Remarkably Inert Metal-Alkyl Linkages in Alkyl Dioxo Complexes of Molybdenum and Tungsten

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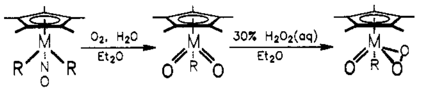
Summary: Protonic acids such as H_2O_2(aq) or HCl in Et_2O transform one of the M=O linkages and *not* the M—C σ bonds of $Cp'M(O)_2R$ complexes [Cp' = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5); M = Mo or W; R = CH_2SiMe_3 or Me]. The respective oxo peroxo and oxo dichloro product complexes $Cp'M(O)(\eta^2\text{-}O_2)R$ and $Cp^*W(O)(Cl)_2R$ are isolable in good yields as air-stable crystalline solids that have been fully characterized by conventional methods, including a single-crystal X-ray crystallographic analysis of $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$.

Reflecting the current interest in transition-metal oxo and peroxo complexes as oxidizing agents, Faller and Ma recently reported that treatment of $Cp^*W(O)_2R$ complexes (Cp* = η^5-C_5Me_5; R = Me or CH_2SiMe_3) with hydroperoxide formed by air oxidation of diethyl ether affords the novel compounds $Cp^*W(O)(\eta^2\text{-}O_2)R$.[2] We now wish to present the preliminary results of our related chemical investigations. Specifically, we report (a) a more general, high-yield synthetic route to such $Cp'M(O)(\eta^2\text{-}O_2)R$ complexes [Cp' = Cp (η^5-C_5H_5) or Cp*] for both molybdenum and tungsten, (b) the unequivocal establishment of the solid-state intramolecular dimensions of one of these η^2-O_2-containing compounds, and (c) the unusual reactions of $Cp^*W(O)_2R$ with HCl. Features (a)–(c) are considered in turn below.

(a) Our general synthetic route is summarized in eq 1.



(1)

Thus, exposure of the 16-electron dialkyl nitrosyl complexes $Cp'M(NO)R_2$ (M = Mo or W)[3,4] to water and molecular oxygen converts them to the corresponding dioxo alkyl compounds $Cp'M(O)_2R$ in higher yields (>80%) than if O_2 alone is employed.[5] Then, treatment of the latter complexes with 30% H_2O_2(aq) results in their clean conversion to the corresponding $Cp'M(O)(\eta^2\text{-}O_2)R$ compounds. Overall yields of the final peroxo alkyl complexes[6] from their dialkyl precursors range from 50% (R = Me) to 80% (R = CH_2SiMe_3). This observation contrasts with the overall yield of 1% (R = Me) or 22% (R = CH_2SiMe_3) for $Cp^*W(O)(\eta^2\text{-}O_2)R$ from $[Cp^*W(CO)_2]_2$ obtained by Faller and Ma.[2] Furthermore, conversions 1 afford *both* the Cp and Cp* derivatives of the two group 6 metals.[7]

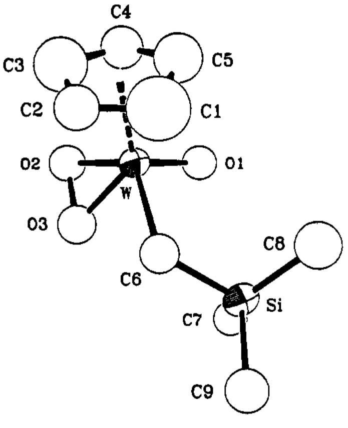
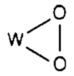


Figure 1. Molecular structure of $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$. Selected bond lengths (Å) and angles (deg): W–O(1) = 1.68 (3), W–O(2) = 1.92 (3), W–O(3) = 1.87 (3), W–C(6) = 2.15 (4), C(6)–Si = 1.84 (4), O(2)–O(3) = 1.44 (3), W–O(2)–O(3) = 66 (2), W–O(3)–O(2) = 70 (2), O(1)–W–C(6) = 99.2 (14), O(1)–W–O(2) = 99.7 (13), O(1)–W–O(3) = 106.5 (14), O(2)–W–O(3) = 44.7 (10), W–C(6)–Si = 119 (2).

(b) A single-crystal X-ray crystallographic analysis of one of the alkyl peroxo complexes, namely, $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$,[8] has established its solid-state molecular structure as being that of a slightly flattened "three-legged piano stool" (Figure 1), the midpoint of the peroxo ligand constituting the terminus of one of the legs. The $W(\eta^2\text{-}O_2)$ intramolecular dimensions (W–O = 1.92 (3) and 1.87 (3) Å and O–O = 1.44 (3) Å are within the ranges (transition-metal–O = 1.80–1.99 Å and O–O = 1.42–1.49 Å) commonly found in peroxo complexes.[9] Furthermore, the W=O, W—alkyl, and W—Cp bond distances are comparable to those found in related compounds.[3,5] In other words, the solid-state molecular structure exhibited by $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ is completely consistent with it being formulated as a 16-electron oxo peroxo complex containing W=O and



linkages. The spectroscopic properties of all our alkyl peroxo complexes[6] indicate that their molecular structures both in solutions and in the solid state are similar to that shown for $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ in Figure 1. In particular, their Nujol mull IR spectra all exhibit bands in the regions 960–930, 875–850, and 575–555 cm^{-1} assignable to $\nu_{M=O}$, ν_{O-O}, and ν_{M-O}, respectively.

(c) Just as in the second step of reactions 1, it is also one of the W=O linkages which is transformed when Cp*W-

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(2) Faller, J. W.; Ma, Y. *Organometallics* 1988, 7, 559 and references therein.

(3) Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

(4) The $Cp^*M(NO)Me_2$ complexes are generated at –65 °C in Et_2O from $[Cp^*M(NO)I_2]_n$ (*n* = 1 or 2) and MeLi and are then allowed to warm to room temperature in the presence of O_2 and H_2O to effect their transformation into the $Cp^*M(O)_2Me$ derivatives.

(5) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1985**, *4*, 1470.

(6) Elemental analysis and spectroscopic data for all new complexes isolated during this work are presented as supplementary material.

(7) We have subsequently learned in a personal communication from Professor Faller that his method[2] also produces 30–40% yields of the $Cp^*Mo(O)(\eta^2\text{-}O_2)R$ complexes from $Cp^*Mo(O)_2Cl$, but it is only applicable to the Cp* derivatives.

(8) Crystals of $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ are orthorhombic with a = 6.531 (6) Å, b = 11.659 (2) Å, c = 32.198 (7) Å, D_{calcd} = 2.08 g cm^{-3}, Z = 8, and space group *Pbca*. The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares procedures using 765 decay- and absorption-corrected reflections with $I \geq 3\sigma(I)$ collected at 22 °C with graphite-monochromated Mo Kα radiation on an Enraf-Nonius CAD4-F diffractometer. Refinement of the tungsten and silicon atoms anisotropically and all other non-hydrogen atoms isotropically (with hydrogens fixed in ideal positions) has been carried out to R = 0.084. Residual electron density in a final difference Fourier map ($\sigma_{max} \simeq 3$ e Å^{-3}) does not suggest any disorder of the three oxygen atoms. Refinement was limited by extensive decay; three standard reflections, measured every hour, had overall intensity decay varying from 68.9% to 78.9%. Initially colorless, the crystals remained intact but became increasingly orange during exposure to X-rays.

(9) Mimoun, H. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; Chapter 15.

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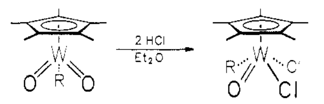
$(O)_2R$ complexes are treated with 2 equiv of HCl in Et_2O (eq 2).[10] The $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ and $Cp^*W(O)$-



(2)

$(Cl)_2Me$ products isolated to date from reactions 2 exhibit IR and ^1H and $^{13}C\{^1H\}$ NMR spectra which are consistent with their possessing the molecular structures shown.[6] These product complexes are also very useful synthetic precursors, e.g. reactions 3 affording the final oxo alkylidene complexes in much higher yields than other routes.[5,6]

$$Cp^*W(O)(Cl)_2R + 2R'MgCl \xrightarrow[-2MgCl_2]{Et_2O}$$

$$Cp^*W(O)(R)(R')_2 \xrightarrow[Et_2O]{\Delta} Cp^*W(O)R[{=}(R' - H)] + R'H \qquad (3)$$

$$R = CH_2SiMe_3;\ R' = CH_2SiMe_3,\ CH_2Ph$$

In essence, the chemical transformations of the M=O links shown in reactions 1 and 2 are those classically found for these functional groups.[9,11,12] *The unusual feature is that the M–C σ bonds remain intact*,[13] there being no evidence for the occurrence of the conversions

$$Cp'M(O)_2R + H\text{–}A \rightarrow Cp'M(O)_2A + R\text{–}H \qquad (4)$$

where H–A = a protonic acid such as H_2O_2 or HCl. Our preliminary investigations also indicate that the applicability of reactions 1 and 2 is only limited by the availability of the requisite dioxo alkyl complexes of which we now have an extended series.[15] Consequently, we are currently extending this work to include a wide range of protonic acids and are endeavoring to ascertain the effects of the M–C σ bonds on the reactivities of the alkyl peroxo and the oxo alkylidene complexes.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and J.T. We also thank Professors Jack Faller and Bob Bergman for stimulating conversations and for informing us of their related work prior to publication.

Registry No. $CpMo(NO)Me_2$, 94620-70-9; $CpMo(NO)(CH_2SiMe_3)_2$, 94620-69-6; $CpW(NO)Me_2$, 109959-57-1; $CpW(NO)(CH_2SiMe_3)_2$, 94620-67-4; $Cp^*Mo(NO)Me_2$, 115364-23-3; $Cp^*Mo(NO)(CH_2SiMe_3)_2$, 115364-24-4; $Cp^*W(NO)Me_2$, 115364-25-5; $Cp^*W(NO)(CH_2SiMe_3)_2$, 109467-45-0; $CpMo(O)_2Me$, 115364-26-6; $CpMo(O)_2(CH_2SiMe_3)$, 115364-27-7; $CpW(O)_2Me$, 115364-28-8; $CpW(O)_2(CH_2SiMe_3)$, 96760-75-7; $Cp^*Mo(O)_2Me$, 115364-29-9; $Cp^*Mo(O)_2(CH_2SiMe_3)$, 115364-30-2; $Cp^*W(O)_2Me$, 112247-12-8; $Cp^*W(O)_2(CH_2SiMe_3)$, 112247-16-2; $CpMo(O)(\eta^2\text{-}O_2)Me$, 115364-31-3; $CpMo(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$, 115364-32-4; $CpW(O)(\eta^2\text{-}O_2)Me$, 115364-33-5; $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$, 115364-34-6; $Cp^*Mo(O)(\eta^2\text{-}O_2)Me$, 115364-35-7; $Cp^*Mo(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$, 115364-36-8; $Cp^*W(O)(\eta^2\text{-}O_2)Me$, 112247-13-9; $Cp^*W(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$, 112247-14-0; $[Cp^*Mo(NO)I_2]$, 115364-37-9; $[Cp^*Mo(NO)I_2]_2$, 115364-38-0; $[Cp^*W(NO)I_2]$, 115364-39-1; $[Cp^*W(NO)I_2]_2$, 115364-40-4; $Cp^*W(O)(Cl)_2Me$, 115364-41-5; $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$, 115364-42-6; $Cp^*W(O)(CH_2SiMe_3)(CHSiMe_3)$, 115364-43-7; $Cp^*W(O)(CH_2SiMe_3)(CHPh)$, 115364-44-8; Me_3SiCH_2MgCl, 13170-43-9; $PhCH_2MgCl$, 6921-34-2.

Supplementary Material Available: Elemental analysis and spectroscopic (IR, ^1H and $^{13}C\{^1H\}$ NMR) data for the nine new complexes and tables of fractional coordinates and isotropic and anisotropic thermal parameters for $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ (6 pages); a listing of structure factors (5 pages). Ordering information is given on any current masthead page.

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(10) Typically, stirred colorless solutions of $Cp'M(O)_2R$ were treated with a slight excess of the requisite reagent (either 30% $H_2O_2(aq)$ or HCl in Et_2O), and the mixtures were stirred for 3–12 h whereupon they remained colorless or became yellow. Removal of volatiles from the final solutions in vacuo and recrystallization of the remaining residues from Et_2O afforded the desired products in 70–95% yields as crystalline, air-stable solids.

(11) See, for example: MacLaughlin, S. A.; Murray, R. C.: Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 796.

(12) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978.

(13) Such inertness of W–C bonds to HCl is quite rare, another example being provided by $W_2O_3(CH_2CMe_3)_6$.[14]

(14) Feinstein-Jaffe, I.; Gibson, D.; Lippard, S. J.; Schrock, R. R.; Spool, A. *J. Am. Chem. Soc.* **1984**, *106*, 6305.

(15) Legzdins, P.; Phillips, E. C.; Sânchez, L., manuscript in preparation.

1,4-Dilithio-1,3-butadienes

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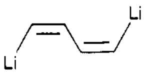
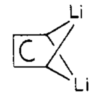
Summary: On treatment with (trimethylstannyl)lithium in THF at −78 °C, 1,4-dichlorobutadienes (**4**) gave the stereoisomeric 1,4-bis(trimethylstannyl)-1,3-butadienes (**5**–**7**). Compounds **5** and **7** may be converted to the corresponding 1,4-dilithio-1,3-butadienes (**1** and **3**) by treatment with excess methyllithium, while **6** and **7** may be converted to **1** by reaction with <1 equiv of methyllithium.

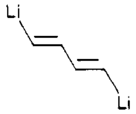
Organopolylithium compounds have attracted considerable attention due to the interest in their unusual structures.[1] Thus, it has been argued that (1*Z*,3*Z*)-1,4-dilithio-1,3-butadiene (1) possesses a symmetrically bridged structure 2,[2] which is stabilized by favorable electrostatic and orbital interactions. Since MO calculations (4-31G//STO-3G) indicate that 1 is 44 kcal/mol more stable than its *E*,*E*-isomer 3,[3] it should be possible to effect conversion of 3 to the more synthetically useful 1.[5] We report here a facile preparation of 1, which provides indirect but convincing evidence for the greater thermodynamic stability of 1 over 3.



1



2



3

The reaction of an isomeric mixture of 1,4-dichloro-1,3-butadienes (4)[6] with an excess of (trimethylstannyl)lithium in THF at −78 °C gave a 60% yield of the 1,4-bis(trimethylstannyl)-1,3-butadienes (5–7) in the ratio of

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(1) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355; **1984**, *56*, 151. Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 354. Maercher, A.; Theis, M. *Top. Curr. Chem.* **1987**, *138*, 1.

(2) An X-ray structure of the tetraphenyl derivative of 1 shows this bridged structure. Schleyer, P. v. R., private communication.

(3) Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1980**, *102*, 7928.

(4) However, see: Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.

(5) (a) Low-yield preparations of 1 have been reported: Ashe, A. J., III; Drone, F. J. *Organometallics* **1985**, *4*, 1478. Ferede, R.; Noble, M.; Cordes, A. W.; Allison, N. T.; Lay, J., Jr. *J. Organomet. Chem.* **1988**, *339*, 1. (b) For substituted 1,4-dilithio-1,3-butadienes: Reich, H. J.; Reich, I. L. *J. Org. Chem.* **1976**, *40*, 2248. Atwell, W. H.; Weyenberg, D. R.; Gilman, H. *J. Org. Chem.* **1967**, *32*, 885. Smith, L. I.; Hoehn, H. H. *J. Am. Chem. Soc.* **1961**, *83*, 4406. Ashe, A. J., III; Drone, F. J. *Organometallics* **1984**, *3*, 495.

(6) Criegee, R.; Hörauf, W.; Schellenberg, W. D. *Chem. Ber.* **1953**, *86*, 126. Bartlett, P. D.; Wallbillich, G. E. H. *J. Am. Chem. Soc.* **1969**, *91*, 409.