Cis-Specific Polymerization of Norbornene Catalyzed by Tungsten Based Complex Catalysts Bearing an O–N–O Tridentate Ligand

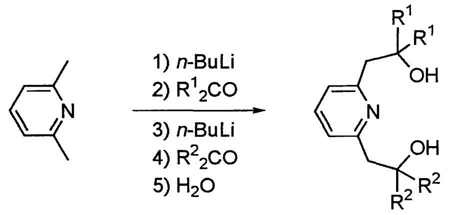
Yuushou Nakayama, Naoko Ikushima, and Akira Nakamura*
Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560

(Received May 14, 1997; CL-970361)

Tungsten complexes bearing O—N—O tridentate ligands, $WOCl_2\{(OCR^1_2CH_2)(OCR^2_2CH_2)(NC_5H_3)\}$ (**3**: R^1 = Ph, R^2 = Me; **4**: $R^1 = R^2$ = Me) were synthesized. The complex **3** was revealed to have octahedral structure with two oxygen atoms of alkoxide in *trans* position by X-ray analysis. These complexes catalyze the polymerization of norbornene upon activation with Et_3Al and the catalyst system **3**/$2Et_3Al$ yielded polynorbornenes with high *cis* content.

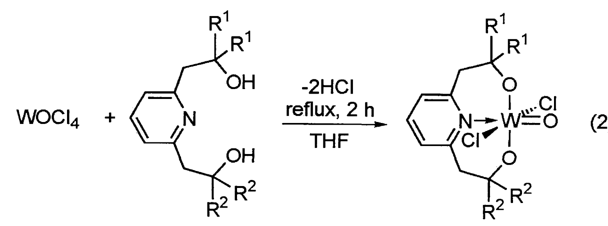
Control in stereoregularity as well as molecular weight and its distribution is one of the most attracting targets in the field of polymer synthesis. Since Brintzinger reported that a bridged metallocene/MAO system afforded isotactic PP in 1985,[1] the design of the catalyst precursors for olefin polymerization has been investigated extensively. On the other hand, the systematic studies to control stereospecificity of the catalysts for the ring opening metathesis polymerization (ROMP) of cyclic olefins are relatively rare.[2-4] Recently, we have reported that the group 5 transition metal complexes bearing a combination of bulky pentamethylcyclopentadienyl and less bulky butadiene ligands can catalyze the *cis*-specific polymerization of norbornene.[5] We tried to apply this strategy to a tungsten catalyst system which is one of the most common systems in ROMP catalysis. In order to make effective coordination environment we designed a chelating O—N—O tridentate ligand, 2-(2-hydroxy-2,2-diphenylethyl)-6-(2-hydroxyisobutyl)pyridine (**1**) in which both of bulky and less bulky alkoxide moieties can be fixed at *trans* position in the complex. Quite recently, Gibson and his coworkers have reported molybdenum complexes having a similar pyridine diolate ligand, $Mo(NC_6H_3Pr^i_2\text{-}2,6)_2(L)\}$ and $Mo(NC_6H_3Pr^i_2\text{-}2,6)(=CHCMe_2Ph)(L)\}$ (L = $(OCPh_2CH_2)_2(NC_5H_3)$).[6] In this communication, we report the *cis*-specific polymerization catalyzed by the tungsten complex having a new tridentate 2,6-pyridinediethanolate ligand.

The ligand **1** was synthesized by the similar reaction to that for 2,6-bis(2-hydroxy-2-methylpropyl)pyridine (**2**)[7] (eqn. 1).[8] The reaction of tungsten oxychloride with **1** or **2** in refluxing THF cleanly afforded the tungsten 2,6-pyridinediethanolate complexes, **3** or **4**, as colorless crystals in 55% and 45% yield, respectively (eqn. 2).[8] Both of the complexes are air- and moisture-stable. Elemental analysis and X-ray crystallography (*vide infra*) of **3** indicated that **3** has one $CHCl_3$ as a crystal solvent.



1: R^1 = Ph, R^2 = Me
2: $R^1 = R^2$ = Me

(1)



(2)

1: R^1 = Ph, R^2 = Me
2: $R^1 = R^2$ = Me

3: R^1 = Ph, R^2 = Me
4: $R^1 = R^2$ = Me

The molecular structure of **3** was revealed by X-ray crystallography as shown in Figure 1.[9] The complex has 6-coordinated distorted octahedral structure. Two oxygen atoms of the pyridinediolate ligand are placed in *trans*-position. The terminal oxide is located at the *trans*-position to pyridine N atom and two chlorine atoms are also trans to each other. The W–N bond distance (2.436(6) Å) is elongated by ca. 0.2 Å compared to typical distances of W–N donor bond found in $W(NBu^t)(NH_2Bu^t)(OC_6H_4Ph\text{-}2)_4$ (2.380(3) Å),[10] and $W(NC_6H_3Pr^i_2\text{-}2,6)\{OCMe(CF_3)_2\}_2$(quinuclidine) (2.273(5) Å)[11] due to the distortion caused by chelating coordination. The short W–O2 (1.843(5) Å) and W–O3 distances (1.864(4) Å) and wide W–O(2)–C(7) (143.8(5) °) and W–O(3)–C(11) (142.3(4) °) angles indicate the contribution of π-donation from O(2) and O(3).

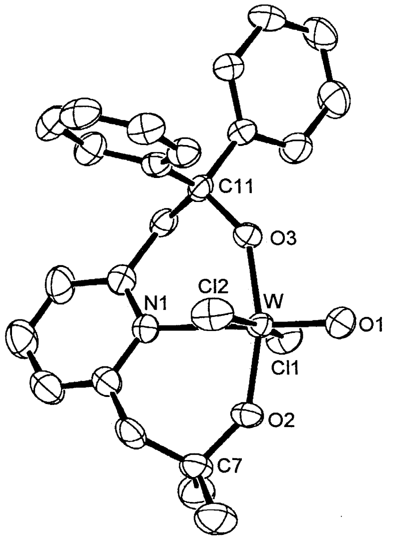


Figure 1. A drawing of **3** with the numbering scheme. Thermal ellipsoids scaled at 20% probability level. The crystal solvent $CHCl_3$ and hydrogen atoms are omitted for clarify. Selected bond distances (Å) and angles (degree): W–Cl(1) 2.377(2), W–Cl(2) 2.359(2), W–O(1) 1.694(5), W–O(2) 1.843(5), W–O(3) 1.864(4), W–N(1) 2.436(6), W–O(2)–C(7) 143.8(5), W–O(3)–C(11) 142.3(4).

Table 1. Polymerization of norbornene by tungsten pyridinediethanolate complexes[a]

run	complex	temp. (°C)	time (h)	yield (%)	$\overline{M}_n$/ 10^3 [b]	$\overline{M}_w$/ $\overline{M}_n$[b]	cis-content(%)
1	**3**	r.t.	1	83	340	2.6	57
2	**3**	0	1	36	90	2.2	86
3	**3**	-78	24	5	38	2.7	92
4	**4**	r.t.	1	72	150	3.0	51
5	**4**	0	1	41	100	1.7	49
6	**4**	-78	24	<1	—	—	—

[a] $[W] = 10$ mM, $[Et_3Al] = 20$ mM, $[\text{norbornene}]_0 = 1$ M.
[b] Determined by GPC analysis in THF, calibrated to a polystyrene standard.

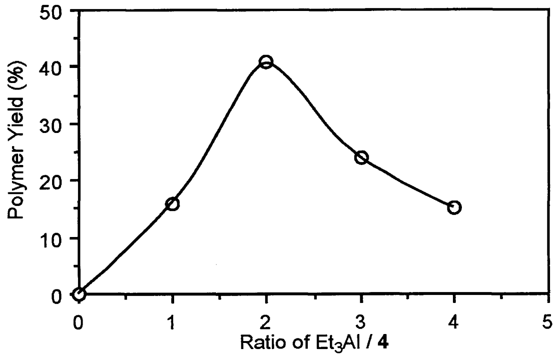


Figure 2. Dependence of the yield of polynorbornene on the molar ratio of complex **4** and co-catalyst triethylaluminum. Polymerization was carried out in toluene at 0 °C for 1 h.

Without cocatalyst, both of the complexes **3** and **4** showed no catalytic activity for the polymerization of norbornene at room temperature. These complexes were found to be activated by the use of Et_3Al. The polymerization of norbornene catalyzed by **4** was carried out in the presence of various molar equiv. of Et_3Al at 0 °C and the results are shown in Figure 2, which shows clearly that the 1:2 ratio for **4**:Et_3Al gave the maximum yield in the norbornene polymerization. Thus, the 1:2 ratio for catalyst:co-catalyst was used consistently for the following polymerization and the results are summarized in Table 1. When the polymerization was carried out at r.t., both of the catalyst systems based on **3** and **4** were moderately active but not stereospecific (runs 1 and 4). Generally, the stereospecificity of polymerization catalysts increases with decreasing polymerization temperature. Thus we investigated the polymerization at lower temperatures. The polymerization of norbornene at 0 °C by **3**/$2Et_3Al$ gave polymers with *cis*-content of 86% (run 2). Although the activities of the **3**/$2Et_3Al$ system was very low at -78 °C, the highest stereospecificity was observed (run 3, *cis* 92%). In sharp contrast to that, the polynorbornene obtained with **4**/$2Et_3Al$ had almost no stereoregularity (run 5) even at 0 °C. The higher activities of the system of sterically more crowded **3** than that of **4** might result from some electronic effect of the phenyl groups.

The stereospecificity of the system can be rationalized by the structure of **3**. Although the initiation mechanism for this polymerization system is not clear, an alkylidene species bearing the 2,6-pyridinediethanolate ligand might be generated. At the insertion step of norbornene to the metal–alkylidene bond to form a metallacyclobutane intermediate, the steric hindrance of the ligand prefers a geometry in which both of the polymer end and the C_5-ring moiety of norbornene are oriented at the opposite side to the Ph_2 moiety of the pyridinediolate ligand to form the *cis*-polymer.

Thus, we have found that coordination of the O—N—O tridentate ligand to the metal enables the effective control of the stereospecificity depending on the substituents on the ligands.

The author (A. N.) is grateful for the financial support of the Ministry of Education, Science and Culture of Japan (Specially Promoted Research No. 06101004).

References and Notes

1 W. Kaminsky, K. Kulper, H. H. Brintzinger, and F. R. W. P. Wild, *Angew. Chem., Int. Ed. Engl.*, **24**, 507 (1985).
2 N. W. Eilerts, and J. A. Heppert, *Polyhedron*, **14**, 3255 (1995).
3 R. H. Grubbs, and W. Tumas, *Science*, **243**, 907 (1989).
4 R. R. Schrock, *Acc. Chem. Res.*, **23**, 158 (1990).
5 w. Mashima, Y. Tanaka, M. Kaidzu, and A. Nakamura, *Organometallics*, **15**, 2431 (1996).
6 V. C. Gibson, E. L. Marshall, C. Redshaw, W. Clegg, and M. R. J. Elsegood, *J. Chem. Soc., Dalton Trans.*, **1996**, 4197.
7 B. Kaptein, G. Barf, R. M. Kellogg, and F. V. Bolhuis, *J. Org. Chem.*, **55**, 1890 (1990).
8 **1**: ^1H NMR (270 MHz, $CDCl_3$, 30 °C) δ 7.47–6.97 (m, 13H, aromatic protons), 3.72 (s, 2H, CH_2), 2.85 (s, 2H, CH_2), 1.07 (s, 6H, CH_3). **1** includes one molucule of H_2O as a solvent molecule. Anal. Found: C, 75.28; H, 7.36; N, 3.89. Calcd for $C_{23}H_{27}NO_3$: C, 75.59; H, 7.45; N, 3.83. **3**: ^1H NMR (270 MHz, $CDCl_3$, 30 °C) δ 7.78–7.72 (m, 13H, aromatic protons), 4.35 (s, 2H, CH_2), 3.65 (s, 2H, CH_2), 1.46 (s, 6H, CH_3). Anal. Found: C, 38.69; H, 3.13; N,1.97%. Calcd for $C_{24}H_{24}Cl_5NO_3W$: C, 39.19; H, 3.29; N, 1.90%. **4**: ^1H NMR (270 MHz, $CDCl_3$, 30 °C) δ 7.78 (t, 1H, 4-H), 7.22 (d, 2H, 3,5-H), 3.59 (s, 4H, CH_2), 1.47 (s, 12H, CH_3). Anal. Found: C, 31.80; H, 3.90; N, 2.91%. Calcd for $C_{13}H_{19}Cl_2NO_3W$: C, 31.73; H, 3.89; N, 2.85%.
9 Crystal and refinement data for **3**: $C_{24}H_{24}NO_3WCl_5$, formula weight = 735.57, monoclinic, space group $P2_1/c$, $a = 8.891(3)$ Å, $b = 10.865(3)$ Å, $c = 27.768(3)$ Å, $V = 2681(1)$ Å^3, $Z = 4$, $d_{calc} = 1.821$ gcm^{-3}, R (R_w) = 0.041 (0.047) for 4592 diffraction data with $I > 3\sigma(I)$ and 287 variables.
10 J. L. Kerschner, J. S. Yu, P. E. Fanwick, and I. P. Rothwell, *Organometallics*, **8**, 1414 (1989).
11 R. R. Schrock, W. E. Crowe, G. C. Bazan, M. DiMare, M. B. O'Regan, and M. H. Schofield, *Organometallics*, **10**, 1832 (1991).