Activation of a *trans*-Dialkyl(oxo)tungsten Complex Bearing a 2,6-Pyridinediethanolate Ligand with Aluminum Cocatalysts to Catalyze the ROMP of Norbornene

Yuushou Nakayama, Naoko Ikushima, Norikazu Ueyama, Akira Nakamura,* and Akira Harada
Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

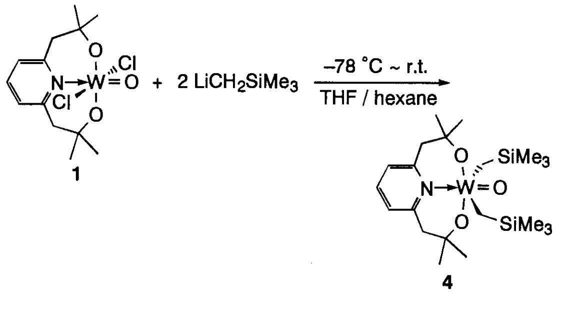
(Received January 20, 2000; CL-000058)

A novel *trans*-bis(trimethylsilylmethyl)(oxo)tungsten complex bearing an O–N–O tridentate ligand, WO(Me_4pyde)-(CH_2SiMe_3)$_2$ (**4**, pyde = 2,6-pyridinediethanolate), was synthesized and was confirmed to have octahedral structure with two alkyl groups in *trans* position by X-ray analysis. Complex **4** catalyzed the polymerization of norbornene although its activity was rather low. The activity of **4** could be dramatically enhanced by the use of $AlEt_3$ or $AlCl_3$ as a cocatalyst.

Ring-opening metathesis polymerization (ROMP) is an important reaction in both scientific and industrial points of view. The active site of ROMP has been established to be a metal alkylidene species.[1,2] Alkylidene complexes having strong π-donor ligands such as imido,[3,4] and oxo[5] are known to be quite effective catalysts for ROMP. Most of such complexes were generated by α-H elimination from the corresponding *cis*-dialkyl compounds.[6,4] Therefore, *cis*-dialkyl complexes are expected to be catalyst precursors for ROMP.[7-9] There are many examples of alkyl(oxo)tungsten complexes,[10] but such complexes have *cis*-dialkyl groups favorable for α-H elimination. On the other hand, *trans*-dialkyl complexes have not been studied in detail as catalyst precursors for ROMP.

We recently reported that the *trans*-dichloro(oxo)tungsten complexes bearing meridional O–N–O tridentate ligands, $WOCl_2\{(OCR^1{}_2CH_2)(OCR^2{}_2CH_2)(NC_5H_3)\}$ (**1**: $R^1 = R^2 = Me$; **2**: $R^1 = R^2 = i\text{-}Pr$; **3**: $R^1 = Me$, $R^2 = Ph$) catalyze the ROMP of norbornene upon activation with Et_3Al to give polynorbornenes with high *cis*-content.[11] In this catalyst system, *trans*-dialkyl complex should be formed at the first step in the reaction with Et_3Al. In order to demonstrate the generation of active species from *trans*-dialkylcomplexes, we synthesized a *trans*-dialkyl(oxo)tungsten complex and investigated its catalytic behavior for the ROMP of norbornene.

The reaction of the *trans*-dichloro(oxo)tungsten complex **1** with two equivalents of $LiCH_2SiMe_3$ in THF/hexane gave a *trans*-bis(trimethylsilylmethyl)tungsten complex, WO(Me_4pyde)-(CH_2SiMe_3)$_2$ (**4**, pyde = 2,6-pyridinediethanolate), as yellow crystals in 5% yield (eq 1).[12] ^1H NMR spectrum of **4** in C_6D_6 indicated that **4** has C_{2v} symmetry in solution.[12]



(1)

The pseudo C_{2v} structure of **4** was confirmed by X-ray crystallography (Figure 1).[13] Complex **4** has two independent molecules in a unit cell, both the molecules have essentially the same structure. Complex **4** has 6-coordinated distorted octahedral geometry in which the two trimethylsilylmethyl ligands are placed in *trans*-position as expected from the structure of the dichloro complexes **2** and **3**.[11] The terminal oxo ligand is located at the *trans*-position to pyridine N atom and two oxygen atoms of the Me_4pyde ligand are also *trans* to each other. The W–C distances (*av.* 2.219 Å) of **4** are longer by 0.06 Å than those of W(=NAr){OC(CF_3)$_2$(tolyl)}(CH_2-CMe_3)$_2$ (*av.* 2.159 Å, Ar = 2,6-diisopropylphenyl)[6] and W(tbp)(PhC≡CPh)R_2 (*av.* 2.154 Å (R = CH_3) and *av.* 2.16 Å (R = CH_2Ph), tbp = 2,2'-thiobis(4-methyl-6-*t*-butylphenoxo))[9] in which two alkyl groups are located in *cis* position. It is notable that the metal–O distances of the Me_4pyde ligand in **4** (*av.* 1.860 Å) are significantly shorter than those of the corresponding Ph_4pyde ligand in Mo(=NAr)$_2$(Ph_4pyde)} (1.940(2) Å) and Mo(=NAr)(=CH-CMe_2Ph)(Ph_4pyde)} (*av.* 1.939 Å)[14] in spite of larger ionic radii of 6-coordinated W^{6+} (0.74 Å) than that of 5-coordinated Mo^{6+} (0.64 Å),[15] indicating the strong tungsten-dπ—oxygen-pπ interaction in **4**.

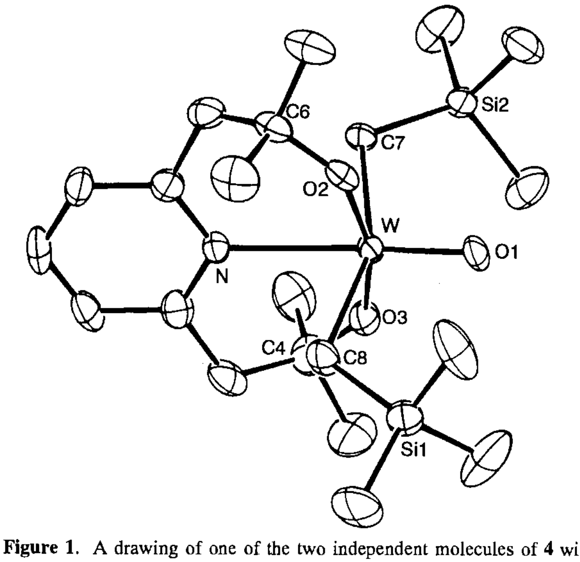


Figure 1. A drawing of one of the two independent molecules of **4** with the numbering scheme. Selected bond distances (molecule A / molecule B, Å) and angles (molecule A / molecule B, degree): W–O1 1.711(9)/1.708(8), W–O2 1.852(2)/1.866(8), W–O3 1.861(9)/1.859(8), W–C7 2.204(12)/2.236(15), W–C8 2.214(15)/2.221(12), W–N 2.476(9)/2.485(9), W–O2–C6 142.9(7)/143.1(7), W–C7–Si2 116.4(6)/115.5(7), W–C8–Si1 118.0(7)/115.7(6).

When the complex **4** was heated to 60 °C in C_6D_6, the color of the solution changed from yellow to yellow brown. ^1H NMR spectrum of the yellow brown solution showed a singlet peak at 9.00 ppm which can be assigned to alkylidene protons (eq 2). The ^1H NMR signal of the alkylidene species was related to a signal at 226 ppm in ^{13}C NMR by HMQC spectrum. However, the yield of the alkylidene species was as low as 5% after 19 h at 60 °C. Elongation of the reaction time did not improve the yield but resulted in decomposition of the complexes to give a complicated mixture.

$$\underset{\mathbf{4}}{WO(Me_4pyde)(CH_2SiMe_3)_2} \xrightarrow[SiMe_4]{\Delta} WO(Me_4pyde)(=CHSiMe_3) \quad (2)$$

The polymerization of norbornene was performed in toluene and the results are summarized in Table 1. Without cocatalyst at 25 °C, complex **4** requires long reaction time to give polynorbornene in high yield (run 1). The polynorbornene obtained by **4** had relatively low molecular weight and narrow molecular weight distribution. Complex **4** did not show any catalytic activity at 60 °C for 24 h (run 2). The activity of **4** was significantly lower than that of W(tbp)(PhC≡CPh)-$(CH_2SiMe_3)_2$ (run 6), in which two alkyl groups are located in *cis* position.[9] These results are in accord with the inefficient generation of alkylidene species from the *trans*-dialkyl complex **4** (*vide supra*).

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

Run	Catalyst system	Temp. / °C	Time / h	Yield / %	$\overline{M}_n$/ 10^3 [b]	$\overline{M}_w$/ $\overline{M}_n$ [b]	*Cis*-content / %
1	**4**	25	150	87	5.0	1.8	56
2	**4**	60	24	<1	–	–	–
3	**4**/$AlEt_3$	25	2	85	30	3.7	43
4	**4**/$AlCl_3$	25	2	83	–[c]	–[c]	~50
5	**1**/2$AlEt_3$[11]	25	1	83	340	2.6	57
6	W(tbp)(PhC≡CPh)$(CH_2SiMe_3)_2$[9]	60	1	62	490	3.4	83

[a] In toluene, [W] = 10 mM, $[norbornene]_0$ = 1 M. [b] Determined by GPC analysis in THF, calibrated to a polystyrene standard. [c] Not determined.

On the other hand, the corresponding multi-component system comprised of the dichloro complex **1** and Et_3Al showed much higher activity (run 5),[11] thus we investigated the effect of the aluminum compounds as cocatalysts. When the complex **4** was combined with Et_3Al (run 3), the catalyst system showed comparable activity to that of the **1**/2Et_3Al system to give polynorbornene with higher molecular weight than that of polynorbornene obtained without cocatalyst. Interestingly, **4** could also be activated with anhydrous $AlCl_3$ (run 4) to show almost identical activity to those of **4**/Et_3Al and **1**/2Et_3Al systems, while **1**/$AlCl_3$ system was inactive. Thus, the role of alkylaluminum cocatalysts in the previous tungsten catalyst systems is not only to alkylate the catalyst precursor but also to accelerate the catalytic process. Similar activation effects of $AlCl_3$ have been reported in oxo alkylidene tungsten systems such as $WO(=CHCMe_3)(PEt_3)Cl_2$[16] and Tp'WO(=$CHCMe_3$)Cl (Tp' = hydrotris(3,5-dimethyl-1-pyrazolyl)borate).[17] A theoretical study has indicated that the Lewis acidic aluminum cocatalysts decrease the activation energy in oxotungsten catalyst system.[18]

Both of the catalyst systems based on complexes **4** and **1** showed essentially no *cis*-specificity for the polymer under these conditions. The *cis*-specificity of the catalyst systems seems to be influenced more significantly by the stereochemistry of the O–N–O ancillary ligands.

Thus, we demonstrated that the *trans*-dialkyltungsten complex could be a catalyst precursor for the ROMP of norbornene without cocatalysts and that its activity could be dramatically enhanced by the addition of $AlEt_3$ or $AlCl_3$ as a cocatalyst.

Y.N. acknowledges the support by the Grant-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

1 R. H. Grubbs and W. Tumas, *Science*, **243**, 907 (1989).
2 R. R. Schrock, *Acc. Chem. Res.*, **23**, 158 (1990).
3 R. R. Schrock, R. T. DePue, J. Feldman, C. J. Schaverien, J. C. Dewan, and A. H. Liu, *J. Am. Chem. Soc.*, **110**, 1423 (1988).
4 P. A. van der Schaaf, D. M. Grove, W. J. J. Smeets, A. L. Spek, and G. van Koten, *Organometallics*, **12**, 3955 (1993).
5 F. J. de la Mata and R. H. Grubbs, *Organometallics*, **15**, 577 (1996).
6 R. R. Schrock, R. T. DePue, J. Feldman, K. B. Yap, D. C. Yang, W. M. Davis, L. Park, M. DiMare, M. Schofield, J. Anhaus, E. Walborsky, E. Evitt, C. Krüger, and P. Betz, *Organometallics*, **9**, 2262 (1990).
7 K. Mashima, Y. Tanaka, M. Kaidzu, and A. Nakamura, *Organometallics*, **15**, 2431 (1996).
8 K. Mashima, M. Kaidzu, Y. Tanaka, Y. Nakayama, A. Nakamura, J. G. Hamilton, and J. J. Rooney, *Organometallics*, **17**, 4183 (1998).
9 Y. Nakayama, H. Saito, N. Ueyama, and A. Nakamura, *Organometallics*, **18**, 3149 (1999).
10 M. W. Whiteley, in "Comprehensive Organometallic Chemistry II", ed by M. J. Winter and S. Woodward, Elsevier Science Ltd., Oxford (1995), Vol. 5, p. 281.
11 Y. Nakayama, N. Ikushima, and A. Nakamura, *Chem. Lett.*, **1997**, 861.
12 ^1H NMR (270 MHz, C_6D_6, 30 °C) d 6.89 (t, 1H, 4-H), 6.36 (d, 2H, 3,5-H), 2.91 (s, 4H, $OC(CH_3)_2CH_2$), 1.20 (s, 12H, $OC(CH_3)_2CH_2$), 0.59 (s, 18H, $CH_2Si(CH_3)_3$), 0.26 (s, 4H, $CH_2Si(CH_3)_3$). Anal. Calcd for $C_{21}H_{41}NO_3Si_2W$: C, 42.35; H, 6.94; N, 2.35%. Found: C, 42.35; H, 6.98; N, 2.33%.
13 The X-ray diffraction data of **4** were collected by using the imaging plate (IP) system DIP3000 developed by MAC Science, Ltd., Japan. Crystal and refinement data for **4**: $C_{21}H_{41}O_3NSi_2W$, formula weight = 595.66, monoclinic, space group $P2_1/c$, a = 17.722(6) Å, b = 17.659(9) Å, c = 19.69(1) Å, β = 115.44(1)°, V = 5563.6 Å^3, Z = 8, d_{calc} = 1.422 gcm^{-3}, R (R_w) = 0.044 (0.048) for 6120 diffraction data with $I > 3\sigma(I)$ and 625 variables.
14 V. C. Gibson, E. L. Marshall, C. Redshaw, W. Clegg, and M. R. J. Elsegood, *J. Chem. Soc., Dalton Trans.*, **1996**, 4197.
15 R. D. Shannon, *Acta Crystallogr.*, **A32**, 751 (1976).
16 J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, and W. J. Youngs, *J. Am. Chem. Soc.*, **102**, 4515 (1980).
17 L. L. Blosch, K. Abboud, and J. M. Boncella, *J. Am. Chem. Soc.*, **113**, 7066 (1991).
18 A. K. Rappe and W. A. Goddard, III, *J. Am. Chem. Soc.*, **104**, 448 (1982).