Synthesis of a Novel Oxotungsten(VI) Complex Having a Chelating Bis(aryloxo) Ligand and Its Catalytic Behavior for Ring-Opening Metathesis Polymerization

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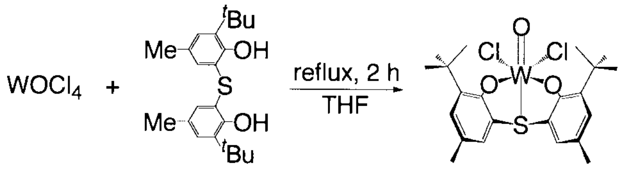
An oxotungsten complex coordinated with O–S–O chelating bis(aryloxo) ligand, $WO\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Cl_2$ (**1**), was synthesized by the reaction of $WOCl_4$ with $2,2'\text{-}S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2OH)_2$. The structure of the complex **1** was determined by single-crystal X-ray analysis to have pseudo C_s symmetry. The catalytic behavior of **1**/$AlEt_3$ system for the ring-opening metathesis polymerization of norbornene was studied. In this catalytic system, strong dependencies of *cis/trans* selectivity on the catalyst concentration and on the polymerization temperature were observed. With increasing catalyst concentration and with lowering polymerization temperature, the resulting poly(norbornene)s tend to have higher *cis*-regularity. Oppositely, *trans*-rich poly(norbornene)s were produced by the polymerization under low catalyst concentration and at high polymerization temperature. We propose that these observations might come from oxotungsten–aluminum interaction.

Since Schrock and coworkers reported alkylidene complexes bearing imido and alkoxo groups, numerous group 6 metal alkylidene complexes have been reported to show catalytic activity for ring-opening metathesis polymerization (ROMP).[1] We have also prepared a series of new tungsten dialkyl complexes bearing diphenylacetylene and O–S–O tridentate chelating bis(aryloxo) ligand, $W(\eta^2\text{-}PhC{\equiv}CPh)\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}R_2$ (R = CH_2SiMe_3, CH_2Ph, CH_3), which initiate the ROMP of norbornene to give poly(norbornene) having high molecular weight ($M_n = 1.7 \times 10^6$) and high *cis*-content (*cis* 93%) at the early stage of the reaction.[2] The high *cis*-selectivity could be attributed to the steric repulsion between the acetylene ligand and the five membered ring of the monomer. On the other hand, various oxotungsten compounds have been known to show high catalytic activity for olefin metathesis reaction.[3–6] Recently, we also reported that the *trans*-dichloro(oxo)tungsten complexes and *trans*-dialkyl(oxo)-tungsten complexes bearing O–N–O tridentate ligands, $WOX_2\{(OCR^1{}_2CH_2)(OCR^2{}_2CH_2)(NC_5H_3)\}$ ($R^1 = R^2$ = Me, X = Cl; $R^1 = R^2 = {}^i$Pr, X = Cl; R^1 = Me, R^2 = Ph, X = Cl; $R^1 = R^2$ = Me, X = CH_2SiMe_3) could be catalyst precursors for the ROMP of norbornene upon activation with $AlEt_3$.[7,8] In order to enhance the catalytic activity and to elucidate the effect of the acetylene ligands in O–S–O chelating system, we synthesized an oxotungsten complex coordinated with an O–S–O chelating bis(aryloxo) ligand, $WO\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Cl_2$ (**1**), and studied its catalytic behavior for ROMP.

The dichlorotungsten complex **1** was prepared as black crystals in 53% yield by refluxing a mixture of $WOCl_4$[9] and 1 equiv of 2,2'-thiobis(4-methyl-6-*tert*-buthylphenol) in THF (Scheme 1).[10] The ^1H–^1H NOESY, HMQC and HMBC spectra of **1** suggested that **1** had C_s symmetric structure, which was also supported by X-ray crystallography (Figure 1).[11] Coordination geometry around the tungsten atom of the complex **1** can be described as pseudooctahedral. The O–S–O chelating bis(aryloxo) ligand and two chloride ligands coordinate to the metal in facial and in *cis* fashion, respectively. The W–S bond distance of **1** (2.751(4) Å) is longer by 0.11 Å than that of the corresponding acetylene complex, $W(\eta^2\text{-}EtC{\equiv}CEt)\{S(4,6\text{-}Me_2C_6H_2O)_2\}Cl_2$ (**2**) (2.638(2) Å),[2] due to the strong *trans* influence of the oxo ligand. The O1-W-O2 angle of **1** (93.1(4)°) is larger than that of **2** (89.4(2)°).



Scheme 1.

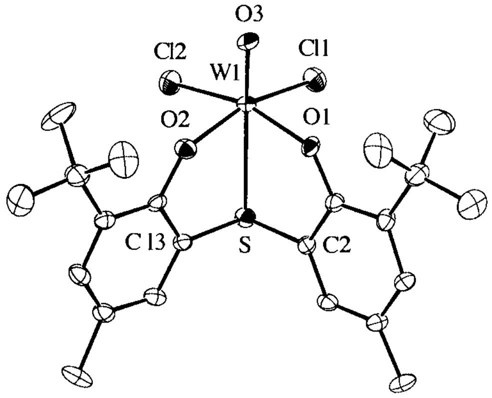


Figure 1. ORTEP drawing of **1**. Selected bond distances (Å) and angles(degree): W-O1 1.901(10), W-O2 1.913(10), W-O3 1.692(9), W-Cl1 2.322(4), W-Cl2 2.324(4), W-S 2.751(4), O1-W-O2 93.1(4), Cl1-W-Cl2 86.8(2), C2-S-C13 102.8(7).

The catalytic behavior of **1**/$AlEt_3$ for the ROMP of norbornene was studied in toluene and the results are summarized in Tables 1 and 2. The catalytic activity of **1**/$AlEt_3$ was significantly higher than that of the corresponding acetylene complexes,[2] and similar or somewhat lower in comparison with those of the reported oxotungsten compounds.[3–8] In the polymerization of norbornene under various catalyst concentration, the lower catalyst concentration ([W] ≤ 2.5 mM) was more suitable to achieve high polymer yield. The *cis* contents of the resulting polymers were found to decrease with decreasing initial catalyst concentration accompanied with a reduction of the molecular weight. The polymerization temperature was also found to strongly effect on the *cis/trans* selectivity. At lower temperature (–15 °C), the resulting polymer had high *cis*-regularity (*cis*-cont. 88%). With raising polymerization temperature, the *cis*-selectivity of the catalyst was decreased and was turned to *trans*-selective above 90 °C. Thus, *cis*-rich polymers were produced by the polymerization at low temperature and/or by that under high concentration. Oppositely, the polymerization under dilute condition and/or that at high temperature gave *trans*-rich polymers. These observations are in sharp contrast to the case of the corresponding acetylene complexes, in which the *cis/trans* selectivity was not so affected by polymerization concentration and temperature.

Table 1. Effects of Concentration on the ROMP of Norbornene by $WO\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Cl_2/AlEt_3$.

[W] mM	Yield %	M_n /10^4 [a]	M_w/M_n[a]	*cis*-Cont.[b]
10	70	46.6	1.6	58
5.0	69	26.2	2.0	54
2.5	99	13.3	2.3	52
1.0	96	6.0	1.7	37
0.1	98	6.6	1.7	32

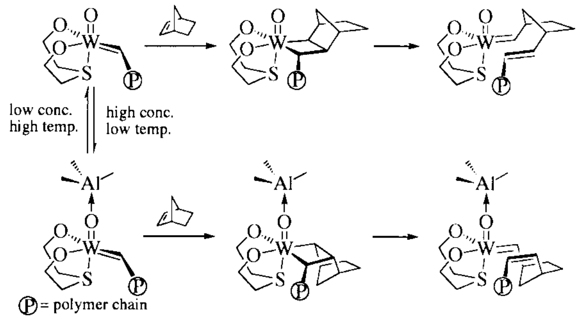
In toluene, at 60 °C, $[Monomer]_0$ / [W] = 100, $[AlEt_3]$ = [W], Time = 1 h.
[a] Determined by GPC analysis calibrated with standard poly(styrene)s.
[b] *cis*-Contents determined by ^1H NMR spectra.

Table 2. Effects of Polymerization Temperature on the ROMP of Norbornene by $WO\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Cl_2/AlEt_3$.

Temp. °C	Yield %	M_n /10^4 [a]	M_w/M_n[a]	*cis*-Cont.[b]
–78	<1	-	-	-
–15	37	23.4	2.6	88
0	42	24.8	2.1	80
30	77	42.0	1.9	42
60	70	46.6	1.6	58
90	73	15.6	1.9	32
110	64	11.1	2.0	31

In toluene, $[Monomer]_0$ = 1 M, [W] = $[AlEt_3]$ = 10 mM, time = 1 h.
[a] Determined by GPC analysis calibrated with standard poly(styrene)s.
[b] *cis*-Contents determined by ^1H NMR spectra.

We propose that such strong dependence of the *cis/trans*-selectivity on the polymerization conditions could come from the interaction between the oxotungsten center and the aluminum compounds $AlEt_nCl_{3-n}$ (Scheme 2). Under high concentration and/or at low temperature, the oxotungsten center would coordinate to the Lewis acidic aluminum compounds, $AlEt_nCl_{3-n}$, which restricts the direction of the coordinating monomer on the tungsten center to produce *cis*-rich polymer. With diluting the polymerization system and/or with raising polymerization temperature, the oxotungsten center would dissociate from the aluminum compounds to decrease *cis*-selectivity for the ROMP of norbornene. The oxotungsten–aluminum interaction was investigated in a model system: **1** and $Al(O^iPr)_3$. The ^1H–^1H NOESY spectra of a 1:1 mixture of **1** and $Al(O^iPr)_3$ in toluene-d_8 ([W] = [Al] = 20 mM) showed a correlation between *tert*-butyl protons of **1** and methine protons of $Al(O^iPr)_3$ at –50 °C but did not show that at 30 °C. This oxotungsten–aluminum interaction may enhance not only *cis*-selectivity but also catalytic activity. Similar activation effects of aluminum cocatalysts have been reported in oxo alkylidene tungsten systems such as $WO(=CHCMe_3)(PEt_3)Cl_2$[3] and Tp'WO(=CHCMe$_3$)Cl (Tp' = hydrotris(3,5-dimethyl-1-pyrazolyl)borate).[4] A theoretical study indicated that the Lewis acidic aluminum cocatalysts decrease the activation barrier between the metallacyclic intermediate and the alkylidene complex in oxotungsten catalyst system.[12]



Scheme 2. Proposed Reaction Mechanism.

In summary, we prepared a new oxotungsten complex having bis(aryloxo) ligand, $WO\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Cl_2$ (**1**), and its structure was determined by single-crystal X-ray analysis to have C_s symmetry. The catalyst system **1**/$AlEt_3$ showed strong dependencies of *cis/trans* selectivity on the catalyst concentration and on the polymerization temperature in ROMP of norbornene. The *cis*-rich poly(norbornene) was produced by the polymerization under high catalyst concentration and/or by that at low polymerization temperature, possibly due to oxotungsten–aluminum interaction.

References and Notes

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10 mp 250–260 °C (dec). ^1H NMR (C_6D_6, 30 °C, 500 MHz): δ 7.18–7.05 (m, 7H, *Toluene*), 7.03 (s, 1H, 3-C_6H_2O), 6.93 (s, 1H, 5-C_6H_2O), 2.16 (s, 4.2H, *Toluene*), 2.00 (s, 3H, 4-*Me*), 1.37 (s, 9H, 6-^{t}*Bu*),. ^{13}C NMR (C_6D_6, 30 °C, 125 MHz): δ 160.31 (1-C_6H_2O), 143.25 (6-C_6H_2O), 137.54 (4-C_6H_2O), 130.39 (5-C_6H_2O), 132.04 (3-C_6H_2O), 132.04 (2-C_6H_2O), 35.45 (6-CMe_3), 29.93 (6-CMe_3), 20.81 (4-*Me*). Anal. Calcd for $WO\{S(4\text{-}Me\text{-}6\text{-}{}^tBuC_6H_2O)_2\}Cl_2\cdot 1.4C_7H_8$: C, 50.50; H, 5.22%. Found: C, 50.47; H, 5.51%. ESI-MS (MeCN) *m/z* 628 (M^-).
11 Crystal data of **1**: formula $C_{29}H_{36}O_3Cl_2SW$, formula weight = 719.42, orthorhombic, space group $P2_12_12_1$ (#19), a = 17.602(3) Å, b = 17.885(4) Å, c = 9.982(4) Å, Z = 4, V = 3142(1) Å^3, D_{calcd} = 1.521 g/cm^3. A total reflection 4039, 1989($I > 2\sigma(I)$) were used in the refinement of 291 parameter: R = 0.044, R_w = 0.047, GOF = 1.30.
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