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Reaction of Cp^*MoCl_4 and Cp^*WCl_4 with H_2O, H_2S, Amines, and Hydrazines. Formation of the Trioxo Anions $[Cp^*Mo(O)_3]^-$ and $[Cp^*W(O)_3]^-$ and the Trisulfido Anion $[Cp^*W(S)_3]^-$

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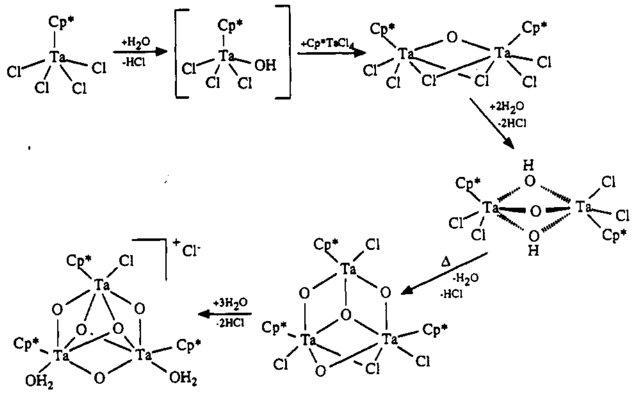
In the presence of aqueous NaOH and air, Cp^*WCl_4 undergoes hydrolysis and oxidation to form $Cp^*W(O)_2Cl$. When air is excluded, two W(V) intermediates are detected in the above reaction for which spectroscopic evidence indicates the formulations $Cp^*WCl_3(OH)$ and $Cp^*WCl_2(OH)_2$. In the absence of air, Cp^*MoCl_4 reacts with NaOH(aq) to cleanly yield the Mo(V) compound $Cp^*Mo(O)Cl_2$, but in the presence of air oxidation occurs to give the Mo(VI) complex $Cp^*Mo(O)_2Cl$. Both Cp^*WCl_4 and Cp^*MoCl_4 react with aqueous Bu^tNH_2 in the presence of air to form the trioxo anions $[Cp^*M(O)_3]^-$, which have been isolated as their $[Bu^tNH_3]^+$ salts. The trioxo anions are also produced upon treatment of $Cp^*M(O)_2Cl$ or $[Cp^*M(O)_2]_2(\mu\text{-}O)$ with aqueous Bu^tNH_2. $[(Ph_3P)_2N]^+$ and $[Bu^n_4N]^+$ salts of $[Cp^*W(O)_3]^-$ were obtained by metathesis reactions, and the reaction of $[Bu^tNH_3][Cp^*W(O)_3]$ with $EtC\{O\}CH{=}CH_2$ gave the salt $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$. The complex Cp^*WCl_4 was also observed to react with anhydrous Bu^tNH_2 in the absence of air to form $Cp^*W(NBu^t)Cl_2$, which in turn gave $Cp^*W(O)(NBu^t)Cl$ upon exposure to moist air. With phenylhydrazine, Cp^*WCl_4 reacted in air to give the bis(hydrazinido) complex $Cp^*W(NNHPh)_2Cl$. With H_2S in air, both Cp^*WCl_4 and Cp^*MoCl_4 reacted to give mixtures of the known dinuclear compounds $[Cp^*M(S)]_2(\mu\text{-}S)_2$ and $[Cp^*M(S)]_2(\mu\text{-}S_2)$, but in the presence of NEt_3, Cp^*WCl_4 and H_2S reacted to give the new trisulfido anion $[Cp^*W(S)_3]^-$. In exploratory reactions of $[Cp^*W(O)_3]^-$ with unsaturated organic substrates, phenylketene was observed to react with this trioxo anion to give a new complex formed via net [2 + 2] cycloaddition of a W=O bond across the ketene C=C bond, and two molecules of $MeO\{O\}CC{\equiv}CC\{O\}OMe$ were taken up by $[Cp^*W(O)_3]^-$ to form a new complex with a six-membered $\overline{WOC(R){=}C(R)C(R){=}C(R)}$ ring. Crystal structures are reported for $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$, $[Bu^tNH_3][Cp^*W(O)_3]\cdot{}^1/_2[Bu^tNH_3]Cl$, $[(Ph_3P)_2N][Cp^*W(O)_3]\cdot 2H_2O$, $[Et_3NH][Cp^*W(S)_3]$, and $[Cp^*W(S)]_2(\mu\text{-}S)_2$.

Introduction

It was earlier reported from these laboratories that Cp^*TaCl_4 ($Cp^* = \eta^5\text{-}C_5Me_5$) undergoes stepwise hydrolysis of the tantalum–chloride bonds to yield the binuclear and trinuclear complexes shown in Scheme I.[1] With the exception of $Cp^*TaCl_3(OH)$, all of the products shown in the scheme were isolated as well-characterized solids,[1] and the binuclear complex $[Cp^*TaCl_2]_2(\mu\text{-}O)(\mu\text{-}OH)_2$ was recently prepared by Curtis *et al.* by an alternative route and was crystallographically characterized.[2] Several related tantalum and niobium compounds have also been described.[3] A significant aspect of this study was its demonstration that oxide ligands could be introduced into organometallic clusters in a stepwise and controlled manner.

Scheme I



As an extension of that work, we have since examined the hydrolysis behavior of the related group VI metal halides Cp^*MoCl_4, **1**,[4] and Cp^*WCl_4, **2**,[4,5] and details of those reactions are described herein. Compounds **1** and **2** have been extensively used as starting materials for a variety of organometallic compounds within the Cp^*MoL_x and Cp^*WL_x families. Although early molecular weight measurements on $W(\eta^5\text{-}C_5Me_4Bu^t)Cl_4$ indicated it to be

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[1] (a) Jernakoff, P.; de Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362. (b) *Ibid. Nouv. J. Chim.* **1988**, *12*, 329.

[2] Kwon, D.; Curtis, M. D.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, *31*, 3489.

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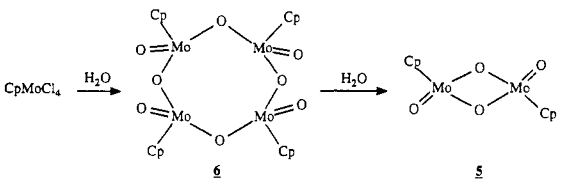
dimeric,[6] presumably with bridging halide ligands, an X-ray diffraction study of the related complex $W(\eta^5\text{-}C_5H_4\text{-}Pr^i)Cl_4$ has shown it to be a monomer,[7] and as recently noted by Schrock *et al.*,[8] it is likely that **1** and **2** are monomeric species. As described earlier in a preliminary communication,[9] particularly interesting products of the hydrolysis and oxidation reactions of **1** and **2** are the new anions $[Cp^*Mo(O)_3]^-$ and $[Cp^*W(O)_3]^-$. These species are highly nucleophilic and as such should prove useful for the preparation of a variety of new inorganic and organometallic compounds. Illustrated herein are the reactions of $[Cp^*W(O)_3]^-$ with phenylketene and $MeOC\{O\}C{\equiv}CC\{O\}OMe$. Also described herein are reactions of **1** and **2** with Bu^tNH_2, $PhNHNH_2$, and H_2S, the latter of which gives the new trisulfido anion $[Cp^*W(S)_3]^-$.

We know of no previous studies of the hydrolysis behavior of the tungsten complex **2** or its Cp-substituted derivatives, but there have been several reports of the hydrolysis of the corresponding cyclopentadienylmolybdenum compounds. As early as 1964, Cousins and Green[10] reported that $CpMoCl_4$ was extremely sensitive to hydrolysis, readily giving $CpMo(O)Cl_2$ (**3**) upon treatment with water, eq 1. This complex, and its substituted Cp

$$\mathrm{CpMoCl_4} \underset{+\mathrm{HCl}}{\overset{+\mathrm{H_2O},\,-\mathrm{HCl}}{\rightleftarrows}} \underset{\mathbf{3}}{\mathrm{CpMo(O)Cl_2}} \xrightarrow{\mathrm{O_2}} \underset{\mathbf{4}}{\mathrm{CpMo(O)_2Cl}} \qquad (1)$$

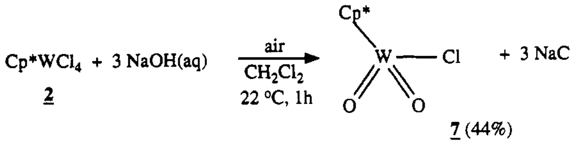
derivatives, have subsequently been prepared by a variety of other means,[3f,11,12] and complex **3** has been crystallographically characterized.[12] Complex **3** was also shown to oxidize readily to give the Mo(VI) species $CpMo(O)_2Cl$, **4**.[10] Further hydrolysis of **3** (or $CpMoCl_4$ via **3**) was shown to occur slowly to form the crystallographically characterized[13] binuclear μ-oxo complex **5**, eq 2, via a red complex **6** that has been proposed to have a tetrameric structure.[11,14] Other $(\eta\text{-}C_5H_4R)MoCl_4$ (R = Me, Pr^i, Bu^n) derivatives behave similarly.[11] Related compounds that have been reported include $(\eta\text{-}C_5H_4R)MoCl_3(OH)$ (R = Pr^i, Bu^n) which formed upon treatment of $\{Mo(O)Cl_3\}_n$ with $Sn(\sigma\text{-}C_5H_4R)Bu^n{}_3$,[11] *syn*-$[Cp^*MoCl]_2(\mu\text{-}Cl)_2(\mu\text{-}O)$, which resulted from treatment of $[Cp^*Mo(CO)_3]_2$ with O_2,[12a] $[CpMo(O)Cl]_2(\mu\text{-}O)$, which formed from oxidation of $\{[CpMoCl]_4(\mu\text{-}O)_6\}\{ZnCl(THF)_2\}$,[12b] and the trimolybdenum complex $(CpMoCl)_3(\mu\text{-}Cl)_4(\mu_3\text{-}O)$ prepared by $CpMoCl_3$ induced abstraction of oxygen from THF solvent.[15a] The Cp* complex $[Cp^*Mo(O)Cl]_2(\mu\text{-}O)$, analogous to the Cp complex mentioned above, was shown to result from treatment of Cp^*MoCl_4 with Na_2WO_4 in THF,[15b] although in water this reaction gave instead the well-known[16] Mo(VI) μ-oxo complex $[Cp^*Mo(O)_2]_2(\mu\text{-}O)$.[15b] It was also claimed in this latter study that $[Cp^*Mo(O)Cl]_2(\mu\text{-}O)$ was formed *in situ* upon reaction of Cp^*MoCl_4 with 1.5 equiv of H_2O in THF and that a species proposed to be $[Cp^*MoCl_2(OH)]_2(\mu\text{-}O)$ resulted upon solvent evaporation.[15b]



(2)

Results and Discussion

Hydrolysis of $[Cp^*WCl_4]_2$ with Aqueous NaOH. Addition of aqueous NaOH to acetone solutions of Cp^*WCl_4, **2**, was observed to induce an immediate color change from orange to green. Admission of air to these solutions induced a further change to yellow over 10 min as the metal was oxidized from W(V) to W(VI) and the known compound $Cp^*W(O)_2Cl$, **7**,[16a] formed, eq 3. This



(3)

latter compound was isolated in good yield and was spectroscopically identified by comparison of its data to those reported.[16a] The use of excess NaOH(aq) in the hydrolysis reaction did not induce displacement of the remaining chloride ligand in **7** to form either $Cp^*W(O)_2OH$ or $[Cp^*W(O)_3]^-$ (see below).

The mechanism proposed to account for the formation of **7** is shown in Scheme II and involves stepwise hydrolysis of the tungsten–chloride bonds along with air oxidation of W(V) to W(VI). In an attempt to identify the W(V) hydrolysis products formed in the initial orange to green color change, the hydrolysis reaction was carried out with the careful exclusion of air. By varying reaction times and equivalents of added base, we were able to isolate two green solids for which spectroscopic data indicated the

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(3) (a) Bottomley, F.; Karslioglu, S. *Organometallics* **1992**, *11*, 326. (b) Bottomley, F.; Keizer, P. N.; White, P. S.; Preston, K. F. *Organometallics* **1990**, *9*, 1916. (c) Gibson, V. C.; Kee, T. P. *J. Chem. Soc., Chem. Commun.* **1989**, 656. (d) Gibson, V. C.; Kee, T. P.; Clegg, W. *J. Chem. Soc., Chem. Commun.* **1990**, 29. (e) Bunker, M. J.; De Cian, A.; Green, M. L. H.; Moreau, J. J. E.; Siganporia, N. *J. Chem. Soc., Dalton Trans.* **1980**, 2155. (f) Bunker, M. J.; DeCian, A.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1977**, 59. (g) Daran, J.-C.; Prout, K.; De Cian, A.; Green, M. L. H.; Siganporia, N. *J. Organomet. Chem.* **1977**, *136*, C4. (h) Prout, K.; Daran, J.-C. *Acta Crystallogr.* **1979**, *B35*, 2882. (i) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037. (j) De la Mata, J.; Fardos, R.; Gomez, M.; Gomez-Sal, P.; Martinez, Carrera, S.; Royo, P. *Organometallics* **1990**, *9*, 2846. (k) Andreu, A. M.; Jalon, F. A.; Otero, A.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1987**, 953. (l) Jalon F. A.; Otero, A.; Royo, P.; Fernandez-G., J. M.; Rosales, M. J.; Toscano, R. A. *J. Organomet. Chem.* **1987**, *331*, C1. (m) Leichtweis, I.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Chem. Ber.* **1991**, *124*, 253.

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(6) Shrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.

(7) Green, M. L. H.; Hubert, J. D.; Mountford, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3793.

(8) O'Regan, M. B.; Vale, M. G.; Payack, J. F.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 1112.

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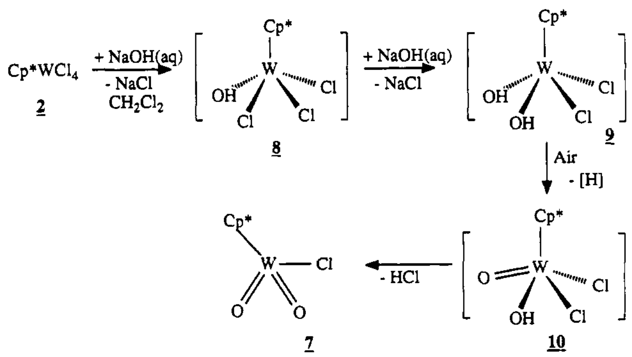
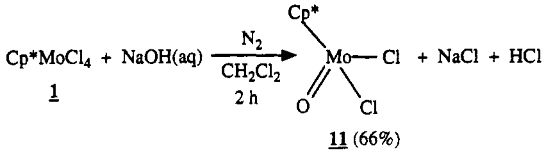
Scheme II



presence of the compounds 8 and 9 shown in Scheme II. After 2 was stirred in CH_2Cl_2 with 2 equiv of aqueous NaOH for 4 h, complex 8 was isolated as a dark green paramagnetic powder by precipitation with hexane. Similarly, compound 9 was obtained as a dark green solid by adding 4 equiv of NaOH(aq) and allowing the reaction to stir for 6 h with a similar workup. Neither compound was obtained pure, with each contaminated with small amounts of each other, 2, 7, and residual NaCl and NaOH. Like the parent compound 2 [^1H NMR (CD_2Cl_2): δ 13.48 (Cp*)],[5] both 8 and 9 showed broad ^1H NMR resonances indicative of a paramagnetic species. For 8, a resonance at δ 8.9 is attributed to the Cp* ligand and a resonance at δ 10.1 is assigned to the coordinated OH group. Compound 9 showed similar broad ^1H NMR resonances at δ 16.1 (Cp*) and 29.1 (OH). In each case, the downfield resonances were absent when 8 and 9 were prepared from NaOD in D_2O solution, consistent with the assignment of these resonances to the coordinated OH groups. Neither compound gave a parent ion in its mass spectrum, but in each case a strong ion was observed at m/z = 407 corresponding to $Cp^*W(O)Cl_2$. However, no $\nu_{W=O}$ vibration in the 890–950-cm^{-1} region was observed for either compound, *indicating the absence of an oxo ligand at this* stage of the hydrolysis. Thus, the $Cp^*W(O)Cl_2$ ion observed in the mass spectra must arise by fragmentation reactions, which for 8 would involve loss of HCl and for 9 loss of water. The presence of two chloride ligands in the $Cp^*W(O)Cl_2$ ion in the mass spectrum indicates that neither 8 nor 9 is $Cp^*W(OH)_3Cl$, which could have also formed in these reactions. No evidence was obtained for this latter species, even when excess base was used in the hydrolysis. Both compounds 8 and 9 showed a broad IR (KBr) band attributable to the OH ligand [8, 3447; 9, 3431 cm^{-1}], with this band stronger for 9 than for 8. When these compounds were prepared from $NaOD/D_2O$, these IR bands shifted to 2519 (8) and 2535 (9) cm^{-1}. A room-temperature ESR spectrum of a solution containing compound 9 showed a signal at $g \cong 1.94$ with a width at half-height of 55 G which compares well to that of 2 ($g \cong$ 1.92, width at half-height = 50 G).[5]

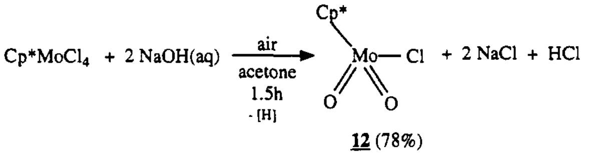
Air-oxidation of both compounds 8 and 9 in solution (rapidly) or in the solid state (slowly) gave high-yield formation of 7. As indicated in Scheme II, we suggest that this proceeds via oxidation to give compound 10, which then forms 7 by rapid loss of HCl.

Hydrolysis of Cp^*MoCl_4 with Aqueous NaOH. As earlier found by Green and co-workers for the Cp analogue of Cp^*MoCl_4 (1),[10,11] hydrolysis of 1 with aqueous NaOH in the absence of air proceeded slowly but smoothly to form $Cp^*Mo(O)Cl_2$, 11, as the only detectable product, eq 4. This compound was isolated as a red-brown solid and was spectroscopically characterized (see Experimental Section). It presumably forms by hydrolysis of two of the Mo–Cl bonds of 1 to form $Cp^*Mo(OH)_2Cl_2$, which then eliminates a molecule of water.



(4)

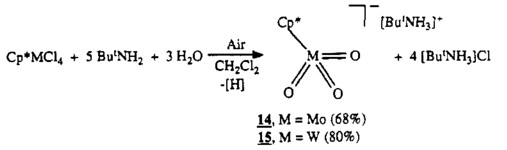
When the hydrolysis of Cp^*MoCl_4 was conducted in air, the known compound $Cp^*Mo(O)_2Cl$, 12,[16a] was obtained in good yield under the conditions given in eq 5.



(5)

However, when the reaction time was 30 min or less, a mixture of compounds 11 and 12 was formed. The former compound is a logical intermediate to 12, and indeed it was observed that 11 reacted in air with 1 equiv of NaOH(aq) to give clean conversion to 12. However, the use of excess NaOH(aq) and longer reaction times gave instead formation of the known dimeric species 13,[16] Scheme III. This latter product likely forms via hydrolysis of 12 to form $Cp^*Mo(O)_2OH$, which undergoes condensation via loss of H_2O to form 13. This was demonstrated by adding excess base to a solution of 12, which led to the clean formation of 13 over a 30-min period.

Formation of the Trioxo Anions $[Cp^*M(O)_3]^-$ (M = Mo, W) via Hydrolysis of Cp^*MCl_4, $Cp^*M(O)_2Cl$, and $[Cp^*M(O)_2]_2(\mu\text{-}O)$ with Bu^tNH_2/H_2O in Air. As noted above, complexes 1 and 2 react with aqueous NaOH to give, after air oxidation, the chloro complexes $Cp^*M(O)_2Cl$. Different results were obtained using the base Bu^tNH_2 in the presence of water. These reactions led to the formation of the new anionic trioxo complexes 14 and 15, which were isolated as their $Bu^tNH_3^+$ salts, eq 6. These trioxo anions also readily result from treatment $Cp^*M(O)_2Cl$ with aqueous Bu^tNH_2, and it was also found that 14 and 15 were cleanly produced by a similar reaction of the μ-oxo compounds $[Cp^*M(O)_2]_2(\mu\text{-}O)$ with aqueous Bu^tNH_2, eq 7. As illustrated, both of these latter reactions likely proceed via formation of the hydroxide complex 17, which is then deprotonated by the aqueous base. It was sometimes observed that small amounts of the μ-oxo complexes 13 and 16 were produced during the hydrolysis



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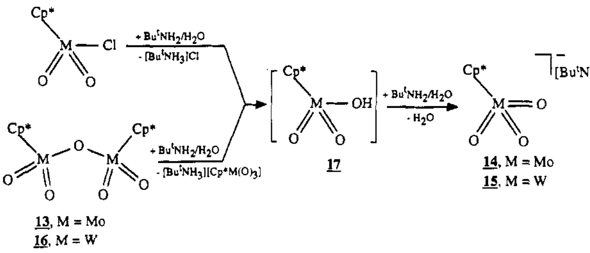
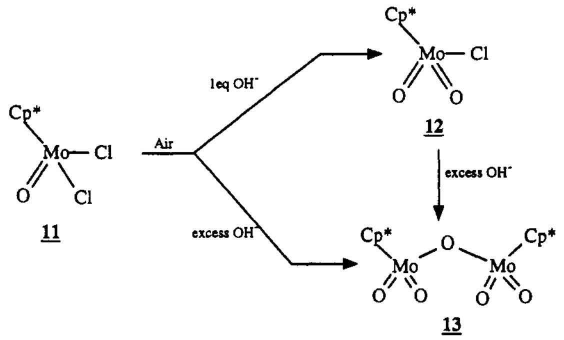


(7)

Scheme III



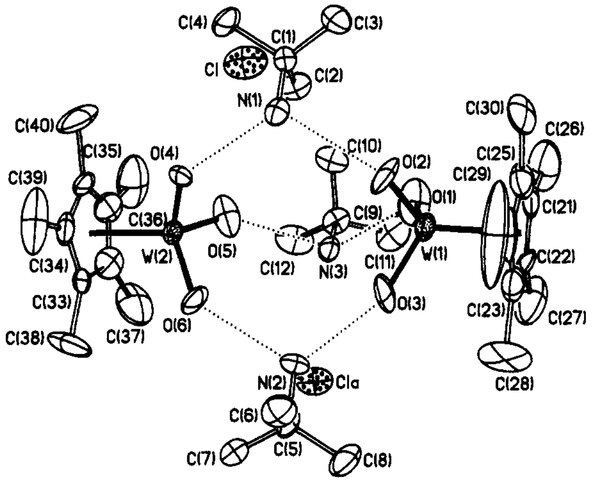


Figure 1. ORTEP drawing for $[Bu^tNH_3][Cp^*W(O)_3]\cdot{}^1/_2[Bu^tNH_3]Cl$, **15a**.

reactions of Cp^*MCl_4, but their formation could be minimized by using excess $Bu^tNH_2(aq)$. Since the time of the original communication of these results,[9] Sundermeyer and co-workers have reported the synthesis of $[Bu^n_4N][Cp^*W(O)_3]\cdot 2H_2O$ via the similar reaction of $[Cp^*W(O)_2]_2(\mu\text{-}O)$ with $[Bu^n_4N][OH]$.[17]

It was also observed that treatment of complexes **14** and **15** with HCl(g) gave clean re-formation of the chloro complexes $Cp^*M(O)_2Cl$. Complexes **14** and **15** were also observed to react with aqueous acetic acid (2 M) to give near quantitative formation of the binuclear μ-oxo complexes **13** and **16**. Both of these reactions likely proceed via protonation of an oxo ligand of **14** and **15** to form the hydroxide complex **17**, which then undergoes condensation to form the μ-oxo complexes or displacement of the hydroxide ligand by chloride to form $Cp^*M(O)_2Cl$.

Complexes **14** and **15** were obtained as spectroscopically characterized yellow and white microcrystalline solids, respectively, and three different salts of **15** have been further defined by X-ray diffraction studies (see Figures 1–3 and below). The preparation of **14** and **15** from Cp^*MCl_4 or $Cp^*M(O)_2Cl$ always gave products containing varying amounts of the $[Bu^tNH_3]Cl$ byproduct, and it has proven difficult to completely separate these salts. The preparation of **14** and **15** from the μ-oxo complexes **13** and **16** does not yield $[Bu^tNH_3]Cl$ as a byproduct, and this represents an important advantage of that synthetic route. A PPN^+ ($PPN^+ = (Ph_3P)_2N^+$) salt of $[Cp^*W(O)_3]^-$ was also obtained as a chloride-free white powder by first treating $[Bu^tNH_3][Cp^*W(O)_3]$ with $[Bu^n_4N]OH$ to form oily $[Bu^n_4N][Cp^*W(O)_3]$. The latter salt is soluble in both polar and nonpolar solvents (CH_2Cl_2, hexane) in contrast to $[Bu^tNH_3][Cp^*W(O)_3]$, which is soluble in CH_2Cl_2 but not in less polar organic solvents. We were unable to solidify $[Bu^n_4N][Cp^*W(O)_3]$, but metathesis with [PPN]Cl led to the formation of $[PPN][Cp^*W(O)_3]$, which was obtained as an analytically pure white solid, albeit in low overall yield. This latter salt could not be obtained by direct treatment of $[Bu^tNH_3][Cp^*W(O)_3]$ with [PPN]Cl since no conditions were found that would give clean metathesis of the cations. The crystal structure of $[PPN][Cp^*W(O)_3]\cdot 2H_2O$ described below shows the presence of two water molecules per formula unit, although we were unable to obtain convincing IR or ^1H NMR evidence for H_2O in the bulk material described above. Also, the C, H analysis was consistent with an anhydrous sample (see Experimental Section) but not with the hydrated formulation. However, given the strong tendency of the oxo ligands of $[Cp^*W(O)_3]^-$ to hydrogen bond with either the cation or with water, as illustrated in the crystal structures described below and in Sundermeyer's independent preparation of $[Bu^n_4N][Cp^*W(O)_3]\cdot 2H_2O$, the presence of water in all of these samples must be regarded as a likely possibility.

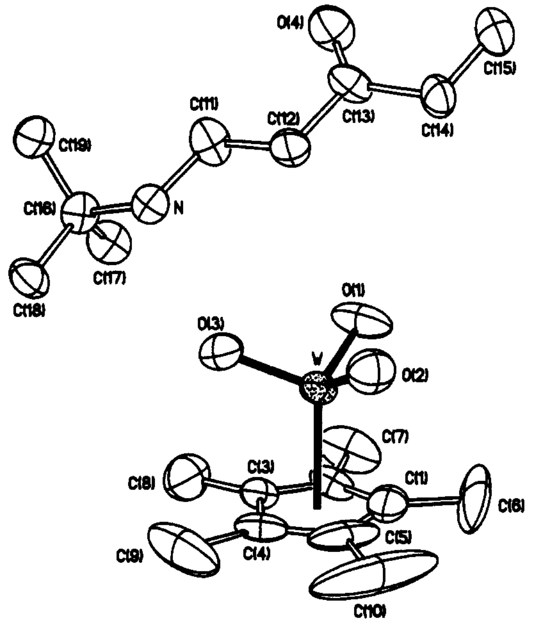


Figure 2. ORTEP drawing for $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$, **15b**.

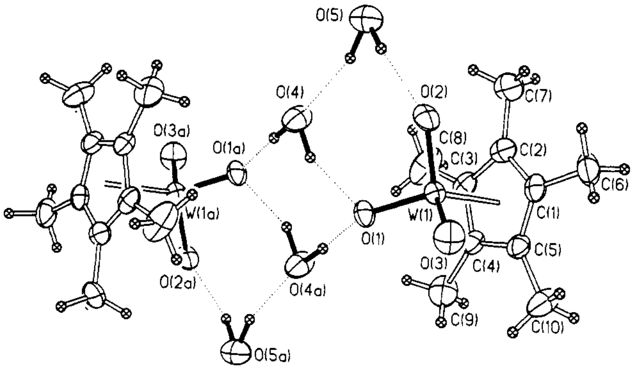


Figure 3. ORTEP drawing for $[PPN][Cp^*W(O)_3]\cdot 2H_2O$, **15**. The $[PPN]^+$ ions have been omitted for clarity.

Before proceeding to a discussion of the characterization of **14** and **15**, we note that these anions are closely related to the Cp^*ReO_3 and Cp^*TcO_3 complexes that have been

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extensively studied by Herrmann and co-workers.[18] The hydridotris(1-pyrazolyl)borate (Tp) and hydridotris{3,5-dimethyl-1-pyrazolyl}borate (Tp*) analogues to **14**, $[TpMo(O)_3]^-$ and $[Tp^*Mo(O)_3]^-$, have also been prepared[19a] as has the σ-aryl derivative $[(\eta^1\text{-}2,4,6\text{-}C_6H_2Me_3)Mo(O)_3]^-$ [19b] and the Tp*–tungsten analogue, $[Tp^*W(O)_3]^-$.[19c] Both the Tp–molybdenum complexes and the σ-aryl derivative have been crystallographically characterized. Related σ-alkyl tungsten trioxo anions $[(Me_3CCH_2)W(O)_3]^-$ and $[(Me_3SiCH_2)W(O)_3]^-$ are also known.[20] An anionic ethylenediaminetetraacetate (EDTA) derivative $[EDTA(Mo(O)_3)_2]^{4-}$ has been reported,[21] and examples of neutral molybdenum trioxo complexes include (1,4,7-triazacyclononane)$Mo(O)_3$[22a] and (diethylenetriamine)$Mo(O)_3$.[22b] A similar Tp* analogue of **7**, $Tp^*W(O)_2Cl$, has also been recently described.[23]

Three different salts of $[Cp^*W(O)_3]^-$, **15**, have been crystallographically characterized in this work. The first was the mixed salt $[Bu^tNH_3][Cp^*W(O)_3]\cdot{}^1/_2[Bu^tNH_3]Cl$ (**15a**) obtained from the preparation of **15** via hydrolysis of Cp^*WCl_4 by aqueous Bu^tNH_2. As indicated in the formula, 0.5 equiv of $[Bu^tNH_3]Cl$ co-crystallized with each 1 equiv of $[Bu^tNH_3][Cp^*W(O)_3]$. A chloride-free salt $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$ (**15b**) was serendipitously obtained in an attempt to induce reaction of the oxo ligands of the anion in $[Bu^tNH_3][Cp^*W(O)_3]$ with $EtC\{O\}CH{=}CH_2$, but instead the *tert*-butylammonium cation added across the olefin double bond to give the cation $[Bu^t(EtC\{O\}CH_2CH_2)NH_2]^+$. The third salt is $[PPN][Cp^*W(O)_3]\cdot 2H_2O$ (**15c**), which resulted from the metathesis of $[Bu^tNH_3][Cp^*W(O)_3]$ with aqueous $[Bu^n{}_4N]OH$ followed by further metathesis with [PPN]Cl. ORTEP drawings are shown in Figures 1–3 and important crystallographic information is given in Tables I–VII. All three structures show the presence of extensive hydrogen bonding between the $[Cp^*W(O)_3]^-$ anion and either the cations (for **15a,b**) or H_2O (for **15c**). In **15c**, the $Cp^*W(O)_3^-$ anions form hydrogen-bonded dimers as shown in Figure 3 involving four water molecules in each dimer. The tungsten–oxygen distances in the three compounds average 1.751, 1.746, and 1.758 Å, while the O–W–O angles average 105.2, 104.6, and 105.3°, respectively, for **15a–c**. The 22 structures with W=O linkages tabulated in an analysis of the Cambridge Crystallographic Data Center's database have an average W=O distance of 1.692 Å with a median value of 1.697 Å.[24] The W=O bonds in **15a–c** are thus longer than typically found. This is consistent with the need for the oxo ligands in **15** to donate only two electrons to the metal to achieve a satisfactory 18 e^- count, in contrast to most metal oxo complexes in which the oxo ligand functions as a four-electron donor (using the electron counting convention of treating all atoms as neutral).[25] Thus the oxo ligands in **15** should be bound more weakly to the metal than in most other W=O complexes and have a correspondingly longer W=O bond. The spectroscopic data summarized below support this conclusion. However, it should be noted that the extensive hydrogen bonding present in **15a–c** may also contribute to the observed lengthening of the W=O bonds.

Table I. Crystal, Data Collection, and Refinement Parameters for $[Bu^tNH_3][Cp^*W(O)_3]\cdot{}^1/_2[Bu^tNH_3]Cl$, 15a, $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$, 15b, and $[PPN][Cp^*W(O)_3]\cdot 2H_2O$, 15c

	15a	**15b**	**15c**
	(a) Crystal Parameters		
formula	$C_{32}H_{66}N_3O_6ClW_2$	$C_{19}H_{35}NO_4W$	$C_{46}H_{49}NO_5P_2W$
fw	991.37	525.34	941.7
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a, Å	13.822(5)	9.508(3)	11.106(4)
b, Å	17.894(7)	15.142(4)	12.935(2)
c, Å	17.277(7)	15.278(4)	29.285(9)
β, deg	95.06(4)	98.45(2)	92.70(2)
V, $Å^3$	4256.5(10)	2175.6(11)	4202.5(20)
Z	4	4	4
μ(Mo Kα), cm^{-1}	58.09	56.29	28.71
D_{calc}, g cm^{-3}	1.547	1.604	1.488
color	colorless	colorless	colorless
size, mm	0.36 × 0.38 × 0.46	0.28 × 0.42 × 0.36	0.10 × 0.28 × 0.30
	(b) Data Collection		
diffractometer	Nicolet R3m	Nicolet R3m	Siemens P4
data (h,k,l)	±16,+21,+20	±11,+17,+17	±12,+14,+33
2θ scan limits, deg	4–48	4–45	4–48
rflns collcd	6926	3124	6751
indpt rflns	6352	2846	6605
rflns ($F_o \geq n\sigma(F_o)$)	3667 ($n = 5$)	1889 ($n = 5$)	4117 ($n = 5$)
T_{max}/T_{min}	0.143/0.052	0.105/0.063	1.13 (STET)
	(c) Refinement		
$R(F)$, %[a]	6.26	4.61	4.04
$R_w(F)$, %	6.26	4.78	4.67
$\Delta(\rho)_{max}$, e $Å^{-3}$	2.4	1.3	0.49
Δ/σ_{max}	0.04	0.004	0.001
GOF	1.241	1.19	0.94
N_o/N_v	9.2	8.6	8.3

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

The spectroscopic data for **14** and **15** are consistent with their indicated formulations. Both the ^1H and ^{13}C NMR spectra of highly purified samples of the $[Bu^tNH_3]^+$ salts of both anions showed the presence of Cp* and Bu^t groups

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Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Parameters ($Å^2 \times 10^3$) for $[Bu^tNH_3][Cp^*W(O)_3]\cdot{}^1/_2[Bu^tNH_3]Cl$, 15a

	x	*y*	*z*	*U*[a]
W(1)	431.4(5)	1020.0(4)	7986.9(5)	52.7(3)
W(2)	4459.5(4)	1103.9(4)	7373.1(4)	43.1(2)
Cl	2930(4)	3971(2)	9212(3)	79(2)
O(1)	911(10)	178(7)	8383(1)	113(8)
O(2)	1106(8)	1735(7)	8467(9)	88(6)
O(3)	787(10)	1040(11)	7053(10)	131(9)
O(4)	4296(7)	1820(6)	8054(6)	54(4)
O(5)	3945(10)	316(7)	7778(10)	96(7)
O(6)	3710(8)	1324(7)	6537(8)	73(5)
N(1)	2914(9)	2192(6)	8992(8)	47(5)
C(1)	3166(1)	1775(9)	9746(10)	54(6)
C(2)	3164(14)	945(8)	9569(11)	62(7)
C(3)	2456(13)	1969(10)	10298(11)	72(8)
C(4)	4177(11)	2019(11)	10068(12)	75(8)
N(2)	1991(10)	753(6)	5953(8)	47(5)
C(5)	1722(11)	1116(8)	5182(11)	49(6)
C(6)	1687(14)	1949(9)	5337(12)	77(9)
C(7)	2524(13)	922(10)	4690(12)	73(8)
C(8)	740(13)	840(11)	4857(13)	87(9)
N(3)	2330(9)	−584(7)	7636(9)	55(5)
C(10)	2833(15)	−1010(8)	8951(11)	73(8)
C(9)	2535(13)	−1274(8)	8112(12)	59(7)
C(11)	1565(15)	−1691(10)	8110(15)	105(11)
C(12)	3325(16)	−1707(10)	7781(13)	95(10)
C(21)	−1054(12)	655(13)	8582(15)	73(9)
C(22)	−1213(12)	551(10)	7781(13)	61(8)
C(23)	−1207(13)	1208(10)	7428(13)	72(8)
C(24)	−1039(12)	1748(10)	7980(18)	94(11)
C(25)	−947(14)	1382(14)	8724(16)	86(11)
C(26)	−1028(17)	10(17)	9164(18)	173(18)
C(27)	−1355(17)	−223(13)	7375(18)	147(16)
C(28)	−1387(23)	1306(19)	6513(15)	206(21)
C(29)	−957(16)	2587(12)	7868(28)	293(34)
C(30)	−735(17)	1744(19)	9488(17)	194(19)
C(31)	5980(15)	436(15)	7616(17)	83(10)
C(32)	5711(15)	400(13)	6867(17)	79(10)
C(33)	5759(11)	1127(13)	6531(11)	60(7)
C(34)	6054(13)	1587(10)	7146(16)	65(9)
C(35)	6168(12)	1171(16)	7817(13)	77(10)
C(36)	5995(18)	−268(14)	8100(20)	166(19)
C(39)	6166(17)	2434(12)	7121(22)	169(20)
C(40)	6460(18)	1428(21)	8630(17)	216(21)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Angles for $[Bu^tNH_3][Cp^*W(O)_3]\cdot{}^1/_2[Bu^tNH_3]Cl$, 15a

(a) Bond Distances (Å)

W(1)–O(1)	1.759(14)	W(2)–O(4)	1.768(11)
W(1)–O(2)	1.749(13)	W(2)–O(5)	1.752(13)
W(1)–O(3)	1.728(18)	W(2)–O(6)	1.747(12)
N(1)···O(2)	2.71(2)	N(1)···O(4)	2.70(2)
N(2)···O(3)	2.68(2)	N(2)···O(6)	2.70(2)
N(3)···O(1)	2.80(2)	N(3)···O(5)	2.75(2)

(b) Bond Angles (deg)

O(1)–W(1)–O(2)	106.0(7)	O(4)–W(2)–O(5)	103.7(6)
O(1)–W(1)–O(3)	104.6(9)	O(4)–W(2)–O(6)	106.6(5)
O(2)–W(1)–O(3)	104.1(8)	O(5)–W(2)–O(6)	106.2(6)

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Parameters ($Å^2 \times 10^3$) for $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$, 15b

	x	*y*	*z*	*U*[a]
W	2124.1(5)	4927.3(3)	6917.6(3)	49.4(2)
O(1)	3532(11)	5596(8)	6679(7)	101(5)
O(2)	656(10)	5638(7)	6819(7)	79(4)
O(3)	1714(11)	4223(6)	6026(6)	84(5)
N	1881(10)	4288(6)	4288(7)	51(4)
C(1)	2681(32)	4934(11)	8478(12)	118(12)
C(2)	3760(15)	4381(9)	8177(10)	69(6)
C(3)	3086(13)	3660(8)	7787(8)	51(5)
C(4)	1705(15)	3685(10)	7896(10)	72(6)
C(5)	1504(28)	4458(15)	8344(14)	135(12)
C(6)	3106(33)	5782(12)	8954(12)	262(22)
C(7)	5393(16)	4583(12)	8199(13)	119(9)
C(8)	3753(20)	2913(10)	7344(11)	111(9)
C(9)	611(20)	2980(13)	7537(13)	151(12)
C(10)	−10(30)	4713(19)	8558(17)	330(25)
C(11)	2552(15)	5132(8)	4057(11)	72(6)
C(12)	1946(15)	5914(8)	4493(10)	67(6)
C(13)	2456(13)	6791(8)	4238(10)	59(5)
C(14)	2074(15)	7568(8)	4787(9)	67(6)
C(15)	2689(19)	8417(9)	4521(11)	102(9)
O(4)	3122(11)	6874(6)	3654(8)	83(5)
C(16)	2600(13)	3463(8)	4044(9)	55(5)
C(17)	4060(14)	3394(9)	4581(10)	77(6)
C(18)	1604(14)	2758(8)	4334(9)	69(6)
C(19)	2581(14)	3416(9)	3067(9)	66(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table V. Selected Bond Distances and Angles for $[Bu^t(EtC\{O\}CH_2CH_2)NH_2][Cp^*W(O)_3]$, 15b

(a) Bond Distances (Å)

W–O(1)	1.759(11)	N···O(2)	2.74(1)
W–O(2)	1.751(10)	N···O(3)	2.68(1)
W–O(3)	1.728(9)		

(c) Bond Angles (deg)

O(1)–W–O(2)	104.4(5)	O(2)–W–O(3)	103.1(5)
O(1)–W–O(3)	106.4(5)		

in a 15:9 intensity ratio. The ^{17}O NMR spectra of the complexes showed only a single resonance in each case (**14**, δ 621.5; **15**, δ 490.5), indicating the presence of equivalent oxo ligands. In both cases, the chemical shifts of these oxo ligands are at the upfield end of the general range observed for other Mo=O and W=O compounds (*e.g.*, δ 701 for $[Mo(O)_3(nitrilotriacetate)]^{3-}$,[26] δ 821 for $[Mo_7(O)_{24}]^{6-}$,[27] δ 844 for **13**, δ 1025 for $Mo(O)_2(acac)_2$,[26] δ 678 for **16**, δ 736 for **7**, δ 775 for $Cp_2W{=}O$[28]). The upfield chemical shift implies a decreased π-bonding to the metal and enhanced electron density on the oxygen atoms in **14** and **15**, as compared to the compounds listed above.[25,27]

A trioxo complex with C_{3v} symmetry should show two M=O bands in the IR, corresponding to symmetric (A_1) and asymmetric (E) modes.[25] Two ν(M=O) vibrations are indeed observed in the IR (KBr) spectra of **14** (ν(Mo=O) = 864, 819 cm^{-1}) and **15** (ν(W=O) = 898, 836 cm^{-1}), as was also found for the related compound $Cp^*Re(O)_3$ (ν(Re=O) = 909, 878 cm^{-1}).[18a] However, the asymmetric bands for **14** and **15** in the IR(KBr) are each split due to the inequivalency of each oxygen in the solid state as a result of hydrogen bonding. A similar splitting was observed for the analogous $[Pr^i_2NH_2]^+$ and $[PPN]^+$ salts of **15**. Kochi and co-workers have observed a similar effect for the complex $[Et_4N][TpMo(O)_3]\cdot 2H_2O$.[19a] The ν(M=O) vibrations of **14** and **15** are significantly lower in energy than typically found for other Mo–oxo and W–oxo complexes [e.g., $[NH_4]_3[Mo(O)_3F_3]$, ν(Mo=O) = 900, 824 cm^{-1};[29] $Mo(O)_3$(diethylenetriamine), ν(Mo=O) = 911, 872 cm^{-1};[29] $[PPh_4][(\eta^1\text{-}2,4,6\text{-}C_6H_2Me_3)Mo(O)_3]$, ν(Mo=O) =

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Table VI. Atomic Coordinates (×10⁴) and Isotropic Parameters (Å² × 10³) for $[PPN][Cp^*W(O)]_3 \cdot 2H_2O$, 15c

	x	*y*	*z*	*U*(eq)[a]
W(1)	1937.5(3)	2142.2(3)	480.5(1)	33.7(1)
P(1)	–2433(2)	1861(2)	2781.1(8)	29.9(8)
P(2)	–4833(2)	1909(2)	3182.5(8)	29.9(7)
O(1)	1343(6)	891(4)	372(2)	46(2)
O(2)	708(6)	2876(5)	651(2)	52(2)
O(3)	2887(6)	2029(6)	971(2)	65(3)
O(4)	–1165(6)	896(5)	159(3)	68(3)
O(5)	–1735(7)	3038(6)	350(3)	82(3)
N	–3791(6)	1576(5)	2865(2)	34(2)
C(1)	3065(9)	3492(8)	132(3)	45(4)
C(2)	1994(9)	3402(9)	–141(3)	52(4)
C(3)	2019(9)	2404(9)	–360(3)	48(4)
C(4)	3111(8)	1923(7)	–211(3)	44(4)
C(5)	3785(9)	2607(7)	83(3)	48(4)
C(6)	3460(10)	4452(8)	407(4)	78(5)
C(7)	1021(10)	4175(9)	–205(4)	87(6)
C(8)	1082(10)	1958(11)	–679(4)	90(6)
C(9)	3514(10)	867(8)	–357(4)	73(5)
C(10)	4987(9)	2400(10)	320(4)	75(5)
C(11)	–1348(8)	3392(7)	3319(3)	43(3)
C(12)	–1102(9)	4412(8)	3443(4)	64(5)
C(13)	–1531(10)	5198(8)	3170(5)	65(5)
C(14)	–2184(10)	4976(8)	2776(4)	61(4)
C(15)	–2418(9)	3983(7)	2652(3)	47(4)
C(16)	–2010(8)	3169(6)	2928(3)	34(3)
C(21)	–1270(8)	2156(8)	1966(3)	44(3)
C(22)	–1066(9)	1939(8)	1517(3)	52(4)
C(23)	–1812(11)	1249(9)	1276(4)	66(5)
C(24)	–2726(12)	784(10)	1488(4)	77(5)
C(25)	–2941(9)	994(8)	1940(3)	51(4)
C(26)	–2195(8)	1664(7)	2185(3)	37(3)
C(31)	–194(8)	997(8)	3002(4)	55(4)
C(32)	588(9)	389(9)	3273(4)	60(4)
C(33)	158(10)	–247(7)	3601(3)	52(4)
C(34)	–1039(10)	–232(8)	3689(3)	55(4)
C(35)	–1820(8)	393(7)	3438(3)	43(3)
C(36)	–1418(8)	1015(6)	3097(3)	31(3)
C(41)	–3762(9)	2477(9)	4015(3)	57(4)
C(42)	–3256(10)	3202(11)	4306(4)	73(5)
C(43)	–3344(11)	4250(13)	4208(5)	86(6)
C(44)	–3957(10)	4576(9)	3832(4)	62(5)
C(45)	–4480(9)	3833(8)	3517(4)	50(4)
C(46)	–4395(7)	2834(8)	3611(3)	40(3)
C(51)	–7061(8)	2884(8)	3052(4)	60(4)
C(52)	–8007(10)	3282(8)	2787(5)	69(5)
C(53)	–7974(10)	3215(9)	2311(5)	74(5)
C(54)	–7031(10)	2806(8)	2113(4)	64(4)
C(55)	–6078(9)	2407(7)	2365(3)	42(3)
C(56)	–6071(8)	2461(7)	2841(3)	40(3)
C(61)	–5240(8)	–177(7)	3272(3)	38(3)
C(62)	–5767(9)	–1029(7)	3460(3)	49(4)
C(63)	–6476(8)	–964(8)	3836(3)	45(4)
C(64)	–6646(9)	1(8)	4026(3)	52(4)
C(65)	–6115(8)	879(7)	3837(3)	42(3)
C(66)	–5432(7)	787(7)	3459(3)	31(3)

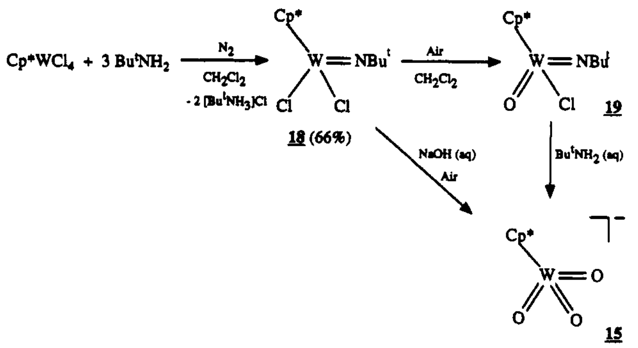
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VII. Selected Bond Distances and Angles for $[PPN][Cp^*W(O)_3] \cdot 2H_2O$, 15c

(a) Bond Distances (Å)			
W(1)–O(1)	1.771(6)	O(4)···O(1a)	2.765(9)
W(1)–O(2)	1.755(7)	O(5)···O(2)	2.813(10)
W(1)–O(3)	1.749(7)	O(5)···O(4)	2.892(10)
O(4)···O(1)	2.829(9)		
(b) Bond Angles (deg)			
O(1)–W(1)–O(2)	104.9(3)	O(2)–W(1)–O(3)	105.0(3)
O(1)–W(1)–O(3)	106.1(3)		

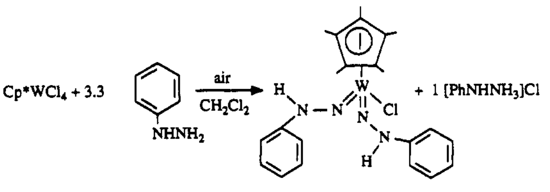
920, 894 cm^{-1};[19b] $[Et_4N][Tp^*Mo(O)_3]$, ν(Mo=O) = 924, 898 cm^{-1}].[19a] This shift to lower energy indicates weaker M=O bonds in **14** and **15** as compared to the compounds above, as also implied by the ^{17}O NMR data.

Scheme IV



Reaction of Bu^tNH_2 and $PhNHNH_2$ with Cp^*WCl_4. In view of the reactions described above using Bu^tNH_2/H_2O, it was of interest to determine how Cp^*WCl_4 would react with Bu^tNH_2 *in the absence of water and air.* Reaction did occur over the course of 3 h to form the dichloro(*tert*-butylimido)tungsten complex **18**, Scheme IV. Longer reaction times did not lead to further chloride displacement, but in moist air, complex **18** was observed to oxidize to form the oxo–imido complex **19**, and in the presence of base, both **18** and **19** give the anionic trioxo complex **15**, Scheme IV. Complex **18** was obtained as a spectroscopically characterized yellow-green solid, is analogous to the molybdenum complexes $(\eta^5\text{-}C_5H_4R)MoCl_2(NR')$ (R = H, Me; R′ = Pr^n, Bu^t, Ph) recently reported by Green *et al.*,[30a] and is similar to the tungsten complex $Cp'W(NBu^t)Cl_3$ (Cp′ = Cp, Cp*) recently described by Sundermeyer *et al.* prepared using a different synthetic approach.[17,30b] Complex **19** is similar to the known[16a] dioxo complex $Cp^*W(O)_2Cl$. The evidence presented above suggests that the reaction of Cp^*WCl_4 with Bu^tNH_2/H_2O/air to form $Cp^*W(O)_2Cl$ occurs via the intermediates **8** and **9** shown in Scheme II, and we also know that $Cp^*W(O)_2Cl$ reacts with Bu^tNH_2/H_2O to form $[Cp^*W(O)_3]^-$, eq 7. However, in light of the reactions shown in Scheme IV, we cannot rule out the possibility of complex **18** being an important intermediate in the formation of $[Cp^*W(O)_3]^-$ from Cp^*WCl_4 and Bu^tNH_2/H_2O.

Phenylhydrazine was also observed to react with Cp^*WCl_4 in air to form the bis(imido) complex **20**, eq 8.



(8)

20 (49%)

This compound was isolated as a dark purple microcrystalline solid and was spectroscopically characterized (see Experimental Section). It is analogous to the bis(imido) complexes $Cp'W(NBu^t)_2Cl$ (Cp′ = Cp, Cp*) recently described by Sundermeyer *et al.*[17,30] and the complex $Cp^*W(NAr)_2Cl$ (Ar = 2,6-$Pr^i_2C_6H_3$) as reported by Wigley.[30d]

Reaction of Cp^*WCl_4 and Cp^*MoCl_4 with H_2S. The reaction of H_2S with the Cp^*MCl_4 complexes was examined

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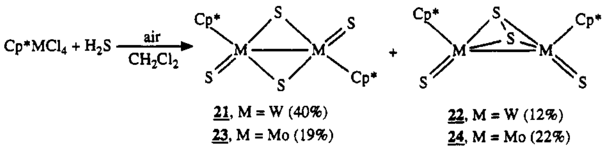
(30) (a) Green, M. L. H.; Konidaris, P. C.; Mountford, P.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1992**, 256. (b) Radius, U.; Sundermeyer, J. *Chem. Ber.* **1992**, *125*, 2183. (c) Sundermeyer, J. *Chem. Ber.* **1991**, *124*, 1977. (d) Huber, S. R.; Baldwin, T. C.; Wigley, D. E. *Organometallics* **1993**, *12*, 91.

Table VIII. Crystal, Data Collection, and Refinement Parameters for *anti*-$Cp^*_2W_2(S)_2(\mu\text{-}S)_2$, 21, and $[Et_3NH][Cp^*W(S)_3]$, 26[a]

	21	26
	(a) Crystal Parameters	
formula	$C_{20}H_{30}S_4W_2$	$C_{16}H_{31}S_3NW$
fw	766.40	517.4
cryst system	monoclinic	orthorhombic
space group	$P2_1/n$	$Pna2_1$
a, Å	7.870(3)	12.904(4)
b, Å	15.095(5)	12.078(2)
c, Å	10.045(3)	12.969(4)
β, deg	105.54(2)	
V, Å^3	1149.7(6)	2021.5(10)
Z	2	4
μ(Mo Kα), cm^{-1}	109.22	60.20
D_{calc}, g cm^{-3}	2.214	1.700
color	black	red
size, mm	0.25 × 0.25 × 0.40	0.35 × 0.35 × 0.41
	(b) Data Collection	
diffractometer	NicoletR3m	Siemens P4
data (h,k,l)	±11,+20,+14	+17,+16,±17
2θ scan limits, deg	4–55	4–58
rflns collcd	2959	5959
indpt rflns	2649	5478
rflns ($F_o \geq n\sigma(F_o)$)	2246 (n = 5)	4566 (n = 4)
T_{max}/T_{min}	0.202/0.112	0.134/0.054
	(c) Refinement	
$R(F)$, %[a]	5.71	4.14
R_w(F), %	5.45	5.18
$\Delta(\rho)_{max}$, e Å^{-3}	1.8	2.0
Δ/σ_{max}	0.001	0.003
GOF	1.69	1.29
N_o/N_v	18.9	24.0

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

in an attempt to prepare sulfido complexes similar to the oxo complexes described above, but quite different chemistry was obtained. First, it was observed that the known[31,32] binuclear complexes 21–24 formed when a stream of $H_2S(g)$ was bubbled through a CH_2Cl_2 solution of Cp^*MCl_4 for 2 min, followed by stirring in air for 30 min, eq 9. All four complexes were identified by comparison of their spectroscopic data to those reported.[31-33] In addition, complex 21 was crystallographically characterized (see Figure 4 and below). In neither reaction was any evidence obtained for the unknown compounds $Cp^*M(S)_2Cl$ which would be analogous to the complexes $Cp^*Mo(O)_2Cl$ and $Cp^*W(O)_2Cl$ formed from the similar reaction of 1 and 2 with water (see eqs 3 and 5).



(9)

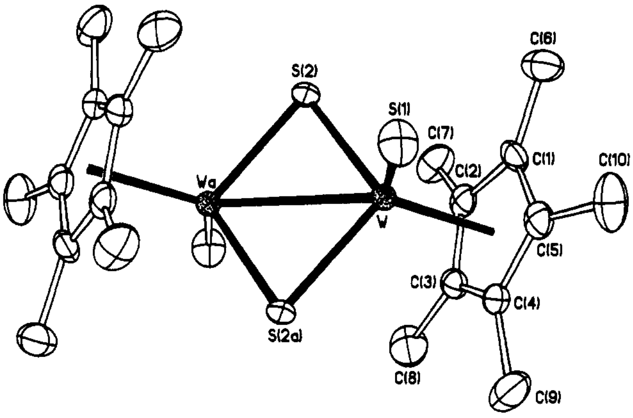


Figure 4. ORTEP drawing for $Cp^*_2W_2(S)_2(\mu\text{-}S)_2$, 21.

Table IX. Atomic Coordinates (×10^4) and Isotropic Parameters (Å^2 × 10^3) for *anti*-$Cp^*_2W_2(S)_2(\mu\text{-}S)_2$, 21

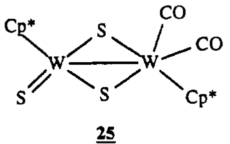
	x	y	z	U[a]
W	268.2(5)	742.5(2)	949.1(4)	22.8(2)
S(1)	1229(5)	1914(2)	174(3)	48(1)
S(2)	2227(3)	−352(2)	746(3)	31.6(8)
C(1)	1457(15)	871(7)	3372(11)	35(4)
C(2)	456(15)	41(8)	3184(10)	35(3)
C(3)	−1314(14)	249(7)	2605(10)	33(3)
C(4)	−1480(14)	1166(9)	2402(11)	38(4)
C(5)	187(16)	1562(8)	2924(11)	38(4)
C(6)	3376(18)	965(11)	4003(15)	56(5)
C(7)	1255(22)	−841(9)	3618(16)	57(6)
C(8)	−2815(21)	−440(12)	2258(16)	69(7)
C(9)	−3178(20)	1710(11)	1896(14)	63(6)
C(10)	655(24)	2532(8)	3129(15)	65(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table X. Selected Bond Distances and Angles for *anti*-$Cp^*_2W_2(S)_2(\mu\text{-}S)_2$, 21

(a) Bond Distances (Å)			
W–S(1)	2.149(3)	W–S(2)	2.306(3)
W–S(2A)	2.305	W–W(A)	2.900(1)
(b) Bond Angles (deg)			
S(1)–W–S(2)	104.4(1)	S(2)–W–W(A)	51.0(1)
S(1)–W–S(2A)	104.8(1)	W–S(2)–S(2A)	77.9(1)
S(1)–W–W(A)	113.6(1)	S(2)–W–S(2A)	102.1(1)

An ORTEP drawing of 21 is shown in Figure 4, and important crystallographic details are given in Tables VIII–X. The crystal structure of the corresponding molybdenum analogue (23) has been previously described,[31] and the two structures are similar. Complex 21 crystallizes in the $P2_1/n$ space group with 2 molecules per unit cell, and the complex has a crystallographically imposed center of symmetry between the tungsten atoms. The W_2S_2 core of the molecule is thus planar, and the terminal sulfido ligands are arranged in an *anti* configuration. The W=S (2.149(3) Å) and the W–(μ-S) bond lengths (average 2.305 Å) compare well to the average W=S (2.153 Å) and W–(μ-S) (2.324 Å) values tabulated in ref 24. The W–S–W bond angle is 77.9(1)°, similar to the 78.38(6)° Mo–S–Mo angle found in 23.[31] The W–W distance of 2.900(1) Å is consistent with the presence of a W–W single bond,[34] and overall the structural parameters are similar to those found in the related compound 25 [W=S = 2.13(1) Å; W–(μ-S) = 2.359 Å (av); W–W = 3.045(2) Å; W–S–W = 80.7(3), 80.4(3)°].[32]



25

Reaction of Cp^*MCl_4 with H_2S in the presence of Et_3N. The presence of a base significantly influences the

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(31) DuBois, M. R.; DuBois, D. L.; VanDerveer, M. C.; Haltiwanger, R. C. *Inorg. Chem.* **1981**, *20*, 3064.

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Table XI. Atomic Coordinates (×10⁴) and Isotropic Parameters (Å² × 10³) for [Et₃NH][Cp*W(S)₃], 26

	x	y	z	U^a
W(1)	2370(1)	4697(1)	2135	34(1)
S(1)	819(2)	4087(2)	2567(2)	45(1)
S(2)	2877(2)	5674(3)	3454(3)	63(1)
S(3)	2095(2)	5906(2)	899(3)	56(1)
N(1)	9482(6)	5967(7)	1407(6)	47(2)
C(1)	2677(8)	2816(8)	1496(7)	42(3)
C(2)	3182(7)	3532(7)	797(6)	38(2)
C(3)	3970(7)	4073(8)	1352(8)	42(3)
C(4)	3965(7)	3649(8)	2369(6)	42(3)
C(5)	3149(8)	2892(8)	2458(6)	41(3)
C(6)	1803(9)	2034(9)	1237(10)	67(4)
C(7)	2994(10)	3636(11)	−329(8)	66(4)
C(8)	4716(9)	4879(10)	837(10)	65(4)
C(9)	4718(9)	3912(10)	3217(9)	63(4)
C(10)	2961(11)	2255(10)	3420(9)	74(5)
C(11)	9363(9)	5708(10)	266(8)	60(4)
C(12)	9404(12)	4478(11)	78(9)	79(5)
C(13)	8594(7)	5532(9)	2026(12)	57(3)
C(14)	7593(9)	6076(13)	1817(15)	87(7)
C(15)	9696(9)	7176(9)	1551(10)	54(4)
C(16)	10064(10)	7438(9)	2643(13)	77(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table XII. Selected Bond Distances and Angles for [Et₃NH][Cp*W(S)₃], 26

(a) Bond Distances (Å)			
W(1)–S(1)	2.2069(2)	W(1)–S(3)	2.198(3)
W(1)–S(2)	2.178(4)		
(b) Bond Angles (deg)			
S(1)–W(1)–S(2)	104.7(1)	S(2)–W(1)–S(3)	105.2(1)
S(1)–W(1)–S(3)	105.1(1)		

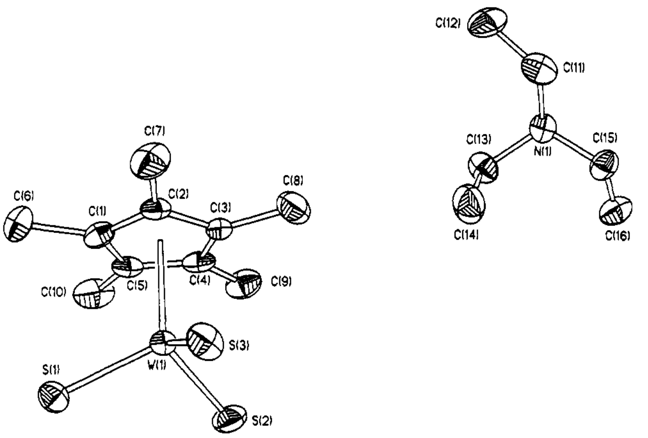
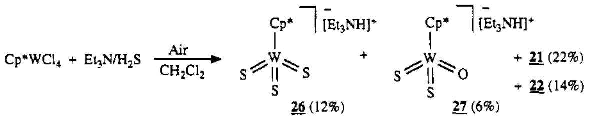


Figure 5. ORTEP drawing for [Et₃NH][Cp*W(S)₃], 26.

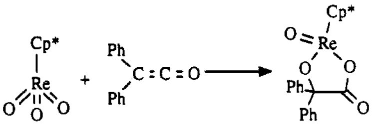
reactions of 1 and 2 with H₂S. For example, when Et₃N and H₂S were added together to Cp*MoCl₄, compound **24** did not form but the yield of **23** increased to 70%. For the reaction of Cp*WCl₄ with H₂S, the presence of Et₃N gave both **21** and **22** in yields of 22% and 14%, respectively, but also isolated in low yield were the new trisulfido and disulfido–oxo anions **26** and **27**, eq 10. The [Et₃NH]⁺ salts of these anions were separated from each other and from **21** and **22** by silica gel chromatography, although we suspect that **27** forms from **26** via hydrolysis of one of the W=S bonds during the chromatographic separation. This was indeed indicated by rechromatography of isolated **26** which resulted in a mixture of **26** and **27**. These salts were respectively obtained as orange-red and yellow-brown microcrystalline solids. Both were spectroscopically characterized, and **26** was further defined by an X-ray diffraction study (see Figure 5 and below). The IR (KBr) spectrum of **26** showed three vibrations at 471 (m), 447 (s), and 432 (s) cm⁻¹, which are in the typical ν(W=S) region (*e.g.*, *anti*-Cp*₂W₂(S)₂(μ-S)₂,[32] ν(W=S) = 481 cm⁻¹; Cp*₂W₂(S)₂(μ-S₂),[32] ν(W=S) = 486 cm⁻¹; [W(S)₃(CH₂Buᵗ)]⁻,[23] ν(W=S) = 490 cm⁻¹). The IR spectrum of **27** showed a single ν(W=O) band at 876 cm⁻¹ and two ν(W=S) bands at 459 and 425 cm⁻¹.



(10)

An ORTEP drawing of **26** is shown in Figure 5, and important crystallographic details are given in Tables VIII, XI, and XII. The [Cp*W(S)₃]⁻ anion has pseudo-C_{3v} symmetry, and there is no hydrogen bonding between the [Et₃NH]⁺ cation and the [Cp*W(S)₃]⁻ anion, in contrast to the strong hydrogen bonding observed in [BuᵗNH₃][Cp*W(O)₃] (see Figure 1). The W=S bond lengths average 2.223 Å and compare well to the average W=S bond length of 2.153 Å tabulated in ref 24. The S–W–S bond angles average 106.1°, similar to the S–Re–S bond angle of 109.9(2)° reported for (η⁵-C₅H₄Me)(Ph₂PCH₂CH₂PPh₂)Ru-S-Re(S)₃[35] and the average S–Ta–S bond angle of 104.9° found in [Cp*Ta(S)₃]²⁻.[36]

Reaction of [PPN][Cp*W(O)₃] with Phenylketene. Herrmann has shown that Cp*Re(O)₃ and [Cp*Re(O)]₂(μ-O)₂ react with diphenylketene to give products that respectively result from net [3 + 2] cycloaddition of the ketene C=C bond across a Re(O)₂ unit to yield **28**, eq 11, and [2 + 2] addition of the ketene C=O bond across a Re=O bond to form **29**, eq 12.[18j,k,o] It was thus of interest to determine if [Cp*W(O)₃]⁻ would behave similarly, and accordingly its reaction with phenylketene was examined. As illustrated in eq 13, the reaction did not follow either of the reaction paths illustrated in eqs 11 and 12, but instead a net [2 + 2] cycloaddition of the W=O bond across the ketene C=C bond occurred to form complex **30**. This species was isolated as a pale yellow microcrystalline solid which showed in the IR a characteristic W(O)₂



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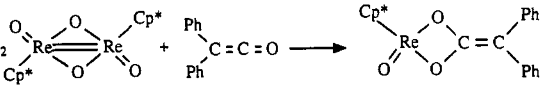
(11)



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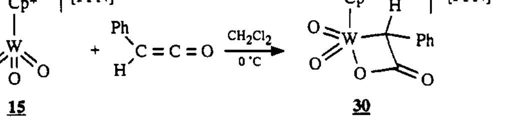
(12)



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30

(13)

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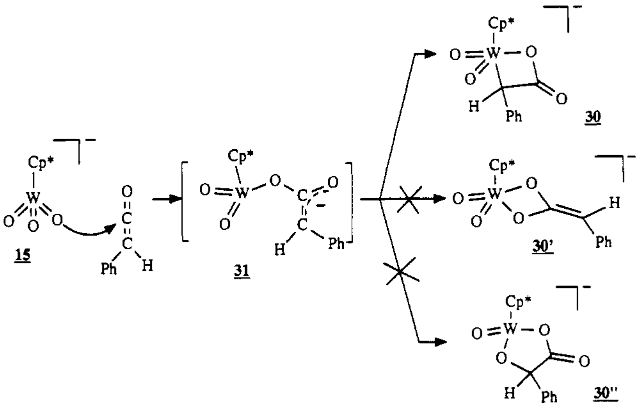
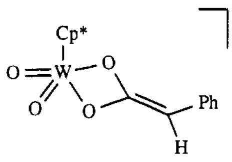
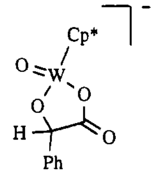
Scheme V



pattern and a strong $\nu_{C=O}$ band at 1720 cm^{-1} assigned to the carbonyl group of the metallacycle. In the ^{13}C NMR, the metallacyclic carbon resonances appeared at δ 175.4 (*C*O) and 43.0 (*C*HPh). These data argue for the proposed structure **30** rather than the alternative structures **30′** and **30″**, which could have resulted via [2 + 2] cycloaddition of the W═O moiety across the ketene C═O bond, reactions which would be analogous to Hermann's reactions shown in eqs 11 and 12. The $\nu_{C=O}$ band observed in the IR spectrum of **30** argues against the formulation **30′**, while **30″** may be ruled out by the W(O)$_2$ IR pattern. In an attempt to force elimination of CO$_2$ from **30** to form an oxo–carbene complex, the compound was heated under vacuum but no reaction was detected up to 110 °C when the solid decomposed without giving tractable products.

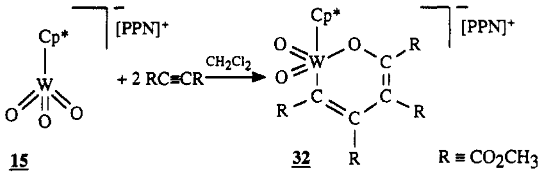

30'


30''

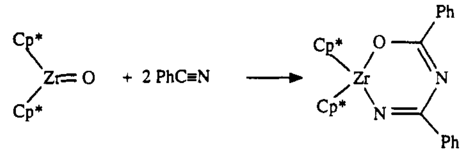
Complex **30** likely forms via the mechanism outlined in Scheme V involving nucleophilic addition of an oxo ligand of **15** to the electrophilic carbon of phenylketene to give an intermediate like **31**. As illustrated in the scheme, this intermediate could undergo ring closure to give **30**, **30′**, or **30″**, but the experimental evidence indicates that only the former occurs.

Reaction of [PPN][Cp*W(O)$_3$], 15, with MeO{O}CC≡CC{O}OMe. Compound **15** also reacted with excess MeO{O}CC≡CC{O}OMe to yield complex **32**, which forms via net [2 + 2 + 2] cycloaddition of two alkynes and one W═O unit, eq 14. A similar [2 + 2 + 2] cycloaddition of nitriles with Cp$_2$Zr═O was earlier reported by Bergman and co-workers, eq 15,[37] and Cp*ReO$_3$ has been found to react with PPh$_3$ in the presence of excess alkyne to form a related six-membered ring, eq 16.[38]

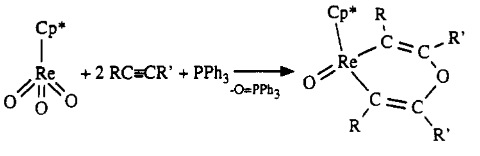
Complex **32** was isolated as a yellow-brown microcrystalline solid and has been spectroscopically characterized. Its IR spectrum showed a characteristic dioxo pattern ($\nu_{W=O}$ = 937 (m), 891 (m) cm^{-1}) and carbonyl bands for the R = CO$_2$Me substituents ($\nu_{C=O}$ = 1728 (vs), 1698 (s), 1658 (s) cm^{-1}). Resonances in the alkynyl region were noticeably absent in the ^{13}C NMR spectrum (δ 65–90), whereas resonances attributable to the alkenyl carbons were observed at δ 168.9, 148.6, 104.1, and 92.8. The ^{13}C NMR spectrum also showed four separate carbonyl resonances at δ 180.6, 171.2, 169.5, and 169.3, four distinct methyl resonances at δ 51.5, 51.0, 50.2, and 50.0, and the Cp* methyl resonance at δ 10.3. The ^{1}H NMR spectrum also showed four inequivalent methyl groups (δ 3.80, 3.69, 3.54, 3.52), consistent with the proposed structure.



(14)



(15)



(16)

Scheme VI outlines a speculative mechanism by which **32** may form. Addition of an oxo ligand of **15** to the electron-deficient alkyne could generate a carbanion intermediate like **33**. This species could be stabilized via electron delocalization onto the ester substituent and could subsequently add to another 1 equiv of alkyne to give **34**, which would yield the observed product **32** upon ring closure. Alternatively, **33** could ring close to give the oxotungstenocyclobutene complex **35**, which could yield **32** via coordination of a second equivalent of alkyne followed by insertion of the alkyne into the tungsten–carbon bond. However, we do not believe the latter route to be likely since **35** is a sterically crowded 18 e$^-$ complex and as such should not readily coordinate a second equivalent of alkyne.

Concluding Remarks

In this work we have shown that Cp*MoCl$_4$ (**1**) and Cp*WCl$_4$ (**2**) readily undergo hydrolysis of the metal–chloride bonds to yield oxo complexes, with the final product dependent upon the nature of the base employed. Hydrolysis using aqueous NaOH in air gave the complexes Cp*M(O)$_2$Cl, but the use of aqueous Bu^{t}NH$_2$ instead led to the formation of the trioxo anions [Cp*Mo(O)$_3$]$^-$ (**14**) and [Cp*W(O)$_3$]$^-$ (**15**), which are undoubtedly stabilized by hydrogen bonding to the Bu^{t}NH$_3^+$ counterion. A particularly significant finding is that aqueous Bu^{t}NH$_2$ also forms the trioxo anions from the chloro complexes Cp*M(O)$_2$Cl and from the oxo-bridged complexes [Cp*M(O)$_2$]$_2$(μ-O). We thus anticipate that the combination of Bu^{t}NH$_2$/H$_2$O should have wide utility for converting other metal halide complexes into oxo species, and such reactions are currently under study in these laboratories. As noted above, complexes **14** and **15** are closely related to the complex Cp*Re(O)$_3$ that has been extensively studied by Herrmann and co-workers.[18] Herrmann's compound has a particularly rich chemistry with

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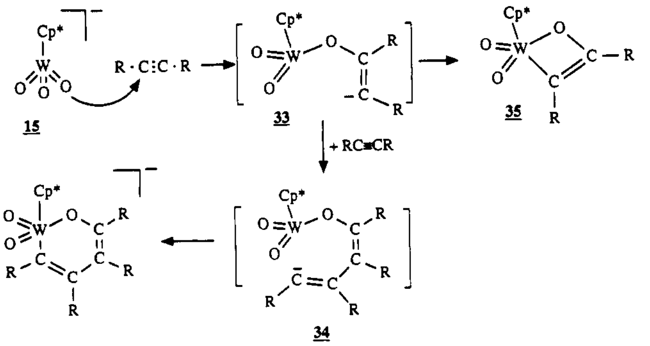
[37] Carney, M. J.; Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1992**, *11*, 761.

[38] de Boer, E. J. M.; de With, J. *J. Am. Chem. Soc.* **1986**, *108*, 8271.

Scheme VI[a]



[a] $R \equiv CO_2CH_3$.

both inorganic and organic substrates, and **14** and **15** should likewise prove profitable to study. Some differences might be expected in the reactions of $[Cp^*Mo(O)_3]^-$, $[Cp^*W(O)_3]^-$, and $Cp^*Re(O)_3$, as already illustrated above for the reactions of these latter two compounds with ketenes (eqs 11 and 13) and alkynes (compare eqs 14 and 16). A very important difference between $Cp^*Re(O)_3$ and $[Cp^*Mo(O)_3]^-$ and $[Cp^*W(O)_3]^-$, **15**, is the anionic character of the latter two compounds. As noted earlier[9] and to be described in more detail in a subsequent publication,[39] the nucleophilic character of the oxo ligands of **15** renders this complex useful for the preparation of a variety of oxo-bridged complexes via displacement of halide ligands from a second metal fragment. A major difference between $Cp^*Re(O)_3$ and $[Cp^*W(O)_3]^-$ is the ability of rhenium to undergo reduction to lower oxidation states, whereas tungsten is more resistant to reduction. This is illustrated by the facile reaction of $Cp^*Re(O)_3$ with PPh_3 to form $Ph_3P{=}O$ and $[Cp^*Re(O)]_2(\mu\text{-}O)_2$ whereas $[Cp^*W(O)_3]^-$ has been found to be inert to PPh_3.

Experimental Section

General Methods. The compounds Cp^*MCl_4 (M = Mo,[4] W[4,5]) were prepared by literature procedures. The following reagents were purchased from the indicated sources and used as received: *n*-butyllithium, 1,2,3,4,5-pentamethylcyclopentadiene, $MgSO_4$, Bu^tNH_2, NaOH, $[Bu^n_4N]OH$, [PPN]Cl, $PhNHNH_2$, Et_3N, HCl(g), H_2S(g), $PhCH_2C\{O\}Cl$, Et_3N, $MeOC\{O\}C{\equiv}CC\{O\}OMe$ (Aldrich), CH_3CO_2H (Fisher Scientific), and ^{17}O-labeled H_2O (MSD Isotopes). All manipulations were performed using standard Schlenk techniques under a N_2 atmosphere unless indicated otherwise. Solvents were dried by refluxing over Na/benzophenone ketyl (tetrahydrofuran (THF), Et_2O), CaH_2 (CH_2Cl_2, pentane, hexane, acetonitrile), and K_2CO_3 (ethyl acetate). IR spectra were recorded on either an IBM FTIR-32 spectrometer or a Perkin-Elmer 225 spectrophotometer operated in the absorbance mode. NMR spectra were obtained using a Brucker AM 300 FT NMR spectrometer, and 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.

Hydrolysis of Cp^*WCl_4 with NaOH(aq) in Air To Form $Cp^*W(O)_2Cl$, 7. Aqueous NaOH (0.66 mL of a 1.99 M solution, 1.30 mmol) was added to a CH_2Cl_2 (100 mL) solution of Cp^*WCl_4 (200 mg, 0.434 mmol) in an open beaker. The solution was stirred for 1 hour while the color of the solution turned from orange to green and then to bright yellow. The solution was dried over $MgSO_4$ to remove any residual H_2O, filtered, and concentrated under reduced pressure. Hexane was added to induce precipitation of **7** as a bright yellow powder which was washed with hexane (3 × 20 mL) and dried under vacuum (73 mg, 0.19 mmol, 44% yield).

7. IR (KBr): $\nu_{W=O} = 940$ (s), 895 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 2.23 (Cp*). ^{17}O NMR (CD_2Cl_2): δ 736.0. MS (EI): $m/z = 386$ (M^+). [Literature:[17a] IR (CS_2) $\nu_{W=O} = 945$ (s), 905 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23 (Cp*)].

Hydrolysis of Cp^*WCl_4 with NaOH(aq) in the Absence of Air To Form 8 and 9. Compound **2** (200 mg, 0.434 mmol) was dissolved in carefully degassed CH_2Cl_2 (25 mL) under a N_2 atm, and 0.22 mL of an aqueous solution of NaOH (1.99 M, 0.43 mmol) that had been degassed by bubbling N_2 for 30 min was added. The solution was stirred under N_2 for 4 h, dried by stirring over $MgSO_4$ for 15–20 min, and then filtered under reduced pressure through a pad of dried Celite. The solvent was reduced to 2 mL by evaporation under reduced pressure, and degassed hexane was added to induce precipitation of **8** along with any remaining NaCl, NaOH, **9**, and unreacted **2** as a dark green solid. The solid was then washed with hexane several times and dried at room temperature under vacuum to yield a dark green powder. Compound **9** was similarly prepared by carrying out the reaction for 6 h and using an additional 2 equivs of NaOH (0.44 mL of 1.99 M, 0.87 mmol). Compound **9** was isolated as a dark green powder containing some NaCl, NaOH, **7**, **8**, and unreacted **2**.

8. ^1H NMR (CD_2Cl_2): δ 8.9 (br, Cp*), δ 10.1 (br, O*H*). MS (EI): $m/z = 407$ ($M^+ - HCl$). IR (KBr): $\nu_{O\text{-}H} = 3447$ cm^{-1} (br, weak); $\nu_{O\text{-}D} = 2519$ cm^{-1} (br, weak) when prepared from NaOD/D_2O.

9. ^1H NMR (CD_2Cl_2): δ 16.1 (br, Cp*), δ 29.1 (br, O*H*). MS (EI): $m/z = 407$ ($M^+ - H_2O$). IR (KBr): $\nu_{O\text{-}H} = 3431$ cm^{-1} (br); $\nu_{O\text{-}D} = 2535$ cm^{-1} (br) when prepared from NaOD/D_2O. ESR (CH_2Cl_2; 25 °C, Varian E-line spectrometer at 9 GHz with a modulation frequency of 100 kHz): $g \cong 1.94$.

Hydrolysis of Cp^*MoCl_4 with NaOH(aq) in the Absence of Air To Form $Cp^*Mo(O)Cl_2$, 11. Compound **1** (200 mg, 0.54 mmol) was dissolved in carefully degassed CH_2Cl_2 (25 mL) under a N_2 atm, and 0.27 mL of an aqueous solution of NaOH (1.99 M, 0.54 mmol) that had been degassed by bubbling N_2 for 30 min was added. The solution was stirred under N_2 for 2 h, dried by stirring over $MgSO_4$ for 10–15 min, and filtered through a pad of dried Celite (under reduced pressure). The solvent was removed by evaporation under reduced pressure, and the red-brown solid was recrystallized from Et_2O and hexane (1:10) to give, after washing with hexane (3 × 10 mL), **11** as a red-brown powder (112 mg, 0.353 mmol, 66% yield).

11. Anal. Calcd for $C_{10}H_{15}OCl_2Mo$: C, 37.76; H, 4.75. Found: C, 37.63; H, 4.48. IR (KBr): $\nu_{Mo=O} = 932$ (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 12.5 (br, Cp*). MS (EI): $m/z = 319$ (M^+).

Hydrolysis of Cp^*MoCl_4 with NaOH(aq) in Air To Form $Cp^*Mo(O)_2Cl$, 12. A 2.0 M solution of NaOH was prepared using distilled H_2O. Compound **1** (200 mg, 0.537 mmol) was dissolved in acetone (100 mL) to which 0.81 mL of a 1.99 M aqueous solution of NaOH (1.61 mmol) had been added. The solution was stirred for 1.5 h, the solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2. $MgSO_4$ was added to remove residual H_2O, and the solution was filtered. After removal of the solvent under reduced pressure, the product was recrystallized from Et_2O and hexane (1:10) to give a yellow solid, which was washed (3 × 10 mL) with hexane to leave the known compound **12** in 78% yield (125 mg, 0.418 mmol).

12. IR (KBr): $\nu_{Mo=O} = 907$ (s), 876 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.09 (Cp*). MS (EI): $m/z = 300$ (M^+). ^{17}O NMR (CD_2Cl_2): δ 905.6. [Literature:[17a] IR (CS_2) $\nu_{Mo=O} = 919$ (s), 888 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (Cp*).]

Formation of $Cp^*Mo(O)_2Cl$, 12, via Hydrolysis of $Cp^*Mo(O)Cl_2$, 11, with NaOH(aq). Equimolar amounts of compound **11** (60 mg, 0.19 mmol) and NaOH(aq) (2.00 M, 0.095 mL) were stirred in acetone in a beaker for 30 min, which gave a color change from red-brown to yellow. The solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2. This solution was dried over $MgSO_4$ and filtered, and the solvent volume was reduced to 2 mL under reduced pressure. Addition

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[39] Rau, M. S.; Kretz, C. M.; Geoffroy, G. L. Manuscript in preparation.

of hexane gave precipitation of **12** as a bright yellow solid, which was washed with hexane (3 × 10 mL) and dried in vacuo (30 mg, 53%).

Formation of $Cp^*Mo(O)_2OMo(O)_2Cp^*$, 13, via Hydrolysis of $Cp^*Mo(O)Cl_2$ and $Cp^*Mo(O)_2Cl$ with Excess NaOH(aq). An excess of NaOH(aq) (2.00 M, 0.29 mL) was added to an acetone solution of $Cp^*Mo(O)Cl_2$ (60 mg, 0.19 mmol). This solution was stirred for 1 h, the solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2. This solution was dried over $MgSO_4$ and filtered. The volume was reduced to 2 mL, and hexane was added to precipitate **13** as a bright yellow solid, which was washed with hexane (3 × 10 mL) and dried under vacuum (39%). A similar reaction using $Cp^*Mo(O)_2Cl$ (47 mg, 0.16 mmol) and an excess of NaOH(aq) (1.99 M, 0.24 mL) in acetone gave **13** in 82% yield.

Formation of $[Cp^*Mo(O)_3]^-$, 14, and $[Cp^*W(O)_3]^-$, 15a, via Hydrolysis of Cp^*MoCl_4 and Cp^*WCl_4 with Bu^tNH_2/H_2O in Air. An excess Bu^tNH_2 (2.4 mL, 23 mmol) and H_2O (0.50 mL, 27 mmol) was added to a CH_2Cl_2 solution (165 mL) of Cp^*WCl_4 (1.0 g, 2.2 mmol) in a 250-mL Schlenk flask, but with no efforts made to exclude air, and the solution was allowed to stir overnight in the sealed flask. The resulting amber colored solution was dried over $MgSO_4$ and filtered through Celite to remove the precipitated $[Bu^tNH_3][Cl]$. The sovlent was reduced in vacuo to 5 mL, and 1:1 Et_2O/hexane was added to induce precipitation of $[Bu^tNH_3][Cp^*W(O)_3]$, **15a**, as a white solid. The product was washed with (3 × 40 mL) and then dried in vacuo. To further purify the sample and remove as much co-crystallized $[Bu^tNH_3][Cl]$ as possible, the solid was dissolved in CH_2Cl_2 (10 mL), the solution was filtered through Celite, and 1:1 Et_2O/hexane was added to induce crystallization. The mixed salt $[Bu^tNH_3][Cp^*W(O)_3]\cdot{}^1/_2[Bu^tNH_3][Cl]$) (**15a**) could be obtained in 80% optimized yield as a white, microcrystlline powder after such a procedure. The salt $[Bu^tNH_3][Cp^*Mo(O)_3]$, **14**, was obtained as a pale yellow solid in 68% yield by similar hydrolysis of Cp^*MoCl_4.

14. Anal. Calcd for $C_{14}H_{27}O_3NMo$: C, 47.59; H, 7.70. Found: C, 47.82; H, 7.58. IR (KBr): $\nu_{Mo=O}$ = 860 (s), 829 (s), 811 (s), 797 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.88 (s, 15H, Cp*), δ 1.18 (s, 9H, Bu^t), δ 7.19 (br, 3H, NH_3). ^{17}O NMR (CD_2Cl_2): δ 624.0. MS (FAB−): m/z = 281 (M^-).

15a. Anal. Calcd for $C_{32}H_{66}N_3O_6ClW_2$: C, 38.74; H, 6.71. Found: C, 39.08; H, 6.96. IR (KBr): $\nu_{W=O}$ = 898 (s), 836 (s), 803 (w, sh), 786 (w, sh) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.27 (Bu^t), 2.01 (Cp*), 8.1 (br, Bu^tNH_3). ^{17}O NMR (CD_2Cl_2): δ 490.5. MS (FAB−): m/z = 367 (M^-).

Metathesis of $[Bu^tNH_3][Cp^*W(O)_3]$ with [PPN]Cl To Form $[PPN][Cp^*W(O)_3]$, 15c. The salt $[Bu^tNH_3][Cp^*W(O)_3]$ (1.00 g, 2.27 mmol), obtained as above, was dissolved in CH_2Cl_2 (50 mL) to which was added $[Bu^n{}_4N]OH$ (40 wt %, aq) (1.48 mL, 2.27 mol). The solution was stirred vigorously for 10 min, $MgSO_4$ was added, and stirring was continued for several min. The solution was then filtered through Celite directly into a flask containing solid [PPN]Cl (976 mg, 1.70 mmol). This solution was stirred for 24 h and then extracted with cold water (3 × 20 mL) to remove $[Bu^n{}_4N]Cl$. The remaining solution was stirred over $MgSO_4$ and filtered through Celite. The solvent was evaporated to leave a white residue, which was dissolved in CH_3CN (1–2 mL). Ethyl acetate (50 mL) was slowly added until the solution just turned cloudy. After being stirred for 3 min, the solution was filtered to remove the white [PPN]Cl precipitate. The solution volume was then decreased to 5–10 mL under reduced pressure, and pentane was added to induce precipitation of white $[PPN][Cp^*W(O)_3]$. The latter steps were repeated if the sample was still contaminated with excess [PPN]Cl. The yield of $[PPN][Cp^*W(O)_3]$ is variable but low (40–50% maximum).

15c. Anal. Calcd for $C_{46}H_{45}P_2NO_3W$: C, 61.01; H, 5.01. Found: C, 60.45; H, 5.14. IR (KBr): $\nu_{W=O}$ = 899 (s), 839 (s), 811 (s), 799 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 1.95 (Cp*), δ 7.45–7.69 (Ph).

Formation of $[Cp^*M(O)_3]^-$ by Treatment of $Cp^*M(O)_2Cl$ and $[Cp^*M(O)_2]_2(\mu\text{-}O)$ with Aqueous Bu^tNH_2. An excess of Bu^tNH_2 (0.08 mL, 0.763 mmol) and H_2O (0.04 mL, 2.22 mmol) was added to a CH_2Cl_2 solution (25 mL) of $Cp^*W(O)_2Cl$ (140 mg, 0.362 mmol). The solution was stirred for 1 h, dried over $MgSO_4$, and filtered through a pad of Celite. The solvent volume was reduced to 2–3 mL, and hexane was added to induce precipitation of $[Bu^tNH_3][Cp^*W(O)_3]$, which was isolated in 86% yield (137 mg, 0.311 mol). The molybdenum analogue $[Bu^tNH_3]$-$[Cp^*Mo(O)_3]$ was similarly prepared in 94% yield. Similar reactions with $[Cp^*M(O)_2]_2(\mu\text{-}O)$ with aqueous Bu^tNH_2 gave the salts $[Bu^tNH_3][Cp^*W(O)_3]$ and $[Bu^tNH_3][Cp^*Mo(O)_3]$ in 82% and 85% yields, respectively.

Addition of CH_3COOH(aq) to $[Bu^tNH_3][Cp^*W(O)_3]$ To Form $[Cp^*W(O)_2]_2(\mu\text{-}O)$. A dilute solution of CH_3COOH in distilled water (2.0 M, 0.55 mL) was added to a CH_2Cl_2 solution (25 mL) of $[Bu^tNH_3][Cp^*W(O)_3]$ (220 mg, 0.500 mmol), and the solution was stirred for 1 h in air in an open beaker. Solid $MgSO_4$ was added, the solution was filtered, the solvent was removed under vacuum, and the resultant yellow solid was recrystallized from CH_2Cl_2/hexane (1:15) to leave the known compound $[Cp^*W(O)_2]_2(\mu\text{-}O)$, **16**, as a pale yellow solid in 67% yield (120 mg, 0.167 mmol). The molybdenum analog $[Cp^*Mo(O)_2]_2(\mu\text{-}O)$, **13**, was similarly prepared in 58% yield.

16. IR (KBr): $\nu_{W=O}$ = 939 (s), 890 (s), $\nu_{W\text{-}O\text{-}W}$ = 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^+). [Literature:[8] IR (CS_2) $\nu_{W=O}$ = 942 (s), 896 (s), $\nu_{W\text{-}O\text{-}W}$ = 820 (broad); ^1H NMR ($CDCl_3$) δ 2.16 (Cp*).]

13. IR (KBr): $\nu_{Mo=O}$ = 906 (s), 876 (s), $\nu_{Mo\text{-}O\text{-}Mo}$ = 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^+). [Literature:[8] IR (CS_2) $\nu_{Mo=O}$ = 912 (s), 882 (s), $\nu_{Mo\text{-}O\text{-}Mo}$ = 771 (br) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (Cp*).]

Reaction of Cp^*WCl_4 with Bu^tNH_2 To Form $Cp^*W(NBu^t)Cl_2$, 18. To a dried and degassed CH_2Cl_2 solution (25 mL) of Cp^*WCl_4 (200 mg, 0.434 mol) was added Bu^tNH_2 (0.460 mL, 4.38 mmol) that had been dried over molecular sieves and degassed by three freeze–pump–thaw cycles. The resultant green solution was stirred for 3 h, the solvent was removed under reduced pressure, and the residue was dissolved in dried and degassed hexane (10 mL). The solution was filtered to remove the salt $[Bu^tNH_3]Cl$. The hexane filtrate was cooled in a liquid nitrogen/2-propanol bath, which induced crystallization of **18** as green-yellow needles. The hexane was removed via cannula, and the needles were dried in vacuo (66% yield).

18. Anal. Calcd for $C_{14}H_{26}NCl_2W$: C, 36.31; H, 5.66. Found: C, 36.10; H, 5.64. ^1H NMR (CD_2Cl_2): δ −1.58 (br, Bu^t), 8.31 (br, Cp*). MS (EI): m/z = 462 (M^+).

Oxidation of $Cp^*W(NBu^t)Cl_2$ To Form $Cp^*W(NBu^t)(O)Cl$, 19. Compound **18** (240 mg, 0.518 mmol) was dissolved in CH_2Cl_2 in a 100-mL Schlenk flask, and the stopcock was opened to admit a small quantity of air. The solution was allowed to stir in air for 30 min, the solvent was reduced in vacuo to 3 mL, and hexane was added to precipitate complex **19** as a yellow powder. The solid was washed with hexane (3 × 10 mL) and dried under vacuum to give **19** in 66% yield (151 mg, 0.170 mmol).

19. ^1H NMR (CD_2Cl_2): δ 1.46 (s, 9H, Bu^t), 2.37 (s, 15H, Cp*). ^{13}C NMR (CD_2Cl_2): δ 12.8 ($C_5(CH_3)_5$), 28.9 ($C(CH_3)_3$), 76.5 ($C(CH_3)_3$), 126.1 ($C_5(CH_3)_5$). MS (EI): m/z = 406 (M^+).

Hydrolysis of $Cp^*W(NBu^t)Cl_2$, 18, with NaOH(aq) To Form $[Bu^tNH_3][Cp^*W(O)_3]$, 15. Excess NaOH(aq) (2.00 M, 0.70 mL) was added to a 50-mL CH_2Cl_2 solution of **18** (160 mg, 0.348 mmol) in an open beaker. The solution was stirred for 30 min, $MgSO_4$ was added, and stirring was continued for several minutes. After filtration, the solvent was reduced to 3 mL, and hexane was added to induce precipitation of **15** as a white solid (50 mg, 33%).

Hydrolysis of $Cp^*W(NBu^t)(O)Cl$, 19, with NaOH(aq) To Form $[Bu^tNH_3][Cp^*W(O)_3]$, 15. Compound **19** (180 mg, 0.408 mmol) was dissolved in 50 mL of CH_2Cl_2 in a beaker to which NaOH(aq) (2.00 M, 0.61 mL) was added. The solution was stirred for 30 min, $MgSO_4$ was added, and stirring was continued for several minutes. The solution was filtered, the solvent volume was reduced to 3 mL, and hexane was added to induce precipitation of **15**, which was isolated in 22% yield.

Reaction of Phenylhydrazine with Cp*WCl$_4$ in Air To Form Cp*W(NNHPh)$_2$Cl, 20. Phenylhydrazine (214 μL, 2.175 mmol) was added to a CH_2Cl_2 (50 mL) solution of Cp*WCl$_4$ (300 mg, 0.651 mmol) in a 100-mL Schlenk flask to which air had been admitted. This solution was stirred at 22 °C for 12 h, during which time the color changed from orange to dark purple and the salt [PhNHNH$_3$]Cl precipitated. The solution was filtered, the solvent was reduced to 5 mL under reduced pressure, and the remaining solution was chromatographed on silica gel with Et_2O as eluent to give a single dark purple band of **20**. This complex was isolated as a dark purple microcrystalline solid by evaporation of solvent and was recrystallized by dissolution in a small amount of hexane and cooling to −78 °C (180 mg, 0.319 mmol, 49%).

20. Anal. Calcd for $C_{22}H_{27}N_4ClW$: C, 46.62; H, 4.80. Found: C, 46.91; H, 4.64. ^{1}H NMR (CD_2Cl_2): δ 2.08 (s, 15H, Cp*), 7.12–7.39 (m, 10H, Ph), 9.33 (br, 2H, (NN*H*Ph). ^{13}C NMR (CD_2Cl_2): δ 9.8 ($C_5(\mathit{C}H_3)_5$), 113.5 ($\mathit{C}_5(CH_3)_5$), 121.9–149.5 (C_6H_5). MS (EI): m/z = 564 (M$^+$).

Reaction of Cp*WCl$_4$ with H$_2$S To Form *anti*-Cp*$_2$W$_2$(S)$_2$(μ-S)$_2$, 21, and Cp*$_2$W$_2$(S)$_2$(μ-S$_2$), 22. Hydrogen sulfide gas was bubbled through a CH_2Cl_2 (25 mL) solution of Cp*WCl$_4$ (150 mg, 0.326 mmol) in a 100-mL Schlenck flask for 2 min, and the solution was then allowed to stir for 30 min with no efforts made to exclude air. The solvent was removed under vacuum, and the amber residue was then chromatographed on silica gel using toluene as eluent to yield the known compound **21**[32] (40%, 50 mg, 0.065 mmol). The eluent was then changed to Et_2O, which eluted **22**[32] (12%, 15 mg, 0.020 mmol).

21. IR (KBr): $\nu_{\mathrm{W=S}}$ = 485 (s); $\nu_{\mathrm{W-S-W}}$ = 432 (w) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.24 (Cp*). MS (EI): m/z = 766 (M$^+$). [Literature:[32] IR (KBr) $\nu_{\mathrm{W=S}}$ = 481 (s), $\nu_{\mathrm{W-S-W}}$ = 430 (vw) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.23 (Cp*).]

22. IR (KBr): $\nu_{\mathrm{W=S}}$ = 490 (m), 477 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.20 (Cp*). MS (EI): m/z = 766 (M$^+$). [Literature:[32] IR (KBr): $\nu_{\mathrm{W=S}}$ = 486 (s); ^{1}H NMR ($CDCl_3$) δ 2.19 (Cp*).]

Reaction of Cp*WCl$_4$ with H$_2$S in the Presence of Et$_3$N To Form 21, 22, [Cp*W(S)$_3$]$^-$, 26, and [Cp*W(S)$_2$(O)]$^-$, 27. H_2S(g) was slowly bubbled through a CH_2Cl_2 solution (25 mL) of Cp*WCl$_4$ (500 mg, 1.09 mmol) in a 100-mL Schlenk flask for 1 min. Excess Et_3N (1.0 mL, 7.17 mmol) was then quickly added, and the solution was allowed to stir for 20 min after which time the solvent was removed under vacuum. The residue was dissolved in THF (30 mL), and the solution was filtered to remove the salt [Et$_3$NH]Cl. The solvent was reduced to a minimum, and the mixture was chromatographed on silica gel. Compounds **21** (22%) and **22** (14%) were removed from the column using neat toluene and toluene/Et_2O (70:30), respectively. The salt [Et$_3$NH][Cp*W(S)$_3$], **26**, eluted with 3:1 Et_2O/THF, and [Et$_3$NH][Cp*W(S)$_2$(O)], **27**, came off the column with neat acetone. The latter compounds were recrystallized by reducing the solvent volume and adding hexane. Compound **26** was obtained as a microcrystalline orange-red solid in 12% yield (65 mg, 0.063 mmol). Compound **27** is a yellow-brown solid and was obtained in 6% yield (30 mg, 0.030 mmol).

26. Anal. Calcd for $C_{16}H_{31}S_3NW$: C, 37.14; H, 6.04. Found: C, 37.24; H, 5.87. IR (KBr): $\nu_{\mathrm{M=S}}$ = 471 (m), 447 (s), 432 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.16 (s, 15H, Cp*), 1.41 (t, J_{HH} = 7.3 Hz, 9H, $CH_2C\mathit{H}_3$), 3.37 (q, J_{HH} = 7.3 Hz, 6H, $C\mathit{H}_2CH_3$), 9.04 (br, 1 H, N*H*). MS (FAB−): m/z = 415 (M$^-$).

27. Anal. Calcd for $C_{16}H_{31}S_2ONW$: C 38.33; H 6.23. Found: C, 38.49; H, 6.38. IR (KBr): $\nu_{\mathrm{M=S}}$ = 459 (m), 425 (m); $\nu_{\mathrm{M=O}}$ = 876 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 2.08 (s, 15H, Cp*), 1.37 (t, J_{HH} = 7.3 Hz, 9H, $CH_2C\mathit{H}_3$), 3.22 (q, J_{HH} = 7.3 Hz, 6H, $C\mathit{H}_2CH_3$), 10.17 (br, 1H, N*H*). MS (FAB−): m/z = 399 (M$^-$).

Reaction of Cp*MoCl$_4$ with H$_2$S To Form *anti*-Cp*$_2$Mo$_2$(S)$_2$(μ-S)$_2$, 23, and Cp*$_2$Mo$_2$(S)$_2$(μ-S$_2$), 24. Hydrogen sulfide was bubbled through a CH_2Cl_2 solution of Cp*MoCl$_4$ (200 mg, 0.538 mmol), and the solution was allowed to stir for several hours. The mixture was separated as described above for the reaction of H_2S with Cp*WCl$_4$ to yield the known compounds **23**[32] (19%) and **24**[32] (22%). If an excess of Et_3N (1.0 mL, 7.17 mmol) was present in the reaction mixture, **23** was obtained in 70% yield, but **24** was not produced.

23. IR (KBr): $\nu_{\mathrm{Mo=S}}$ = 490 (s); $\nu_{\mathrm{Mo-S-Mo}}$ = 448 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.04 (Cp*). MS (EI): m/z = 590 (M$^+$). [Literature:[32] IR (KBr): $\nu_{\mathrm{Mo=S}}$ = 485 (s); $\nu_{\mathrm{Mo-S-Mo}}$ = 442 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.01 (Cp*).]

24. IR (KBr): $\nu_{\mathrm{Mo=S}}$ = 488 (s); $\nu_{\mathrm{Mo-S-Mo}}$ = 444 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.05 (Cp*). MS (EI): m/z = 590 (M$^+$). [Literature:[32] IR (KBr): $\nu_{\mathrm{Mo=S}}$ = 479 (s); $\nu_{\mathrm{Mo-S-Mo}}$ = 439 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.06 (Cp*).]

Reaction of [PPN][Cp*W(O)$_3$] with Phenylketene. Phenylketene was generated in situ by following the published methods[40] and was then added dropwise (0.279 mmol) via an addition funnel over a period of 15 min into a chilled CH_2Cl_2 solution of [PPN][Cp*W(O)$_3$] (253 mg, 0.279 mmol). This solution was then stirred at 0 °C for 3 h, during which time it changed from colorless to an intense bright yellow. The solvent was removed under vacuum, and the residue was extracted into THF. Addition of pentane to this solution precipitated a pale yellow solid, which was washed with pentane (3 × 10 mL) and dried under reduced pressure to give **30** in 44% yield (125 mg, 0.122 mmol).

30. Anal. Calcd for $C_{54}H_{51}O_4P_2NW$: C, 63.35; H, 5.02. Found: C, 63.74; H, 4.83. IR (KBr): $\nu_{\mathrm{W=O}}$ = 937 (s), 891 (s) cm^{-1}, $\nu_{\mathrm{C=O}}$ = 1720 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.11 (s, 15H, Cp*), 3.56 (s, 1H, C*H*Ph), 7.03–7.25 (m, 5H, CH*Ph*), 7.36–7.65 (m, 30H, PPN-Ph). ^{13}C NMR ($CDCl_3$): δ 10.2 ($C_5(\mathit{C}H_3)_5$), 43.0 (*C*HPh), 120.1 ($\mathit{C}_5(CH_3)_5$), 125.8–127.6 (CH*Ph*), 129.3–136.5 (PPN-Ph), 175.4 (*C*O). MS (FAB−): m/z = 485 (M$^-$).

Reaction of [PPN][Cp*W(O)$_3$] with MeO{O}CC≡CC{O}OMe. A 2-fold excess of MeO{O}CC≡CC{O}OMe (38 μL, 0.309 mmol) was added to a CH_2Cl_2 solution of [PPN][Cp*W(O)$_3$] (140 mg, 0.154 mmol), and the mixture was allowed to stir for 3 h at room temperature. The solvent was removed from the resultant yellow-red solution, and the residue was extracted with THF. The THF was removed under reduced pressure, and the residue was recrystallized from THF/pentane to give a golden yellow powder, which was washed several times with pentane (10 mL) and dried under vacuum to give **31** in 71% yield (130 mg, 0.143 mmol).

31. Anal. Calcd for $C_{58}H_{57}O_{11}P_2NW$: C, 58.55; H, 4.83. Found: C, 58.75; H, 4.53. IR (KBr): $\nu_{\mathrm{W=O}}$ = 937 (w), 891 (w) cm^{-1}; ν_{CO} = 1728 (s), 1698 (m), 1658 (m). ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 15H, Cp*), 3.52 (s, 3H, Me), 3.54 (s, 3H, Me), 3.69 (s, 3H, Me), 3.80 (s, 3H, Me), 7.40–7.70 (m, 30H, PPN). ^{13}C NMR ($CDCl_3$): δ 10.3 ($C_5(\mathit{C}H_3)_5$), 50.0 (Me), 50.2 (Me), 51.0 (Me), 51.5 (Me), 92.8 (W–*C*CO$_2$Me)═C), 104.3 (W–C(CO$_2$Me)═*C*), 148.5 (W–O–C(CO$_2$Me)═*C*), 168.9 (W–O–*C*(CO$_2$Me)═C), 120.1 ($\mathit{C}_5(CH_3)_5$), 126.1–133.8 (PPN), 169.3, 169.5, 171.2, 180.7 (CO).

Crystal Structure Determinations for [Bu^{t}NH$_3$][Cp*W(O)$_3$], 15a, [Bu^t(EtC{O}CH$_2$CH$_2$)NH$_2$][Cp*W(O)$_3$], 15b, [PPN][Cp*W(O)$_3$]·2H$_2$O, 15c, *anti*-Cp*$_2$W$_2$(S)$_2$(μ-S)$_2$, 21, and [Et$_3$NH][Cp*W(S)$_3$], 26. Crystallographic data for the structures of **15a–c**, **21**, and **26** are collected in Tables I and VIII. All specimens were sealed with epoxy cement in thin-walled capillary tubes. Photographic characterization revealed 2/*m* Laue symmetry for **15a–c** and **21** and *mmm* symmetry for **26**. Systematic absences in the diffraction data were uniquely consistent with the assignment of *P*2$_1$/*n* for **15a**, **15b**, and **21** and of *P*2$_1$/*c* for **15c**, and either of the orthorhombic space groups *Pna*2$_1$ or *Pnam* for **26**. *E*-statistics initially suggested the noncentrosymmetric alternative for **26**; this choice was supported by the absence of mirror-plane symmetry and the results of refinement. The hand for **26** was established by the Rogers test (multiplier = 0.92(3)). Data were collected using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 296 K. Three standard reflections were monitored

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(40) Brady, W. T.; Shieh, C. H. *J. Heterocycl. Chem.* **1985**, *22*, 357.

every 197 data; variation in the standards was less than 2% in all cases. For **15c** no correction for absorption was required (T_{max}/T_{min}). All other data sets were empirically corrected for absorption effects.

Patterson maps were used to obtain the W-atom positions, and the structures were completed by subsequent difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were treated as idealized contributions for **15a**, **15b**, **21**, and **26** and for the methyl groups of **15c**. The hydrogen atoms of the two water molecules of **15c** were found and isotropically refined. Computations for **15a**, **15b**, and **21** used SHELXTL (version 5.1) for the Data General Eclipse S-30 and for **15c** and **26** SHELXTL-PC (version 4.2) for MS-DOS computers (G. Sheldrick, Siemens, Madison, WI).

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Supplementary Material Available: For **15a–c**, **21**, and **26**, tables of atomic coordinates, anisotropic temperature factors, complete bond lengths and bond angles, and calculated hydrogen atom positions (19 pages). Ordering information is given on any current masthead page.

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