Reactions of Tris(ethanediolato)tungsten and Tungsten Oxytetrachloride with Aminotris(phenol)s: Alkoxide, Chloro, and Alkyl Derivatives of Oxotungsten(VI) Complexes with Tetradentate [O₃N]-Type Ligands

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Trisdiolatotungsten(VI) complex [W(eg)₃] (eg = 1,2-ethanediolato dianion) reacts in refluxing toluene solution with phenolic ligand precursors tris(2-hydroxy-3,5-dimethylbenzyl)amine (H₃L^Me) and tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (H₃L^tBu) to form monomeric oxotungsten(VI) complexes [WO(L^Me)(Heg)] and [WO(L^tBu)(Heg)], respectively. These complexes undergo chloride-for-alkoxide substitution when treated with SOCl₂ in CH₂Cl₂, which leads to the formation of corresponding chloro complexes [WO(L^Me)Cl] and [WO-(L^tBu)Cl]. Identical chloro complexes are also formed in the reaction between these phenolic ligand precursors and [WOCl₄]. The reaction of [WO(L^R)Cl] complexes with Grignard reagents yields corresponding monoalkyl derivatives [WO(L^R)(Me)] and [WO(L^R)(CH₂CMe₂Ph)]. These alkyl derivatives are stable in ambient atmosphere. All new compounds are mononuclear molecules, in which the tripodal aminotris(phenolate) group has coordinated as a tetradentate ligand through three oxygen donors and one nitrogen donor, whereas the nitrogen donor is located trans to the terminal oxo group.

Introduction

The increasing interest in the development of early-transition-metal chemistry with chelating multifunctional phenols is prompted by their significance in organometallic chemistry and catalysis.[1] Particularly, well-presented examples of group IV and group V metal compounds with such ligands have attracted attention, as they can catalyze living polymerization of terminal alkenes.[2] Various molybdenum and tungsten complexes with such chelating aryloxides are known in industrially and scientifically interesting applications of olefin metathesis reactions.[3] For example, oxotungsten(VI) complexes with several 1,1′-coupled or -bridged biphenols have been used successfully as catalyst precursors in metathesis polymerization of cyclic alkenes.[3c−e] High-

valent molybdenum and tungsten oxo complexes have also found applications as catalysts in diverse oxo transfer processes, including various enzymatic processes as well as industrially important selective epoxidation of alkenes.[4] In the context of a broader program aimed at developing transition metal catalysts for olefin metathesis reaction, our laboratory has recently become interested in the chemical manipulation of molybdenum and tungsten aryloxide complexes. In the course of these studies, we have introduced the dianionic aminobis(phenolato) (O,N,O donors) and diaminobis(phenolato) (O,N,N,O donors) ligands to oxomolybdenum(VI) and oxotungsten(VI) chemistry and reported several catalytic applications of formed complexes.[5−7] We have now extended these studies to include tungsten(VI) complexes with atrane-type aminotris(phenol)s. Aminotris(phenol)s are a contemporary group of chelating phenols, which are known to react as tetradentate trianionic ligands with main group elements as well as with early transition metals.[8−12] At present, the chemistry of these ligands has been focused mainly on group IV and group V metals, whereas the

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reports on molybdenum or tungsten complexes with these ligands are still scarce.[13] In this article we describe new coordination and organometallic chemistry of oxotungsten(VI) complexes chelated by aminotris(phenolato) ligands tris(2-hydroxy-3,5-dimethylbenzyl)amine (H_3L^{Me}) and tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (H_3L^{tBu}).

Experimental Section

General Comments. Starting complexes [W(eg)$_3$] (**1**) and [WOCl$_4$] (**2**) and ligand precursors H_3L^R were prepared and purified according to the literature.[14−16] Other chemicals were of reagent grade and were used as purchased. ^1H NMR (200 MHz) and ^{13}C spectra (200 MHz) were recorded in CDCl$_3$ solutions and were referenced internally to SiMe$_4$. IR spectra were recorded as Nujol mulls. Analytical samples were dried in vacuo at 40 °C for 2 h prior to elemental and spectral analyses.

Syntheses of [WO(L^R)(Heg)]. Tungsten precursor **1** (364 mg, 1.00 mmol) was heated with 1 equiv of H_3L^{Me} (420 mg) or H_3L^{tBu} (672 mg) in 60 mL of toluene at reflux temperature for 6 h to form a orange-red solution. The H$_2$eg that formed during reaction was removed as a toluene azeotrope. Remaining solvent was evaporated, and an orange solid residue was purified by silica column chromatography using toluene as an eluent.

[WO(L^{Me})(Heg)] (3a). Yield: 620 mg (92%). Anal. Calcd for C$_{29}$H$_{35}$NO$_6$W: C, 51.42; H, 5.21; N, 2.07. Found: C, 51.78; H, 5.44; N, 2.05. IR (Nujol): 3555 m, 1460 s, 1377 s, 1298 w, 1240 s, 1219 vs, 1159 s, 1084 s (br), 1030 s (br), 984 w, 947 vs, 899 m, 860 s, 826 s, 756 w, 729 m, 694 w, 606 s, 559 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 7.22 (1H), 6.94 (2H), 6.74 (2H), 6.53 (1H), 4.41 (2H, t, *J* = 8.8 Hz), 3.97−3.41 (6H, several overlapping peaks), 3.36 (2H, t, *J* = 8.8 Hz), 2.43 (3H), 2.29 (12H), 2.21 (3H). ^{13}C NMR (CDCl$_3$): δ 154.39, 131.79, 131.58, 131.04, 130.87, 129.01, 128.19, 127.96, 127.31, 125.83, 124.68, 64.17, 60.58, 59.00, 20.44, 16.06. Mp > 260 °C (dec).

[WO(L^{tBu})(Heg)] (3b). Yield: 630 mg (67%). Anal. Calcd for C$_{47}$H$_{71}$NO$_6$W: C, 48.80; H, 10.03; N, 1.96. Found: C, 48.61; H, 9.98; N, 1.87. IR (Nujol): 3557 m, 1460 s, 1377 s, 1302 m, 1238 s (br), 1204 s, 1169 vs, 1136 w, 1121 w, 1086 s, 1032 vs, 984 w, 961 vs, 914 m, 909 m, 876 s, 856 vs, 841 s, 810 w, 758 m, 729 w, 694 w, 623 m, 606 m, 561 s cm^{-1}. ^1H NMR (CDCl$_3$): δ 7.40 (1H), 7.39 (2H), 7.02 (1H), 6.98 (2H), 4.22 (2H, t, *J* = 8.0 Hz), 3.98−3.64 (6H, several overlapping peaks), 3.06 (2H, t, *J* = 8.8 Hz), 1.58 (9H), 1.44 (18H), 1.29 (18H), 1.27 (9H). ^{13}C NMR (CDCl$_3$): δ 144.77, 130.79, 130.01, 129.91, 128.87, 127.11, 128.19, 127.96, 125.06, 123.88, 123.61, 63.97, 60.96, 59.95, 35.01, 34.35, 31.59, 29.96. Mp > 280 °C (dec).

Chloride-for-Alkoxide Substitutions of [WO(L^R)(Heg)]. General Procedure. [WO(Heg)(L^R)] (0.20 mmol) was dissolved in 5 mL of CH$_2$Cl$_2$ in a screw cap vial and subsequently treated with 2.0 mmol (0.15 mL) of SOCl$_2$. The reaction mixtures were then heated at 100 °C (*Caution, pressure!*) for 3 (**3a**) or 20 (**3b**) h. Volatiles were then evaporated, and the

remaining red solids were purified by silica column chromatography using a hexane−toluene mixture (1:1) as an eluent. X-ray quality crystals of **4b** were grown at 4 °C from acetonitrile.

[WO(L^{Me})Cl] (4a). Yield: 81 mg (62%). Anal. Calcd for C$_{27}$H$_{30}$ClNO$_4$W: C, 49.75; H, 4.64; N, 2.15. Found: C, 49.92; H, 4.51; N, 2.01. IR (Nujol): cm^{-1} 1462 s, 1377 s, 1240 s, 1217 vs, 1159 s, 1076 m, 953 vs, 870 s, 843 m, 824 m, 756 w, 730 w, 690 w, 596 m, 556 m cm^{-1}. ^1H NMR (CDCl$_3$): δ 6.94 (2H), 6.83 (1H), 6.73 (2H), 6.39 (1H), 4.42 (1H), 4.35 (1H), 3.53 (2H), 3.46 (1H), 3.39 (1H), 2.38 (3H), 2.31 (12H), 2.13 (3H). ^{13}C NMR (CDCl$_3$): δ 150.08, 144.84, 137.68, 133.72, 132.33, 131.25, 130.84, 128.64, 127.33, 125.96, 125.55, 62.76, 59.02, 20.57, 15.96. Mp > 200 °C (dec).

[WO(L^{tBu})Cl] (4b). Yield: 161 mg (89%). Anal. Calcd for C$_{45}$H$_{66}$ClNO$_4$W: C, 59.77; H, 7.36; N, 1.55. Found: C, 59.60; H, 7.30; N, 1.81. IR (Nujol): 1460 s, 1378 s, 1258 m, 1240 vs (br), 1204 s, 1169 vs, 1125 m, 1070 w, 945 vs, 916 s, 878 vs, 851 vs, 816 m, 764 m, 737 m, 694 w, 602 m, 565 m cm^{-1}. ^1H NMR (CDCl$_3$): δ 7.41 (1H), 7.39 (2H), 7.06 (1H), 6.98 (2H), 3.77−3.63 (several peaks, 6H), 1.53 (12H), 1.47 (16H), 1.31 (26H), 0.44 (3H). ^{13}C NMR (CDCl$_3$): δ 154.95, 152.59, 145.28, 144.21, 140.13, 126.69, 125.75, 124.36, 124.18, 123.80, 60.92, 59.95, 42.15, 35.20, 34.42, 31.61, 30.10. Mp: 250 °C.

Reaction of H_3L^R with [WOCl$_4$]. Reactions were carried out under a N$_2$ atmosphere by using standard benchtop techniques. Toluene used as a reaction medium was distilled over sodium prior to use.

[WO(L^{Me})Cl] (4a). Starting compound **2** (340 mg, 1.0 mmol) was suspended in 30 mL of toluene and subsequently treated with 1 equiv of H_3L^{Me} (420 mg) to obtain an intense red mixture. Reaction mixture was allowed to reflux for 2 h. Volatiles were then evaporated in a vacuum, and the red solid thus obtained was purified as described above. Yield: 455 mg (70%).

[WO(L^{tBu})Cl] (4b). Starting compound **2** (260 mg, 0.76 mmol) was suspended in 30 mL of toluene and subsequently treated with H_3L^{tBu} (520 mg, 0.76 mmol) to obtain an intense red mixture, which was stirred under reflux for 2 h. One equivalent of NaH-dispersion (50% in oil, 40 mg) was added to the reaction mixture, and the reaction was allowed to continue for 1 h. Volatiles were then evaporated in a vacuum, and the red solid thus obtained was purified as described above. Yield: 480 mg (69%).

General Procedure for the Preparation of [WO(L^R)-(Me)]. To the solution of [WO(L^R)Cl] (0.30 mmol) in anhydrous toluene (20 mL) was added dropwise a solution of freshly prepared MeMgI (ca. 1 mmol) in diethyl ether (2 mL). During the addition, the mixture turned from intense red to a yellow solution. The solution was stirred under N$_2$ atmosphere for 1 h at room temperature and subsequently filtered through a short pad of silica. All the volatiles were then removed under reduced pressure, and a brownish-yellow residue was recrystallized from hot acetonitrile (10 mL) to obtain organometallic products as air-stable, yellow crystals.

[WO(L^{Me})(Me)] (5a). Yield: 120 mg (63%). Anal. Calcd for C$_{28}$H$_{33}$NO$_4$W: C, 53.26; H, 5.27; N, 2.22. Found: C, 52.91; H, 4.97; N, 2.21. IR (Nujol): cm^{-1} 1462 s, 1373 s, 1256 s, 1238 vs, 1217 vs, 1161 s, 1040 m, 953 vs, 934 m, 858 s, 832 s, 750 w, 730 w, 696 w, 604 m, 564 m, 552 m cm^{-1}. ^1H NMR (CDCl$_3$): δ 6.95 (2H), 6.92 (1H), 6.71 (2H), 6.61 (1H), 3.87 (1H), 3.80 (1H), 3.55 (1H), 3.52 (2H), 3.47 (1H), 2.39 (3H), 2.30 (6H), 2.28 (6H), 2.21(3H), 0.57 (3H). ^{13}C NMR (CDCl$_3$): δ 153.70, 152.51, 131.95, 130.76, 130.52, 128.57, 127.75, 127.12, 125.52, 124.85, 124.61, 60.51, 59.02, 40.73, 20.10, 15.68. Mp > 280 °C (dec).

[WO(L^{tBu})(Me)] (5b). Yield: 175 mg (66%). Anal. Calcd for C$_{46}$H$_{69}$NO$_4$W: C, 62.51; H, 7.87; N, 1.58. Found C, 62.80; H, 5.72; N, 1.67. IR (Nujol): 1460 s, 1378 s, 1258 m, 1238 s, 1204 m, 1169 s, 1125 m, 1070 w, 951 vs, 914 s, 878 vs, 860 s, 849 vs, 812 m, 764 m, 741 m, 694 w, 602 m, 536 m cm^{-1}. ^1H NMR (CDCl$_3$): δ 7.39 (1H), 7.33 (2H), 7.01 (1H), 6.96 (2H), 4.06−

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Scheme 1. Preparation of Complexes [WO(L^R)X] (coordinated aminotris(phenolate) ligands are presented in a simplified fashion for clarity)^a
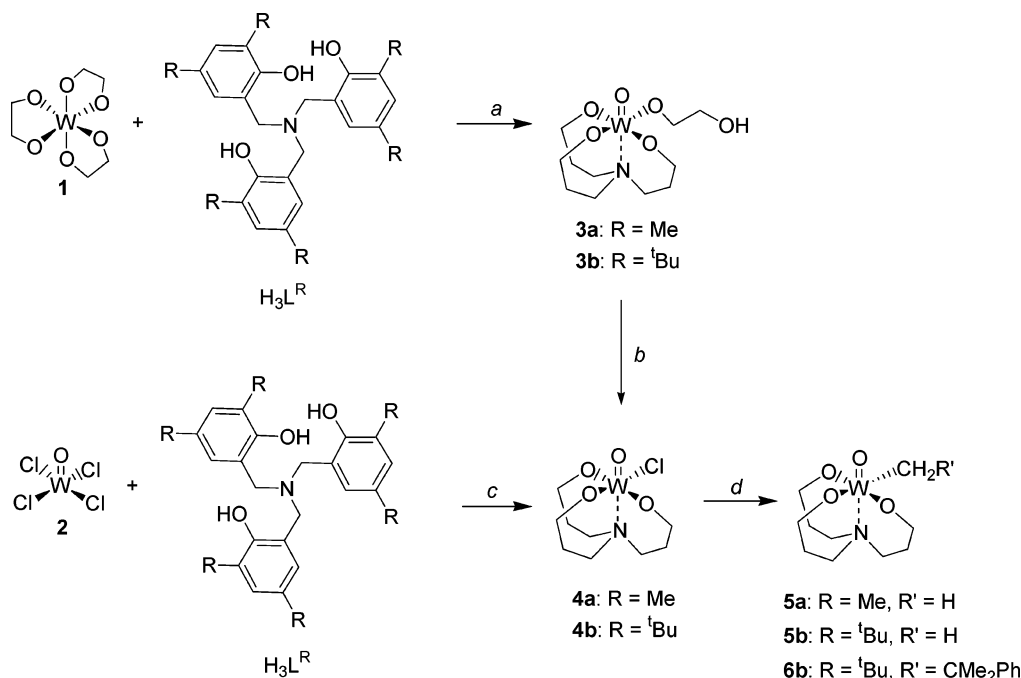
^{a} Conditions: (a) toluene, reflux, distillation of PhMe-H$_2$eg azeotrope; (b) CH$_2$Cl$_2$, SOCl$_2$; (c) toluene, reflux; (d) PhMe, Et$_2$O, RMgX.

3.65 (several peaks, 6H), 1.55 (12H), 1.47 (16H), 1.29 (26H). ^{13}C NMR (CDCl$_3$): δ 155.32, 154.48, 146.30, 146.08, 140.20, 139.96, 126.91, 126.34, 124.55, 123.91, 61.40, 60.06, 35.17, 34.46, 31.61, 30.36, 29.70. Mp > 300 °C (dec).

Preparation of [WO(L^{tBu})(CH$_2$CMe$_2$Ph)] (6b). To the solution of [WO(L^{tBu})Cl] (0.30 mmol, 270 mg) in anhydrous toluene (20 mL) was added dropwise a solution of freshly prepared PhMe$_2$CCH$_2$MgCl (ca. 1 mmol) in diethyl ether (2 mL). The deep purple reaction mixture was stirred under N$_2$ atmosphere for 1 h at room temperature, and all the volatiles were subsequently evaporated under reduced pressure. Intense red, solid **6b** was recrystallized from hot acetonitrile (10 mL) to obtain air-stable, deep purple crystals. Yield: 175 mg (58%). Anal. Calcd for C$_{55}$H$_{79}$NO$_4$W: C, 65.90; H, 7.95; N, 1.40. Found: C, 66.19; H, 8.12; N 1.38. IR (Nujol): 1460 vs, 1414 w, 1378 s, 1364 s, 1254 m, 1236 s, 1204 m, 1171 s, 1128 m, 1070 w, 972 s, 914 m, 874 s, 860 s, 851 s, 810 w, 766 m, 741 w, 700 m, 563 m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 7.33–6.97 (multiple peaks, 10H), 6.26 (1H), 4.51 (1H), 4.45 (1H), 3.44 (1H), 3.40 (2H), 3.37 (1H), 2.01 (2H), 1.82 (3H), 1.65 (5H), 1.42–1.28 (several peaks, 45H), 0.96 (7H). ^{13}C NMR (CDCl$_3$): δ 150.75, 148.60, 142.70, 138.14, 134.65, 135.90, 126.91, 127.43, 123.19, 121.74, 121.47, 120.65, 120.09, 119.41, 118.49, 116.86, 114.24, 61.36, 59.08, 38.34, 29.98, 29.38, 27.57, 26.86, 25.08, 24.36, 22.59, 21.93 (the signals due to the α-carbon of the CH$_2$CMe$_2$-Ph ligand may be covered by the strong solvent triplet[17]). Mp > 252 °C.

X-ray Crystallography. Crystals of **3b**, **5a**, and **6b** suitable for X-ray measurements were grown from acetonitrile. The crystal data for the compounds along with other experimental details are summarized in Table 1. Single-crystal data collections, reduction, and subsequent calculations were performed essentially as described in our earlier papers.[5,6] *MULABS*[18] absorption correction was tested for the data of all three compounds, but was only used for the data of **6b**. Crystals of

Table 1. Summary of Crystallographic Data for 3b, 5a, and 6b at 173(2) K

	3b	**5a**	**6b**
formula	C$_{47}$H$_{71}$NO$_6$W	C$_{28}$H$_{33}$NO$_4$W	C$_{55}$H$_{79}$NO$_4$W· 0.2C$_2$H$_3$N
M_r	929.90	631.40	1010.25
cryst syst	monoclinic	orthorhombic	monoclinic
space group (no.)	$P2_1/c$ (14)	$Pcab$ (61)	$P2_1/a$ (14)
a/Å	10.5201(3)	16.2251(4)	12.6104(3)
b/Å	19.9157(3)	16.5889(3)	26.2334(7)
c/Å	21.8690(6)	18.8273(4)	16.4217(2)
$α$/deg	90	90	90
$β$/deg	97.9050(10)	90	103.4180(10)
$δ$/deg	90	90	90
V/Å^3	4538.35(19)	5067.49(19)	5284.2(2)
Z	4	8	4
D_c/g cm^{-1}	1.361	1.655	1.270
$μ$(Mo Kα)/cm^{-1}	25.91	45.93	22.29
no. of obsd reflns	9939	4686	9537
R_{int}	0.0380	0.0395	0.0582
no. of params	517	314	469
R1^a	0.052 (0.032)^b	0.060 (0.030)	0.058 (0.036)
wR2	0.061 (0.055)	0.060 (0.053)	0.076 (0.070)

^{a} R1 = Σ||F$_o$| − |F$_c$||/Σ|F$_o$|. wR2 = {Σ[w(F$_o$^{2} − F$_c$^{2})^2]/Σ[w(F$_o$^{2})^2]}$^{1/2}$ and w = 1/[σ^2(F$_o$^{2}) + (aP)^2 + bP)], where P = (2F$_c$^{2} + F$_o$^{2})/3. ^{b} Values in parentheses for reflections with $I > 2.0σ(I)$.

6b contain 0.2 molecule of acetonitrile in the lattice. Figures were drawn with *Ortep-3 for Windows*.[19] Further details are provided in the Supporting Information.

Results and Discussion

Syntheses of Complexes [WO(L^R)(Heg)]. Stirred suspensions of alkoxide starting complex **1** in toluene were reacted with stoichiometric amounts of the ligand precursors H$_3$L^R at reflux temperature (Scheme 1a). Under these conditions, the reactions proceeded efficiently, the colorless suspensions turning rapidly to

(17) For example, the ^{13}C NMR spectrum of [MoCl(NAr)(NBu^t)(CH$_2$-CMe$_2$Ph)] in C$_6$D$_6$ solution shows this α-carbon signal at δ 71.16. See: Gibson, V. C.; Redshaw, C.; Walker, G. L. P.; Clegg, W.; Elsegood, M. R. J. *J. Organomet. Chem.* **2004**, *689*, 332–344.

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orange-red solutions. The reactions were promoted by distilling out the liberated 1,2-ethanediol as a toluene azeotrope. Evaporation of toluene followed by crystallization from hot acetonitrile afforded air-stable tungsten(VI) compounds as orange solid crystalline materials, which are moderately soluble in toluene, THF, and chlorinated solvents. ^{1}H NMR spectra of studied compounds showed predictable resonances for coordinated aminotris(phenolato) ligands. In the aliphatic region of the spectra two distinct multiplets for the 1,2-ethanediolate groups are observed, implying that there are two different environments for these methylene protons. IR spectra showed absorption bands at 3555 cm^{-1}, which were assigned as free OH groups. Strong absorptions in the range 1000−1200 cm^{-1} are typical for alkoxide O−C stretching frequencies, whereas the W−O stretches were seen as medium to strong intensity peaks around 600 cm^{-1}.[20] Intense absorption bands at 947 cm^{-1} (**3a**) and 961 cm^{-1} (**3b**) are characteristic for W=O moieties.[21] On the grounds of our earlier studies on aminobis(phenolato) complexes of tungsten(VI), we supposed that the coordination of aminotris(phenolate)s may be associated with the formation of terminal oxo groups.[5,7] X-ray structure determinations of **3b** (see below) confirmed that the aminotris(phenolate) has been bonded as a tetradentate, trianionic ligand, whereas the ethanediolate ligand is monoanionic and monodentate. As expected, the sixth coordination site has been occupied by a terminal oxo ligand. Although the formation of terminal oxo groups was predictable, the source of these oxo moieties still remains vague. In principle, high-valent metal alkoxides can decompose by an elimination process, which yields ether and the corresponding oxometal compounds.[22] On the other hand, water is the most likely supplier of unanticipated oxo groups, while it is practically impossible to exclude the diminutive amount of water necessary to carry out the hydrolysis reaction. Analogous reactions with other phenolic ligands,[23] e.g., calix(4)arenes or methylene-bridged biphenols, do not produce related oxo complexes, so the nitrogen donors of the ligand precursors seem to be necessary for these transformations. Conceivably, the role of the amino groups may just be to make these ligand precursors sufficiently hygroscopic to carry a required amount of water into the reaction.

Syntheses of Complexes [WO(L^R)Cl]. Metal alkoxide moieties can be transformed into halides by various substitution reactions.[24] The direct addition of anhydrous HCl is the most straightforward method to the stepwise substitution of alkoxides, whereas other successful procedures utilize diverse chlorinating reagents. In our earlier studies, we have found SOCl$_2$ as a convenient reagent for chloride-for-alkoxide substitutions.[5,25] In the present study, intense red solutions were obtained when orange solutions of [WO(L^R)(Heg)] in

CH$_2$Cl$_2$ were treated with a 10-fold excess of SOCl$_2$ (Scheme 1b). The reaction mixtures were heated at 100 °C in screw cap vials, while the reactions were monitored by TLC. Consequently, complex **3a** reacted with SOCl$_2$ in a few hours to produce **4a** as the only isolable product in an adequate yield, whereas sterically more hindered complex **3b** required a substantially longer reaction time to give chlorinated derivative **4b** nearly quantitatively. Compounds **4** are soluble in chlorinated solvents, THF, and toluene. NMR spectra of **4** confirmed the loss of an ethanediolate group presenting typical signals for aminotris(phenol) ligands. IR spectra showed C−O, W−O, and W=O stretches essentially similar to those found for compounds **3**.

The routine syntheses for oxotungsten(VI) phenoxides employ a straightforward reaction of [WOCl$_4$] (**2**) with a stoichiometric amount of phenolic ligand precursors in a proper solvent. When **2** was treated with ligand precursor H$_3$L^{Me} in refluxing toluene, the reaction proceeded smoothly, yielding an intense red solution (Scheme 1c). Evaporation of solvent and HCl coproduct afforded a red solid, which was further purified by column chromatography to obtain dark red chlorocomplex **4a** in synthetically beneficial yields. Analogous reaction with sterically bulkier ligand precursor H$_3$L^{tBu} was more time-consuming, and additional base was needed to complete the reaction. Evaporation of toluene followed by column chromatography and recrystallization from MeCN afforded dark red crystals of **4b** in a good yield.

Syntheses of Alkyl Complexes. The tungsten alkyl complexes [WO(L^R)(Me)] (**5**) were readily prepared by treating [WO(L^R)Cl] (**4**) with the Grignard reagent MeMgI (Scheme 1d). When an etheral solution of methylmagnesium iodide was added to the intense red solutions of **4** in toluene, the reaction mixtures rapidly turned yellow (Scheme 1d). Solutions were filtered and subsequently evaporated to obtain brownish-yellow solids, which are reasonably soluble in toluene and chlorinated solvents. Recrystallization from acetonitrile afforded complexes **5** as yellow crystals in 60−70% yields. IR spectra of **5** in Nujol were practically identical with those of **4**, presenting W=O stretches at 953 and 951 cm^{-1} for **5a** and **5b**, respectively. ^{1}H NMR spectra of these compounds in CDCl$_3$ showed signals at 0.57 ppm (**5a**) and 0.46 ppm (**5b**) for W−CH$_3$ protons, whereas related signals in the ^{13}C NMR spectra were seen at 40.7 and 42.2 ppm for **5a** and **5b**, respectively. In the solid state, complexes **5** are stable in air, but their solutions are moderately sensitive to moisture. Corresponding transmetalation reactions of **4** with neophyl Grignard reagent were also studied. Addition of an etheral solution of neophylmagnesium chloride to the toluene solution of **4a** gave a brownish-red mixture. TLC analyses indicated the formation of a new red product, but all attempts to isolate this compound led to the formation of poorly soluble brownish material. Reaction of neophyl Grignard reagent with **6b** in toluene solution gave a deep purple solution, which was stirred for an hour at room temperature. The filtered solution was evaporated, and air-stable complex **6b** was isolated in ca. 60% yield by crystallization from hot acetonitrile.

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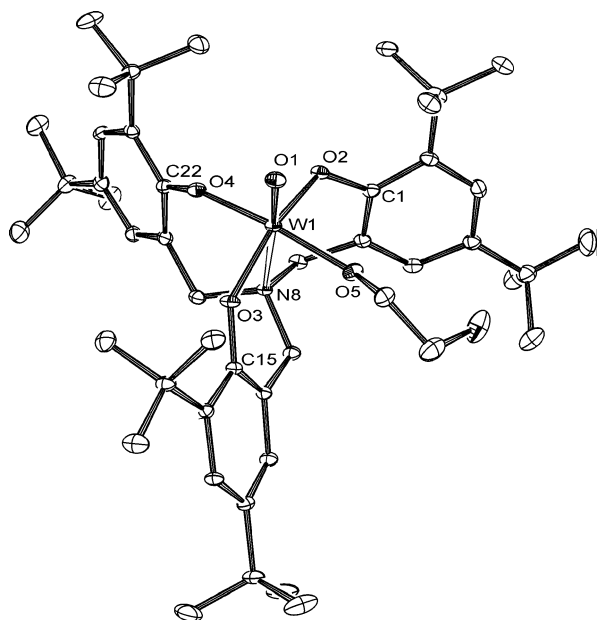
Figure 1. Molecular structure of [WO(L^{tBu})(Heg)] (**3b**). Thermal ellipsoids have been drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.

**Table 2. Selected Bond Lengths [Å] and Angles [deg] for 3b, 5a, and 6b**

|	**3b**	**5a**	**6b**
W1−O1	1.706(2)	1.714(3)	1.700(3)
W1−O2	1.941(2)	1.916(3)	1.900(3)
W1−O3	1.905(2)	1.889(3)	1.891(3)
W1−O4	1.900(2)	1.949(3)	1.968(3)
W1−N8	2.421(2)	2.476(3)	2.450(3)
W1-X	1.904(2)^a	2.187(5)^b	2.230(4)^c
O1−W1−N8	176.13(9)	176.98(14)	179.60(13)
O2−W1−O3	158.40(9)	155.75(13)	161.01(12)
O2−W1−O4	87.88(9)	91.49(13)	90.92(11)
O4−W1-X	162.71(9)	164.54(16)	162.41(14)
C1−O2−W1	126.0(2)	131.1(3)	144.8(3)
C15−O3−W1	138.54(19)	139.8(3)	139.0(2)
C22−O4−W1	141.90(19)	143.8(3)	127.7(2)

^{a} W1−O5 distance. ^{b} W1−C29 distance. ^{c} W1−C47 distance.

Deep purple complex **6b** is soluble in common organic solvents, and crystals for X-ray analyses can be easily obtained from acetonitrile. Crystals of **6b** are stable in air, but in solutions this complex decomposes slowly. NMR spectra of this compound are quite futile; that is, resonances for aromatic protons of the neophyl group are overlapping with those of the aminotris(phenolato) ligand, whereas methyl and methylene protons of the neophyl group seem to overlap with multiple resonances of the *tert*-butyl groups.

Structural Studies. Single crystals of complexes **3b**, **5a**, and **6b** were obtained from hot acetonitrile solutions upon slow cooling, and their molecular structures were verified by X-ray diffraction measurements. Complex **3b** forms monomeric molecules in which the tripodal aminotris(phenolate) group has coordinated as a tetradentate ligand through three oxygen donors and one nitrogen donor (Figure 1). The nitrogen donor is located trans to the terminal oxo group. The sixth coordination site is occupied by a monoanionic, monodentate ethanediolato ligand. In the solid-state structure of **3b**, the W−O$_{aryloxide}$ bond lengths vary from 1.900(2) to 1.941(2) Å, whereas the W−O$_{alkoxide}$ bond is 1.904(2) Å. The bonding between the metal center and the amino-
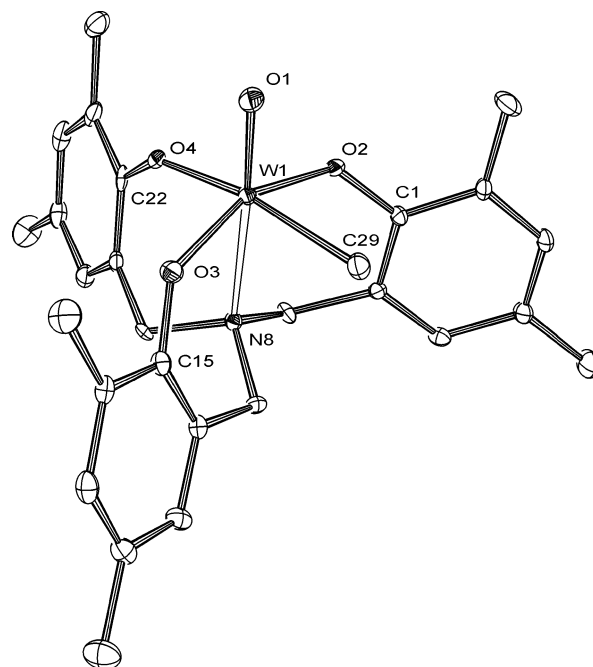
Figure 2. Molecular structure of [WO(L^{Me})(Me)] (**5a**). Thermal ellipsoids have been drawn at the 30% probability level. The hydrogen atoms are omitted for clarity.
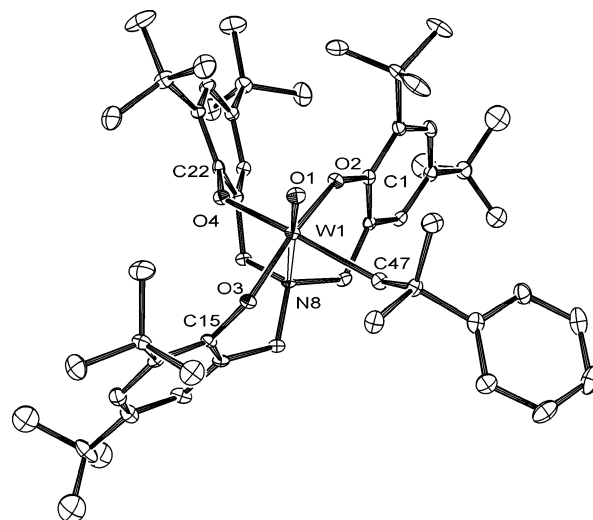
Figure 3. Molecular structure of [WO(L^{tBu})(CH$_2$CMe$_2$Ph)] (**6b**). Thermal ellipsoids have been drawn at the 30% probability level. Only the main components of distorted *tert*-butyl groups have been presented. The hydrogen atoms are omitted for clarity.

tris(phenolato) ligand is unexceptional, although the W−O bond distances are slightly longer and W−N distances are slightly shorter than in comparable oxotungsten(VI) complexes with tridentate aminobis-(phenolates).[5]

In alkyl complexes **5a** and **6b**, the distorted octahedral WO$_4$NC units are generally similar, as indicated by the bond parameters presented in Table 2 (Figures 2 and 3). The overall geometry around the central tungsten atom is comparable to that in complex **3b**, although the W1−O4 distances in alkyl complexes **5a** and **6b** (1.949(3) and 1.968(3) Å, respectively) are clearly longer than the corresponding distance in **3b** (1.900(2) Å). The W−C$_{alkyl}$ bond distances are 2.187(5) and 2.230(3) Å for

5a and **6b**, respectively, which are typical values for six-coordinated oxotungsten(VI) alkyl complexes.[26]

Conclusion

In conclusion, we have found that trisdiolato tungsten(VI) complex $[W(eg)_3]$ reacts with phenolic ligand precursors tris(2-hydroxy-3,5-dimethylbenzyl)amine (H_3L^{Me}) and tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)amine (H_3L^{tBu}) to form monomeric oxotungsten(VI) complexes $[WO(L^R)(Heg)]$ (R = Me, *t*-Bu). These complexes react further with chlorinating reagents, which leads to the formation of corresponding chloro complexes of type $[WO(L^R)Cl]$. Identical chloro complexes were also prepared by the reaction between phenolic ligand precursors and $[WOCl_4]$. These chloro complexes can react with Grignard reagents to form corresponding monoalkyl derivatives $[WO(L^R)(Me)]$ and $[WO(L^R)(CH_2CMe_2Ph)]$, which are stable in normal laboratory conditions.

Supporting Information Available: Crystallographich data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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