phosphide anion. The phosphido bridge of 5 can be opened again by protonation with CH_3CO_2H to give complex 7. Note that 7 differs from 3 only by loss of a CO from Os and formation of the W–Os bond. However, complex 7 cannot be directly formed from 3 since heating the latter induces CO *and* H_2 loss to give 4.

Complex 7 can be converted back to 5 by deprotonation with MeLi. However, note that a CO ligand must migrate from one metal to the other as these reactions occur. The hydride ligand of 5 can be removed by addition of $[(CH_3)_3O]BF_4$ to yield 4, and this latter complex is also produced by heating 7 to induce H_2 loss. Complex 4 is the thermodynamic sink in this series of complexes, and once formed it does not convert into the other derivatives under any conditions that we have explored. Particularly interesting would be hydrogenation of 4 to give 7 or 3 (in the presence of CO), but neither of these reactions occur. Complex 4 was recovered unchanged when heated under 1000 psi of CO/H_2 (1:1) at 110 °C for 24 h or 1000 psi of CO at 110 °C for 24 h.

Protonation of 5 could occur at the metal or directly at phosphorus. Protonation at Os seems unlikely on two grounds. First, an Os–PPh_2H ligand is produced whereas the most reasonable consequence of Os protonation followed by (μ-PPh_2)–H coupling would be a PPh_2H ligand on W. Also, recall that the deuterium labeling study showed that the initial Os hydride ligand remains on Os and does not participate in the bridge elimination. If protonation occurred at Os, some interchange between the two hydride ligands would seem likely and the isotopic purity of the labeled product would be lost. Our data do not allow us to distinguish between protonation at W followed by hydride–phosphide coupling or direct protonation at phosphorus.

In summary, the results reported herein further demonstrate the facility with which phosphido ligands can be generated and eliminated in bimetallic complexes. These ligands are not inert and their chemistry must be considered in reactivity studies of such bridged complexes.[1-16]

Acknowledgment. We thank the National Science Foundation (Grant CHE 8201160) for their generous support of this research and in providing support to the University of Delaware for the purchase of the diffractometer, Englehard Corp. for the loan of osmium metal, and the SOHIO Corp. for fellowship support of S.R.

Registry No. 3, 96393-02-1; 3-d_1, 96393-04-3; 4, 88904-57-8; 5, 88904-60-3; 6a, 96348-81-1; 6b, 96393-03-2; 7, 96348-82-2; 7-d_1, 96348-83-3; W, 7440-33-7; Os, 7440-04-2.

Supplementary Material Available: Table of anisotropic thermal parameters, complete lists of bond angles and bond lengths, calculated hydrogen atom positions, and structure factors (35 pages). Ordering information is given on any current masthead page.

Preparation of Anionic Tungsten(VI) Alkyl Complexes Containing Oxo or Sulfido Ligands and the X-ray Structure of $[N(C_2H_5)_4]\{WO_2[OC(CH_3)_2C(CH_3)_2O][CH_2C(CH_3)_3]\}$

Irene Feinstein-Jaffe, John C. Dewan, and Richard R. Schrock*

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received November 26, 1984

$W(CCMe_3)(OCMe_3)_3$ reacts with 1 equiv of $[NEt_4][OH]$ in water to give colorless $[NEt_4][WO_3(CH_2CMe_3)]$ in high yield. $[NEt_4][WO_3(CH_2CMe_3)]$ is stable in air and is hydrolyzed only by strong acid or base. A similar reaction between $W(CSiMe_3)(OCMe_3)_3$ and $[NEt_4][OH]$ gives $[NEt_4][WO_3(CH_2SiMe_3)]$. $[NEt_4][WO_3(CH_2CMe_3)]$ reacts with 1 equiv of pinacol to give $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$. $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$ crystallizes in the space group $I2/c$ where $a = 21.294$ (3) Å, $b = 10.175$ (1) Å, $c = 22.331$ (3) Å, $\beta = 90.97$ (1)°, $V = 4837.7$ Å^3, and $Z = 8$. It is approximately a trigonal-bipyramidal molecule in which the two oxo ligands lie in the equatorial plane (W=O = 1.712 (5) and 1.720 (5) Å; O—W—O = 110.4 (3)°), the O—W—O angle is 75.6 (2)° in the pinacolato ligand, and W—C = 2.170 (6) Å and W—C_α—C_β = 123.1 (5)° in the neopentyl ligand. $[NEt_4][WO_3(CH_2CMe_3)]$ reacts with $S(SiMe_3)_2$ in acetonitrile to give $[NEt_4][WS_3(CH_2CMe_3)]$ as yellow-orange needles.

Introduction

In general d^0 transition-metal alkyl complexes are either thermally or hydrolytically unstable.[1] Some notable exceptions are members of the small family of d^0 oxo alkyl complexes. Examples are ReO_3Me,[2] $V(O)(CH_2SiMe_3)_3$,[3] and ReO_2Me_3.[4] Complexes of the type MoO_2R_2(bpy) have been prepared where R = methyl, benzyl, or neopentyl,[5] and complexes of the type $MoO_2(R)(Br)$(bpy)[6a] (R = Me, Et, etc.) hydrolyze to give species that have been formulated as $[MoO_3R]^-$ on the basis of ^1H NMR and hydrolysis studies;[6b] the $[MoO_3R]^-$ species are hydrolyzed relatively

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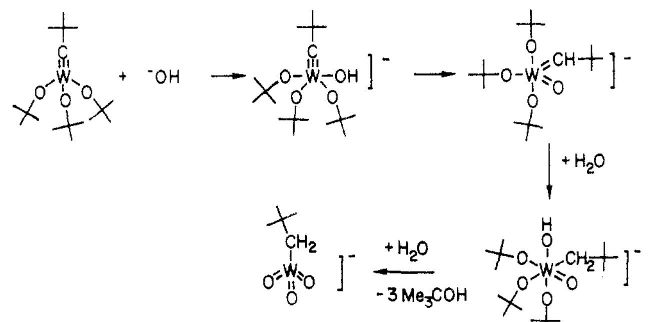
Scheme I. Proposed Mechanism of Hydrolysis of $W(CCMe_3)(OCMe_3)_3$ by Aqueous Base



slowly at pH 7 and are stable in water in the air.

Recently we discovered that tungsten neopentylidyne complexes are hydrolyzed to give oxo neopentyl complexes that are also remarkably stable to water and air.[7] One of these is $[W(O)(CH_2CMe_3)_3]_2(\mu\text{-}O)$,[8] formed upon treating $W(CCMe_3)(CH_2CMe_3)_3$[9] with water. The second is $[WO_3(CH_2CMe_3)]^-$, formed by treating $W(CCMe_3)(OCMe_3)_3$[9] with water. Here we report the full details of the preparation of $[NEt_4][WO_3(CH_2CMe_3)]$ and several related species and a crystal structure of $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$.

Results and Discussion

Preparation of $[NEt_4][WO_3R]$. $W(CCMe_3)(OCMe_3)_3$ reacts with 1 equiv of $[Et_4N][OH]$ in water to give colorless $[Et_4N][WO_3(CH_2CMe_3)]$ (1). Compound 1 is soluble and stable in water at pH 7 or in dichloromethane. It is also stable in air in the solid state or in solution for several days. Unfortunately, we were not able to find conditions that give crystals suitable for an X-ray study, even though the white, granular product was analytically and spectroscopically pure. ^1H or ^{13}C NMR spectra of 1 in either D_2O or CD_2Cl_2 clearly show the presence of the neopentyl ligand. In CD_2Cl_2 the methylene proton signal is sharp, and satellites due to ^{183}W coupling ($J_{HW} = 14$ Hz) are observed. In D_2O, however, the methylene proton signal is relatively broad. Since we have seen no evidence that the α-protons in the neopentyl ligand exchange with deuterium in D_2O over a period of many days at pH 7, we must attribute the broadening to various degrees of solvation of the anion or rapid and reversible formation of a significant amount of an actual hydrate, i.e., $[WO_2(OH)_2(CH_2CMe_3)]^-$ (cf. $[WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]^-$ later). There is no evidence (e.g., low value for J_{CH_α}) that suggests that the neopentyl ligand is distorted to any significant extent, i.e., that the $W\text{-}C_\alpha\text{-}C_\beta$ angle is larger than $\sim 125°$.[10] A similar reaction involving NaOH instead of NEt_4OH gave a water-soluble white product that presumably is a sodium salt of $[WO_3(CH_2CMe_3)]^-$, although we only noted that its ^1H NMR spectrum in D_2O was identical with that of $[NEt_4][WO_3(CH_2CMe_3)]$.

The proposed mechanism of hydrolysis at high pH is shown in Scheme I. We have observed before that neopentylidyne complexes can be transformed into oxo neopentylidene complexes of the type $W(O)(CHMe_3)L_2Cl_2$ (L $= PMe_3$ or PEt_3)[11] upon treatment with 1 equiv of water. $[W(O)(CHCMe_3)(OCMe_3)_3]^-$ should be susceptible to further attack by water, either to give $[W(O)(CH_2CMe_3)(OH)(OCMe_3)_3]^-$ or, equally likely, some anionic alkylidene or alkyl complex containing at least one more oxo ligand in place of two *tert*-butoxide ligands, e.g., $[WO_2(CHCMe_3)(OCMe_3)]^-$. Formation of $[WO_3(CHCMe_3)]^{2-}$, however, seems relatively unlikely in view of the fact that we have never observed even H/D exchange into the methylene group in $[WO_3(CH_2CMe_3)]^-$ in D_2O at high pH.

An analogous reaction between $W(CSiMe_3)(OCMe_3)_3$ and aqueous $[NEt_4][OH]$ gave $[NEt_4][WO_3(CH_2SiMe_3)]$ (2) in ~60% yield. The physical properties of 2 are essentially identical with those of 1.

So far we have not succeeded in preparing other examples of $[WO_3R]^-$ complexes. We noted in the preliminary communication[7] that hydrolysis of $W(CPh)(OCMe_3)_3$ yielded $[NEt_4][WO_3(CH_2Ph)]$. Unfortunately, we still have obtained only a very low yield (~5%) of a pale yellow oily residue whose ^1H NMR spectrum shows a peak at ~4.6 ppm in CD_2Cl_2 (in addition to NEt_4 peaks), *consistent* with a species of the type $[NEt_4][WO_3(CH_2Ph)]$, but hardly definitive. Unfortunately, we also have not been able to obtain an FD mass spectrum that confirms the presence of such a species. We speculate that since benzyl complexes are among the most stable and readily prepared d^0 transition-metal alkyl complexes, there may be an important steric factor involved in formation of the $[WO_3R]^-$ species, perhaps prevention of adverse intermolecular reactions or slowing down of hydrolysis. However, we saw no indication that hydrolysis of $W(C\text{-}2,6\text{-}C_6H_3Me_2)(OCMe_3)_3$ was any more successful than hydrolysis of $W(CPh)(OCMe_3)_3$.

In view of the above problems, we did not expect to be able to form $[WO_3R]^-$ complexes in which R contains β-hydrogens. Addition of aqueous $[NEt_4][OH]$ to $W(CEt)(OCMe_3)_3$ yielded a dark brown mixture from which no $[NEt_4][WO_3(CH_2CH_2CH_3)]$ could be extracted. Hydrolysis of $W(CCH_2CMe_3)(OCMe_3)_3$ likewise failed to produce $[NEt_4][WO_3(CH_2CH_2CMe_3)]$. Although it is unclear at this point that such $[WO_3R]^-$ species would be stable toward decomposition processes involving β-hydrogen atoms or toward relatively rapid further hydrolysis, species of the type $[MoO_3R]^-$ (R = Me, Et, Pr, etc.) *have* been observed in solution.[6b] Therefore at this juncture we suspect that a molecule such as $[WO_3Et]_-$ may be stable, but it cannot be prepared by the double protonation of an alkylidyne ligand in $W(CR)(OCMe_3)_3$ complexes.

Since an amide ligand is likely to behave like an alkoxide in a hydrolysis reaction, we were curious as to whether hydrolysis of $W(CCMe_3)(NR_2)_3$[9] would yield $[WO_3(CH_2CMe_3)]^-$. Some $[NEt_4][WO_3(CH_2CMe_3)]$ could be observed by ^1H NMR upon hydrolysis of $W(CCMe_3)[N(CHMe_2)_2]_3$ by aqueous $[NEt_4][OH]$, but the yield was clearly relatively poor (50% at best) and other products were present that contained a *tert*-butyl group. As expected, the hydrolysis of $W(CEt)(NMe_2)_3$ was decidedly unsuccessful.

Hydrolysis of $[NEt_4][WO_3(CH_2CMe_3)]$ (1) by Base. Hydrolysis of 1 in D_2O containing at least 5 equiv of NaOD (in order to preserve pH) was studied by ^1H NMR using dioxane as an internal standard. Only 1 mg of 1 was employed in order to slow the rate of hydrolysis and to allow us to adjust the pH to lower values. Under these condition (~1 mL total volume D_2O) we found that 1 was not hy-

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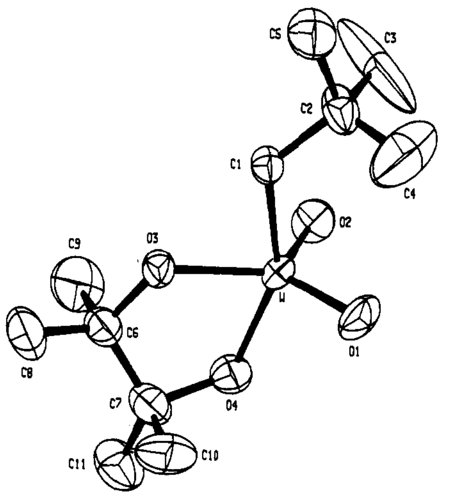

Figure 1. Geometry of $[WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]^-$ showing the atom labeling scheme. Thermal ellipsoids are depicted at the 30% probability level. Hydrogen atoms have been omitted for clarity.

drolyzed at a significant rate until a pH of ~14 was reached, where $t_{1/2}$ for hydrolysis at ~25 °C was ~20 min. A plot of the data showed that the rate of disappearance of 1 was first order. However, the data were not judged sufficiently accurate to determine rate constants, and therefore the dependence upon pH; we can only assume for now that the rate of hydrolysis probably depends linearly upon OH^- concentration. A signal for the hydrolysis product was coincident with that for neopentane and decayed with time. Moreover, hydrolysis of 1 with excess NaOH in water to give 0.9 (1) equiv of neopentane (by GLC). We presume that the metal-containing product of hydrolysis in base is $[WO_4]^{2-}$, although this has not been confirmed. It should be noted that $[MoO_3(CH_2CMe_3)]^-$ (prepared in situ) is also hydrolyzed (pH 11, 70 °C, $t_{1/2}$ = 282 min) by base to give neopentane and $[MoO_4]^{2-}$.[6b]

Compound 1 is also hydrolyzed by aqueous HCl, but this process was not studied in any detail. We know that 1 is stable in aqueous HCl down to pH ~1 and that a white solid precipitates as hydrolysis proceeds. We would expect the products of hydrolysis ultimately to be neopentane and tungstic acid. Hydrolysis of $MoO_2(Br)(CH_2CMe_3)(bpy)$ in aqueous acid was observed to give neopentane and an insoluble white solid.[6b]

Preparation and X-ray Structure of $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$. $[NEt_4][WO_3(CH_2CMe_3)]$ reacts with 1 equiv of pinacol in toluene to give $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$ (3) quantitatively. Compound 3 does not hydrolyze completely back to 1 in D_2O; a mixture of 1, 3, and free pinacol is observed by ^1H NMR. Interestingly, 3 is soluble in toluene and benzene. It can be recrystallized from toluene as clear rods which proved suitable for an X-ray study.

$[WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]^-$ is only very approximately a trigonal-bipyramidal molecule (Figure 1). Although O(1), O(2), and O(3) lie in a plane, the C(1)–W–O(4) angle is only ~150° (Table III). The W–O(1) and W–O(2) bonds are both short (1.712 (5) and 1.720 (5) Å, respectively), and the angle between them is 110.4(3)°. Overall this geometry is what one would expect for a five-coordinate d^0 tungsten species containing two strongly π-bonded ligands. In $W(O)(CHCMe_3)Cl_2(PEt_3)$,[12] for example, the oxo (W–O = 1.661 (11) Å) and neopentylidene (W–C = 1.882 (14) Å) ligands lie in the equatorial plane, the angle between them is 106.7 (6)°, and the P–W–Cl_{ax} angle is 163.4°. One could propose that the O(4)–W–C(1) angle in $[WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]^-$ (75.6 (2)°) is as small as it is as a result of the pinacolate ligand being unable to span ligand sites 90° apart (but see later). The pinacolate ligand is twisted, as one would expect, with unexceptional distances and angles within the WO_2C_2 ring system (W–O(3) = 2.000 (4) Å and W–O(4) = 1.945 (5) Å; W–O(3)–C(6) = 118.2 (4)°, and W–O(4)–C(7) = 119.9 (4)°).

The neopentyl ligand is bonded to the metal in an unexceptional manner with W–C(1) = 2.170 (6) Å and W–C(1)–C(2) = 123.1 (5)°. These structural results corroborate the spectroscopic and chemical results for $[WO_3(CH_2CMe_3)]^-$ which suggested that the neopentyl ligand is not inclined to lose an α-proton to give $[WO_3(CHCMe_3)]^{2-}$, a plausible relative of $[WO_4]^{2-}$. We now feel that an α-proton is lost to the metal, to a leaving group such as an alkyl ligand, or possibly directly to an external base, only when relatively few π-bonding ligands (either covalently or datively π-bonding) are already present. In tungsten chemistry the currently most extreme example of α-hydrogen abstraction in the presence of a π-donor ligand is the decomposition of $W(NPh)(CH_2SiMe_3)_4$ to $W(NPh)(CHSiMe_3)(CH_2SiMe_3)_2$.[13] Because of the π-donating ability of the oxo ligand and the overall dianionic charge, the neopentylidene α-carbon atom in hypothetical $[WO_3(CHCMe_3)]^{2-}$ probably would be extremely basic.

It is interesting to compare the structure of $[WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$ with three structures of molecules of the type $MoO_2R_2(bpy)$ where R = Me,[5a] CH_2Ph,[5c] or CH_2CMe_3[5b] (Table IV). The values for W–C(1) (2.170 (6) Å), W–O (1.712 and 1.720 Å), O(1)–W–O(2) (110.4 (3)°), O(3)–W–O(4) (75.6 (2)°), O(4)–W–C(1) (150.3 (2)°), and W–C(1)–C(2) (123.1 (5) Å) all are similar to the analogous bond distances and angles observed in the six-coordinate Mo species. In particular note that the pinacolate ligand fits the axial/equatorial coordination sites rather well (N–Mo–R = 74–81° in $MoO_2R_2(bpy)$); i.e., contrary to what we postulated above, the structure of $[WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]^-$ probably is *not* determined to any significant extent by the relatively small bite of the pinacolate ligand. The difference between the W–C(1) bond length and the Mo–alkyl bond lengths is not especially significant; it could be ascribed simply to systematic differences in bond lengths in a five-coordinate vs. a six-coordinate complex (cf. the shorter metal ligands bond lengths in $W(O)(CHCMe_3)(PEt_3)Cl_2$[12] vs. those in $W(O)(CHCMe_3)(PMe_3)_2Cl_2$.[14]

Preparation of $[NEt_4][WS_3(CH_2CMe_3)]$. The successful reaction between oxo complexes and $S(SiMe_3)_2$ to give analogous sulfido complexes[15] provided us with the opportunity of preparing $[WS_3(CH_2CMe_3)]^-$ from $[WO_3(CH_2CMe_3)]^-$. This reaction proceeds rapidly and smoothly in acetonitrile at 25 °C using excess $S(SiMe_3)_2$ to give what we propose is $[NEt_4][WS_3(CH_2CMe_3)]$ (4) as fine, yellow-orange needles. The ^1H NMR spectrum of 4 in CD_2Cl_2 differs from that of 1 only in the shift of the resonance for the methylene protons at 2.10 ppm (vs. 1.68 ppm in 1). In the ^{13}C NMR spectrum the main difference is the shift of the methylene carbon atom resonance of 74.09 ppm in 4 from 54.67 ppm in 1. The strongest peak in the IR spectrum of 4 is found at 490 cm^{-1}. The positive mode FD mass spectrum of 4 showed a $[NEt_4]_2[WS_3(CH_2CMe_3)]^+$ ion at *m/e* 611. All of these data suggest that the yellow-orange product is the sulfido analogue of $[NEt_4]$-

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$[WO_3(CH_2CMe_3)]$. An alternate formulation such as $[NEt_4][WS_2(SCH_2CMe_3)]$ (W(IV)) does not seem reasonable in view of the unsaturated nature of the metal center in what is apparently a monometallic complex. A formulation such as $[NEt_4][W(S)(S_2)(CH_2CMe_3)]$ (S_2^{2-} bound to W(IV)) is not as easily excluded, although this species also would be essentially three-coordinate about the metal. We doubt that either of the above W(IV) complexes would be at all stable in water or air. Therefore, in spite of the fact that an X-ray structural study on the NEt_4^+ derivative could not be undertaken, we feel confident our proposal that the $[NEt_4][WS_3(CH_2CMe_3)]$ species contains W(VI) is sound.

When 4 is dissolved in D_2O, a yellow solution is obtained in which two broad signals are observed in the ^1H NMR spectrum in the region where methylene proton resonances are found for 1 in D_2O. The one at ~1.7 ppm in a relative amount of ~30% we attribute to the neopentyl methylene protons in 4. The signal at 1.9–2.0 ppm most likely should be ascribed to the methylene protons in 1 (found at ~1.9 ppm in pure 1 in D_2O). The NMR spectrum does not change appreciably over a period of 24 h. Therefore it appears that 4 is hydrolyzed incompletely to 1 in water. Since the final ratio of 4:1 varies from sample to sample (20–40% 4), we suspect that 1 can also back react with H_2S to give 4. We should point out that we cannot be certain that no significant amounts of the expected intermediates $[WS_2(O)(CH_2CMe_3)]^-$ and $[W(S)O_2(CH_2CMe_3)]^-$, or some W(SH) or W(OH) species, are present, but we have no reason to suspect at this time that they might be. Further investigations into the chemistry of $[NEt_4][WS_3(CH_2CMe_3)]$ should resolve this question.

Conclusion

The results reported here demonstrate that d^0 tungsten oxo neopentyl and trimethylsilylmethyl complexes of the type $[WO_3R]^-$ are remarkably stable. We cannot conclude yet that similar species where R contains β-protons are inherently unstable, only that we cannot prepare them by the route we have discovered, i.e., double protonation of an α-carbon atom in complexes of the type $W(CR')(OCMe_3)_3$. The fact that two oxo ligands can be replaced by a pinacolato ligand or that all three oxo ligands can be replaced by sulfido ligands further confirms the relative inertness of the alkyl ligand and at the same time suggests that other anionic W(VI) neopentyl complexes containing ligands that commonly are found in W(VI) complexes (e.g., imido) might be stable.

Experimental Section

$W(CCMe_3)(OCMe_3)_3$ was made from $[NEt_4][W(CCMe_3)Cl_4]$[9] by the addition of 3 equiv of $LiOCMe_3$, or, alternatively, from the metathesis reaction of $W_2(OCMe_3)_6$ with *tert*-butyl methylacetylene.[16,17] $W(CCMe_3)(OCMe_3)_3$ was stored under nitrogen until the hydrolysis step; $[NEt_4][WO_3(CH_2CMe_3)]$ may be handled in air. $(Me_3Si)_2S$ was purchased from Petrarch Systems, Inc. $W(CCH_2CMe_3)(OCMe_3)_3$ was prepared by the reaction of $W_2(OCMe_3)_6$ with $N{\equiv}CCH_2CMe_3$[16] followed by sublimation at ~60 °C and <0.1 μm. $W(C\text{-}2,6\text{-}C_6H_3Me_2)(OCMe_3)_3$ was prepared similarly from $W_2(OCMe_3)_6$ and $2,6\text{-}C_6H_3Me_2CN$ and purified by sublimation at ~50 °C and <0.1 μm. $W(CEt)(NMe_2)_3$ was prepared by treating $W(CEt)(OCMe_3)_3$ with 3 equiv of $LiNMe_2$ at −60 °C in ether. It was separated from $LiOCMe_3$ by two sublimations at ~50 °C and <0.1 μm (M.L. Listemann, unpublished results). $W(CSiMe_3)(OCMe_3)_3$ was prepared by adding bis(trimethylsilyl)acetylene to a solution of $W(CMe)(OCMe_3)_3$ prepared in situ from $W_2(OCMe_3)_6$ and 2-butyne in pentane followed by a 40 °C sublimation at <0.1 μm.[17] Coupling constants are quoted in hertz, and values for J_{CH} in ^{13}C NMR spectra are in the range 125–130 Hz, unless otherwise noted. The FD and FAB mass spectra showed the expected isotope envelope; only the peak for the compound containing ^{184}W is quoted.

Preparations. $[N(CH_2CH_3)_4][WO_3(CH_2CMe_3)]$ (1). $W(CCMe_3)(OCMe_3)_3$ (1.0 g, 2.1 mmol) was dissolved in ~30 mL of dry tetrahydrofuran under N_2 in a septum-stoppered 100-mL flask. A solution of NEt_4OH (1.45 mL of 1.45 M solution in water, 2.1 mmol) in ~10 mL of water was thoroughly degassed in a stream of dry nitrogen and then rapidly added to the flask with a syringe. The reaction mixture turned brown briefly but then steadily lightened over 10 min to give a colorless solution. After ~2 h the water was removed in vacuo, the dry, white residue was extracted with dichloromethane, and the extract was filtered. Removal of the dichloromethane in vacuo left 0.75 g (82%) of analytically pure $[NEt_4][WO_3(CH_2CMe_3)]$: ^1H NMR (CD_2Cl_2) δ 3.35 (q, 8, $NC\mathit{H}_2CH_3$), 1.68 (s, 2, J_{HW} = 14 Hz, $C\mathit{H}_2CMe_3$), 1.34 (t, 12, ($NCH_2C\mathit{H}_3$), 1.02 (s, 9, CMe_3); ^1H NMR (D_2O) δ 3.06 (q, 8, $NC\mathit{H}_2CH_3$), 1.93 (br s, 2, $C\mathit{H}_2CMe_3$)8 1.07 (tt, 12, $NCH_2C\mathit{H}_3$), 0.86 (s, 9, CMe_3); ^{13}C NMR (CD_2Cl_2) δ 54.67 (t, $\mathit{C}H_2CMe_3$), 52.84 (t, $N\mathit{C}H_2CH_3$), 33.60 (q, $C\mathit{Me}_3$), 31.68 (s, $\mathit{C}Me_3$), 7.82 (q, $NCH_2\mathit{C}H_3$); IR (Nujol, cm^{-1}) 980 (vs), 925 (vs), 800 (s), 690 (vs), 655 (vs). The $\{[NEt_4]_2[WO_3(CH_2CMe_3)]\}^+$ ion at *m/e* 563 and $\{[WO_3(CH_2CMe_3)]\}^-$ ion at *m/e* 303 were observed in the positive mode FD mass spectrum and negative mode of FAB mass spectrum, respectively. Anal. Calcd for $WC_{13}H_{31}NO_3$: C, 36.04; H, 7.21. Found: C, 36.41; H, 7.33.

$[NEt_4][WO_3(CH_2SiMe_3)]$ (2). A reaction essentially identical with that described above employing $W(CSiMe_3)(OCMe_3)_3$ (0.275 g, 0.56 mmol), ~20 mL of tetrahydrofuran, and NEt_4OH (0.39 mL of 1.45 N in water, 0.56 mmol) in ~10 mL of water yielded 0.155 g (62%) of pure $[NEt_4][WO_3(CH_2SiMe_3)]$: ^1H NMR (CD_2Cl_2) δ 3.34 (q, 8, $NC\mathit{H}_2CH_3$), 1.31 (t, 12, $CH_2C\mathit{H}_3$), 0.55 (s, 2, J_{HW} = 15 Hz, $C\mathit{H}_2SiMe_3$), 0.04 (s, 9, $CH_2Si\mathit{Me}_3$); ^{13}C NMR (CD_2Cl_2) δ 53.12 (t, $N\mathit{C}H_2CH_3$), 23.85 (t, $\mathit{C}H_2SiMe_3$), 7.98 (q, $NCH_2\mathit{C}H_3$), 1.22 (q, $CH_2Si\mathit{Me}_3$). The $\{[NEt_4]_2[WO_3(CH_2SiMe_3)]^+\}$ ion (*m/e* 579) was observed in positive mode FD and positive mode FAB mass spectra. Anal. Calcd for $WC_{12}H_{31}NO_3Si$: C, 32.06; H, 6.94. Found: C, 32.25; H, 7.20.

$[NEt_4][WO_2(OCMe_2CMe_2O)Np]$ (3). Pinacol (0.038 g, 0.32 mmol) in dichloromethane (~5 mL) was quickly added to $[NEt_4][WO_3(CH_2CMe_3)]$ (0.14 g, 0.32 mmol) dissolved in dichloromethane (~15 mL). After several hours the solvent was removed in vacuo to give granular, white $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$ quantitatively. This species is soluble in benzene or toluene, from which it may be recrystallized as clear rods: ^1H NMR (C_6D_6) δ 2.76 (q, 8, $N\mathit{C}H_2CH_3$), 2.14 (s, 2, J_{HW} = 12 Hz, $C\mathit{H}_2CMe_3$), 1.52 (s, 9, CMe_3), 1.48 (s, 12, $OCMe_2CMe_2O$), 0.83 (t, 12, $NCH_2C\mathit{H}_3$); ^{13}C NMR (C_6D_6) δ 92.73 (t, $\mathit{C}H_2CMe_3$), 77.30 (s, $O\mathit{C}Me_2\mathit{C}Me_2O$), 59.34 (t, $N\mathit{C}H_2CH_3$), 41.28 (q, $OC\mathit{Me}_2C\mathit{Me}_2O$), 40.61 (s, $\mathit{C}Me_3$), 34.14 (q, $CH_2C\mathit{Me}_3$), 14.28 (q, $NCH_2\mathit{C}H_3$); IR (Nujol, cm^{-1}) 930 (vs), 885 (vs), 785 (s), 695 (s), 595 (s). The $\{[NEt_4]_2[WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]\}^+$ ion (*m/e* 663) was observed in the positive mode FAB mass spectrum. Anal. Calcd for $WC_{19}H_{43}NO_4$: C, 42.76; H, 8.12. Found: C, 43.08; H, 8.20.

$[NEt_4][WS_3(CH_2CMe_3)]$ (4). $S(SiMe_3)_2$ (2.88 mL, 14.50 mmol) was added all at once via syringe to $[NEt_4][WO_3(CH_2CMe_3)]$ (0.30 g, 0.69 mmol) dissolved in acetonitrile (~50 mL). The solution immediately turned yellow-orange. After 16 h the solvent was removed in vacuo and the crude product was washed with pentane (~50 mL). The product can be recrystallized as fine yellow-orange needles by dissolving it in dichloromethane, adding ether, and cooling the mixture to −30 °C: ^1H NMR (CD_2Cl_2) δ 3.30 (q, 8, $NC\mathit{H}_2CH_3$), 2.1 (s, 2, J_{HW} = 11 Hz, $C\mathit{H}_2CMe_3$), 1.36 (t, 12, $NCH_2C\mathit{H}_3$), 1.00 (s, 9, CMe_3); ^{13}C NMR (CD_2Cl_2) δ 74.09 (t, CH_2CMe_3), 53.36 (t, NCH_2CH_3), 33.92 (q, $C\mathit{Me}_3$), 8.07 (q, NCH_2CH_3); IR (Nujol, cm^{-1}) 490 (s). The $\{[NEt_4]_2[WS_3(CH_2CMe_3]\}^+$ ion (*m/e* 611) was observed in the positive mode FD mass spectrum. Anal. Calcd for $WC_{13}H_{31}NS_3$: C, 32.41; H, 6.49. Found: C, 32.57; H, 6.50.

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Table I. Crystal Data for $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$

a = 21.294 (3) Å
b = 10.175 (1) Å
c = 22.331 (3) Å
β = 90.97 (1)°
V = 4837.7Å^3
space group = $I2/c^a$
Z = 8
mol wt = 533.17 g
ρ(calcd) = 1.464 g cm^{-3}
μ = 45.6 cm$^{-1\,b}$

[a] A nonstandard setting of $C2/c$ where the general equivalent positions are (x,y,z), $(x, -y, {}^1/_2 + z)$, $(-x, -y, -z)$, and $(-x, y, {}^1/_2 - z)$ plus the four positions obtained by adding $({}^1/_2, {}^1/_2, {}^1/_2)$. [b] An empirical absorption correction was applied based on the ψ scans of three reflections with $\chi \approx 90°$.

Table II. Final Positional Parameters for the Non-Hydrogen Atoms of $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]^{a,b}$

atom	x	y	z
W	0.123340 (10)	0.15427 (3)	0.387320 (10)
O(1)	0.1139 (3)	0.0903 (7)	0.4575 (2)
O(2)	0.0979 (2)	0.0442 (5)	0.3338 (2)
O(3)	0.1619 (2)	0.3262 (4)	0.3648 (3)
O(4)	0.0536 (2)	0.2777 (6)	0.3871 (3)
C(1)	0.2234 (3)	0.1149 (6)	0.3838 (3)
C(2)	0.2517 (4)	−0.0172 (8)	0.3985 (5)
C(3)	0.2283 (7)	−0.1210 (10)	0.3559 (11)
C(4)	0.2415 (7)	−0.0597 (19)	0.4594 (8)
C(5)	0.3234 (4)	−0.0139 (10)	0.3901 (6)
C(6)	0.1213 (4)	0.4324 (7)	0.3507 (5)
C(7)	0.0659 (4)	0.4188 (8)	0.3873 (5)
C(8)	0.1583 (5)	0.5575 (9)	0.3564 (6)
C(9)	0.1032 (6)	0.4136 (12)	0.2811 (5)
C(10)	0.0796 (5)	0.4552 (11)	0.4522 (4)
C(11)	0.0042 (4)	0.4856 (9)	0.3652 (5)
N	0.0988 (3)	−0.0070 (5)	0.1402 (2)
C(12)	0.0660 (5)	0.1135 (9)	0.1208 (4)
C(13)	0.0947 (5)	0.1706 (8)	0.0597 (4)
C(14)	0.0866 (6)	−0.1161 (10)	0.0930 (5)
C(15)	0.0213 (5)	−0.1363 (10)	0.0766 (5)
C(16)	0.0651 (4)	−0.0493 (10)	0.1973 (4)
C(17)	0.0918 (6)	−0.1832 (9)	0.2212 (5)
C(18)	0.1661 (4)	−0.0003 (12)	0.1495 (5)
C(19)	0.1844 (5)	0.1166 (11)	0.1985 (5)

[a] Atoms of the anion are labeled as indicated in Figure 1. Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter. [b] Atoms of the cation are labbeled N and C(12)–C(19).

Base Hydrolysis of 1. $[NEt_4][WO_3(CH_2CMe_3)]$ (1 mg) was dissolved in a solution of NaOD/D_2O (1 mL, 0.7 N) in an NMR tube and kept at 0 °C. Dioxane (0.5 μL) was added as an internal standard. The sample was warmed to 25 °C and the hydrolysis reaction followed by ^1H NMR.

Crystallography. A suitable sized colorless crystalline fragment of $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]$ was cut from a larger crystalline mass. Data were collected at room temperature on a CAD4F-11 diffractometer using Mo Kα radiation. The data collection and reduction procedures, as well as the refinement procedures, used in the laboratory have been described in detail elsewhere.[18] A total of 7043 reflections $(+h,+k,\pm l)$ were collected in the range $3° < 2\theta < 60°$ with the 4207 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (231 variables) using SHELX-76. Final $R_1 = 0.040$ and $R_2 = 0.050$.

Table III. Selected Interatomic Distance (Å) and Angles (deg) for the Anion of $[NEt_4][WO_2(OCMe_2CMe_2O)(CH_2CMe_3)]^a$

Bond Distances			
W–O(1)	1.712 (5)	W–C(1)	2.170 (6)
W–O(2)	1.720 (5)	O(3)–C(6)	1.416 (8)
W–O(3)	2.000 (4)	O(4)–C(7)	1.460 (10)
W–O(4)	1.945 (5)	C(1)–C(2)	1.506 (9)
Bond Angles			
O(1)–W–O(2)	110.4 (3)	O(3)–W–O(4)	75.6 (2)
O(1)–W–O(3)	128.2 (3)	O(3)–W–C(1)	75.2 (2)
O(1)–W–O(4)	98.4 (3)	O(4)–W–C(1)	150.3 (2)
O(1)–W–C(1)	95.3 (3)	W–O(3)–C(6)	118.2 (4)
O(2)–W–O(3)	121.4 (2)	W–O(4)–C(7)	119.9 (4)
O(2)–W–O(4)	100.8 (3)	W–C(1)–C(2)	123.1 (5)
O(2)–W–C(1)	98.8 (3)		

[a] See footnote a, Table II. Distances have not been corrected for thermal motion.

Table IV. Some Selected Metal–Ligand Bond Lengths (Å) and Angles (deg) in Molecules of the Type $MoO_2R_2(bpy)$

	R = Me[5a]	R = CH_2Ph[5b]	R = CH_2CMe_3[5c]
O–Mo–O	110.20 (9)	110.2 (6)	110.0 (2)
R–Mo–R	149.03 (10)	155.5 (8)	145.8 (2)
N–Mo–R	76.3–78.4	77.6–81.3	73.8–78.8
Mo–C	2.189 (3)	2.24 (2)	2.237 (5)
Mo–C′	2.194 (2)	2.26 (2)	2.235 (5)
Mo–O	1.707 (2)	1.68 (1)	1.709 (3)
Mo–O′	1.708 (2)	1.71 (1)	1.706 3)
Mo–C_α–C_β		123–128	118–120

The anisotropic temperature factors for C(3) (U_{33} = 0.62 Å^2) and C(4) (U_{22} = 0.40 Å^2; U_{33} = 0.30 Å^2) are rather large, suggesting that the *tert*-butyl group may be disordered even though the temperature factors for C(5) are reasonable. It was not possible, however, to refine a disordered model for this group. No evidence for disorder was seen elsewhere in the structure. All hydrogen atoms were placed in geometrically calculated positions and constrained to "ride" on the carbon atom to which they are bound (C–H = 0.95 Å; H–C–H = 109.5°). A final difference Fourier map showed no significant features.

Crystal data appear in Table I, final non-hydrogen atom positional parameters appear in Table II, and selected interatomic distances and angles within the anion are given in Table III. Figure 1 shows the geometry of the anion along with the atom-labeling scheme.

The structure of the cation is normal. The atoms are labeled N and C(12)–C(19).

Acknowledgment. R.R.S. thanks the National Science Foundation for support (Grant CHE84-02892), and I.F.-J. thanks the Bantrell Foundation for a post-doctoral fellowship. We also thank Dr. Catherine Costello and Dr. Henrianna Pang for obtaining FD mass spectra (NIH Grant RR 00317 to K. Biemann), and the Biomedical Research Support Shared Instrumentation Grant Program, Division of Research Resources, for funds to purchase the X-ray diffraction equipment (NIH Grant S10RR02243-01).

Registry No. 1, 87615-69-8; 2, 96364-07-7; 3, 96364-09-9; 4, 96364-11-3; $W(CCMe_3)(OCMe_3)_3$, 78234-36-3; $W(CSiMe_3)(OCMe_3)_3$, 96364-12-4; $[NEt_4][WO_2(OH)_2(CH_2CMe_3)]$, 96364-14-6; $Na[WO_3(CH_2CMe_3)]$, 96364-15-7; $W(CEt)(OCMe_3)_3$, 82228-88-4; $[NEt_4][WO_3(CH_2CH_2CH_3)]$, 96364-17-9; $W(CCMe_3)[N(CH_2Me_2)_3]_3$, 96394-18-2; $W(CEt)(NMe_2)_3$, 96364-18-0; $(Na)_2[WO_4]$, 13472-45-2; $S(SiMe_3)_2$, 3385-94-2; tungstic acid, 7783-03-1; pinacol, 76-09-5; neopentane, 463-82-1.

Supplementary Material Available: Tables S1–S3, listing hydrogen atom positional parameters, final thermal parameters, and final observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.