Finally, it should be noted that the η^2-diene-carbonyl complex (**20**) requires somewhat more forcing conditions for its preparation than do the related phosphine compounds (**18** and **19**). Thus, when L = CO in reaction 8, a hexanes solution of the organometallic reactant must be subjected to 60 psig of carbon monoxide at room temperature for 5 days in order to effect complete conversion. This observation again gives a clear indication of the relatively high inertness of the Mo–η^4-*trans*-diene linkage in **8** to undergo substitution reactions. Even more surprising is the fact that no $CpMo(NO)(CO)_2$, the disubstituted product, is formed during this transformation.

Clearly, further studies of the characteristic reactivities of compounds **1**–**14** must be effected so that their chemical properties can be discussed in the proper context. Such studies are currently in progress.

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Registry No. 1, 102418-61-1; **2A**, 119008-47-8; **2B**, 119008-40-1; 3, 95123-26-5; **4A**, 118920-36-8; **4B**, 119008-41-2; **5A**, 118920-37-9; **5B**, 119008-46-7; **6**, 118920-38-0; **7A**, 119008-42-3; **7B**, 119008-43-4; **8**, 95123-27-6; **9**, 118920-39-1; **10**, 119008-45-6; **11A**, 118920-40-4; **11B**, 119008-44-5; **12**, 118920-41-5; **13**, 102418-60-0; **14**, 118920-42-6; **15**, 119008-48-9; **16**, 118920-46-0; **17**, 100448-74-6; **18**, 118920-43-7; **19**, 118920-44-8; **20**, 118920-45-9; $[CpMo(NO)I_2]_2$, 12203-25-7; $H_2C{=}CHCH{=}CH_2$, 106-99-0; $H_2C{=}C(Me)CH{=}CH_2$, 78-79-5; $H_2C{=}C(Me)C(Me){=}CH_2$, 513-81-5; (*E*)-$H_2C{=}CHCH{=}CHMe$, 2004-70-8; $(Me)_2C{=}CHC(Me){=}CH_2$, 1000-86-8; (*E*,*E*)-$MeCH{=}CHCH{=}CHMe$, 5194-51-4; (*E*,*Z*)-$MeCH{=}CHCH$<<ΔbdCHMe, 5194-50-3; $(Me)_2C{=}CHCH{=}C(Me)_2$, 764-13-6; (*E*,*E*)-$PhCH{=}CHCH{=}CHPh$, 538-81-8; $[CpW(NO)I_2]_2$, 71341-43-0; $[CpMo(NO)I]_2$, 37368-74-4; $[Cp^*Mo(NO)I_2]_21$, 115364-38-0; $C_4H_6Mg(THF)_2$, 83995-88-4; cycloheptatriene, 544-25-2; 1,3-cyclooctadiene, 1700-10-3; 1,5-cyclooctadiene, 111-78-4; cyclooctatetraene, 629-20-9; 1,3-cyclohexadiene, 592-57-4; 1,4-pentadiene, 591-93-5; 2,3-butanedione, 431-03-8; 3-buten-2-one, 78-94-4; diphenylacetylene, 501-65-5; ethylene, 74-85-1; norbornadiene, 121-46-0.

New Types of Organometallic Oxo Complexes Containing Molybdenum and Tungsten

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Treatment of solutions of the 16-electron dialkyl compounds $Cp'M(NO)R_2$ (Cp' = Cp (η^5-C_5H_5) or Cp* (η^5-C_5Me_5); M = Mo or W; R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, CH_2Ph, or Me) with either dioxygen or aqueous hydrogen peroxide in Et_2O at ambient temperatures and pressures produces novel dioxo alkyl complexes $Cp'M(O)_2R$ which can be isolated in moderate yields (45–60%). The results of labeling studies with $^{18}O_2$ are consistent with the first steps of the reactions involving O_2 proceeding via the coordination of the diatomic molecule to the metal centers in the organometallic reactants. The preferred sites of reactivity in the dioxo alkyl complexes are their M=O linkages. Thus, exposure to 30% H_2O_2 in Et_2O converts them cleanly to the oxo peroxo derivatives $Cp'M(O)(\eta^2\text{-}O_2)R$ and treatment of representative $Cp'W(O)_2R$ species with HCl (or PCl_5 or Me_3SiCl) in Et_2O produces the corresponding $Cp'W(O)(Cl)_2R$ compounds in high yields. These dichloro oxo complexes are very useful synthetic precursors in their own right, undergoing metathesis with alkyllithium or alkyl Grignard reagents to produce the oxo trialkyl compounds $Cp'W(O)R_nR'_{3-n}$ in which R and R′ represent selected alkyl groups. Sterically crowded members of this class of compounds are not isolable under ambient conditions since they spontaneously convert to the corresponding oxo alkylidene species, presumably via intramolecular α-H abstraction. The isolable oxo trialkyl complexes can be induced to undergo the same conversions simply by gentle warming of their solutions. All the new oxo complexes isolated during this work have been fully characterized by conventional spectroscopic techniques. Their physical properties indicate that they are all monomeric 16-valence-electron species possessing piano-stool molecular structures and containing the metal in its highest oxidation state of +6.

Introduction

The first examples of organometallic oxo complexes were the vanadium-containing species $CpV(O)X_2$ (Cp = η^5-C_5H_5; X = Cl or Br), obtained by Fischer and Vigoureux in the late 1950s.[2] Shortly thereafter, Cousins and Green described some cyclopentadienyl oxo compounds of molybdenum,[3] but this area of research then remained relatively dormant until recently. During the past 5 years, many research groups have shown a renewed interest in the synthesis and chemistry of higher oxidation state organometallic oxo complexes, this interest being manifested by the appearance of reports describing such diverse complexes as $CpRe(O)_3$,[4] $Cp^*Re(O)_3$ (Cp^* = η^5-C_5Me_5),[4,5] $CpReOMe_2$,[4b] $Re(O)I(MeC{\equiv}CMe)_2$,[6] $W_2O_3(CH_2CMe_3)_6$,[7] $CpW(O)(C_2H_4)Me$,[8] $CpW(O)(C_2H_4)COMe$,[8] $MeReO_3$,[9] and

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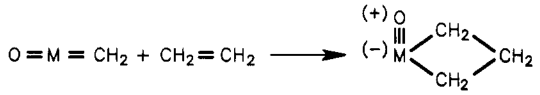
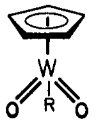
Me_2ReO_3.[9] Indeed, the reports of organometallic oxo compounds have proliferated to such an extent that the recent, excellent review of this subject by Bottomley and Sutin is both timely and appropriate.[10] The renewed interest in these compounds results in part from the anticipation that a detailed understanding of their characteristic chemistry may provide some insight into how metal oxides function as catalysts for organic reactions and as oxidizing agents for organic compounds.[11] It has been argued on theoretical grounds[12] that the role of the oxo ligands during these catalytic and stoichiometric processes is to stabilize various metallacyclic intermediates by an increase in the metal–oxygen bond order, e.g. during olefin metathesis



In general, however, the detailed mechanisms of such reactions are not yet known with certainty.

Our interest in organometallic oxo complexes stems from our original investigations of the chemical properties of $CpW(NO)(CH_2SiMe_3)_2$,[13] during which we encountered the first examples of three new types of cyclopentadienyl oxo alkyl complexes, namely, **1**–**3** (R = CH_2SiMe_3).[14] Our initial discoveries of complexes **1**–**3** were somewhat serendipitous, to say the least. Compound **1** was obtained by exposing a hexanes solution of $CpW(NO)(CH_2SiMe_3)_2$ to air, compound **2** was formed as a byproduct during the preparation of the parent dialkyl complex, and compound **3** resulted from the thermal decomposition of the dialkyl compound in the solid state.[14] Nevertheless, we were sufficiently intrigued by these classes of compounds to embark on a study of their chemistry. In this paper we report full details of this study, a portion of which has been previously communicated.[15] Specifically, we describe reliable synthetic routes leading to all three classes of complexes **1**–**3** for a range of alkyl ligands R, for both cyclopentadienyl- and pentamethylcyclopentadienyl-containing species, and for both molybdenum and tungsten as the central metal. Furthermore, we present some of the characteristic chemistry of these 16-electron, coordinatively unsaturated complexes, aspects of which may well relate to how metal oxides both affect and effect various organic transformations.



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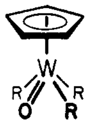

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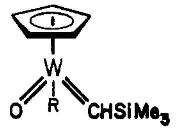

3

Experimental Section

Most reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. General procedures routinely employed in these laboratories have been described in detail previously.[16] The requisite $Cp'M(NO)R_2$ reagents (Cp′ = Cp, M = Mo or W, R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, or CH_2Ph;[13] Cp′ = Cp*, M = W, R = CH_2SiMe_3)[17] were prepared by the published procedures. Other reagents were synthesized by literature methods or were purchased from commercial suppliers, and their purities were ascertained by elemental analyses and ^1H NMR spectroscopy. The dioxygen used during this work was purchased from Medigas in 99.5% purity and was used as received. The $^{18}O_2$ and HCl gases were purchased from Matheson in 98% isotopic purity and 99.0% purity, respectively, and were not purified further before use. The hydrogen peroxide reagent was obtained as a 30% by weight aqueous solution from BDH Chemicals, and the phosphorus pentachloride and the trimethylsilyl chloride reagents were purchased from Aldrich.

The ^{13}C NMR spectra were recorded at 75 MHz on a Varian Associates XL-300 spectrometer with reference to the ^{13}C signal of the solvent employed (usually benzene-d_6). All ^{13}C chemical shifts are reported in parts per million downfield from Me_4Si.

Preparation of $Cp^*Mo(NO)(CH_2SiMe_3)_2$. Unlike the other dialkyl nitrosyl complexes which may be readily obtained by treatment of $[Cp'M(NO)X_2]_n$ (Cp′ = Cp or Cp*, M = Mo or W, X = I or Cl, n = 1 or 2) with 4 equiv of the appropriate Grignard reagent,[13] $Cp^*Mo(NO)(CH_2SiMe_3)_2$ can only be synthesized by employing the dichloro complex as the precursor. The experimental procedure employed to synthesize and isolate this complex was as described below.

To a stirred, brown suspension of $[Cp^*Mo(NO)Cl_2]_2$[18] (2.10 g, 3.16 mmol) in Et_2O (150 mL) at room temperature was added dropwise from an addition funnel 12 mL of a 1.0 M Et_2O solution of Me_3SiCH_2MgCl[19a] (12 mmol). The reaction mixture immediately changed color, first becoming black and then purple, and a white precipitate slowly deposited. After being stirred for an additional hour at ambient temperature, the reaction mixture was taken to dryness in vacuo. The remaining purple and white solid was extracted with pentane (60 mL), and the volume of the purple pentane extracts was slowly reduced under reduced pressure until the first signs of crystallization were evident. Cooling of this mixture to −20 °C overnight induced the crystallization of 0.62 g (25% yield) of purple $Cp^*Mo(NO)(CH_2SiMe_3)_2$ as an extremely air-sensitive solid. The crystals were collected by filtration and dried at 5×10^{-3} mm and 20 °C for 2 h.

Anal. Calcd for $C_{18}H_{37}ONSi_2Mo$: C, 49.63; H, 8.56; N, 3.21. Found: C, 49.47; H, 8.71; N, 3.06. IR (Nujol mull): ν_{NO} 1595 (s) cm^{-1}. IR (hexanes): ν_{NO} 1601 (s) cm^{-1}. ^1H NMR (C_6D_6): δ 2.20 (d, 2 H, $^2J_{H_A-H_X}$ = 10.8 Hz, 2 $CH_AH_XSiMe_3$), 1.49 (s, 15 H, $C_5(CH_3)_5$), 0.37 (s, 18 H, 2 $Si(CH_3)_3$), −1.17 (d, 2 H, $^2J_{H_A-H_X}$ = 10.8 Hz, 2 $CH_AH_XSiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 110.52 (s, $C_5(CH_3)_5$), 66.54 (s, CH_AH_X), 9.97 (s, $C_5(CH_3)_5$), 2.59 (s, $Si(CH_3)_3$). Low-resolution mass spectrum (probe temperature 100 °C): m/z 437 (P^+, ^{98}Mo). Melting point: 72–73 °C.

Preparation of $Cp^*W(NO)(CH_2Ph)_2$. A stirred solution of $[Cp^*W(NO)Cl_2]_2$[18] (1.5 g, 1.8 mmol) in THF (150 mL)/Et_2O (25 mL) at room temperature was treated dropwise with a Et_2O solution (11.1 mL, 0.65 M, 7.21 mmol) of $PhCH_2MgCl$[19b] by using an addition funnel. The reaction mixture slowly changed from green to brown-orange as the addition proceeded. The final reaction mixture was stirred at room temperature for 1 h whereupon 0.5 mL of deaerated water was added, resulting in the formation of a sticky white precipitate and a deep red supernatant solution. This mixture was then taken to dryness under reduced pressure, and CH_2Cl_2 (20 mL) was added. The resulting mixture was chromatographed on an alumina column (Fisher neutral, 80–200 mesh, activity 3, 6 × 3 cm) made up in hexanes using CH_2Cl_2 as eluant. A single orange band developed and was eluted

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Table I. Analytical and IR Data for the Oxo Complexes

		analytical data				IR data (Nujol, cm^{-1})				
		C		H		$\nu_{M=O}$				
complex	mp, °C	calcd	found	calcd	found	asym	sym	ν_{O-O}	ν_{Si-Me}	ν_{M-O}
CpMo(O)$_2$(CH$_2$SiMe$_3$)	95–97	38.57	38.56	5.75	5.70	924	895		1246	
CpMo(O)$_2$Me	95 dec	34.64	34.53	3.88	3.95	926	902			
Cp*Mo(O)$_2$(CH$_2$SiMe$_3$)	104–106	48.12	48.19	7.50	7.60	912	893		1242	
Cp*Mo(O)$_2$Me	104–106	47.49	47.43	6.52	6.62	918	887			
CpW(O)$_2$(CH$_2$SiMe$_3$)	110–111	29.44	29.34	4.36	4.34	948	907		1248	
CpW(O)$_2$Me	112–115	24.34	24.19	2.72	2.69	951	910			
Cp*W(O)$_2$(CH$_2$SiMe$_3$)	118–119	38.36	38.20	5.98	5.96	937	901		1242	
Cp*W(O)$_2$Me	119–120	36.08	36.40	4.95	4.87	943	899			
CpW(O)$_2$(CH$_2$CMe$_3$)		34.11	34.00	4.58	4.49	952	906			
CpW(O)$_2$(CH$_2$CMe$_2$Ph)	154 dec	43.50	43.25	4.38	4.45	951	907			
CpW(O)$_2$(CH$_2$Ph)	163 dec	38.70	38.43	3.25	3.26	947	901			
Cp*W(O)$_2$(CH$_2$Ph)	148–150	46.17	45.81	5.01	4.79	939	899			
CpMo(O)(η^2-O$_2$)(CH$_2$SiMe$_3$)	85 dec	36.49	36.37	5.44	5.40	943		875	1238	569, 557
CpMo(O)(η^2-O$_2$)Me		32.17	32.49	3.60	3.86	949		878		575, 565
Cp*Mo(O)(η^2-O$_2$)Me	97 dec	44.90	44.87	6.17	6.13	934		875		565
CpW(O)(η^2-O$_2$)(CH$_2$SiMe$_3$)	107–108	28.15	27.95	4.20	4.33	955		852	1238	563
CpW(O)(η^2-O$_2$)Me	127 dec	23.10	23.36	2.58	2.70	955		864		569
Cp*W(O)(η^2-O$_2$)(CH$_2$SiMe$_3$)	110–111	37.01	37.11	5.77	5.80	941		868	1238	567, 559
Cp*W(O)(η^2-O$_2$)Me	116 dec	34.57	34.55	4.75	4.70	949		860		571
CpW(O)(Cl)$_2$(CH$_2$SiMe$_3$)	75 dec	25.55	25.80	3.81	3.92	951			1244	
Cp*W(O)(Cl)$_2$(CH$_2$SiMe$_3$)	83 dec	34.09	34.14	5.31	5.38	939			1244	
Cp*W(O)(Cl)$_2$Me	102	31.38	31.67	4.31	4.38	939				
CpW(O)(CH$_2$SiMe$_3$)$_3$	84 dec	38.78	38.48	7.22	7.64	941			1259, 1242	
Cp*W(O)(Me)$_2$(CH$_2$SiMe$_3$)	106 dec	42.48	42.85	7.13	7.45	933			1240	
Cp*W(O)(Me)(CH$_2$Ph)$_2$	99 dec	56.41	56.66	6.06	6.17	935				
CpW(O)(=CHSiMe$_3$)(CH$_2$SiMe$_3$)	74 dec	35.61	35.80	5.93	6.06	956			1255, 1240	
Cp*W(O)(=CHSiMe$_3$)(CH$_2$SiMe$_3$)	127 dec	42.51	42.88	7.13	7.33	949			1250, 1238	
Cp*W(O)(=CHPh)(CH$_2$SiMe$_3$)	107 dec	49.22	49.40	6.29	6.40	939			1238	

from the column. The volume of the collected eluate was reduced in vacuo to approximately 10 mL, and an equal volume of hexanes was added. Cooling of this mixture to −20 °C overnight induced the formation of 1.22 g (64% yield) of red crystals of Cp*W(NO)(CH$_2$Ph)$_2$ which were collected by filtration.

Anal. Calcd for C$_{24}$H$_{29}$ONW: C, 54.25; H, 5.50; N, 2.64. Found: C, 54.45; H, 5.45; N, 2.80. IR (Nujol mull): ν_{NO} 1566 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.37–6.80 (m, 10 H, 2 C$_6$$H_5$), 2.24 (d, 2 H, $^2J_{H_A-H_X}$ = 9.1 Hz, 2 CH_AH$_X$Ph), 1.81 (s, 15 H, C$_5$(CH_3)$_5$), 0.55 (d, 2 H, $^2J_{H_A-H_X}$ = 9.1 Hz, 2 CH$_A$$H_X$Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 133.6, 132.2, 132.1, 128.4, 127.1 (all s, C_6H$_5$), 108.2 (s, C_5(CH$_3$)$_5$), 42.9 (s, CH$_2$Ph), 10.3 (s, C$_5$(CH$_3$)$_5$). Low-resolution mass spectrum (probe temperature 200 °C): *m/z* 531 (P$^+$, ^{184}W). Melting point: 160–162 °C.

Preparations of the Cp′M(O)$_2$R Complexes By Employing Dioxygen. All of these syntheses involved treating the appropriate Cp′M(NO)R$_2$ precursors (Cp′ = Cp or Cp*, M = Mo or W, R = CH$_2$SiMe$_3$, CH$_2$CMe$_3$, CH$_2$CMe$_2$Ph, or CH$_2$Ph) with an excess of dioxygen. The experimental procedure, using CpW(NO)(CH$_2$SiMe$_3$)$_2$ as a representative example, was as follows.

Analytically pure CpW(NO)(CH$_2$SiMe$_3$)$_2$ (0.906 g, 2.00 mmol) was dissolved in hexanes (20 mL) at room temperature, and most of the dinitrogen atmosphere above the resulting dark purple solution was removed in vacuo. An excess of molecular oxygen was then introduced into the reaction vessel until a pressure of 10 psig was attained. The reaction vessel was then sealed, and the reaction mixture was stirred, whereupon a color change from purple to red occurred within 1 h. After 6 h, the final reaction mixture consisted of a fine brown precipitate and a red-brown supernatant solution. The volume of the final mixture was reduced to approximately 10 mL under reduced pressure, and the brown precipitate was collected by cannula filtration, washed with cold (0 °C) hexanes (15 mL), and dried at 5 × 10^{-3} mm. Recrystallization of this solid from Et$_2$O at −20 °C afforded 0.41 g (56% yield) of CpW(O)$_2$(CH$_2$SiMe$_3$) as an analytically pure, white, crystalline solid.

The isolated yields of the other dioxo products were similar, generally being in the 45–60% range. In the cases when R = CH$_2$CMe$_2$Ph and CH$_2$Ph, optimum yields of the desired products were obtained only if 1:1 hexanes/Et$_2$O and toluene, respectively, were employed as the solvents in order to obtain initially homogeneous reaction mixtures. The analytical, mass spectral, IR, and ^{1}H and ^{13}C NMR data for these and all the other new oxo complexes synthesized during this work are presented in Tables I and II.

Preparations of the Cp′M(O)$_2$R Complexes By Employing Hydrogen Peroxide. In general, these conversions were more rapid than those involving O$_2$, being usually complete in less than 1 h and producing comparable isolated yields of the CpM(O)$_2$R products. However, the stoichiometry of the oxidizing agent had to be carefully controlled in order to avoid further conversion of the desired CpM(O)$_2$R compounds to their CpM(η^2-O$_2$)(O)R derivatives (vide infra). Again, the preparation of CpW(O)$_2$(CH$_2$SiMe$_3$) is described below as a representative example.

To a stirred, purple solution of CpW(NO)(CH$_2$SiMe$_3$)$_2$ (1.20 g, 2.65 mmol) in Et$_2$O (50 mL) was added a 30% by weight aqueous solution of H$_2$O$_2$ (0.22 mL, 2.8 mmol of H$_2$O$_2$) by microsyringe. The initial purple color of the reaction mixture faded over the course of 1 h to a pale yellow. An IR spectrum of the final yellow solution was devoid of absorptions due to the nitrosyl reactant. Volatiles were removed from the final reaction mixture under reduced pressure to obtain a sticky yellow solid which was dried at 20 °C and 5 × 10^{-3} mm for 2 h. Recrystallization of the resulting pale yellow solid from 1:1 Et$_2$O/hexanes at −20 °C afforded 0.50 g (51% yield) of CpW(O)$_2$(CH$_2$SiMe$_3$) as a white microcrystalline solid.

When the pentamethylcyclopentadienyl analogue Cp*W(O)$_2$(CH$_2$SiMe$_3$) was prepared in a manner similar to that described in the preceding paragraph for the cyclopentadienyl species, the oxo peroxo complex Cp*W(O)(η^2-O$_2$)(CH$_2$SiMe$_3$) was also obtained as a byproduct in ca. 10% yield. The two organometallic oxo complexes could be conveniently separated by chromatography on Florisil with Et$_2$O as eluant (vide infra).

Preparations of the Cp′M(O)$_2$Me Complexes. All these syntheses involved first treating the appropriate [Cp′M(NO)X$_2$]$_n$ precursors (Cp′ = Cp or Cp*, M = Mo or W, X = Cl or I, *n* = 1 or 2) with the requisite amount of MeLi at low temperatures to generate Cp′M(NO)Me$_2$ in situ and then exposure of these latter complexes to H$_2$O$_2$. The representative experimental procedure employed to synthesize Cp*W(O)$_2$Me was as follows.

A stirred suspension of green Cp*W(NO)I$_2$[20] (1.50 g, 2.48 mmol) in Et$_2$O (200 mL) was cooled to −78 °C by using a dry ice/acetone

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[20] Dryden, N. H.; Einstein, F. W. B.; Jones, R. H.; Legzdins, P. *Can. J. Chem.* **1988**, *66*, 2100.

bath. Dropwise addition of a 1.4 M solution of MeLi in Et_2O (3.55 mL, 4.97 mmol, diluted with 10 mL of Et_2O) to the cooled mixture resulted in it gradually becoming an orange-red solution over the course of 1 h as the organometallic reactant was consumed. The cold bath was then removed, and the reaction mixture was permitted to warm slowly to room temperature. While being warmed, the mixture was treated with a 30% by weight aqueous solution of H_2O_2 (0.3 mL, 3.8 mmol) which was injected by syringe. After being stirred for 1 h at 20 °C, the final orange solution was first concentrated in vacuo to ca. 10 mL and then chromatographed on a Florisil column (2 × 4 cm) using Et_2O as the eluant. The pale yellow band that developed was eluted from the column and collected. The eluate was slowly concentrated under reduced pressure until white crystals began to deposit, and the mixture was then maintained at -20 °C overnight to complete the crystallization. The white crystals were collected by filtration the next day to obtain 0.45 g (50% yield) of analytically pure $Cp^*W(O)_2Me$.

The congeneric $Cp^*Mo(O)_2Me$ compound was prepared from $[Cp^*Mo(NO)Cl_2]_2$ in a similar manner in 52% isolated yield. The yields of the analogous $CpM(O)_2Me$ (M = Mo or W) complexes were only in the range of 10–15%, however, since appreciable amounts of the $CpM(\eta^2\text{-}O_2)(O)Me$ compounds were also formed as byproducts. Use of dioxygen in place of hydrogen peroxide did not afford higher yields of the desired dioxo methyl products.

Preparations of the $Cp'M(O)(\eta^2\text{-}O_2)R$ Complexes (Cp′ = Cp or Cp*, M = Mo or W, R = Me or CH_2SiMe_3). Only in the case of $Cp^*W(NO)(CH_2SiMe_3)_2$ did the treatment of the $Cp'M(NO)R_2$ complexes with an excess of H_2O_2 result in a high yield of the corresponding $Cp'M(O)(\eta^2\text{-}O_2)R$ species. In general, these latter compounds were best synthesized by employing the isolated dioxo alkyl complexes as the synthetic precursors. The preparation of $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ in this manner as a representative example was as detailed below.

To a stirred, colorless solution of $CpW(O)_2(CH_2SiMe_3)$ (0.30 g, 0.81 mmol) in Et_2O (25 mL) at ambient temperature was added by microsyringe a 30% by weight aqueous solution of H_2O_2 (0.32 mL, 4.1 mmol of H_2O_2). After 5 h, there had been no apparent change in the appearance of the reaction mixture; it was taken to dryness in vacuo to obtain a pale yellow solid. Recrystallization of this solid from Et_2O at -25 °C gave colorless plates of analytically pure $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ (0.25 g, 80% yield).

The synthesis of the permethylcyclopentadienyl analogue $Cp^*W(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ in this manner was monitored during the course of the reaction by periodically removing aliquots from the reaction mixture and taking them to dryness in vacuo. Nujol mull IR spectra of the dried residues showed the gradual diminution in intensity with time of the two $\nu_{W=O}$'s due to $Cp^*W(O)_2(CH_2SiMe_3)$ at 937 (asym) and 901 (sym) cm^{-1} and the appearance and growth of new absorptions due to $Cp^*W(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ at 941 ($\nu_{W=O}$), 868 (ν_{O-O}), and 567 and 559 (ν_{W-O}) cm^{-1}.

Preparations of the $Cp^*W(O)(Cl)_2R$ Complexes (R = CH_2SiMe_3 or Me) By Employing HCl, PCl_5, or Me_3SiCl as the Chlorinating Agents. A. With HCl. To a stirred, colorless solution of $Cp^*W(O)_2(CH_2SiMe_3)$ (0.85 g, 1.9 mmol) in Et_2O (20 mL) was added by microsyringe a 6 M solution of HCl in Et_2O (1.0 mL, 6.0 mmol HCl).[21] The reaction mixture immediately became yellow; stirring of the mixture was continued for 12 h whereupon a yellow precipitate also formed. Removal of the solvent in vacuo and recrystallization of the resulting yellow solid from Et_2O/hexanes at room temperature afforded 0.87 g (91% yield) of $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ as a yellow crystalline solid which was isolated by filtration.

B. With PCl_5. To a stirred, white suspension of PCl_5 (0.20 g, 0.96 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added solid $Cp^*W(O)_2(CH_2SiMe_3)$ (0.42 g, 0.96 mmol). Immediately, the reaction mixture became dark yellow, but the color lightened to yellow-green as stirring was continued for 0.5 h. At the end of this time, the mixture was allowed to warm to room temperature, and the solvent was then removed under reduced pressure to obtain a yellow-green solid. Crystallization of this solid from Et_2O at -20 °C produced yellow-green microcrystals of $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ (0.32 g, 68% yield).

C. With Me_3SiCl. To a stirred, colorless solution of $Cp^*W(O)_2(CH_2SiMe_3)$ (0.61 g, 1.4 mmol) in Et_2O (10 mL) at room temperature was added Me_3SiCl (1.0 mL, 7.9 mmol) by syringe. The reaction mixture became yellow immediately. After being stirred for 48 h, the reaction mixture consisted of a yellow microcrystalline precipitate and a yellow supernatant solution. Volatiles were then removed in vacuo, and the yellow solid remaining was recrystallized from 1:1 Et_2O/hexanes at -20 °C to obtain 0.67 g (97% yield) of yellow $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$.

Yellow $Cp^*W(O)(Cl)_2Me$ was obtained in an analogous manner by treating $Cp^*W(O)_2Me$ with an excess of Me_3SiCl in Et_2O and was isolated in 60% yield by recrystallizing the collected resulting precipitate from Et_2O at -20 °C.

Preparation of $CpW(O)(Cl)_2(CH_2SiMe_3)$. This complex was prepared by utilizing HCl as the chlorinating agent in a manner analogous to that outlined above in method A for its permethylcyclopentadienyl analogue. This reaction was performed over 4 h at 0 °C, however, and the final product compound precipitated as a yellow crystalline solid in 54% isolated yield when the final reaction mixture was maintained at -20 °C for 2 days.

Preparation of $CpW(O)(CH_2SiMe_3)_3$. A stirred yellow solution of freshly prepared $CpW(O)(Cl)_2(CH_2SiMe_3)$ (0.16 g, 0.38 mmol) in Et_2O (25 mL) at approximately -40 °C (maintained by a saturated aqueous $CaCl_2$/dry ice bath) was treated dropwise with a 1.0 M Et_2O solution of Me_3SiCH_2MgCl (0.78 mL, 0.78 mmol). The reaction mixture immediately developed a brown color, but it was stirred at this temperature for 30 min before being permitted to warm to room temperature to ensure completion of the reaction. The final mixture was filtered through a short (4 × 2 cm) column of Florisil supported on a medium-porosity frit. The filtrate was taken to dryness in vacuo, and the remaining yellow solid was crystallized from pentane at -20 °C to obtain 0.08 g (40% yield) of yellow needlelike crystals of $CpW(O)(CH_2SiMe_3)_3$. The ^1H NMR spectrum of the product complex in C_6D_6 at 20 °C (Table II) also exhibits small signals due to the corresponding oxo alkylidene compound $CpW(O)(=CHSiMe_3)(CH_2SiMe_3)$ (Table II), which increase in intensity with time.

Preparation of $Cp^*W(O)(Me)_2(CH_2SiMe_3)$. To a stirred, yellow solution of $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ (0.42 g, 0.85 mmol) in Et_2O (30 mL) at approximately -40 °C was added dropwise a 1.4 M solution of MeLi in Et_2O (1.4 mL, 1.96 mmol). Immediately the solution became green in color, and a white precipitate formed. After being stirred for 1 h, the reaction mixture was permitted to warm slowly to room temperature by removing the surrounding cold bath. The solvent was then removed from the final reaction mixture to obtain an oily blue residue. This residue was extracted with hexanes (2 × 10 mL), and the blue-green extracts were chromatographed on a Florisil column (2 × 4 cm) using Et_2O as the eluant. The single yellow band that developed was eluted from the column and collected. Solvent was removed from the eluate under reduced pressure, and the resulting oily yellow solid was crystallized from pentane at -20 °C to obtain 0.26 g (62% yield) of $Cp^*W(O)(Me)_2(CH_2SiMe_3)$ as analytically pure, large yellow crystals.

Preparation of $Cp^*W(O)(Me)(CH_2Ph)_2$. To a stirred, yellow solution of $Cp^*W(O)(Cl)_2Me$ (0.22 g, 0.52 mmol) in Et_2O (30 mL) at ca. -40 °C was added dropwise a 1.1 M solution of $PhCH_2MgCl$ in Et_2O (0.99 mL, 1.09 mmol). The reaction mixture immediately became somewhat cloudy and developed a green-brown coloration. After being stirred for 1 h at this temperature, the mixture was permitted to warm to room temperature and was then filtered through a short (2 × 4 cm) column of Florisil supported on a medium-porosity frit. The yellow filtrate was taken to dryness in vacuo, and the remaining residue was recrystallized from 1:1 Et_2O/hexanes at -20 °C overnight to obtain 0.12 g (44% yield) of $Cp^*W(O)(Me)(CH_2Ph)_2$ as a yellow crystalline solid.

Preparation of $CpW(O)(=CHSiMe_3)(CH_2SiMe_3)$. A stirred, yellow solution of $CpW(O)(CH_2SiMe_3)_3$ (0.30 g, 0.57 mmol) in benzene (15 mL) was maintained at 50 °C for 2 days. Removal of all volatiles from the final reaction mixture in vacuo produced a yellow solid which was recrystallized from Et_2O to obtain 0.24 g (95% yield) of $CpW(O)(=CHSiMe_3)(CH_2SiMe_3)$ as analytically

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[21] This solution was prepared by bubbling HCl gas through dry, deaerated Et_2O and was standardized by titration with 1.0 M aqueous NaOH.

Table II. Mass Spectral and ^1H and $^{13}C\{^1H\}$ NMR Data for the Oxo Complexes

complex	low-resolution mass spectral data[a] m/z[b]	^1H NMR data (C_6D_6) δ	$^{13}C\{^1H\}$ NMR data (C_6D_6)[c] δ
$CpMo(O)_2(CH_2SiMe_3)$	267, $[P - Me]^+$	5.61 (s, 5 H, $C_5\mathit{H}_5$)	109.5 (C_5H_5)
		1.20 (s, 2 H, CH_2)	24.6 ($\mathit{C}H_2$)
		0.32 (s, 9 H, $Si\mathit{CH}_3$)	0.6 ($Si\mathit{C}H_3$)
$CpMo(O)_2Me$	210, $[P]^+$	5.42 (s, 5 H, $C_5\mathit{H}_5$)	109.3 (C_5H_5)
		1.19 (s, 3 H, CH_3)	11.6 ($\mathit{C}H_3$)
$Cp^*Mo(O)_2(CH_2SiMe_3)$	352, $[P]^+$	1.59 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	117.4 ($\mathit{C}_5(CH_3)_5$)
		0.63 (s, 2 H, CH_2)	28.8 ($\mathit{C}H_2$)
		0.37 (s, 9 H, $Si\mathit{CH}_3$)	10.5 ($C_5(\mathit{C}H_3)_5$)
			0.8 ($Si\mathit{C}H_3$)
$Cp^*Mo(O)_2Me$	280, $[P]^+$	1.57 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	117.4 ($\mathit{C}_5(CH_3)_5$)
	265, $[P - Me]^+$	0.90 (s, 3 H, CH_3)	15.8 ($\mathit{C}H_3$)
			10.4 ($C_5(\mathit{C}H_3)_5$)
$CpW(O)_2(CH_2SiMe_3)$	353, $[P - Me]^+$	5.69 (s, 5 H, $C_5\mathit{H}_5$)	109.5 (C_5H_5)
	337, $[P - 2Me]^+$	0.88 (s, 2 H, CH_2, $^2J_{HW}$ = 12 Hz)	19.2 ($\mathit{C}H_2$, $^1J_{CW}$ = 135 Hz)
		0.28 (s, 9 H, $Si\mathit{CH}_3$)	0.7 ($Si\mathit{C}H_3$)
$CpW(O)_2Me$	296, $[P]^+$	5.49 (s, 5 H, $C_5\mathit{H}_5$)	109.2 (C_5H_5)
	281, $[P - Me]^+$	1.14 (s, 3 H, CH_3, $^2J_{HW}$ = 12 Hz)	8.6 ($\mathit{C}H_3$, $^1J_{CW}$ = 144.5 Hz)
$Cp^*W(O)_2(CH_2SiMe_3)$	423, $[P - Me]^+$	1.67 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	116.5 ($\mathit{C}_5(CH_3)_5$)
		0.41 (s, 2 H, CH_2, $^2J_{HW}$ = 10.7 Hz)	24.5 ($\mathit{C}H_2$, $^1J_{CW}$ = 135 Hz)
		0.36 (s, 9 H, $Si\mathit{CH}_3$)	10.5 ($C_5(\mathit{C}H_3)_5$)
			0.97 ($Si\mathit{C}H_3$)
$Cp^*W(O)_2Me$	366, $[P]^+$	1.64 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	116.7 ($\mathit{C}_5(CH_3)_5$)
	351, $[P - Me]^+$	0.88 (s, 3 H, CH_3, $^2J_{HW}$ = 11.2 Hz)	13.85 ($\mathit{C}H_3$, $^1J_{CW}$ = 140.7 Hz)
			10.22 ($C_5(\mathit{C}H_3)_5$)
$CpW(O)_2(CH_2CMe_3)$	352, $[P]^+$	5.50 (s, 5 H, $C_5\mathit{H}_5$)	109.5 (C_5H_5)
	337, $[P - Me]^+$	2.19 (s, 2 H, CH_2, $^2J_{HW}$ = 11.4 Hz)	50.4 ($\mathit{C}H_2$, $^1J_{CW}$ = 144.4 Hz)
	295, $[P - 2Me]^+$	1.30 (s, 9 H, $C(\mathit{CH}_3)_3$)	33.3 ($\mathit{C}(CH_3)_3$)
			32.8 ($C(\mathit{C}H_3)_3$)
$CpW(O)_2(CH_2CMe_2Ph)$	414, $[P]^+$	7.5–7.2 (m, 5 H, $C_6\mathit{H}_5$)	128–125.9 (m, C_6H_5)
	399, $[P - Me]^+$	5.45 (s, 5 H, $C_5\mathit{H}_5$)	109.5 (C_5H_5)
	296, $[P - CMe_2Ph]^+$	2.52 (s, 2 H, CH_2, $^2J_{HW}$ = 11.8 Hz)	50.5 ($\mathit{C}H_2$, $^1J_{CW}$ = 145.4 Hz)
			39.75 ($\mathit{C}Me_2Ph$)
	281, $[P - CH_2CMe_2Ph]^+$	1.67 (s, 6 H, $C(\mathit{CH}_3)_2$)	30.8 ($C(\mathit{C}H_3)_2$)
$CpW(O)_2(CH_2Ph)$	372, $[P]^+$	7.22–7.18 (m, 5 H, $C_6\mathit{H}_5$)	145.3 (quaternary C of Ph)
		5.44 (s, 5 H, $C_5\mathit{H}_5$)	136.9, 129.8, 128.5, 125.0 (Ph C)
		3.42 (s, 2 H, CH_2)	109.8 (C_5H_5)
			36.8 ($\mathit{C}H_2$, $^1J_{CW}$ = 134.8 Hz)
$Cp^*W(O)_2(CH_2Ph)$	442, $[P]^+$	7.36 (d, 2 H, o-$C_6\mathit{H}_5$)	146.0 (quaternary C of Ph)
	351, $[P - C_7H_7]^+$	7.15 (t, 2 H, m-$C_6\mathit{H}_5$)	129.9, 128.4, 124.8 (aromatic C)
		6.87 (t, 1 H, p-$C_6\mathit{H}_5$)	117.1 ($\mathit{C}_5(CH_3)_5$)
		2.84 (s, 2 H, CH_2, $^2J_{HW}$ = 13.8 Hz)	44.0 ($\mathit{C}H_2$, $^1J_{CW}$ = 133.2 Hz)
		1.64 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	10.4 ($C_5(\mathit{C}H_3)_5$)
$CpMo(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$	282, $[P - O]^+$	5.36 (s, 5 H, $C_5\mathit{H}_5$)	
	267, $[P - O,Me]^+$	2.06 (d, 1 H, $C\mathit{H}_AH_B$, $^2J_{HH}$ = 12.4 Hz)	
		1.35 (d, 1 H, $CH_A\mathit{H}_B$, $^2J_{HH}$ = 12.4 Hz)	
		0.35 (s, 9 H, $Si(\mathit{CH}_3)_3$)	
$CpMo(O)(\eta^2\text{-}O_2)Me$	226, $[P]^+$	5.26 (s, 5 H, $C_5\mathit{H}_5$)	109.3 (C_5H_5)
	210, $[P - O]^+$	1.96 (s, 3 H, CH_3)	24.9 ($\mathit{C}H_3$)
$Cp^*Mo(O)(\eta^2\text{-}O_2)Me$	296, $[P]^+$	1.67 (s, 3 H, CH_3)	118.1 ($\mathit{C}_5(CH_3)_5$)
	280, $[P - O]^+$	1.47 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	29.9 ($\mathit{C}H_3$)
	265, $[P - O,Me]^+$		9.81 ($C_5(\mathit{C}H_3)_5$)
$CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$	368, $[P - O]^+$	5.42 (s, 5 H, $C_5\mathit{H}_5$)	109.6 (C_5H_5)
	353, $[P - O,Me]^+$	1.47 (d, 1 H, $C\mathit{H}_AH_B$, $^2J_{HH}$ = 13 Hz, $^2J_{HW}$ = 13 Hz)	28.1 ($\mathit{C}H_2$, $^1J_{CW}$ = 92.7 Hz)
		0.86 (d, 1 H, $CH_A\mathit{H}_B$, $^2J_{HH}$ = 13 Hz, $^2J_{HW}$ = 8 Hz)	1.7 ($Si(\mathit{C}H_3)_3$)
		0.34 (s, 9 H, $Si(\mathit{CH}_3)_3$)	
$CpW(O)(\eta^2\text{-}O_2)Me$	312, $[P]^+$	5.35 (s, 5 H, $C_5\mathit{H}_5$)	109.0 (C_5H_5)
	296, $[P - O]^+$	1.56 (s, 3 H, CH_3, $^2J_{HW}$ = 8.7 Hz)	20.1 ($\mathit{C}H_3$, $^1J_{CW}$ = 96 Hz)
	281, $[P - O,Me]^+$		
$Cp^*W(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$	438, $[P - O]^+$	1.58 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	117.2 ($\mathit{C}_5(CH_3)_5$)
	423, $[P - O,Me]^+$	0.93 (d, 1 H, $C\mathit{H}_AH_B$, $^2J_{HH}$ = 12.6 Hz, $^2J_{HW}$ = 10 Hz)	33.1 ($\mathit{C}H_2$, $^1J_{CW}$ = 97.4 Hz)
		0.52 (d, 1 H, $CH_A\mathit{H}_B$, $^2J_{HH}$ = 12.6 Hz, $^2J_{HW}$ = 6.9 Hz)	9.9 ($C_5(\mathit{C}H_3)_5$)
		0.45 (s, 9 H, $Si(\mathit{CH}_3)_3$)	1.5 ($Si(\mathit{C}H_3)_3$)
$Cp^*W(O)(\eta^2\text{-}O_2)Me$	382, $[P]^+$	1.56 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	117.0 ($\mathit{C}_5(CH_3)_5$)
	366, $[P - O]^+$	1.39 (s, 3 H, CH_3, $^2J_{HW}$ = 8.4 Hz)	25.2 ($\mathit{C}H_3$, $^1J_{CW}$ = 101.3 Hz)
	351, $[P - O,Me]^+$		9.7 ($C_5(\mathit{C}H_3)_5$)
$CpW(O)(Cl)_2(CH_2SiMe_3)$	371, $[P - H,Cl,Me]^+$	5.47 (s, 5 H, $C_5\mathit{H}_5$)	113.1 (C_5H_5)
		2.80 (d, 1 H, $C\mathit{H}_AH_B$, $^2J_{HH}$ = 10.7 Hz)	60.4 ($\mathit{C}H_2SiMe_3$)
	352, $[P - 2Cl]^+$	1.26 (d, 1 H, $CH_A\mathit{H}_B$, $^2J_{HH}$ = 10.7 Hz)	1.95 ($Si(\mathit{C}H_3)_3$)
		0.42 (s, 9 H, $Si(\mathit{CH}_3)_3$)	
$Cp^*W(O)(Cl)_2(CH_2SiMe_3)$	456, $[P - H,Cl]^+$	2.23 (d, 1 H, $C\mathit{H}_AH_X$, $^2J_{HH}$ = 9.8 Hz, $^2J_{HW}$ = 6.3 Hz)	122.1 ($\mathit{C}_5(CH_3)_5$)
	426, $[P - H,Cl,2Me]^+$	1.75 (s, 15 H, $C_5(\mathit{CH}_3)_5$)	63.3 ($\mathit{C}H_2$, $^1J_{CW}$ = 72 Hz)
		0.80 (d, 1 H, $CH_A\mathit{H}_X$, $^2J_{HH}$ = 9.8 Hz, $^2J_{HW}$ = 6.3 Hz)	12.0 ($C_5(\mathit{C}H_3)_5$)
		0.49 (s, 9 H, $Si(\mathit{CH}_3)_3$)	2.2 ($Si(\mathit{C}H_3)_3$)

Table II (Continued)

complex	low-resolution mass spectral data[a] m/z[b]	^{1}H NMR data (C_6D_6) δ	$^{13}C\{^1H\}$ NMR data (C_6D_6)[c] δ
$Cp^*W(O)(Cl)_2Me$	385, $[P - H,Cl]^+$ 371, $[P - H,Cl,Me]^+$	1.78 (s, 3 H, CH_3, $^2J_{HW} = 5.5$ Hz) 1.70 (s, 15 H, $C_5(CH_3)_5$)	121.5 ($C_5(CH_3)_5$) 52.2 (CH_3, $^1J_{CW} = 90.5$ Hz) 11.5 ($C_5(CH_3)_5$)
$CpW(O)(CH_2SiMe_3)_3$	511, $[P - Me]^+$ 439, $[P - CH_2SiMe_3]^+$	5.39 (s, 5 H, C_5H_5) 1.41 (d, 2 H, CH_AH_B, $^2J_{HH} = 13.9$ Hz) 1.22 (d, 2 H, CH_AH_B, $^2J_{HH} = 13.9$ Hz) 0.64 (s, 2 H, CH_2Si, $^2J_{HW} = 7.9$ Hz) 0.36 (s, 9 H, $Si(CH_3)_3$) 0.28 (s, 18 H, 2 $Si(CH_3)_3$)	107.3 (C_5H_5) 38.5 (CH_2Si, $^1J_{CW} = 75$ Hz) 32.3 ($2CH_2Si$, $^1J_{CW} = 61$ Hz) 4.5 ($Si(CH_3)_3$) 2.2 (2 $Si(CH_3)_3$)
		Isomer A: Trans Me Groups	
$Cp^*W(O)(Me)_2(CH_2SiMe_3)$	437, $[P - Me]^+$ 407, $[P - 3Me]^+$	1.47 (s, 15 H, $C_5(CH_3)_5$) 1.35 (s, 2 H, CH_2Si) 1.33 (s, 6 H, $2CH_3$) 0.50 (s, 9 H, $Si(CH_3)_3$)	112.7 ($C_5(CH_3)_5$) 39.4 (CH_2Si, $^1J_{CW} = 61.7$ Hz) 31.20 (CH_3, $^1J_{CW} = 66.7$ Hz) 10.48 ($C_5(CH_3)_5$) 4.63 ($Si(CH_3)_3$)
		Isomer B: Cis Me Groups	
		1.49 (s, 15 H, $C_5(CH_3)_5$) 1.30 (s, 3 H, CH_3) 0.74 (d, 1 H, CH_AH_XSi, $^2J_{HH} = 4.2$ Hz) 0.47 (s, 9 H, $Si(CH_3)_3$) −0.09 (s, 3 H, CH_3)	112.3 ($C_5(CH_3)_5$) 39.44 (CH_2Si, $^1J_{CW} = 61.7$ Hz) 36.33 (CH_3, $^1J_{CW} = 60.5$ Hz) 33.76 (CH_3, $^1J_{CW} = 57.6$ Hz) 10.60 ($C_5(CH_3)_5$) 2.44 ($Si(CH_3)_3$)
$Cp^*W(O)(Me)(CH_2Ph)_2$	440, $[P - Me,Ph]^+$	7.58 (d, 4 H, 2 o-PhH, $^2J_{HH} = 7.3$ Hz) 7.13 (t, 4 H, 2 m-PhH, $^2J_{HH} = 7.6$ Hz) 6.87 (t, 2 H, 1 p-PhH, $^2J_{HH} = 7.3$ Hz) 3.37 (d, 2 H, 2 CH_AH_BPh, $^2J_{HH} = 9.5$ Hz, $^2J_{HW} = 12.1$ Hz) 2.38 (d, 2 H, 2 CH_AH_BPh, $^2J_{HH} = 9.5$ Hz, $^2J_{HW} = 4.5$ Hz) 1.44 (s, 15 H, $C_5(CH_3)_5$) 0.29 (s, 3 H, CH_3)	148.1 (quaternary C of Ph) 130.9, 127.2, 124.5 (aromatic C) 112.8 ($C_5(CH_3)_5$) 57.6 (CH_2, $^1J_{CW} = 64$ Hz) 43.5 (CH_3) 10.7 ($C_5(CH_3)_5$)
$CpW(O)({=}CHSiMe_3)(CH_2SiMe_3)$[d]		10.34 (d, 1 H, $=CH$, $^2J_{HW} = 10.0$ Hz) 5.39 (s, 5 H, C_5H_5) 0.85 (d, 1 H, CH_AH_BSi, $^2J_{HH} = 12.9$ Hz) 0.68 (d, 1 H, CH_AH_BSi, $^2J_{HH} = 12.9$ Hz) 0.49 (s, 9 H, $CHSi(CH_3)_3$) 0.16 (s, 9 H, $CH_2Si(CH_3)_3$)	246.6 ($=CH$) 103.6 (C_5H_5) 5.71 (CH_2Si) 1.78 ($CHSi(CH_3)_3$) 1.30 ($CH_2Si(CH_3)_3$)
$Cp^*W(O)({=}CHSiMe_3)(CH_2SiMe_3)$[d]		8.89 (s, 1 H, $=CH$, $^2J_{HW} = 7.1$ Hz) 1.62 (s, 15 H, $C_5(CH_3)_5$) 0.49 (s, 9 H, $CHSi(CH_3)_3$) 0.36 (s, 9 H, $CH_2Si(CH_3)_3$) 0.10 (s, 2 H, CH_2Si)	239.5 ($=CH$) 111.8 ($C_5(CH_3)_5$) 16.3 (CH_2, $^1J_{CW} = 119$ Hz) 2.16 ($CHSi(CH_3)_3$) 1.6 $CH_2Si(CH_3)_3$)
$Cp^*W(O)({=}CHPh)(CH_2SiMe_3)$[d]		9.74 (s, 1 H, $=CH$, $^2J_{HW} = 11.0$ Hz) 7.27 (d, 2 H, C_6H_5) 7.19–7.08 (m, 2 H, C_6H_5) 6.86 (t, 1 H, C_6H_5) 2.57 (d, 2 H, CH_2Si, $^2J_{HH} = 3.5$ Hz, $^2J_{HW} = 27.8$ Hz) 1.56 (s, 15 H, $C_5(CH_3)_5$) 0.18 (s, 9 H, $Si(CH_3)_3$)	249.3 ($=CH$, $^1J_{CW} = 161$ Hz) 152.9 (quaternary C of Ph) 129.1, 128.1, 123.2 (aromatic C) 111.9 ($C_5(CH_3)_5$) 37.74 (CH_2, $^1J_{CW} = 119.1$ Hz) 10.69 ($C_5(CH_3)_5$) 1.19 ($Si(CH_3)_3$)
$Cp^*W(O)({=}CHSiMe_3)(Me)$[e]		9.69 (s, 1 H, $=CH$, $^2J_{HW} = 11.6$ Hz) 1.64 (s, 15 H, $C_5(CH_3)_5$) 0.75 (s, 3 H, CH_3) 0.54 (s, 9 H, $Si(CH_3)_3$)	243.3 ($=CH$, $^1J_{CW} = 157$ Hz) 111.7 ($C_5(CH_3)_5$) 31.65 (CH_3) 10.7 ($C_5(CH_3)_5$) 1.92 ($Si(CH_3)_3$)
$Cp^*W(O)({=}CHPh)(Me)$[e]		9.86 (s, 1 H, $=CH$, $^2J_{HW} = 8.6$ Hz) 7.9 (d, 2 H, 2 o-PhH, $^2J_{HH} = 7.5$ Hz) 7.31 (t, 2 H, 2 m-PhH, $^2J_{HH} = 7.5$ Hz) 7.0 (t, 1 H, 1 p-PhH) 1.64 (s, 15 H, $C_5(CH_3)_5$) 0.86 (s, 3 H, CH_3, $^2J_{HW} = 9.6$ Hz)	252.9 ($=CH$, $^1J_{CW} = 150.1$ Hz) 145.2 (quaternary C of Ph) 129.5, 129.3, 128.5, 125.6 (Ph C) 111.6 ($C_5(CH_3)_5$) 31.9 (CH_3) 10.9 ($C_5(CH_3)_5$)

[a] Probe temperatures 100–150 °C. [b] Assignments involve the most abundant naturally occurring isotopes in each species (e.g. ^{98}Mo, ^{184}W, etc.). [c] All signals are singlets unless indicated otherwise. [d] Reliable mass spectral data for this complex could not be obtained because of its extreme air- and moisture-sensitivity. [e] This complex was not isolated but was simply generated by heating a solution of its oxo trialkyl precursor in an NMR tube.

pure, yellow needles which were collected by filtration.

This conversion was also effected in benzene-d_6 while being monitored by ^{1}H NMR spectroscopy. This monitoring confirmed the clean conversion of the oxo trialkyl compound into the oxo alkylidene complex, the only byproduct being Me_4Si.

Preparations of $Cp^*W(O)(=R')(CH_2SiMe_3)$ (R' = $CHSiMe_3$ or CHPh). Both of these complexes were synthesized and isolated in a similar manner. The experimental procedure, using the case when $R' = CHSiMe_3$ as a typical example, was as follows.

A yellow solution of $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ (0.45 g, 0.91 mmol) in Et_2O (50 mL) was cooled to ca. −40 °C by employing a saturated aqueous $CaCl_2$/dry ice bath. To this stirred solution was added dropwise a colorless solution containing 2.5 mL of a 0.82 M solution (2.0 mmol) of Me_3SiCH_2MgCl in Et_2O diluted with an additional 15 mL of Et_2O. The reaction mixture instantaneously became green in color and then slowly changed to brown as the addition of the Grignard reagent continued. After this addition was complete, the final reaction mixture was stirred for an additional 30 min at ca. −40 °C before being permitted to warm slowly to room temperature by removal of the cold bath. Solvent was then removed in vacuo, and the remaining brown solid was extracted with hexanes (2 × 10 mL). The brown hexanes extracts were concentrated to ca. 5 mL under reduced pressure and were chromatographed on a short (3 × 2 cm) column of Florisil with Et_2O as eluant. The single brown band that developed was eluted from the column and collected. Solvent was removed from the eluate in vacuo, and the remaining red-brown solid was recrystallized from pentane at −20 °C to obtain 0.27 g (58% yield) of highly air-sensitive $Cp^*W(O)(=CHSiMe_3)(CH_2SiMe_3)$ as large, black needles.

Yellow-green needles of $Cp^*W(O)(=CHPh)(CH_2SiMe_3)$ were obtained in an analogous manner in 69% isolated yield when $PhCH_2MgCl$ was used in place of Me_3SiCH_2MgCl in the above procedure.

Preparations of $Cp^*W(O)(=R')(Me)$ (R' = $CHSiMe_3$ or CHPh). Both of these complexes were generated by gently warming (50–60 °C) C_6D_6 solutions of their oxo trialkyl precursors (i.e. $Cp^*W(O)(Me)_2(CH_2SiMe_3)$ and $Cp^*W(O)(Me)(CH_2Ph)_2$, respectively) in NMR tubes. The oxo alkylidene product complexes were characterized spectroscopically (Table II) but were not isolated.

Results and Discussion

Syntheses and Some Physical Properties of the $Cp'M(O)_2R$ Complexes (Cp' = Cp or Cp^*, M = Mo or W, R = CH_2SiMe_3, CH_2CMe_3, CH_2CMe_2Ph, CH_2Ph, or Me). Treatment of solutions of the 16-electron dialkyl compounds $Cp'M(NO)R_2$ in various organic solvents with an excess of dioxygen at ambient temperatures and pressures produces novel alkyl dioxo complexes $Cp'M(O)_2R$ which can be isolated in moderate yields (45–60%). The general transformation is summarized in eq 1, the conversions being relatively rapid and straightforward in most cases.

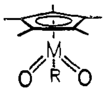
$$Cp'M(NO)R_2 \xrightarrow[6\text{-}12\ h,\ 20°C]{excess\ O_2} Cp'M(O)_2R \quad (1)$$

The dialkyl reactants need not be isolable species but may be generated in situ by the alkylation of their halo precursors with either alkyllithium or alkyl Grignard reagents. At present, the principal limitation of conversions 1 is the availability of the requisite dialkyl reactant complexes which so far is restricted to compounds containing alkyl ligands that do not possess β-hydrogens. This limitation notwithstanding, the synthetic route summarized by eq 1 does afford a range of dioxo alkyl complexes for both molybdenum and tungsten as evidenced by the first 12 entries in Tables I and II which present the physical properties of the compounds prepared in this manner. It should be noted that two of the $Cp'M(O)_2R$ compounds listed in these tables, namely, $Cp^*W(O)_2(CH_2SiMe_3)$ and $Cp^*W(O)_2Me$, have been recently prepared by Faller and Ma via a different route.[22]

Interestingly, the presence of adventitious water during the occurrence of reactions 1 is a help and not a hindrance, the isolated yields of the dioxo alkyl products generally increasing by 10–15% under these conditions. Why this is so is not clear at the present time. Furthermore, conversions 1 can also be effected by employing aqueous hydrogen peroxide in Et_2O as the oxidizing agent. Under these latter conditions, the yields of the desired $Cp'M(O)_2$ complexes are comparable to those obtained with O_2 alone, but stoichiometric amounts of the oxidant must be employed to prevent further conversion of the products to their oxo peroxo analogues $Cp'M(O)(\eta^2\text{-}O_2)R$ (vide infra).

All 12 dioxo alkyl complexes isolated during our work are white, diamagnetic solids which are very soluble in common organic solvents such as benzene, Et_2O, CH_2Cl_2, and THF and are somewhat less soluble in hexanes. Species containing Cp^* and Me_3SiCH_2 ligands are the most soluble members of this class of compounds. Unfortunately, solutions of the various dioxo alkyl compounds (particularly in CH_2Cl_2) slowly decompose and develop a yellow coloration over a few days even when maintained at −20 °C under N_2. All the $Cp'M(O)_2R$ compounds are quite thermally stable as solids, however, and are unaffected by exposure to air under ambient conditions. Many of them melt reversibly without decomposition, and samples of $CpM(O)_2(CH_2SiMe_3)$ (M = Mo or W) may be sublimed unchanged at 80 °C and 10^{-3} mm onto a water-cooled probe. The formulations of these complexes as monomeric, 16-electron entities are supported by their elemental analysis and low-resolution mass spectral data (Tables I and II).

The spectroscopic properties of all the $Cp'M(O)_2R$ compounds (Tables I and II) are consistent with their possessing the familiar three-legged piano-stool molecular structures having mirror symmetry at the central metal atom, i.e.



a fact that has been established for $CpW(O)_2(CH_2SiMe_3)$ in the solid state by a single-crystal X-ray crystallographic analysis.[14] This analysis has also determined that the tungsten–oxygen bond lengths of 1.716 (5) and 1.723 (5) Å are consistent with the existence of W=O double bonds in this compound. Accordingly, IR spectra of Nujol mulls of all the $Cp'M(O)_2R$ complexes exhibit two strong absorptions in the region 960–885 cm^{-1} attributable to the asymmetric and symmetric stretching vibrations of their $M(=O)_2$ groups. The $\nu_{M=O}$ frequencies exhibited by these compounds are similar to those observed previously for the related $CpM(O)_2X$[3] and $[CpM(O)_2]_2O$[22,23] complexes (M = Mo or W, X = halide). The $\nu_{M=O}$ values of the dioxo alkyl compounds are relatively insensitive to the alkyl group present but do decrease by ca. 20 cm^{-1} in going from W to Mo and by ca. 10 cm^{-1} in going from Cp to Cp^*. The ^1H and $^{13}C\{^1H\}$NMR spectra of the $Cp'M(O)_2R$ complexes (Table II) are relatively simple and can be interpreted in a straightforward manner. Particular spectral features worthy of note are that the ^1H NMR spectra of the $Cp'W(O)_2(CH_2SiMe_3)$ compounds display normal methylene singlets which generally exhibit 14% ^{183}W satellites with $^2J_{HW}$ being in the range of ca. 11–13 Hz, as expected for a monomeric species.[24] In a complementary manner, the $^{13}C\{^1H\}$NMR spectra of these same compounds contain resonances due to the methylene carbons in the range δ 20–50 ppm, the $^1J_{CW}$ value being 130–145 Hz. Furthermore, the $^{13}C\{^1H\}$NMR spectra of the $Cp'M(O)_2Me$ species exhibit methyl carbon signals in the range δ 8–16 ppm. Consequently, the physical properties of the dioxo alkyl compounds indicate that their monomeric molecular structures persist both in solutions as well as in the solid state.

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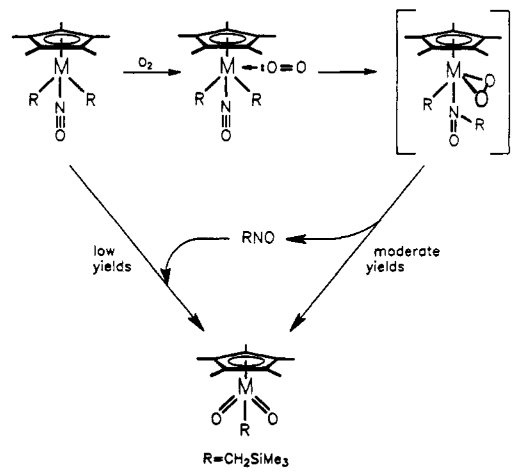
[22] (a) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59. (b) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559.

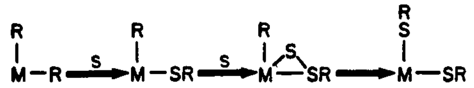
[23] Herberhold, M.; Kremnitz, W.; Razavi, A.; Shoellhorn, H.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 601.

[24] Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 7971.

Scheme I



Possible Mechanisms for the Reactions of the $Cp'M(NO)R_2$ Complexes with Molecular O_2. The most striking feature of reactions 1, especially in so far as the $Cp'W(NO)(CH_2SiMe_3)_2$ complexes are concerned, is that they apparently bear no resemblance whatsoever to the reactions undergone by these reactants when exposed to the heavier chalcogen sulfur. Treatment of the precursor dialkyl nitrosyl complexes with elemental sulfur results in the sequential insertion of sulfur into the W–C σ bonds as summarized in eq 2 (M = Cp'W(NO) and R = CH_2SiMe_3), each of the intermediate complexes shown



$$\mathrm{M{-}R} \xrightarrow{S} \overset{R}{\mathrm{M}}\mathrm{{-}SR} \xrightarrow{S} \overset{R\;\;S}{\mathrm{M}}\mathrm{{-}SR} \longrightarrow \overset{\overset{R}{S}}{\mathrm{M}}\mathrm{{-}SR} \qquad (2)$$

having been isolated and fully characterized for both the Cp-[13] and Cp*-containing[25] systems. There is no evidence in either of the reactions 2 for the formation of $Cp'W(S)_2(CH_2SiMe_3)$ (Cp' = Cp or Cp*), the dithio analogues of the dioxo products formed in reactions 1. Conversely, there is also no evidence during reactions 1 involving the tunsten reactants for the formation of alkoxy complexes such as $Cp'W(NO)(OCH_2SiMe_3)_2$ (the formal oxo analogues of the final dithiolate products of reactions 2), this despite the fact that such alkoxy complexes are known to result from the treatment of other 16-electron dialkyl complexes with elemental oxygen.[26] Clearly, the elucidation of the mechanisms operative during reactions 1 is of both fundamental significance and interest and is worthy of the expenditure of some investigative effort.

Plausible mechanistic pathways for reactions 1 using $Cp'W(NO)(CH_2SiMe_3)_2$ (Cp' = Cp or Cp*) as representative reactants are presented in Scheme I. The first step involves coordination of molecular oxygen to the 16-electron metal center in the dialkyl nitrosyl reactant, a demonstrated Lewis acid,[13] to form a simple 1:1 adduct. The second step involves migratory insertion of the bound nitrosyl group into one of the W–C σ bonds, a process for which there is ample precedent in the chemical literature.[27] [The alternative insertion of the bound dioxygen into one of the W–C σ bonds to form an alkyl peroxo complex would be expected to lead to a bis(alkoxy) complex as the final product.[26]] The resulting peroxo alkylnitroso complex could then expel the nitrosoalkane from the metal's coordination sphere in the final step and rearrange concomitantly to the final dioxo alkyl product. If such a mechanism is indeed operative, the byproduct of reactions 1 involving the $Cp'W(NO)(CH_2SiMe_3)_2$ reactants should then be the nitrosoalkane Me_3SiCH_2NO. It is unlikely that this byproduct would persist long enough to be detected in the reaction mixture since (a) such nitrogen oxides are known to be very useful oxidizing agents for the preparation of transition-metal organometallic oxo compounds[10] and (b) we have established independently that PhNO in Et_2O consumes the tungsten dialkyls completely even at −60 °C to produce 20–25% isolated yields of $Cp'W(O)_2(CH_2SiMe_3)$ as well as other products whose identities remain to be ascertained. In other words, it is our expectation that any nitrosoalkane produced during reactions 1 would itself be capable of functioning as the oxidant for these transformations, at least to some extent. Consequently, we have also included this pathway in Scheme I.

Table III. Assignments of the $\nu_{W=O}$ Values to the $Cp^*W(O)_2(CH_2SiMe_3)$ Isotopomers

isotopomer	$\nu_{W=O}$ (Nujol mull, cm^{-1}) ν_3	ν_1	ν_2
$Cp^*W(^{16}O)_2(CH_2SiMe_3)$	939	901	378
$Cp^*W(^{16}O)(^{18}O)(CH_2SiMe_3)$	926	868	
$Cp^*W(^{18}O)_2(CH_2SiMe_3)$	891	858	355

Regrettably, reactions 1 are not sufficiently clean to permit a straightforward kinetic analysis to be performed on them. Therefore, in an attempt to gain some direct evidence for the mechanistic possibilities outline in Scheme I, we first effected the reactions of $Cp'W(NO)(CH_2SiMe_3)_2$ with O_2 in benzene-d_6 and monitored their progress by ^1H NMR spectroscopy[28] and then performed the reaction of $Cp^*W(NO)(CH_2SiMe_3)_2$ in hexanes with labeled $^{18}O_2$ and analyzed the organometallic product mixture by IR spectroscopy. The ^1H NMR monitoring only reveals the conversion of the dialkyl nitrosyl reactants to the dioxo alkyl product complexes, no signals attributable to intermediate Cp'W-containing species or Me_3SiCH_2NO being evident. The ^1H NMR spectra of the final mixtures do, however, also exhibit several signals in the δ 0.1–0 ppm range attributable to alkyl protons. A Nujol mull IR spectrum of the dried final reaction mixture of the labeling experiment exhibits six absorptions of varying intensities at 939, 926, 901, 891, 868, and 858 cm^{-1} attributable to $\nu_{W=O}$. These absorptions may be assigned to the various isotopomers of the $Cp^*W(O)_2(CH_2SiMe_3)$ product by essaying the approximation that the organic ligands contribute little to its W=O vibrations and by treating the complex as a simple triatomic, O=W=O, having C_{2v} symmetry according to the method outlined by Herzberg.[29] If this is done, the assignments listed in Table III are obtained, the validity of these assignments being confirmed by agreements of better than 1% between the observed and calculated isotope effects.[30] Given these assignments, the ratios of the various isotopomers in the final reaction mixture are calculable from the intensity ratios of these absorptions in the final Nujol mull IR spectrum. In this

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[25] (a) Legzdins, P.; Sânchez, L. *J. Am. Chem. Soc.* **1985**, *107*, 5525. (b) Legzdins, P.; Martin, L. R., unpublished observations.

[26] (a) Brindley, P. B.; Scotton, M. J. *J. Chem. Soc., Perkin Trans. 2* **1981**, 419. (b) Blackburn, T. F.; Labinger, J. A.; Schwartz, J. *Tetrahedron Lett.* **1975**, 3041. (c) Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424 and references therein.

[27] Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6110 and references therein.

[28] Preliminary experiments indicate that these reactions also occur between solid $Cp'W(NO)(CH_2SiMe_3)_2$ and gaseous O_2 over a period of 4–5 days and may well afford fewer byproducts than those that occur between these two reactants in solutions.

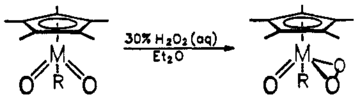
[29] Herzberg, G. *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: Toronto, 1966.

[30] Reference 29, pp 228–231.

manner, it can be determined that the final residue contains ca. 12% of $Cp^*W(^{16}O)_2(CH_2SiMe_3)$, ca. 35% of $Cp^*W(^{16}O)(^{18}O)(CH_2SiMe_3)$, and ca. 53% of $Cp^*W(^{18}O)_2(CH_2SiMe_3)$. In other words, the majority of the dioxo alkyl product formed during the labeling study does indeed contain two labeled oxo ligands, as would be expected if the principal mechanistic pathway presented in Scheme I is operative. The fact that appreciable amounts of unlabeled or partially labeled dioxo products are formed during the reaction involving labeled dioxygen can be attributed to some of them being formed by the reaction with the Me_3SiCH_2NO byproduct (as shown in Scheme I) and the rest resulting from slower exchange reactions of the labeled species with adventitious $^{16}O_2$.[31] In summary, then, the basic conclusion that emanates from these NMR and IR studies is that they are fully in accord with the mechanistic proposals outlined for reactions 1 in Scheme I.

Characteristic Chemistry of the Cp′M(O)₂R Complexes. The remarkable aspect of the reactivity exhibited to date by the representative dioxo alkyl complexes prepared during this work is that their metal–alkyl linkages remain unaffected by reagents that would normally be expected to cleave them. Instead, it is their M=O groups that are the preferred sites of reactivity. This aspect is particularly well illustrated by the behavior of the dioxo alkyls upon treatment with hydrogen peroxide and hydrogen chloride. Each of these reactions will now be considered in turn.

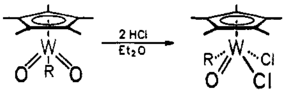
A. With H_2O_2. Treatment of representative members of the 16-electron dioxo alkyl complexes with 30% H_2O_2(aq) in Et_2O results in their clean conversion to the corresponding $Cp'M(O)(\eta^2\text{-}O_2)R$ compounds as summarized in eq 3 where M = Mo or W, R = Me or CH_2SiMe_3,



(3)

and the cyclopentadienyl ring represents either C_5H_5 or C_5Me_5. It should be noted that two of the $Cp^*W(O)(\eta^2\text{-}O_2)R$ compounds, namely, $Cp^*W(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$ and $Cp^*W(O)(\eta^2\text{-}O_2)Me$, have recently been prepared by Faller and Ma via a different route.[22b] The oxo peroxo product complexes are white (M = W) to pale yellow (M = Mo) air-stable solids which are isolable from reactions 3 in good yields (ca. 80%). Their solubility properties are comparable to those exhibited by their dioxo alkyl precursors (vide supra), and their spectroscopic properties (summarized in Tables I and II) are consistent with their possessing the molecular structures shown in eq 3 both in solutions and in the solid state. A single-crystal X-ray crystallographic analysis of one of these complexes, namely, $CpW(O)(\eta^2\text{-}O_2)(CH_2SiMe_3)$,[15] has established its solid-state molecular structure as being that of a slightly flattened three-legged piano stool whose intramolecular dimensions are fully in accord with it being formulated as a 16-electron complex containing W=O and $W(\eta^2\text{-}O_2)$ linkages. Interestingly, the introduction of the extra oxygen atom into the metal's coordination sphere has a significant effect on the methyl and methylene signals in the ^1H and ^{13}C NMR spectra of the peroxo complexes. The inequivalent methylene protons give rise to AB patterns in the ^1H NMR spectra (Table II), and both the methyl and methylene resonances occur some 0.5–1.0 (^1H) and 10 ppm (^{13}C) downfield from those exhibited by their dioxo alkyl precursors (Table II). Furthermore, the $^1J_{CW}$ values diminish by approximately 40 Hz, thereby reflecting the different electron density at the metal center extant in the $Cp'W(O)(\eta^2\text{-}O_2)R$ species. We are currently investigating the possibility that these oxo peroxo complexes may be able to function as selective oxidants during various organic transformations of interest.

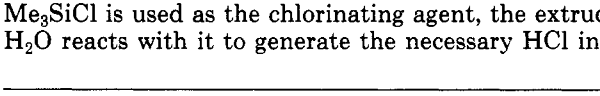
B. With HCl. Just as in reactions 3, it is also one of the W=O links which is transformed when $Cp'W(O)_2R$ (Cp′ = Cp or Cp*, R = Me or CH_2SiMe_3) complexes are treated with a slight excess of HCl in Et_2O (eq 4). There is absolutely no evidence, however, during the occurrence of conversions 4 for the formation of any of the $Cp'W(O)_2Cl$ products even though these are well-known species[22] that might reasonably be expected to result from the reaction of a transition-metal alkyl with a hydrogen halide.[32] The net organometallic conversions shown in eq 4 can also be effected with PCl_5 or Me_3SiCl as the chlorinating agents. The congeneric molybdenum dioxo alkyls initially appear to react with HCl in a manner similar to that shown in eq 4 but then convert to other products whose identities have yet to be determined.



(4)

The tungsten dichloro oxo products are isolable in high yields (>90%) from reactions 4 as yellow, crystalline solids which may be handled in air for short periods of time without the occurrence of noticeable decomposition. These solids are less soluble in common organic solvents than are their dioxo alkyl precursors. Their mass, IR, and ^1H and ^{13}C NMR spectra (Tables I and II) are consistent with their possessing monomeric four-legged piano-stool molecular structures with cis chloride ligands. The cis nature of the chloride ligands is indicated by their ^1H and $^{13}C\{^1H\}$NMR spectra (Tables I and II). For instance, the methylene protons of the CH_2SiMe_3 ligands give rise to AB patterns in the ^1H NMR spectra ($^2J_{HH}$ = ca. 10 Hz), and the ^{13}C gated decoupled NMR spectrum of $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ in C_6D_6 exhibits a low field resonance at δ 63.3 ppm assignable to the methylene carbon which displays coupling to two inequivalent protons ($^1J_{CH}$ = 116 and 129 Hz). Thus, like all the other oxo complexes encountered during this work, the $Cp'W(O)(Cl)_2R$ compounds appear to be monomeric 16-electron species containing the metal in its highest oxidation state of +6. We are currently endeavoring to grow suitable single crystals of $Cp^*W(O)(Cl)_2(CH_2SiMe_3)$ for a confirmation of its solid-state molecular structure by an X-ray crystallographic analysis.

Since oxidative addition to the tungsten(VI) center in the dioxo alkyl reactant is unlikely, reactions 4 probably proceed via initial addition of HCl across one of the W=O bonds as shown in eq 5. The resulting hydroxo chloro



(5)

compound would then react rapidly with a second equivalent of HCl to afford the final organometallic product, water being extruded as the byproduct. Presumably, when Me_3SiCl is used as the chlorinating agent, the extruded H_2O reacts with it to generate the necessary HCl in an

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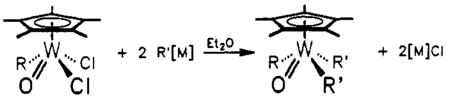
(31) That such exchange reactions do occur can be demonstrated by simply exposing an Et_2O solution of the final labeled reaction mixture to $^{16}O_2$ for 2 days. A Nujol mull IR spectrum of the dried reaction residue after this time clearly exhibits increased intensities of the $\nu_{W=O}$'s due to the ^{16}O-containing dioxo alkyl complexes (Table III).

(32) Powell, P. *Principles of Organometallic Chemistry*, 2nd ed.; Chapman and Hall: London, 1988.

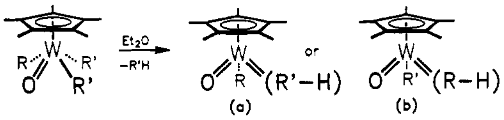
autocatalytic fashion. Regrettably, monitoring of the various conversions 4 by ^1H NMR spectroscopy fails to reveal any evidence pro or con these putative intermediates.

The dichloro oxo alkyl products of reactions 4 are very useful synthetic precursors in their own right. In particular, they provide reliable synthetic routes to complexes of types 2 and 3 considered in the Introduction via the sequential transformations summarized in eq 6 and 7 in which the cyclopentadienyl ring represents either C_5H_5 or C_5Me_5. Thus, treatment of the tungsten dichloro oxo compounds with 2 equiv of an alkyllithium or alkyl Grignard reagent affords the oxo trialkyl complexes of type 2 which, when isolable, may be obtained in ca. 60% yields from reactions 6 as yellow, crystalline solids. The presence of the three alkyl ligands in these compounds imparts to them a greater solubility in common organic solvents than that exhibited by their dichloro precursors. Indeed, their solubilities are even greater than those of the related dioxo alkyl species; e.g., Cp*W(O)$(Me)_2(CH_2SiMe_3)$ is very soluble in pentane. The isolable oxo trialkyl complexes (Tables I and II) appear to be reasonably stable when exposed to air and moisture both as solids or in solutions.



(6)

R=CH_2SiMe_3 ; [M]=Li ; R'=Me
R=CH_2SiMe_3 ; [M]=MgCl ; R'=CH_2SiMe_3 or CH_2Ph
R=Me ; [M]=MgCl ; R'=CH_2Ph



(7)

	product
R=CH_2SiMe_3 ; R'=CH_2SiMe_3 or CH_2Ph	(a)
R=CH_2SiMe_3 ; R'=Me	(b)
R=Me ; R'=CH_2Ph	(a)

The spectroscopic properties of the Cp'W(O)R_3 complexes indicate that they possess normal monomeric four-legged piano-stool molecular structures. The intramolecular dimensions of one of these species, namely, CpW(O)$(CH_2SiMe_3)_3$, have been established previously[14] by single-crystal X-ray crystallography. When two of the alkyl ligands are different from the third, as in Cp*W(O)$(Me)_2(CH_2SiMe_3)$ and Cp*W(O)(Me)$(CH_2Ph)_2$, their piano-stool molecular structures should result in their existing as cis and trans isomers. This feature is readily evident in the solution NMR spectra of Cp*W(O)$(Me)_2(CH_2SiMe_3)$ (Table II), the two isomers being designated as A (trans Me groups) and B (cis Me groups). The ratio of the two isomers in benzene-d_6 at 30 °C is A:B = 63:37. Interestingly, Cp*W(O)(Me)$(CH_2Ph)_2$ does not exhibit similar isomerism, existing exclusively as the trans $(CH_2Ph)_2$ isomer under identical conditions. Presumably, steric factors play the principal role in determining the thermodynamically most stable isomers of these trialkyl oxo complexes. Steric factors also appear to be dominant in determining whether the oxo trialkyl product complexes of reactions 6 are sufficiently thermally stable to be isolable in the first place under ambient conditions. When the coordination environment around the central metal is sufficiently congested, as for Cp*W(O)$(CH_2SiMe_3)_3$ and Cp*W(O)$(CH_2SiMe_3)(CH_2Ph)_2$, the oxo trialkyl complexes do not persist at temperatures above −20 °C. Instead, alkane elimination (presumably via intramolecular α-H abstraction) occurs as shown in eq 7, and the new oxo alkylidene complexes result. For those oxo trialkyl complexes which are isolable at ambient temperatures, reactions 7 may be induced by gently warming solutions of them to 50–60 °C. For example, ^1H NMR monitoring of the thermal conversion of Cp*W(O)(Me)$(CH_2Ph)_2$ in C_6D_6 at 50 °C indicates the clean formation of Cp*W(O)(Me)(=CHPh), the conversion being complete within 3 days. Under identical experimental conditions, Cp*W(O)$(Me)_2(CH_2SiMe_3)$ similarly converts to Cp*W(O)(Me)(=$CHSiMe_3$), the notable feature being that the trans isomer converts more rapidly than its cis analogue. Whether external heating is required or not, reactions 7 afford the final oxo alkylidene products in high yields (40–70%). Again, the physical properties of these complexes (Tables I and II) are consistent with their having the molecular structures shown in eq 7. Aspects of the characteristic chemistry of these oxo alkylidene complexes are currently being investigated.

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