(26–30) ring in **13** from the distorted thermal ellipsoids and high Δ/σ values for the positional parameters for these atoms. Crystallographic computations used SHELXTL software in various versions (G. Sheldrick, Siemens XRD, Madison, WI).

Acknowledgment. We gratefully acknowledge the U.S. Department of Energy, Office of Basic Energy Sciences, for support of this research and the National Science Foundation for assisting with the purchase of the diffractometer at the University of Delaware. A. Benesi is thanked for his assistance with the ^{17}O NMR experiments.

Supplementary Material Available: For **13**, **14**, **20**, and **26**, tables of atomic coordinates and isotropic parameters, anisotropic thermal parameters, bond lengths, bond angles, and hydrogen atom coordinates (27 pages). Ordering information is given on any current masthead page.

OM9307920