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Tungsten(VI) Complexes with Aminobis(phenolato) [O,N,O] Donor Ligands

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The reaction between trisdiolatotungsten(VI) complex $[W(eg)_3]$ (**1**) (eg = 1,2-ethanediolato dianion) and phenolic ligand precursor methylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenol) (H_2L^{Me}) or methylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol) (H_2L^{tBu}) affords monomeric oxotungsten complex $[WO(eg)(L^{Me})]$ (**2**) or $[WO(eg)(L^{tBu})]$ (**3**), respectively. These complexes react further with chlorinating reagents, which leads to the displacement of ethanediolato ligands from the complex units and formation of cis and trans isomers of the corresponding dichloro complexes $[WOCl_2(L^{Me})]$ (**4**) and $[WOCl_2(L^{tBu})]$ (**5**), respectively. Identical dichloro complexes were also prepared by the reaction between the above-mentioned phenolic ligand precursors and $[WOCl_4]$. Molecular structures of **3**, *cis*-**4**, *trans*-**4**, and *cis*-**5** were verified by X-ray crystallography. Complexes **2**–**5** can be activated by Et_2AlCl to catalyze ring-opening metathesis polymerization of norbornene.

Introduction

The increased interest in the development of early-transition-metal complexes with chelating bis(phenolato) ligands is driven by their relevance in organometallic and catalytic chemistry.[1] Various molybdenum and tungsten compounds with such ligands have attracted considerable attention as they catalyze scientifically and industrially interesting olefin metathesis reactions. 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.[2−4] On the other hand, aminobis(phenol)s are a topical group of chelating phenols, which are known to react as tridentate ligands with various transition metals.[5,6] Particularly, Kol and coworkers have introduced a new family of group IV metal complexes with aminobis(phenolato) ligands featuring a variety of side arm donors.[7] These compounds are promising catalyst precursors, as they can exhibit high activity in living polymerization of 1-hexene. However, at present the reports on molybdenum and tungsten complexes with aminobis(phenolato) ligands are scarce.[8]

The reaction of metal alkoxides with phenols is a practical approach to the corresponding metal phenoxides. Especially, if suitable metal alkoxides can be easily prepared from metal oxides, it is feasible to avoid the use of air- and moisture-sensitive metal chlorides. Previously we have synthesized several tungsten(VI) phenoxide complexes of types $[W(eg)_2(OAr)_2]$ and $[W(eg)_2(bife)]$ [eg = 1,2-ethanediolate dianion, OAr = substituted phenolate, bife = 1,1′-coupled or -methylene-bridged bis(phenolate)] using a trisdiolato complex, $[W(eg)_3]$ (**1**), as a starting compond.[9] In the course of these studies, we have found that complexes with monodentate

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phenolato ligands can react with HCl to form *trans*-[W(eg)-$Cl_2(OAr)_2$],[10] though the reactions of bis(phenolato) complexes with halogenating reagents do not produce isolable products, most likely due to the rigidity of the bis(phenolato) moiety, which may prevent the essential reorganization of the ligands. To obtain bis(phenolato) complexes with more flexible ligand backbones and consequently higher activity, we decided to use methylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenol) (H_2L^{Me}) and methylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol) (H_2L^{tBu}) as chelating ligand precursors. In this Article we describe the syntheses of six new oxotungsten(VI) complexes with the aforesaid ligands. As these complexes appear as potential catalyst precursors for ring-opening metathesis polymerization (ROMP), also some preliminary catalytic studies are reported.

Table 1. Isolated Yields of $WOCl_2(L^R)$ Isomers in Various Experiments

		$WOCl_2(L^{Me})$ (**4**)		$WOCl_2(L^{tBu})$ (**5**)	
reaction	solvent	yield, % (mg)[a]	cis/trans[b]	yield, % (mg)[a]	cis/trans[b]
$WO(eg)(L^R) + HCl$	CH_2Cl_2	26 (15)	−:100	31 (20)	−:100
	THF	76 (43)	94:6	80 (52)	37:63
	toluene	5 (3)	−:100		
$WO(eg)(L^R) + Me_3SiCl$	CH_2Cl_2	5 (3)	−:100		
	THF	72 (41)	100:−	84 (55)	26:74
	toluene	71 (40)	93:7		
$WO(eg)(L^R) + SOCl_2$	CH_2Cl_2	75 (43)	63:37	83 (54)	36:64
	THF	61 (35)	100:−	65 (42)	31:69
	toluene	74 (42)	49:51	78 (51)	33:67
$WOCl_4 + H_2L^R$	CH_2Cl_2	83 (47)	6:94	90 (59)	12:88
	THF	90 (51)	100:−	91 (60)	18:82
	toluene	73 (41)	62:38	93 (61)	16:84

[a] Total yields of cis and trans isomers. [b] Relative yields of each isomer.

Experimental Section

General Information. Starting complexes **1** and [$WOCl_4$] were prepared and purified according to the literature.[11,12] Ligand precursors H_2L^R were prepared using a known procedure and crystallized from hot hexane.[13] The purities of the ligand precursors were checked by ^1H NMR. Toluene and hexane used in the preparation of complexes **2** and **3** were distilled over sodium. Acetonitrile used in recrystallizations was distilled over CaH_2. Other chemicals were of reagent grade and were used as purchased. NMR spectra were recorded using Bruker AM 200 (^1H) and Bruker AV 500 (^{13}C) spectrometers in $CDCl_3$ solutions and were referenced internally to $SiMe_4$. IR spectra were recorded as Nujol mulls using a Mattson Galaxy FTIR spectrometer. Elemental analyses were obtained using a Perkin-Elmer CHNS analyzer 2400. Analytical samples were dried in vacuo at 40 °C for 2 h prior to elemental and spectral analyses.

Syntheses of [WO(eg)(L^R)]. Syntheses were carried out under a N_2 atmosphere (99.999% purity) using standard benchtop techniques.[14] Tungsten precursor **1** (364 mg, 1.00 mmol) was heated with 1 equiv of H_2L^{Me} (299 mg) or H_2L^{tBu} (383 mg) in 60 mL of toluene at reflux temperature for 4 h to form a yellow solution. The H_2eg that formed during reaction was removed as a toluene azeotrope. Remaining solvent was evaporated, and a yellow solid residue was crystallized from acetonitrile (**2**) or a hexane−toluene mixture (**3**).

Data for [WO(eg)(L^{Me})] (2). Yield: 505 mg (91%). Anal. Calcd for $C_{21}H_{27}NO_5W$: C, 45.2; H, 4.9; N, 2.5. Found: C, 45.0; H, 4.9; N, 2.2. ^1H NMR ($CDCl_3$): δ 7.04 (2H, s, Ar), 6.75 (2H, s, Ar), 5.20 (2H, m, OCH_2), 4,95 (2H, m, OCH_2), 3.66 (4H, m, NCH_2), 2.40 (6H, s, $ArCH_3$), 2.32 (6H, s, $ArCH_3$), 2.24 (3H, s, NCH_3). ^{13}C NMR ($CDCl_3$): δ 154.9, 141.4, 132.0, 128.8, 127.0, 126.1, 80.3, 61.5, 46.3, 21.0, 16.1. IR (Nujol): 1464 s, 1377 s, 1312 m, 1242 vs, 1221 s, 1161 s, 1069 vs, 990 w, 949 vs, 920 w, 864 vs (br), 841 m, 748 w, 629 m, 604 m, 561 m, 513 m cm^{-1}.

Data for [WO(eg)(L^{tBu})] (3). Yield: 530 mg (83%). Anal. Calcd for $C_{27}H_{39}NO_5W$: C, 50.5; H, 6.1; N, 2.2. Found: C, 50.1; H, 6.3; N, 2.1. ^1H NMR ($CDCl_3$): δ 7.17 (2H, s, Ar), 6.80 (2H, s, Ar), 5.20 (2H, m, OCH_2), 4.97 (2H, m, OCH_2), 3.56 (4H, m, NCH_2), 2.35 (6H, s, $ArCH_3$), 2.32 (3H, s, NCH_3), 1.48 (18H, s, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 153.9, 140.8, 132.4, 128.1, 127.4, 126.6, 80.2, 61.2, 46.5, 34.8, 30.9, 30.1, 21.0. IR (Nujol): 1458 s, 1377 s, 1362 s, 1312 m, 1268 s, 1240 vs, 1215 s, 1155 s, 1086 m, 1069 vs (br), 951 vs, 940 s, 920 w, 885 vs, 860 vs, 840 s, 765 m, 696 w, 623 s, 595 s, 579 s, 565 m, 513 s cm^{-1}.

Sealed Ampule Reaction. An 18 mg sample of **1** (0.050 mmol) and 15 mg of H_2L^{Me} (0.050 mmol) were mixed with 0.7 mL of toluene-d_8 in a sealed NMR tube. The reaction mixture was heated at 120 °C for 24 h and subsequently analyzed by ^1H NMR.

Chloride-for-Alkoxide Substitutions of [WO(eg)(L^R)]. General Procedure. [WO(eg)(L^R)] (0.10 mmol) was dissolved in 5 mL of solvent (CH_2Cl_2, THF, toluene) in a screw cap vial and subsequently treated with 1.0 mmol of chlorinating reagent ($SOCl_2$, Me_3SiCl) or a slow stream of gaseous HCl (bubbled through the reaction mixture for 5 min). The reaction mixtures were then heated at 100 °C (*caution: pressure!*) for 30 min (**2**) or 180 min (**3**), respectively, and the mixture of cis and trans isomers of [$WOCl_2(L^R)$] thus obtained was separated by silica column chromatography using a hexane−toluene mixture (40:60) as an eluent. Table 1 presents isolated yields from each experiment.

Reaction of H_2L^R with [$WOCl_4$]. General Procedure. Reactions were carried out under a N_2 atmosphere (99.999% purity) by using standard benchtop techniques.[14] [$WOCl_4$] (100 mg, 0.30 mmol) was dissolved in 30 mL of solvent (CH_2Cl_2, THF, toluene) and subsequently treated with 1 equiv of H_2L^{Me} (90 mg) or H_2L^{tBu} (128 mg) to obtain an intense red mixture. The reaction mixture was allowed to reflux for 2 h. Volatiles were then evaporated in a vacuum, and the mixture of cis and trans isomers of [$WOCl_2(L^R)$] thus obtained was separated by silica column chromatography. Table 1 presents isolated yields from each experiment.

Data for *cis*-[$WOCl_2(L^{Me})$] (*cis*-4). Anal. Calcd for $C_{19}H_{23}Cl_2NO_3W$: C, 40.2; H, 4.1; N, 2.5. Found: C, 40.4; H, 4.3; N, 2.2. ^1H NMR ($CDCl_3$): δ 7.12 (2H, s, Ar), 6.86 (2H, s, Ar), 3.91(2H, br, NCH_2), 3.58 (2H, d, $J = 15$ Hz, NCH_2), 2.47 (6H, s, $ArCH_3$), 2.45 (3H, s, NCH_3), 2.43 (6H, s, $ArCH_3$). ^{13}C NMR ($CDCl_3$): δ 155.2, 135.7, 131.3, 129.4, 127.8, 127.1, 61.5, 48.6, 20.7, 16.0. IR (Nujol): 1460 s, 1377 s, 1298 w, 1236 s, 1219 vs, 1157 s, 1144 m, 1080 w, 1038 w, 980 s, 966 vs, 941 w, 880 s, 862 vs, 839 m, 745 w, 665 w, 602 m, 563 m cm^{-1}.

Data for *trans*-[$WOCl_2(L^{Me})$] (*trans*-4). Anal. Calcd for $C_{19}H_{23}Cl_2NO_3W$: C, 40.2; H, 4.1; N, 2.5. Found: C, 40.4; H, 4.1; N, 2.3. ^1H NMR ($CDCl_3$): δ 7.13 (2H, s, Ar), 6.86 (2H, s, Ar), 4,01 (2H, d, $J = 8$ Hz, NCH_2), 3.06 (2H, d, $J = 8$ Hz, NCH_2), 2.52 (6H, s, $ArCH_3$), 2.45 (6H, s, $ArCH_3$), 2.00 (3H, s, NCH_3). ^{13}C

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Table 2. Summary of Crystallographic Data for **3**, *trans*-**4**, *cis*-**4**, and *cis*-**5** at 173(2) K

	3	*trans*-**4**	*cis*-**4**	*cis*-**5**
empirical formula	$C_{27}H_{39}NO_5W$	$C_{19}H_{23}Cl_2NO_3W$	$C_{19}H_{23}Cl_2NO_3W$	$C_{25}H_{23}Cl_2NO_3W$
M_r	641.44	568.13	568.13	652.29
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group (No.)	$C2/c$ (15)	$P2_1/m$ (11)	$P2_12_12_1$ (19)	$P2_1/n$ (14)
a/Å	35.0371(12)	7.6686(3)	14.0191(3)	17.4438(9)
b/Å	9.6461(4)	16.1120(12)	15.4816(2)	7.7968(2)
c/Å	16.8845(5)	8.0662(5)	18.2990(5)	19.9166(12)
α/deg	90	90	90	90
β/deg	108.104(2)	93.129(4)	90	106.417(2)
δ/deg	90	90	90	90
V/Å^3	5424.0(3)	995.15(10)	3971.58(15)	2598.3(2)
Z	8	2	8	4
D_c/g cm^{-1}	1.571	1.896	1.900	1.667
μ(Mo Kα)/cm^{-1}	42.95	60.91	61.05	46.77
no. of obsd reflns	6166	2198	8734	5441
R_{int}	0.0531	0.0585	0.0633	0.0715
no. of param	307	127	469	272
R1[b]	0.045 (0.029)[a]	0.052 (0.036)	0.052 (0.034)	0.074 (0.038)
wR2[c]	0.058 (0.054)	0.070 (0.066)	0.062 (0.058)	0.076 (0.067)

[a] Values in parentheses for reflections with $I > 2.0\sigma(I)$. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP)]$, where $P = (2F_c^2 + F_o^2)/3$.

NMR ($CDCl_3$): δ 155.1, 135.7, 131.6, 129.1, 128.6, 127.3, 62.7, 47.2, 21.0, 16.1. IR (Nujol): 1458 s, 1377 s, 1320 w, 1240 s, 1219 s, 1157 s, 1076 s (br), 964 vs, 920 w, 874 vs, 840 m, 749 w, 667 w, 598 m, 571 m cm^{-1}.

Data for *cis*-[WOCl$_2$(L^{tBu})] (*cis*-5). Anal. Calcd for $C_{25}H_{35}Cl_2NO_3W$: C, 46.1; H, 5.4; N, 2.2. Found: C, 46.3; H, 5.8; N, 2.0. ^{1}H NMR ($CDCl_3$): δ 7.14 (2H, s, Ar), 6.88 (2H, s, Ar), 3.90 (2H, br, NCH_2), 3.58 (2H, d, $J = 14$ Hz, NCH_2), 2.46 (6H, s, $ArCH_3$), 2.45 (3H, s, NCH_3), 1.60 (18H, s, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 156.2, 135.1, 131.1, 129.0, 126.8, 126.1, 61.3, 46.6, 34.7, 31.6, 29.9, 20.7, 15.3. IR (Nujol): 1458 vs, 1377 s, 1364 s, 1235 s, 1223 s, 1152 m, 1134 m, 1078 s (br), 970 vs, 922 m, 885 m, 860 vs, 839 m, 756 w, 669 w, 596 w, 581 m cm^{-1}.

Data for *trans*-[WOCl$_2$(L^{tBu})] (*trans*-5). Anal. Calcd for $C_{25}H_{35}Cl_2NO_3W$: C, 46.0; H, 5.4; N, 2.2. Found: C, 46.2; H, 5.5; N, 2.5. ^{1}H NMR ($CDCl_3$): δ 7.32 (2H, s, Ar), 6.90 (2H, s, Ar), 4,93 (2H, d, NCH_2), 3.15 (2H, d, $J = 8$ Hz, NCH_2), 2.48 (6H, s, $J = 7$ Hz, $ArCH_3$), 2.18 (3H, s, NCH_3), 1.57 (18H, s, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): δ 153.8, 140.1, 132.2, 128.0, 127.3, 126.4, 61.9, 47.4, 33.9, 31.5, 30.0, 21.7, 15.1. IR (Nujol): 1456 s, 1377 s, 1364 m, 1289 m, 1238 s, 1225 vs, 1215 s, 1150 s, 1092 m, 974 s, 964 s, 934 m, 916 s, 876 vs (br), 845 s, 760 m, 687 m, 598 s, 571 vs, 513 w cm^{-1}.

Isomerization of *cis*-[WOCl$_2$(L^R)]. Samples (0.10 mmol) of *cis*-**4** and *cis*-**5** were dissolved in 5 mL of xylene in screw cap vials and heated at 140 °C in an oil bath for 24 h. Reactions produced the corresponding trans isomers, which were isolated by column chromatography in ca. 90% yields.

X-ray Crystallography. Crystals of **3** suitable for X-ray measurements were grown at 21 °C from hot hexane. Other compounds were crystallized at 4 °C from a hexane−toluene mixture (*cis*-**4** and *cis*-**5**) or acetonitrile (*trans*-**4**). Crystal data for compounds **3**, *trans*-**4**, *cis*-**4**, and *cis*-**5** along with other experimental details are summarized in Table 2. The crystallographic data were collected at −100 °C on a Nonius Kappa CCD area-detector diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The data collection was performed using φ and ω scans. The data were processed using DENZO-SMN v0.93.0.[15] MULABS[16] absorption correction was applied for the data of **3** and *trans*-**4**, and SHELXA[17] absorption correction was applied for the data of *cis*-**4** and *cis*-**5**.

The structures were solved by direct methods, and full-matrix least-squares refinements on F^2 were performed using SHELXL-97.[18] For all compounds the heavy atoms were refined anisotropically. The CH hydrogen atoms were included at fixed distances with fixed displacement parameters from their host atoms. In *cis*-**5** the ligand is disordered, showing two orientations around N8 as shown in Figure 4. Figures were drawn with Ortep-3 for Windows.[19]

Catalyst Studies. Polymerizations were performed at ambient temperature as well as at 80 °C under a nitrogen atmosphere employing a 1:5:200 tungsten precatalyst:activator:monomer ratio. The precatalyst (2×10^{-5} mol) was dissolved in 4 mL of 1 M norbornene monomer (4.0 mmol) solution in toluene. The reaction mixture was stirred for 5 min and subsequently treated with 0.05 mL of Et_2AlCl solution (1.8 M in toluene, 9×10^{-5} mol). After 15 min of stirring the solution was treated with 10 mL of methanol to precipitate polymer as a white solid. Polymers were swelled in toluene, reprecipitated by methanol, and dried in vacuo at 40 °C for 8 h.

Results and Discussion

Syntheses of Complexes [WO(eg)(L^R)]. Stirred suspensions of alkoxide starting complex **1** in toluene were treated with stoichiometric amounts of the ligand precursors H_2L^R at reflux temperature while the reactions were promoted by fractionating out the liberated 1,2-ethanediol as a toluene azeotrope (Scheme 1). Under these conditions, the reactions proceeded efficiently, the colorless suspensions rapidly turning yellow. Evaporation of toluene followed by crystallization afforded new tungsten compounds as yellow solid crystalline materials which are soluble in toluene, THF, and halogenated solvents.

Spectroscopic analyses of the yellow products indicated that the simple alkoxide displacement reactions were associ-

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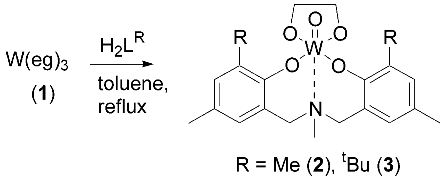
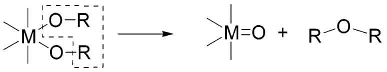
Scheme 1. Preparation of Complexes [WO(eg)(L^R)]



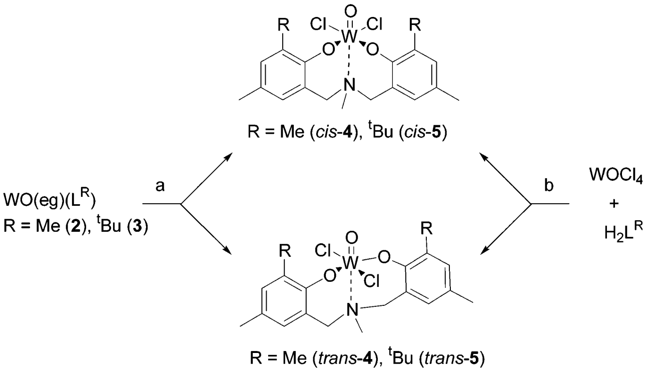
Scheme 2. Ether Elimination Reaction of Metal Alkoxides



ated with some other significant modifications in the ligand environment. ^{1}H NMR spectra of studied compounds showed anticipated resonances for coordinated aminobis(phenolato) ligands.[6−8] In the aliphatic region of the spectra two distinct multiplets for the ethanediolate groups are observed, implying that there are two different environments for these methylene protons. However, relative intensities indicated the presence of one eg ligand in addition to one aminobis(phenolato) ligand, instead of the expected 2:1 stoichiometry. IR spectra showed strong absorption bands at 950 cm^{-1}, which is characteristic for a W═O moiety.[20] X-ray crystal structure analysis of **3** (see below) verified finally the presence of unpredicted terminal oxo groups. As water is the most likely supplier of unexpected oxo groups, toluene and aminobis(phenol)s were carefully dried and atmospheric moisture was rigorously excluded during the ligand displacement reactions. However, as it is virtually impossible to eliminate the diminutive amount of water necessary to accomplish the transformation, the involvement of trace water in the reaction cannot be entirely excluded. On the other hand, it is known that several high-valent molybdenum, tungsten, and rhenium alkoxide derivatives can decompose by an elimination process, which yields ether and the corresponding oxometal species (Scheme 2).[21]

Consequently, we can assume that the studied tungsten complexes undergo an ether elimination reaction upon ligand displacements, which moreover consents to the tridentate coordination of aminobis(phenolato) ligands. Undesirably, characterization of any ether byproducts, e.g., oxirane or di(ethylene glycol) proved difficult. The ^{1}H NMR spectrum of toluene distillate in $CDCl_3$ showed a resonance at 3.78 ppm for ethylene glycol in addition to a signal at 3.65 ppm, possibly due to 1,4-dioxane.[22] These resonances might also indicate the presence of di(ethylene glycol), although more accurate analyses failed due to the low concentration of these byproducts. The reaction of **1** with H_2L^{Me} was as well carried out in a sealed NMR tube at 120 °C while the reaction was monitored by ^{1}H NMR. The reaction equilibrium was reached in a few hours. At that time the NMR spectrum presented several overlapping signals at 3.5−3.7 ppm, which can be characterized as methylene protons of complex **3**, liberated H_2eg, unreacted H_2L^{Me}, or ether byproducts. Nevertheless, the nitrogen donor of the bis(phenol) ligand has apparently a crucial role in each likely reaction mechanism (i.e., hydrolysis or ether elimination), as analogous ligand substitutions with comparable 1,1′-coupled or -methylene-bridged biphenols do not produce related oxo complexes.[9c]

Scheme 3. Formation of $WOCl_2(L^R)$ Isomers[a]



[a] Conditions: (a) chlorinating reagent (HCl, Me_3SiCl, or $SOCl_2$), solvent (CH_2Cl_2, THF, or toluene), 100 °C; (b) solvent (CH_2Cl_2, THF, or toluene), reflux.

Chloride-for-Alkoxide Substitution of [WO(eg)(L^R)]. Metal alkoxides can be transformed into the corresponding mixed-ligand complexes composed of alkoxides and halides by various substitution reactions.[23] Direct addition of anhydrous HCl is the most straightforward method to the substitution of alkoxides, whereas other successful procedures utilize chlorinating agents, e.g., AcCl or Me_3SiCl, where the reagent can initially react with proton sources, e.g., trace amounts of alcohol, to form HCl, the actual reacting species. In the present study we used selected reagents (HCl, Me_3SiCl, and $SOCl_2$) in a variety of solvents (CH_2Cl_2, THF, and toluene) to optimize reaction conditions for chloride-for-alkoxide substitution of [WO(eg)(L^R)].

Intense red solutions were obtained when yellow solutions of [WO(eg)(L^R)] were treated with an excess of the appropriate chlorinating reagents (Scheme 3, reaction a). The reaction mixtures were heated for 30−180 min at 100 °C in screw cap vials while the reactions were monitored by TLC. As a result, complex **2** reacted smoothly in each experiment to produce a mixture of cis and trans isomers of dichloro complex **4** in varied ratios. Resultant isomeric mixtures were separated by column chromatography to obtain individual isomers as red crystalline solids (Table 1). Interestingly, the reaction with gaseous HCl yielded *trans*-**4** as the only isolable product, whereas the reaction with $SOCl_2$ in THF produced predominantly the cis isomer, which provides practical syntheses for these pure isomers. Sterically more hindered complex **3** required longer reaction times with HCl or $SOCl_2$ to produce dichloro complex **5** in notable yields. Again, the reaction with HCl afforded only the trans isomer, whereas other reactions provided *trans*-**5** as a major component along with minor amounts of *cis*-**5**. Unfortunately, selective reac-

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[20] Nugent, W. M.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

[21] (a)Turova, N. Ya.; Kessler, V. G.; Kucheiko, S. I. *Polyhedron* **1991**, *10*, 2617−2628. (b) Shcheglov, P. A.; Drobot, D. V.; Seisenbaeva, G. A.; Gohil, S.; Kessler, V. G. *Chem. Mater*. **2002**, *14*, 2378−2383.

[22] Free 1,2-ethanediol shows a singlet at 3.76 ppm, while 1,4-dioxane shows a singlet at 3.71 ppm. See: Gottlieb H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem*. **1997**, *62*, 7512−7515.

[23] Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Vol. 2, Chapter 15.3, pp 335−364.

tion conditions for *cis*-**5** were not found. All complexes **4** and **5** are stable in air at room temperature and are soluble in aromatic hydrocarbons, acetonitrile, chlorinated solvents, and ethers. They are as well soluble in ethanol and 2-propanol but decompose slowly in alcohol solutions.

Formation of cis isomers as a result of chloride-for-alkoxide substitution seems reasonable, as the two newly introduced chlorides replace two oxygen atoms of one eg ligand which are, by necessity, in cis positions. Conversely, formation of trans isomers is not so obvious, as it results in the substantial rearrangement of the ligands. A similar reorganization was earlier perceived in chloride-for-alkoxide substitution of $[W(eg)_2(OAr)_2]$ complexes (OAr = substituted phenol), which yields only *trans*-$[WCl_2(eg)(OAr)_2]$.[11] Even so, cis isomers of complexes $[WOCl_2(L^R)]$ can be transformed into trans isomers by heating in xylene solution at 140 °C; thus, trans isomers seem to be thermodynamically more favorable.

Reaction of H_2L^R with $[WOCl_4]$. The standard procedure for oxotungsten(VI) phenoxides comprises a straightforward reaction of $[WOCl_4]$ with a stoichiometric amount of phenolic ligand precursor in an appropriate solvent.[24] In our initial experiments, the ligand precursors H_2L^R were reacted with $[WOCl_4]$ in toluene solutions at reflux temperature. Under these conditions, the reactions proceeded rapidly, yielding the corresponding oxodichloro complexes $[WOCl_2(L^R)]$ in nearly quantitative yields (Scheme 3, reaction b). The ^1H NMR spectra of the isolated dark red materials indicated the presence of both cis and trans isomers. The reactions were repeated in various solvents, whereupon it appeared that H_2L^{Me} reacts with $WOCl_4$ in refluxing THF to form almost exclusively the cis isomer, whereas the parallel reaction in CH_2CH_2 leads to the formation of the trans isomer as the sole product (see Table 1). However, the reaction with sterically more hindered aminobis(phenol) H_2L^{tBu} did not show a similar solvent dependency; thus, the product was obtained as a mixture of cis and trans isomers in an approximately 1:5 ratio in various solvents.

Structural Studies. The solid-state structures of four new compounds were verified by X-ray studies. Crystals of **3** were obtained as orange blocks from hot hexane upon cooling to room temperature. The compound forms mononuclear molecules in which one ethanediolato ligand (two oxygen donors), one aminobis(phenolato) ligand (two oxygen donors and one nitrogen donor), and one terminal oxo ligand bond to the central W(VI) ion, which has therefore a 5 + 1 coordination geometry (Figure 1). The main features of this structure are the following: (1) the nitrogen donor is located trans to the oxo group (the O−W−N angle is 172.20(11)°), (2) the O(diolato)−W−O(diolato) angle is 78.87(11)°, and (3) the O(phenolato)−W−O(phenolato) angle is 99.89(10)°. The O−W−O angles vary from their ideal values of 90° due to the rigidity of the diolato and phenolato ligands. The

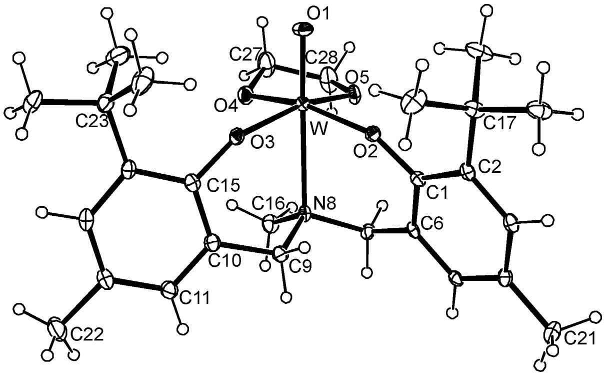

Figure 1. Molecular structure of $[WO(eg)(L^{tBu})]$ (**3**). Thermal ellipsoids have been drawn at the 30% probability level.

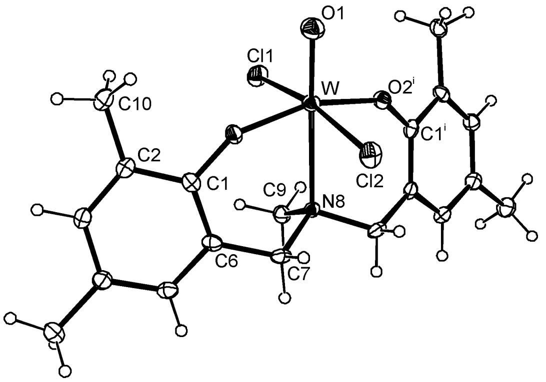

Figure 2. Molecular structure of *trans*-$[WOCl_2(L^{Me})]$ (*trans*-**4**). Thermal ellipsoids have been drawn at the 30% probability level. Symmetry operation i = x, $-y + 1/2$, z.

W═O bond length is 1.722(2) Å, W−O(phenolato) bond distances are 1.888(2) and 1.907(2) Å, and W−O(diolato) bond distances are 1.928(2) and 1.929(3) Å, which are typical values for these kinds of ligands.[9,23] The W−N distance is 2.498(3) Å, which is slightly longer than found in dioxotungsten(VI) complexes with tetradentate aminobis(phenol)s.[8]

Crystals of *trans*-**4** were grown from acetonitrile at 4 °C. In this compound the tungsten(VI) cation has adopted a distorted octahedral coordination geometry with chloro ligands in trans orientation, and the molecule has a σ-symmetry (Figure 2). Selected bond parameters for *trans*-**4** are presented in Table 3. The overall structure of the central WCl_2NO_3 unit resembles moderately that found in pyridinedialkoxide complex $WOCl_2$(pydi)—a cis-specific ROMP catalyst (H_2pydi = α,α-dimethyl-α′,α′-diphenyl-2,6-pyridinediethanol).[25] As well, core parameters, e.g., W−O and W−Cl distances along with $O_{Ar}-W-O_{Ar}$ and Cl−W−Cl angles, are of the same magnitude as typically found in square-pyramidal $WOCl_2(OAr)_2$ complexes.[24]

Intense red crystals of *cis*-**4** and *cis*-**5** were grown from a hexane−toluene mixture at 4 °C. The asymmetric unit of *cis*-**4** contains two chemically equivalent molecules with chloro ligands is cis positions (Figure 3). Selected bonding parameters for two crystallographically inequivalent molecules are compared in Table 3. In both molecules, the coordination mode of aminobis(phenolate) is rather similar

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(24) (a) Bell, A. *J. Mol. Catal.* **1992**, *76*, 165−180. (b) Nugent, W.; Feldman, J.; Calabrese, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 8992−8998. (c) Gómez, F. J.; Manak, M. S.; Abboud, K. A.; Wagener, K. B. *J. Mol. Catal. A: Chem.* **2000**, *160*, 145−156. (d) Lehtonen, A.; Sillanpää, R. *Polyhedron* **2002**, *21*, 349−352.

(25) Nakayama, Y.; Ikushima, N.; Nakamura, A. *Chem. Lett.* **1997**, 861−862.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-**4**, *cis*-**4**, and *cis*-**5**

	trans-**4**	*cis*-**4**	*cis*-**4**[a]	*cis*-**5**
W−O1	1.696(5)	1.677(3)	1.688(3)	1.688(3)
W−O2	1.867(3)	1.860(4)	1.868(4)	1.857(4)
W−O3	1.867(3)	1.885(3)	1.885(4)	1.869(4)
W−N8	2.512(5)	2.500(4)	2.518(4)	2.492(4)
W−Cl1	2.3608(17)	2.3733(16)	2.3417(16)	2.3448(14)
W−Cl2	2.3706(4)	2.3406(15)	2.3329(16)	2.3577(16)
O1−W−N8	177.2(2)	174.38(17)	174.81(18)	175.87(16)
O2−W−O3	158.5(2)[b]	97.95(18)	97.79(18)	96.15(17)
Cl1−W−N8	86.05(12)	88.25(11)	86.61(10)	86.07(10)
Cl2−W−N8	82.37(12)	85.03(11)	82.93(12)	85.33(11)
Cl1−W−Cl2	168.41(7)	84.56(7)	85.08(6)	85.08(6)
C1−O2−W	143.8(3)	147.7(4)	146.5(4)	147.1(3)
C15−O3−W		137.7(4)	137.7(3)	139.8(3)

[a] Parameters for a molecule labeled as W2, O11, O12, O13, Cl11, Cl12, N28, C21, and so on. [b] O2−W−O2^{i}, where symmetry operation i = x, $-y + 1/2$, z.

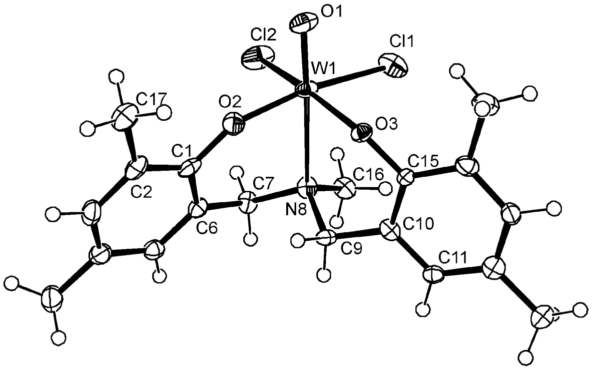

Figure 3. Molecular structure of *cis*-$[WOCl_2(L^{Me})]$ (*cis*-**4**). Thermal ellipsoids have been drawn at the 30% probability level.

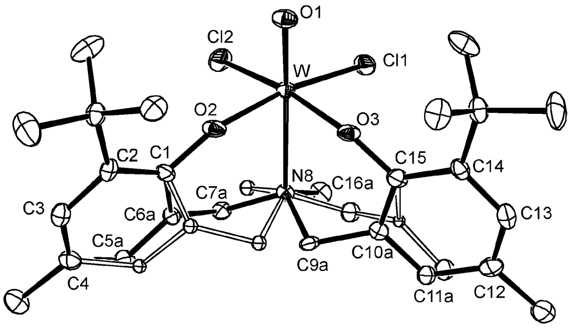

Figure 4. Molecular structure of *cis*-$[WOCl_2(L^{tBu})]$ (*cis*-**5**). Thermal ellipsoids have been drawn at the 30% probability level. The main component (80%) of the disordered ligand is drawn in black. The hydrogen atoms are omitted for clarity.

to that in **3**. However, in *cis*-**4** some small differences can be seen between two molecules in the asymmetric unit, e.g., the dihedral angles between C1, ..., C6 and C10, ..., C15 and C21, ..., C26 and C30, ..., C35 are distinct, being 51.2(2)° and 48.1(2)°, respectively. These deviations indicate that although the [O,N,O] framework is rather rigid, it still has enough flexibility to accommodate slightly different arrangements due to packing reasons. The molecular structure of *cis*-**5** is closely related to that of *cis*-**4** (Figure 4), though the aminobis(phenolato) group can adopt different orientations in solution, which can also result in a disordered solid-state structure. In the asymmetric unit of *cis*-**5** can be seen two different orientations in a 4:1 ratio. In general, the coordination sphere around the W(VI) ion in *cis*-**4** and *cis*-**5** is comparable with that of other known *cis*-dichlorotungsten(VI) complexes with chelating bis(phenolate)s.[26]

Catalytic Studies. A number of tungsten(VI) complexes with easily replaceable ligands can be activated by main-group organometallics to obtain active metathesis catalysts.[27] The role of these activators is most probably to interchange two labile ligands on tungsten with alkyl groups; the resultant organotungsten intermediate would then undergo an α-elimination reaction to afford the corresponding alkylidene derivative.

Catalytic activities of complexes **2**−**5** in ROMP of norbornene were studied in toluene solutions using a Et_2AlCl cocatalyst while the overall conversion of monomer to insoluble polymers was used as a measure of activity. Tungsten complexes were dissolved in a toluene−norbornene mixture to form yellow (for **2** and **3**) or red (for **4** and **5**) solutions, which were treated with a toluene solution of Et_2AlCl. As a result, the solutions changed rapidly from to an intense red color, and simultaneous gel formation started, leading quickly to the completion of the reaction. The monomer conversions after 15 min of reaction at room temperature were within 10% of the quantitative yield for experiments carried out with compounds **2**, **4**, and **5**, while no differences in activities between cis and trans isomers were seen. Sterically hindered precursor **3** showed moderate activity for polymerization, as the yield of polymer was 32%. At 80 °C all precatalysts produced polynorbornene as an insoluble rubber-like material in practically quantitative yields. Et_2AlCl was required for polymerizations, as other main-group organometallics (MeMgI, Me_2Zn) did not activate studied precatalysts in these experimental conditions.

Conclusion. In conclusion, we have found that trisdiolatotungsten(VI) complex $[W(eg)_3]$ reacts with phenolic ligand precursors H_2L^{Me} and H_2L^{tBu} to form oxotungsten(VI) complexes $[WO(eg)(L^{Me})]$ and $[WO(eg)(L^{tBu})]$, respectively. These complexes react further with chlorinating reagents, which leads to the formation of cis and trans isomers of the corresponding dichloro complexes $[WOCl_2(L^{Me})_2]$ (**4**) and $[WOCl_2(L^{tBu})_2]$ (**5**), respectively. Identical dichloro complexes were also prepared by the reaction between phenolic ligand precursors and $[WOCl_4]$. All studied oxotungsten complexes can catalyze ROMP of norbornene when activated by Et_2AlCl.

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

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