Isomerization and α-H Elimination of Dialkyltungsten Complexes Stabilized by a Sulfur-Bridged Chelating Diaryloxo Ligand

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Dichlorotungsten complexes bearing an O−S−O chelating dialkoxo and a diphenylacetylene ligand, W(η^2-RC≡CR)[S(4-R′-6-R″$C_6H_2O)_2$]Cl_2 (R = Ph, R′ = Me, R″ = ^{t}Bu (**3a**); R = Et; R′ = R″ = Me (**3b**)), were prepared by the reaction of W(η^2-RC≡CR)Cl_4 and S(4-R′-6-R″C_6H_2-OH)$_2$. Their C_s structures were confirmed by NMR study of these complexes and X-ray crystallography of **3b**. Complex **3a** reacted with Mg($CH_2SiMe_3)_2$ in diethyl ether to give initially a C_s symmetric dialkyltungsten complex, W(η^2-PhC≡CPh)[S(4-Me-6-^{t}Bu$C_6H_2O)_2$](CH_2-$SiMe_3)_2$ (**5**). In solution at room temperature, **5** isomerizes to the C_1 symmetric isomer **6,** whose structure was probed by the NMR spectroscopy. The thermodynamic parameters for the isomerization were determined to be $G^{\ddagger}$(45 °C) = 23.8 ± 0.4 kcal mol^{-1} and $S^{\ddagger}$(45 °C) = −3.3 ± 0.7 cal K^{-1} mol^{-1}. Upon heating to 60 °C, the generation of metal−alkylidene species occurs. A similar reaction of **3a** with dimethyl- and dibenzylmagnesium directly gives C_1 symmetric dialkyltungsten complexes, W(η^2-PhC≡CPh)[S(4-Me-6-^{t}Bu$C_6H_2O)_2$]R_2 (R = Me (**7**), CH_2Ph (**8**)), whose structures were determined by X-ray crystallography. The ring-opening metathesis polymerization (ROMP) of norbornene was initiated in the presence of these dialkyl complexes as catalyst precursors to give poly(norbornene) having high molecular weight (M_n = 1.7 × 10^6) and high cis content (cis 93%) at the early stage of the reaction. At a polymerization temperature of 60 °C, the molecular weight and the cis content of the resulting poly(norbornene) are lowered due to the second metathesis reactions.

Introduction

High-valent group 6 metal complexes are of much interest as catalysts for the ring-opening metathesis polymerization (ROMP) of the cyclic olefins to provide polymers with unique functions.[1−7] In particular, alkylidene complexes having strong π-donor ligands such as imido, oxo, and alkoxo, M(=$NC_6H_3{}^iPr_2$-2,6)$(OR)_2$(=CHR′) (M = Mo, W; R = ^{t}Bu, $CMe_2(CF_3)$, $CMe(CF_3)_2$, etc.),[8] W(=NPh)(C_6H_4-2-CH_2NMe_2)(=CH$SiMe_3$)(CH_2-$SiMe_3$),[9] and W(=O)$(OR)_2$(=CHR′),[10] are well-known to be effective catalysts for ROMP.

We have been interested in the syntheses and reactivities of tungsten complexes bearing chelating dialkoxo ligands such as catecholate[11] and 2,6-pyridinediethanolate,[12] both of which are effective for ROMP. The tridentate ligand, 2,2′-thiobis(4-methyl-6-*tert*-butylphenoxo) (^{t}Bu_2tbp), which was previously used as a ligand in titanium complexes for olefin polymerization,[13,14] was found to coordinate to the metal ion in a *fac* fashion.[15,16] A theoretical study suggested that the sulfur atom coordination was essential to reduce the activation energy for olefin insertion into a metal−carbon bond.[17] We also introduced alkyne ligands as π-donors that can be regarded as dianionic,[18] such as imido or oxo ligands.

(1) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1983.
(2) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cyclo-Olefins*; John Wiley & Sons: New York, 1985.
(3) *Olefin Metathesis and Polymerization Catalysts*; Imamoglu, Y., Zümreoglu-Karan, B., Amass, A. J., Eds.; Kluwer Academic Publishers: Dordrecht, 1990.
(4) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907.
(5) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.
(6) Eilerts, N. W.; Heppert, J. A. *Polyhedron* **1995**, *14*, 3255.
(7) Schuster, M.; Blechert, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2036.
(8) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169. (c) Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807. (d) Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2973. (e) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988**, *21*, 1885. (f) Knoll, K.; Krouse, S. A.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4424. (g) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (h) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (i) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Dawis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378. (j) Bazan, G. C.; Schrock, R. R.; Cho, H.-N.; Gibson, V. C. *Macromolecules* **1991**, *24*, 4495. (k) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899. (l) Bazan, G. C.; Schrock, R. R. *Macromolecules* **1991**, *24*, 817. (m) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831. (n) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185. (o) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759. (p) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (q) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414. (r) Schrock, R. R. *Polyhedron* **1995**, *14*, 3177. (s) Schrock, R. R.; Lee, J.-K.; O'Dell, R.; Oskam, J. H. *Macromolecules* **1995**, *28*, 5933. (t) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erichson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713. (u) Fujimura, O.; de la Mata, F.; Grubbs, R. H. *Organometallics* **1996**, *15*, 1865. (v) Pu, L.; Wagaman, M. W.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1138.

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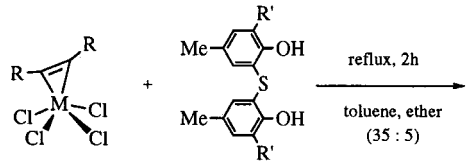
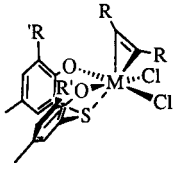
Here we report the synthesis and reactivity of *cis*-dialkyltungsten complexes having both ^{t}Bu$_2$tbp and disubstituted acetylene ligands.

Results and Discussion

Synthesis and Structures of Dichloro Complexes. The dichlorotungsten complexes W(η^2-RC≡CR)(R′$_2$tbp)Cl$_2$ (R = Ph, R′ = ^{t}Bu (**3a**); R = Et; R′ = Me (**3b**)) were prepared as red crystals by refluxing a mixture of W(η^2-RC≡CR)Cl$_4$ (R = Ph (**1a**), R = Et (**1b**); M = Mo, R = Ph (**2**)) and 1 equiv of (R′$_2$tbp)H$_2$ (R′$_2$tbp = 2,2′-thiobis(4-methyl-6-R′phenoxo)) in toluene−THF (93:7). A molybdenum analogue, Mo(η^2-PhC≡CPh)(^{t}Bu$_2$-tbp)Cl$_2$ (**4**), was obtained as black crystals in a similar manner. The ^{1}H NMR spectra of these complexes suggest that they have symmetric structures, and the X-ray crystallography of Me$_2$tbp complex **3b** confirmed a C_s structure (vide infra). In the ^{13}C NMR spectrum of **3** and **4**, the alkyne carbon resonance appears at δ 230−244 ppm, indicating that the diphenylacetylene donates four electrons to the metal center.



1a: M = W, R = Ph R' = Me, ^{t}Bu
1b: M = W, R = Et
2: M = Mo, R = Ph



(1)

3a: M = W, R = Ph, R' = ^{t}Bu
3b: M = W, R = Et, R' = Me
4: M = Mo, R = Ph, R' = ^{t}Bu

Crystal Structure of 3b. The C_s structure of **3b** is confirmed by the single-crystal X-ray analysis (Figure 1). Selected bond distances and angles are summarized in Table 1. If the 1-hexyne ligand is considered to occupy one coordination site, the coordination geometry around the tungsten atom of **3b** can be described as pseudo-octahedral. The Me$_2$tbp ligand coordinates to tungsten in a facial fashion, and the alkyne ligand is located at the trans position to the sulfur atom of the Me$_2$tbp ligand. The W−S bond distance (2.638(2) Å) of **3b** is slightly shorter than the Ti−S distances in [Ti(^{t}Bu$_2$tbp)-Cl$_2$]$_2$ (2.664(2) Å)[19] and [Ti(^{t}Bu$_2$tbp)(O^{i}Pr)$_2$]$_2$ (2.719(1) Å)[15,16] taking into account the similar ionic radii of W^{6+} (0.74 Å) and Ti^{4+} (0.745 Å).[20] The bond angles O−W−O, O−W−Cl, and Cl−W−Cl are 89.4(2)°, 89.0(1)°, and 86.65(7)°, respectively. The W−C distances, W−C17 (2.015(8) Å) and W−C18 (2.014(7) Å), are comparable to those of [PPh$_4$][WCl$_5$(η^2-PhC≡CH)] (2.002(15) and 2.032(10) Å),[21] [WCl$_3$(μ-Cl)(η^2-Me$_3$SiC≡CSiMe$_3$)]$_2$ (2.025-(11) and 2.028(11) Å),[22] and WCl$_2$(OC$_6$H$_3$Ph$_2$-2,6)$_2$(η^2-EtC≡CEt) (2.021(8) and 2.027(8) Å)[23] but shorter than the corresponding dialkyl complexes (vide infra).

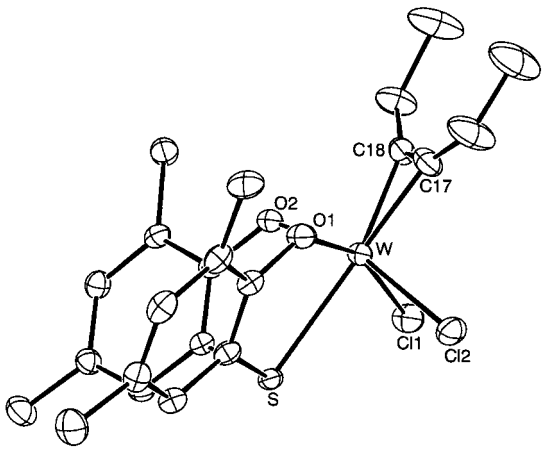
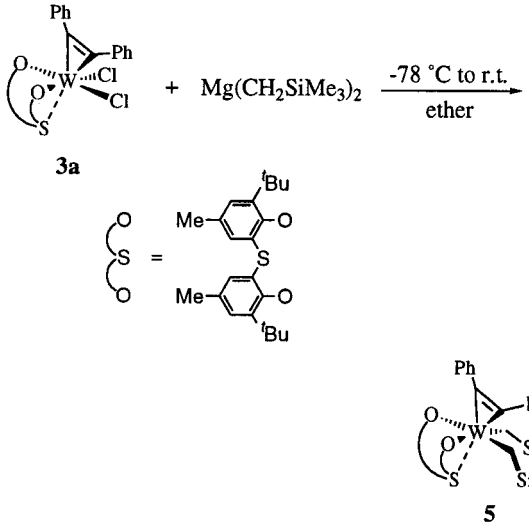


Figure 1. ORTEP drawing of W(η^2-EtC≡CEt)(Me$_2$tbp)-Cl$_2$ (**3b**) with a numbering scheme.

Preparation of Bis(trimethylsilylmethyl) Complexes. A bulky dialkyl complex, W(η^2-PhC≡CPh)(^{t}Bu$_2$-tbp)(CH$_2$SiMe$_3$)$_2$ (**5**), was obtained as red crystals in 94% yield from the reaction of **3a** with 1 equiv of bis-(trimethylsilylmethyl)magnesium in diethyl ether (eq 2). Complex **5** was characterized by elemental analysis



(2)

5

and NMR spectroscopy. In the ^{1}H NMR spectrum of **5**, the proton signals of the trimethylsilylmethyl, *tert*-butyl, and methyl groups appear as singlets at −0.11, 1.17, and 2.03 ppm, respectively, indicating that **5** has a C_s symmetric structure. The AB-type signals at 2.67 and

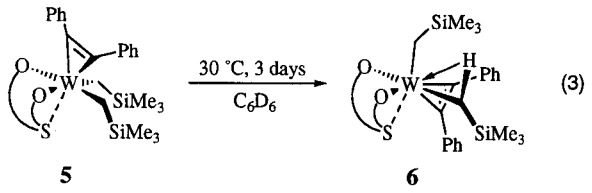
(9) (a) van der Schaaf, P. A.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 3955. (b) van der Schaaf, P. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 717. (c) van der Schaaf, P. A.; Abbenhuis, R. A. T. M.; van der Noort, W. P. A.; de Graaf, R.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 1433.
(10) de la Mata, F. J.; Grubbs, R. H. *Organometallics* **1996**, *15*, 577.
(11) Nakayama, Y.; Saito, H.; Nakamura, A. *Chem. Lett.* **1996**, 691.
(12) Nakayama, Y.; Ikushima, N.; Nakamura, A. *Chem. Lett.* **1997**, 861.
(13) Miyatake, T.; Mizunuma, K.; Seki, Y.; Kakugo, M. *Macromol. Chem., Rapid Commun.* **1989**, *10*, 349.
(14) van der Linden, A.; Schaverien, C. J.; Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.
(15) Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069.
(16) Porri, L.; Ripa, A.; Colombo, P.; Miano, E.; Capelli, S.; Meille, S. V. *J. Organomet. Chem.* **1996**, *514*, 213.
(17) Froese, R. D. J.; Musaev, D. G.; Matsubara, T.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 7190.
(18) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 3b, 7, and 8

complex	3b	7	8
		Bond Distances	
W−O	1.931(5) (O1)	2.053(4) (O1)	2.019(5) (O1)
	1.945(5) (O2)	1.912(4) (O2)	1.941(5) (O2)
W−S	2.638(2)	2.697(2)	2.637(2)
W−C(alkyne)	2.015(8) (C17)	2.060(6) (C7)	2.054(7) (C27)
	2.014(7) (C18)	2.062(5) (C8)	2.053(7) (C28)
W−C(alkyl)		2.148(7) (C50)	2.173(8) (C1)
		2.160(8) (C51)	2.15(1) (C11)
W−Cl	2.350(2) (Cl1)		
	2.394(2) (Cl2)		
C−C(alkyne)	1.28(1)	1.319(8)	1.274(9)
		Bond Angles	
O−W−O	89.4(2)	89.6(2)	89.9(2)
C−S−C	102.7(3)	101.1(3)	104.0(3)
X−W−X	86.65(7) (X = Cl)	100.2(3) (*X* = Me)	111.3(4) (X = CH_2Ph)
W−C−C(alkyl)			125.4(6) (C1)
			126.3(7) (C11)
W−O−C	130.3(4) (O1)	128.4(4) (O1)	128.5(5) (O1)
	127.2(4) (O2)	135.6(4) (O2)	132.1(5) (O2)

1.80 ppm ($^2J_{HH}$ = 12.5 Hz) are assignable to the α-methylene protons of W−CH_2SiMe$_3$. In the ^{13}C NMR spectrum, the α-methylene carbon signal is observed at 57 ppm (t, $^1J_{CH}$ = 112 Hz), and the alkyne carbon resonance was observed at 240 ppm. The structure of **5** was confirmed by the ^{1}H−^{1}H COSY and ^{1}H−^{1}H NOESY spectra, the latter showing a correlation between trimethylsilyl groups and *o*-, *m*-H of diphenylacetylene, indicating that both trimethylsilylmethyl groups are cis to the diphenylacetylene ligand. A correlation between *tert*-butyl group and *o*-H of diphenylacetylene indicates that the alkyne is cis to the oxygen atoms of the ^{t}Bu$_2$-tbp ligand.

Isomerization of the Bis(trimethylsilylmethyl) Complex. When **5** was kept in C_6D_6 at 30 °C for 3 days, the structure of **5** changed from a C_s structure to a C_1 one (**6**: eq 3). Unfortunately, efforts to crystallize **6** were



5 **6** (3)

not successful. The ^{1}H NMR spectra of **6** revealed no symmetry element at the metal ion. The diastereotopic methylene protons of one of the trimethylsilylmethyl groups were observed at 2.33 and 0.20 ppm. The large upfield shift of one methylene proton suggests an α-agostic interaction with the tungsten metal center. The α-protons of the other trimethylsilylmethyl group were observed at 3.56 and 3.48 ppm. In the ^{13}C NMR spectrum, the two α-carbon signals of trimethylsilylmethyl groups appear at 79.5 (t, $^1J_{CH}$ = 112 Hz) and 82.3 ppm (dd, $^1J_{CH}$ = 116, 107 Hz). The latter signal can be assigned to the α-carbon of the trimethylsilylmethyl group with an α-agostic interaction and is related with the signal of one of the two trimethylsilyl protons at −0.06 ppm by a ^{13}C−^{1}H HMBC spectrum. A ^{1}H−^{1}H NOESY experiment revealed a close proximity of the bis(trimethylsilyl)methyl group without agostic interaction to both the two *tert*-butyl groups of the ^{t}Bu$_2$tbp ligand, indicating that it is cis to the two oxygen atoms of the ^{t}Bu$_2$tbp ligand. The resonance of the diphenylacetylene alkyne carbons appears at 213.9 and 210.6 ppm, shifted more than 30 ppm upfield compared to those of **5**, indicating that the donation from diphenylacetylene ligand was decreased in **6** compared with the case of **5**.[24] This can be attributed to the increasing electron density at the tungsten center due to the α-H agostic interaction. The negative ESI-MS spectrum of **6** did not show any of the molecular ion peaks but a signal assignable to [W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)(CH$_2$-SiMe$_3$)(O)]$^-$. These results of MS came from decomposition of **6** during measurement operations. The structure of **6** shown in eq 3 was also supported by the crystal structures of the corresponding dibenzyl and dimethyl complexes (vide infra).

Table 2. Observed Rate Constants and Half-Lives at Various Temperatures for the Isomerization of 5 to Give 6

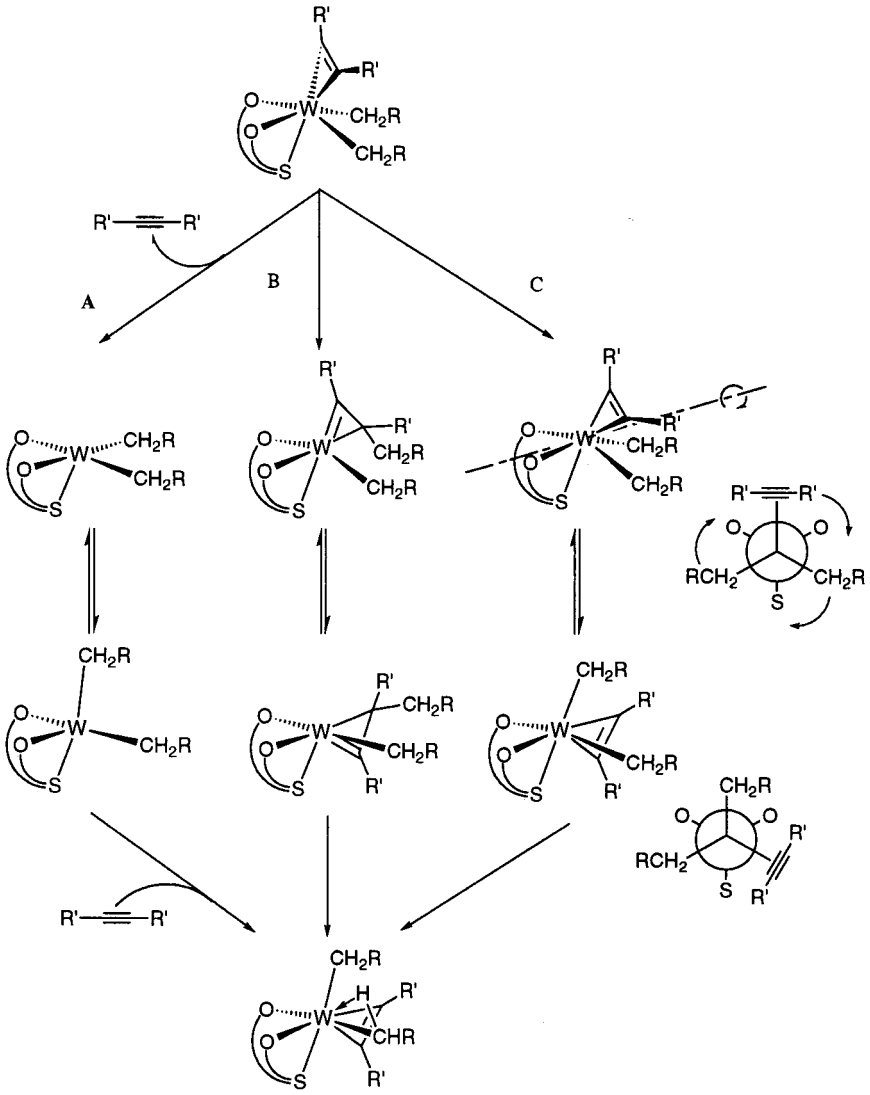
temp (°C)	$10^4 k_{obs}$ (s^{-1})	$t_{1/2}$ (m)
60	7.95	14.9
55	4.71	24.5
50	2.64	43.8
45	1.47	78.6
40	0.80	145

The rate of the transformation of **5** to **6** in C_6D_6 was measured in the temperature range 40−60 °C. The decrease of **5** followed first-order kinetic behavior (Table 2); an Arrhenius plot afforded the activation data $G^‡$(45 °C) = 23.8 ± 0.4 kcal mol^{-1} and $S^‡$(45 °C) = −3.3 ± 0.7 cal K^{-1} mol^{-1}. The small $S^‡$ value indicates that the isomerization is an intramolecular process.[25]

We speculate that this isomerization is controlled by both electronic and steric effects. If the alkyne ligand is located trans to the oxygen atom of the ^{t}Bu$_2$tbp ligand, it would compete with the oxygen ligand for π-donation to the same d orbital of the metal. Thus, the stereo-

(19) Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A. To be published.
(20) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(21) Kersting, M.; Dehnick, K.; Fenske, D. *J. Organomet. Chem.* **1988**, *346*, 201.
(22) Hey, E.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 18.
(23) Kriley, C. E.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2051.
(24) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.
(25) Lee, D.; Suh, M. P.; Lee, J. W. *J. Chem. Soc., Dalton Trans.* **1997**, 577.

Scheme 1



chemistry having the alkyne ligand cis to the aryloxo of the ^{t}Bu$_2$tbp ligand may be electronically more favorable especially for electron-deficient complexes such as the C_s dichloro complex **3a**. When the two chloro ligands of **3a** were replaced by two alkyl groups to increase electron density around the metal center, π-donation from the aryloxo decreases and the steric repulsion between the diphenylacetylene and the ^{t}Bu$_2$tbp ligands may overcome this electronic preference to result in the isomerization. In the C_1 isomer, π-donation from the aryloxo oxygen trans to diphenylacetylene disturbs the donation from diphenylacetylene to the same d orbital. This reduced donation is clearly indicated by the change of the ^{13}C chemical shifts of the acetylenic carbons. Since the steric bulk of the alkyl groups hinders the isomerization of **5** (C_s isomer), the observed direct formation of C_1 isomers in the case of the methyl and the benzyl complexes (vide infra) is rationalized.

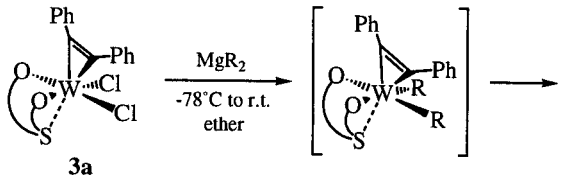
Three plausible routes for the isomerization are shown in Scheme 1. In route A, the diphenylacetylene ligand is dissociated to generate a five-coordinated square-pyramidal intermediate which changes to a trigonal-bipyramidal structure, and then the diphenylacetylene recoordinates to the metal ion. The next pathway (B) includes an alkyl migratory insertion to the diphenylacetylene ligand followed by the rotation of the acetylene moiety and β-alkyl elimination. Such an exchange process of the metal-bound and the alkyne-bound alkyl groups has been reported in Tp*NbCl(CH$_2$R)(PhC≡CR′) (Tp* = hydrotris(3,5-dimethylpyrazolyl)borate).[26] The last pathway (C) is based on the simple rotation of the two alkyl groups and one diphenylacetylene ligand around the axis through the center of those three ligands and tungsten. In the case of path A, the dissociation of diphenylacetylene is the rate-determining step and $\Delta G^{\ddagger}$ should be larger than the observed value. If path B is the case, the alkyl groups should replace the phenyl group on diphenylacetylene or should not react with diphenylacetylene ligand. Thus we speculate that the path C is the most likely.

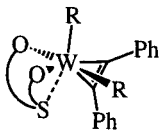
At higher temperature (60 °C), complex **5** underwent α-H elimination following the isomerization. The ^{1}H NMR spectra of **5** treated at 60 °C for 4 h showed the absence of the signals for **5** and **6,** and new signals appeared at 9.76 and 10.69 ppm, which can be assigned as the α-H protons of *syn*- or *anti*-alkylidenetungsten

(26) Etienne, M.; Mathieu, R.; Donnadieu, B. *J. Am. Chem. Soc.* **1997**, *119*, 3218.

complexes. We have not succeeded in isolating an alkylidene complex.

Preparation of Dimethyl (7) and Dibenzyl (8) Complexes. We synthesized the dimethyl and dibenzyl complexes W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)(R)$_2$ [R = CH$_3$ (**7**), CH$_2$Ph (**8**)] from the reaction of **3a** with dimethyl and dibenzylmagnesium, respectively (see eq 4). In both





(4)

7: R = Me
8: R = CH$_2$Ph

cases, the C_s complexes corresponding to **5** were not detected, and the C_1 complexes **7** and **8** were directly produced as indicated by NMR spectroscopy and X-ray analysis (vide infra). A signal for one of the four benzyl α-protons in **8** appeared at significantly high field (1.52 ppm), indicating an α-agostic interaction with the tungsten metal center as already observed in bis(trimethylsilylmethyl) complex **6**. The ^{1}H−^{1}H NOESY spectrum shows a correlation between the agostic α-proton and the *tert*-butyl groups of ^{t}Bu$_2$tbp ligand. This suggests that the agostic benzyl ligand is located trans to sulfur. In the ^{13}C NMR spectrum, a signal of the benzyl α-carbon having the agostic proton was observed at δ 96.9 ppm (dd, $^1J_{CH}$ = 140, 120 Hz), and the other benzyl α-carbon showed a resonance at δ 72.7 ppm ($^1J_{CH}$ = 125 Hz). The alkyne signals appeared at δ 208.1 and 205.8 ppm, suggesting that it can be regarded as a 2-electron donor ligand. In the case of dimethyl complex **7**, the methyl protons were observed as two singlets at 2.30 and 0.45 ppm in the ^{1}H NMR spectra, indicating a large difference in the magnetic shielding.

Crystal Structure of Dimethyl (7) and Dibenzyl (8) Complexes. The X-ray analysis of complexes **7** and **8** confirmed their C_1 symmetry as shown in Figures 2 and 3; the structural parameters **7** and **8** are included in Table 1. If the diphenylacetylene ligand occupies one coordination site around the metal, both **7** and **8** can be best described as distorted octahedrons, in which the ^{t}Bu$_2$tbp coordinates to tungsten in a facial fashion and the diphenylacetylene ligand is located trans to the oxygen atom of the ^{t}Bu$_2$tbp ligand. The distortion of the dibenzyl complex **8** (∠(C1−W−C11) = 111.3(4)°) from the octahedral geometry is larger than that of the dimethyl complex **7** (∠(C50−W−C51) = 100.2(3)°). The W−S bond distances of the dimethyl (**7**) and the dibenzyl (**8**) complexes are 2.697(2) and 2.637(2) Å, respectively, indicating weak coordination of sulfur to tungsten. The W−C(alkyl) bond distances [**7**, 2.148(7) Å; **8**, 2.15(1) Å,] trans to sulfur are shorter by ca. 0.02 Å than those [**7**, 2.160(8) Å; **8**, 2.173(8) Å,] trans to the phenoxo moiety due to the weak trans influence of the thioether. The W−O1 bond distances [**7**, 2.053(4) Å; **8**, 2.019(5) Å] are

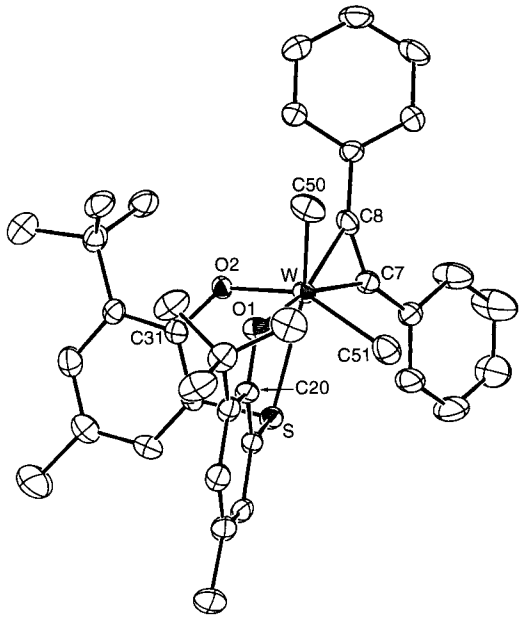


Figure 2. ORTEP drawing of W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)-Me$_2$ (**7**) with a numbering scheme.

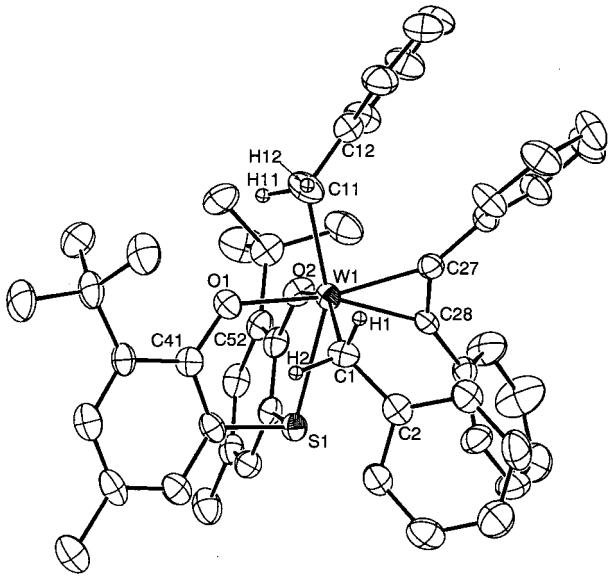


Figure 3. ORTEP drawing of W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)-(CH$_2$Ph)$_2$ (**8**) with a numbering scheme.

longer than the W−O2 ones [**7**, 1.912(4) Å; **8**, 1.941(5) Å] due to the trans influence of a π-donor diphenylacetylene ligand. Although both the solution and the solid-state ^{13}C CP/MAS NMR spectrum of **8** indicate that the α-methylene of the benzyl group trans to sulfur participates in the α-agostic interaction, we could not find any structural feature characteristic of the α-agostic interaction such as wide M−Cα−Cβ and narrow M−Cα−H angles (∠(W−Cα−Cβ) = 125.4(6)° and 126.3(9)°). In the solid state, the motion of the benzyl groups might be constrained to a geometry preferable for the α-agostic interaction.

Generation of Alkylidene Species from the Dibenzyl Complex. When a C_6D_6 solution of **8** was heated to 60 °C in an NMR tube, the generation of an alkylidene species was not observed due to contamination by paramagnetic byproducts, while bis(trimethylsilylmethyl) complex **5** was observed to generate alky-

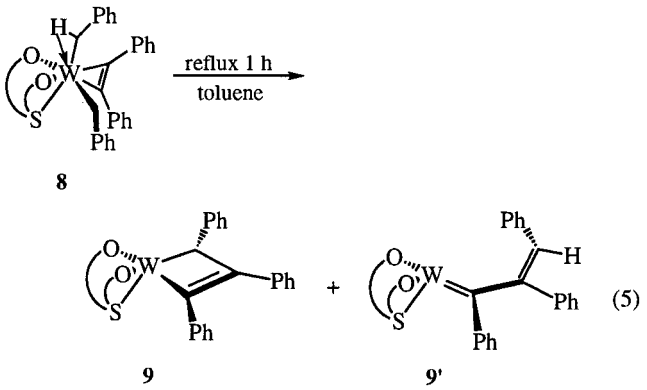
Table 3. ROMP of Norbornene by W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)R$_2$ in Benzene for 1 h[a]

run	catalyst	temp (°C)	time (h)	yield (%)	$M_n/10^5$ [b]	M_w/M_n [b]	cis content (%)[c]
1	R = CH_2SiMe_3 (**5**)[d]	30	1	1.6	>20	1.7	93
2		30	6	19	19	1.7	93
3		30	12	65	19	1.8	77
4		30	24	82	6.9	2.6	79
5		30	48	87	3.4	2.6	75
6		60	1	62	4.9	3.4	83
7		60	24	89	0.2	2.8	54
8	R = CH_2Ph (**8**)	30	1	6.4	17	1.8	83
9		60	1	22	bimodal		81
10	R = CH_3 (**7**)	30	1	<1			
11		60	1	8.4	0.8	3.0	89

[a] [Monomer]$_0$ = 1 M, [Catalyst] = 10 mM. [b] Determined by GPC analysis calibrated with standard poly(styrene)s. [c] Determined by ^{1}H NMR spectra. [d] Heated to 60 °C for 1 h before addition of monomer.

lidene species by NMR (vide supra). When complex **8** was kept at room temperature in CD_2Cl_2 for several months, new signals assignable to the α-protons of alkylidene complexes appeared at 9.83 ppm in the ^{1}H NMR spectrum and at 281 ppm in the ^{13}C NMR spectrum. This encouraged us to isolate the alkylidene complex.

When complex **8** was refluxed in toluene for 1 h followed by extraction with hexane and recrystallization from toluene−hexane (2:1), brown crystals were obtained. The elemental analysis of the product indicates that it has the same composition as the expected benzylidene complex. However, ^{1}H and ^{13}C NMR spectra of the product revealed it to be a mixture of tungstacyclobutene complex (**9**) and 1,2,3-triphenyl-2-propenylidene complex (**9′**) (eq 5), and we could not separate



(5)

these two species. In the ^{1}H NMR spectrum of the product, a signal of the α-H proton of **9** was observed at 3.08 ppm, while the γ-H proton signals of **9′** appeared at 8.57 and 9.67 ppm (syn and anti isomers). The ^{13}C NMR spectrum showed the signals of the metallacyclobutene of **9** at 102.3 (CHPh), 210.6 (α-CPh), and 160.6 (β-CPh) ppm and those of the γ-C of **9′** at 96.6 and 77.6 ppm. The signals for α- and β-carbons were not detected.

Polymerization of Norbornene Catalyzed by the Dialkyltungsten Complexes. The dialkyltungsten complexes were found to initiate the polymerization of norbornene without any cocatalysts, and the results are summarized in Table 3. The catalytic activity at 60 °C increased with increasing bulkiness of the alkyl groups (run 6, run 9, run 11). This indicates that the α-H abstraction occurs more easily with increasing steric congestion. In the polymerization at 30 °C by **5**, an interesting time dependence of the molecular weight

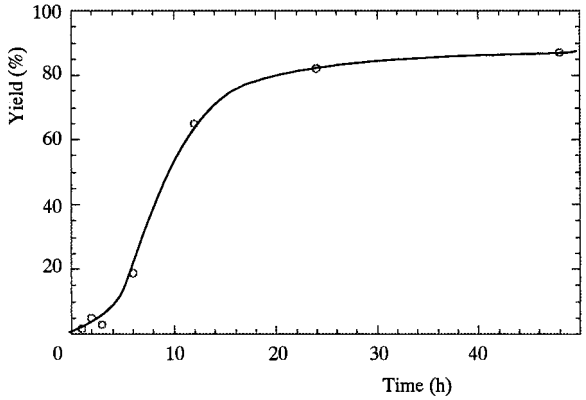


Figure 4. Time-conversion curve of the ROMP of norbornene in the presence of W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)(CH_2SiMe_3)$_2$ (**5**) as catalyst in benzene at 30 °C.

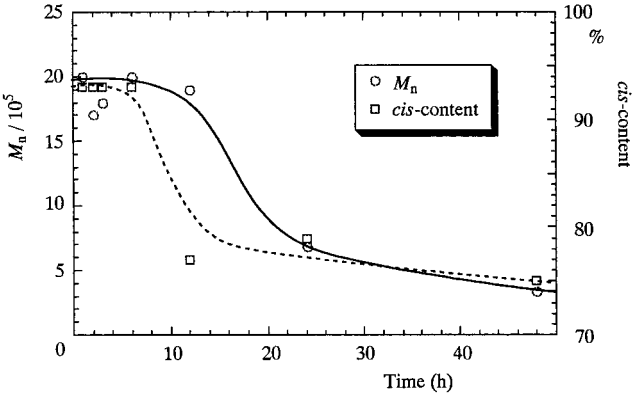


Figure 5. Time-dependence of molecular weight and cis content for the ROMP of norbornene in the presence of W(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)(CH_2SiMe_3)$_2$ (**5**) as a catalyst in benzene at 30 °C.

and of the stereoregularity (Table 3 runs 1−5, Figure 5) was found. At the initial stage of the polymerization, the produced polymer had extremely high molecular weight ($M_n > 10^6$) and high stereoregularity (cis content > 90%), although the polymer yield was low. With longer reaction time, the polymer yield became higher, but the molecular weight and stereoregularity of the polymer were reduced. Such phenomena may result from the second metathesis reaction.[27] The isomerization of the C−C double bonds in the polymer occurs prior to the decrease of the molecular weights, as shown in

(27) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964.

Table 4. ROMP of Norbornene by Using Mo(η^2-PhC≡CPh)(^{t}Bu$_2$tbp)Cl$_2$ (4)/Cocatalyst[a]

run	cocatalyst	temp (°C)	time (min)	yield (%)	$M_n/10^5$ [b]	M_w/M_n [b]	cis content (%)[c]
1	none	60	60				
2	$Mg(CH_2SiMe_3)_2$	30	15	11	8.1	3.3	67
3		30	30	17	9.4	3.6	60
4		30	60	26	19	2.3	58
5		60	60	79	> 20	2.0	54

[a] In benzene, [Monomer]$_0$ = 1 M, [Catalyst] = 10 mM. [b] Determined by GPC analysis calibrated with standard poly(styrene). [c] Determined by ^{1}H NMR spectra.

Table 5. Comparison of Group 6 Metal Complexes in the ROMP of Norbornene

catalyst system	temp (°C)	time (h)	yield (%)	$M_n/10^5$ [a]	M_w/M_n [a]	cis content (%)[b]	ref
5[c]	30	1	1.6	>20	1.7	93	this work
	30	6	19	>20	1.7	93	this work
4/$Mg(CH_2SiMe_3)_2$[c]	30	0.25	11	8.1	3.3	67	this work
	30	1	26	19	2.3	58	this work
W(CH^{t}Bu)(NAr)(O^{t}Bu)$_2$[c]	25	0.16	quant.	0.2	1.05	40	8b
W(CH^{t}Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$[d]	−20	2−3	quant.	4	1.6	>95	8b
W(=NPh)(C$_6$H$_4$-2-CH$_2$NMe$_2$)(=CHSiMe$_3$)(CH$_2$SiMe$_3$)[e]	rt	0.16	quant.	n.d.	n.d.	>90	9a

[a] Determined by GPC analysis calibrated with standard poly(styrene). [b] Determined by ^{1}H NMR spectra. [c] [Monomer]$_0$/[Cat] = 100. [d] [Monomer]$_0$/[Cat] = 288. [e] [Monomer]$_0$/[Cat] = 200.

Figures 4 and 5. The active species for cis−trans isomerization are thus different from that for the decrease of the molecular weight.

Unfortunately, we could not isolate the corresponding dialkyl complexes of molybdenum, which is expected to be more active than the corresponding tungsten catalyst. Thus, we investigated the activity of a multicomponent catalyst system, **4**/$Mg(CH_2SiMe_3)_2$, and the results are summarized in Table 4. Indeed, the **4**/$Mg(CH_2SiMe_3)_2$ system showed a higher activity than that of the tungsten systems. The molecular weight of the resulting polymer increased with increasing the polymer yield, indicating that the second metathesis reaction is suppressed in the molybdenum system compared with the corresponding tungsten systems. The molecular weight distributions of the polymers were broader than those in tungsten systems. This might be attributed to the slow initiation step. The stereospecificity of the molybdenum system was lower than that of the tungsten systems. We speculate that the lower stereospecificity of the molybdenum system can be attributed to the higher Lewis acidity of dichloro complex **4** than those of the dialkyl complexes **5**−**8**, and the higher Lewis acidity of **4** should promote isomerization.

Table 5 shows the comparison of the catalytic behavior of the catalyst systems reported here with those of the Schrock-type catalysts. Although the activity is low, **5** affords poly(norbornene) with extremely high molecular weight and high stereoregularity compared to the other catalyst systems.

Although the initiator efficiency was very low and the active species were unidentified, we speculate a mechanism for the cis-specific polymerization of norbornene as shown in Scheme 2. A key intermediate, metallacyclobutane, was assumed to be formed at the position of the two alkyl groups in the X-ray structures of **7** and **8** without significant geometrical change of the ^{t}Bu$_2$tbp and diphenylacetylene ligands. The active alkylidene species should consist of anti (**10**) and syn (**11**) isomers. The anti isomer may be more favorable than the syn isomer due to the smaller steric repulsion between the polymer chain and the diphenylacetylene ligand. At the metallacycle-forming step, norbornene monomer may coordinate to the metal ion to avoid steric hindrance, resulting in the preferable formation of metallacycle **13** to give the cis polymer.

Conclusion

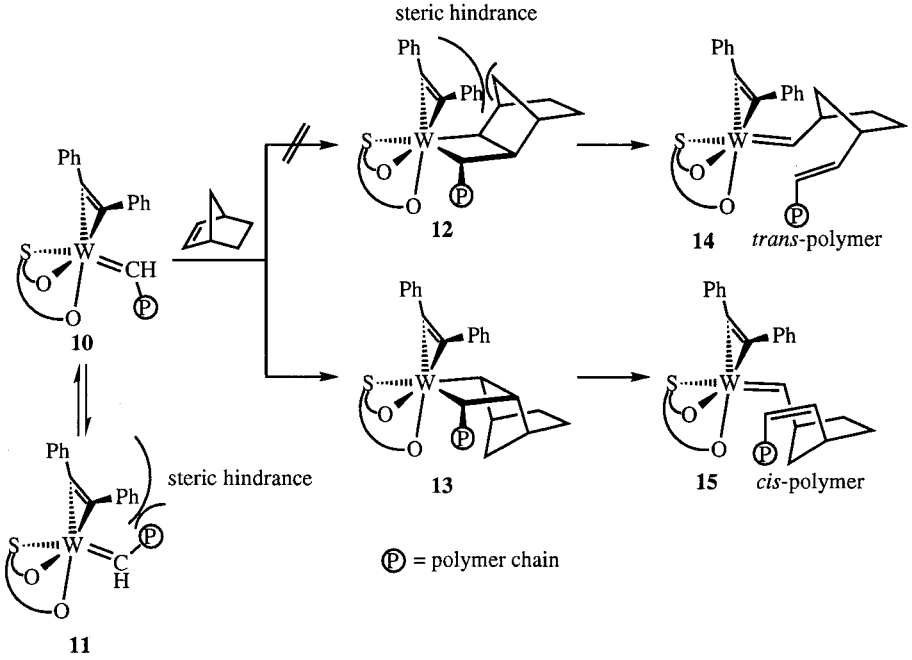
A series of new *cis*-dialkyltungsten complexes bearing a bulky tridentate diaryloxo ligand was prepared. In the case of the bis(trimethylsilylmethyl) complex, isomerization from a C_s structure to a C_1 structure proceeds at 30 °C prior to α-H elimination, while the corresponding dimethyl and dibenzyl complexes were directly obtained as C_1 complexes. At 60 °C, α-H elimination occurs to generate reactive alkylidene species which initiate the ROMP of norbornene. Under certain conditions, these complexes yield polynorbornene with extremely high molecular weight and high cis content.

Experimental Section

General Procedure. All manipulations involving air- and moisture-sensitive compounds were carried out by use of the standard Schlenk techniques under argon. Complexes, M(η^2-RC≡CR)Cl$_4$ [M = W, R = Ph (**1a**); M = W, R = Et (**1b**); M = Mo, R = Ph (**2**)][28,29] and dialkylmagnesium[30] were prepared according to the literature. *n*-Hexane, THF, toluene, benzene, and diethyl ether were purified by distillation under argon after drying over sodium benzophenone ketyl. Dichloromethane was distilled under argon after drying over phosphorus pentoxide. Dichloromethane-d_2 and chloroform-d_1 were distilled from phosphorus pentoxide. Benzene-d_6 was dried over sodium/potassium alloy and thoroughly degassed by trap-to-trap distillation prior to use. 2,2′-Thiobis(4-methyl-6-*tert*-butylphenol) was supplied by Ciba-Geigy AG. 2,2′-Thiobis(4,6-dimethylphenol)[31] was prepared according to the literature. Norbornene (bicyclo[2.2.1]hept-2-ene) purchased from Aldrich Chemical Co., Inc., was refluxed over sodium and distilled prior to use.

(28) Hey, E.; Weller, F.; Dehnicke, K. Z. *Anorg. Allg. Chem.* **1984**, *514*, 25.
(29) Theopold, K. H.; Holmes, S. J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1010.
(30) Andersen, R. A.; Wilkinson, G.; Lappert, M. F.; Pearce, R. *Inorg. Synth.* **1979**, *19*, 262.
(31) Pastor, S. D.; Denney, D. Z. *Phosphorus Sulfur* **1987**, *32*, 105.

Scheme 2



The ^{1}H (600, 500, and 400 MHz), and ^{13}C (150, 125, and 100 MHz) NMR spectra in benzene-d_6, dichloromethane-d_2, and chloroform-d_1 were measured on a Varian-Unity-600, a JEOL JNM-LA500, or a JEOL JNM-GSX400 spectrometer. Assignments for ^{1}H and ^{13}C NMR peaks for some complexes were aided by 2D ^{1}H−^{1}H NOESY, 2D ^{1}H−^{1}H COSY, and 2D ^{13}C−^{1}H COSY spectra. The solid-state NMR (CP/MAS) spectra were measured on a Chemmagnetics CMX-300 spectrometer. Elemental analysis was performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points of complexes were measured in sealed tubes under an argon atmosphere and were not corrected. ESI-MS measurements were performed on a Perkin-Elmer/Sciex API III plus spectrometer.

Preparation of W(η^2-PhC≡CPh)[S(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$]Cl$_2$(thf) (3a). A solution of 2,2′-S(4-Me-6-^{t}BuC$_6$H$_2$OH)$_2$ (0.31 g, 0.86 mmol) in toluene (5 mL) was added to a solution of W(η^2-PhC≡CPh)Cl$_4$ (**1a**) (0.43 g, 0.86 mmol) in a mixture of toluene (35 mL) and THF (2.5 mL) at −78 °C. The reaction mixture was stirred for 10 min and then allowed to warm to ambient temperature, followed by refluxing for 2 h. The color of the solution was changed from red to dark red. All volatiles were removed under reduced pressure to give microcrystals. Recrystallization from a mixture of THF and *n*-hexane gave W(η^2-PhC≡CPh)[S(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$]Cl$_2$(thf) (**3a**) (0.22 g, 33%) as red crystals, mp 128−130 °C. ^{1}H NMR (C$_6$D$_6$, 30 °C, 400 MHz): δ 8.39 (dd, 4H, *o-Ph*C), 7.33 (t, 4H, *m-Ph*C), 7.30 (s, 2H, 3-C$_6H_2$O), 7.18 (t, 2H, *p-Ph*C), 7.09 (s, 2H, 5-C$_6H_2$O), 3.62 (m, 4H, *thf*), 2.07 (s, 6H, *Me*), 1.46 (m,4H, *thf*), 1.17 (s, 18H, ^{t}*Bu*). ^{13}C NMR (C$_6$D$_6$, 30 °C, 100 MHz): 236.5 (Ph*C*), 167.1 (4-*C*$_6$H$_2$O), 142.6, 138.4 (6-*C*$_6$H$_2$O), 134.7 (*o-Ph*C), 132.5 (*p-Ph*C), 131.4 (3-*C*$_6$H$_2$O), 130.7 (5-*C*$_6$H$_2$O), 129.0 (*m-Ph*C), 122.7, 35.3 (*C*Me$_3$), 30.3 (C*Me*$_3$), 20.7 (*Me*). Anal. Calcd for C$_{40}$H$_{46}$Cl$_2$O$_3$S$_1$W$_1$: C, 55.76; H, 5.38. Found: C, 55.66; H, 5.22.

Preparation of W(η^2-EtC≡CEt)[S(4,6-Me$_2$C$_6$H$_2$O)$_2$]Cl$_2$ (3b). This complex was prepared and isolated in a manner similar to that for **3a** as black crystals in 73% yield, mp 261−264 °C. ^{1}H NMR (C$_6$D$_6$, 30 °C, 400 MHz): δ 7.09 (s, 2H, 3-C$_6H_2$O), 6.60 (s, 2H, 5-C$_6H_2$O), 4.21 (q, 4H, CH_2CH$_3$), 2.04 (s, 6H, 6-*Me*), 1.94 (s, 6H, 4-*Me*), 1.36 (t, 6H, CH$_2$CH_3). ^{13}C NMR (C$_6$D$_6$, 30 °C, 100 MHz): 244.5 (Et*C*), 166.3 (4-*C*$_6$H$_2$O), 134.4 (3-*C*$_6$H$_2$O), 133.9, 130.8 (5-*C*$_6$H$_2$O), 129.3, 121.2, 32.5 (*C*H$_2$CH$_3$), 20.4 (4-*Me*), 16.8 (6-*Me*), 14.1 (CH$_2$*C*H$_3$). Anal. Calcd for C$_{22}$H$_{26}$Cl$_2$O$_2$S$_1$W$_1$: C, 43.37; H, 4.30. Found: C, 43.52; H, 4.22.

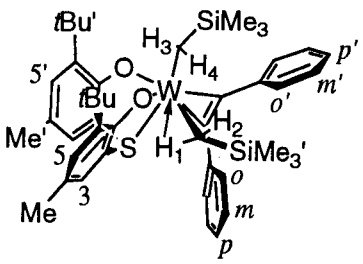
Preparation of Mo(η^2-PhC≡CPh)[S(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$]Cl$_2$(thf) (4). This complex was prepared and isolated in a manner similar to that for **3a** as black crystals in 54% yield, mp 110−112 °C. ^{1}H NMR (CD$_2$Cl$_2$, 30 °C, 400 MHz): δ 8.40 (dd, 4H, *o-Ph*C), 7.69 (t, 4H, *m-Ph*C), 7.65 (t, 2H, *p-Ph*C), 7.48 (s, 2H, 3-C$_6H_2$O), 7.17 (s, 2H, 5-C$_6H_2$O), 3.67 (br, 4H, *thf*), 2.36 (s, 6H, *Me*), 1.80 (br, 4H, *thf*), 0.97 (s, 18H, ^{t}*Bu*). ^{13}C NMR (CD$_2$Cl$_2$, 30 °C, 100 MHz): 233.1 (Ph*C*), 168.0 (4-*C*$_6$H$_2$O), 140.3, 135.4, 134.3 (6-*C*$_6$H$_2$O), 133.6 (*o-Ph*C), 133.0 (*p-Ph*C), 130.6 (3-*C*$_6$H$_2$O), 130.0 (5-*C*$_6$H$_2$O), 128.3 (*m-Ph*C), 121.1, 34.6 (*C*Me$_3$), 29.4 (C*Me*$_3$), 20.3 (*Me*). Analytically pure sample was obtained as Mo(η^2-PhC≡CPh)[S(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$]Cl$_2$·C$_7$H$_8$ upon recrystallization from toluene−hexane. Anal. Calcd for C$_{43}$H$_{46}$Cl$_2$MoO$_2$S: C, 65.07; H, 5.84. Found: C, 65.09; H, 5.72.

Preparation of W(η^2-PhC≡CPh)[S(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$](CH$_2$SiMe$_3$)$_2$(thf) (5). A solution of Mg(CH$_2$SiMe$_3$)$_2$ (0.22 mmol, 1 equiv) in diethyl ether was added to a solution of **3a** (0.17 g, 0.22 mmol) in diethyl ether (30 mL) via syringe at −78 °C. After stirring for 20 min, the reaction mixture was allowed to warm to ambient temperature and stirred for 4 h. The color of the solution changed from dark purple to red. All volatiles were removed under reduced pressure, followed by extraction with *n*-hexane (25 mL) from the resulting residue. After the extract was dried in vacuo, recrystallization from THF (2 mL) and *n*-hexane (8 mL) at −20 °C afforded W(η^2-PhC≡CPh)[S(4-Me-6-^{t} BuC$_6$H$_2$O)$_2$](CH$_2$SiMe$_3$)$_2$(thf) (**5**) as red crystals in 36% yield, mp 122 °C. ^{1}H NMR (C$_6$D$_6$, 30 °C, 400 MHz): δ 8.31 (dd, 4H, *o-Ph*C), 7.43 (t, 4H, *m-Ph*C), 7.39 (s, 2H, 3-C$_6H_2$O), 7.20 (t, 2H, *p-Ph*C), 7.01 (s, 2H, 5-C$_6H_2$O), 3.62 (m, 4H, *thf*), 2.68 (d, 2H, $^2J_{H^AH^B}$ = 12.5 Hz, $^2J_{WH}$ = 8.7 Hz, CH_A H$_B$Si), 2.03 (s, 6H, *Me*), 1.80 (d, 2H, $^2J_{H^BH^A}$ = 12.6 Hz, $^2J_{WH}$ = 8.7 Hz, CH$_A$H$_B$ Si), 1.47 (m, 4H, *thf*), 1.17 (s, 18H, ^{t}*Bu*), −0.11 (s, 18H, CH$_2$Si*Me*$_3$). ^{13}C NMR (C$_6$D$_6$, 30 °C, 100 MHz): 244.1 (Ph*C*), 167.2 (4-*C*$_6$H$_2$O), 141.6, 141.0 (6-*C*$_6$H$_2$O), 131.8 (*o-Ph*C), 131.1 (*p-Ph*C), 130.9 (3-*C*$_6$H$_2$O), 130.5 (5-*C*$_6$H$_2$O), 129.9 (*m-Ph*C), 121.6, 67.8 (*thf*), 56.7 (t, $^1J_{CH}$ = 112 Hz, *C*H$_2$Si), 35.6 (*C*Me$_3$), 30.5 (C*Me*$_3$), 25.8 (*thf*), 20.8 (*Me*), 3.9 (Si*Me*$_3$). Anal. Calcd for C$_{48}$H$_{68}$O$_3$S$_1$Si$_2$W$_1$: C, 59.73; H, 7.10. Found: C, 59.37; H, 7.08.

Table 6. Crystal Data and Data Collection Parameters of 3b, 7, and 8

	3b	7	8
formula	$C_{22}H_{26}Cl_2O_2SW$	$C_{38}H_{44}O_2SW$	$C_{50}H_{52}O_2S_1W_1$
fw	609.26	748.67	900.87
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	11.280(4)	10.587(6)	12.245(4)
b, Å	11.295(4)	16.959(6)	16.728(4)
c, Å	9.596(2)	19.427(5)	11.321(3)
α, deg	96.48(3)		100.19(2)
β, deg	100.32(4)	98.65(3)	90.41(3)
γ, deg	72.64(3)		110.60(2)
Z	2	4	2
V, Å^3	1145.7(8)	3448(2)	2130(1)
D_{calcd}, g/cm^3	1.766	1.442	1.404
$F(000)$	596	1512	916
radiation	Mo Kα	Mo Kα	Mo Kα
abs coeff, cm^{-1}	53.86	34.45	28.01
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
temp, °C	23	23	23
scan speed, deg/min	16	16	8
scan width, deg	$1.63 + 0.35 \tan\theta$	$1.73 + 0.35 \tan\theta$	$1.52 + 0.35 \tan\theta$
$2\theta_{max}$, deg	55.0	55.0	55.0
no. of unique data	5275	8184	9760
no. of unique data ($I > 3\sigma(I)$)	3903	5282	5597
no. of variables	253	379	503
R	0.037	0.039	0.043
R_w	0.039	0.042	0.043
GOF	1.56	2.12	1.37
Δ, e Å^{-3}	1.38, −1.57	1.53, −1.37	1.14, −0.92

Chart 1



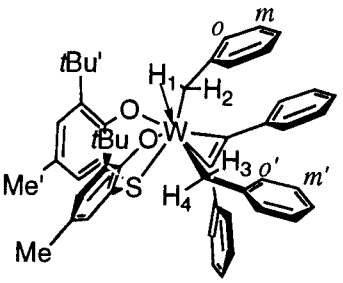
Isomerization of 5. Complex **5** was dissolved in C_6D_6 (0.6 mL) in a 5 mm NMR tube, which was sealed under argon and placed for 3 days at room temperature. The color changed from red to orange, and the ^{1}H and ^{13}C NMR spectra of the solution were measured. A numbering scheme is shown in Chart 1. ^{1}H NMR (C_6D_6, 22.5 °C, 600 MHz): δ 7.83 (dd, 2H, *o-Ph*C), 7.76 (dd, 2H, *o′-Ph*C), 7.59 (s, 1H, 3-C_6H_2O), 7.40 (t, 2H, *m-Ph*C), 7.33 (s, 1H, 3′-C_6H_2O), 7.23 (s, 1H, 5-C_6H_2O), 7.15 (t, 1H, *p-Ph*C), 7.12 (t, 2H, *m′-Ph*C), 6.81 (s, 1H, 5′-C_6H_2O), 6.94 (t, 1H, *p′-Ph*C), 3.62 (m, 4H, *thf*), 3.56 (d, 1H, $^2J_{H^3H^4} = 7.69$ Hz, C*H*^{3} H^{4}Si), 3.48 (d, 1H, $^2J_{H^4H^3} = 7.69$ Hz, C*H*^{4} H^{3}Si), 2.33 (d, 1H, $^2J_{H^2H^1} = 11.54$ Hz, C*H*^{2} H^{1}Si), 2.21 (s, 3H, *Me*), 1.95 (s, 3H, *Me′*), 1.80 (s, 9H, ^{t}*Bu*), 1.46 (m, 4H, *thf*), 1.19 (s, 9H, ^{t}*Bu′*), 0.31 (s, 9H, Si*Me*$_3$), 0.20 (d, 1H, $^2J_{H^1H^2} = 11.54$ Hz, C*H*^{1} H^{2}Si), −0.07 (s, 9H, Si*Me*$_3$′). ^{13}C NMR (C_6D_6, 22.5 °C, 150 MHz): 213.9 (Ph*C*), 210.6 (Ph*C*), 167.4 (4-*C*$_6$H$_2$O), 165.6 (4′-*C*$_6$H$_2$O), 144.1, 142.8, 141.3 (6-*C*$_6$H$_2$O), 139.2 (6′-*C*$_6$H$_2$O), 131.0 (*o-Ph*C), 130.84 (3-*C*$_6$H$_2$O), 130.76 (5-*C*$_6$H$_2$O), 130.0 (*p′-Ph*C), 129.7 (5′-*C*$_6$H$_2$O), 129.3 (*o′-Ph*C), 129.2 (3′-*C*$_6$H$_2$O), 129.0 (*m′-Ph*C), 128.9 (*m-Ph*C), 128.5 (*p-Ph*C), 122.2, 121.4, 82.3 (*C*H^{1}H^{2}Si, $^1J_{CH^1} = 116$ Hz, $^1J_{CH^2} = 107$ Hz), 79.5 (*C*H^{3}H^{4}Si, $^1J_{CH} = 113$ Hz), 67.8 (*thf*), 35.7 (*C*Me$_3$), 35.0 (*C*Me$_3$′), 30.5 (C*Me*$_3$), 29.9 (C*Me*$_3$′), 25.8 (*thf*), 20.7 (*Me*), 20.6 (*Me′*), 4.3 (Si*Me*$_3$), 2.4 (Si*Me*$_3$′). ESI-MS for ^{184}W *m/z*, 821 [(M − CH_2SiMe_3 + O)$^-$]. All attempts to isolate **6** failed because it was highly soluble even in hexane at −78 °C.

Kinetic Study for Isomerization of 5 to 6. Complex **5** (0.063 g, 0.071 mmol) was dissolved in C_6D_6 (4.00 mL) at room temperature, and the solution (0.018 M) was divided equally among five NMR tubes. Each of them was sealed under argon and kept at −20 °C until used. Reaction temperatures were maintained within ±0.1 °C by the GSX400 temperature controller, and progress of isomerization was monitored by ^{1}H NMR. The value [**5**]$_t$, which refers to the concentration of **5** at the reaction time t, was determined by the sum of intensities of areas assignable to 18 protons (Si*Me*$_3$) in **5**. Treatment of the data is described in the text.

Preparation of W(η^2-PhC≡CPh)[S(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$]-(CH$_3$)$_2$ (7). This complex was prepared and isolated in a manner similar to that for **5** as orange crystals in 46% yield, mp 122 °C (dec 150 °C). ^{1}H NMR (CD_2Cl_2, 30 °C, 500 MHz): δ 7.64 (dd, 2H, *o-Ph*C), 7.61 (dd, 2H, *o′-Ph*C), 7.60 (t, 2H, *m-Ph*C), 7.44 (t, 2H, *m′-Ph*C), 7.40 (t, 1H, *p-Ph*C), 7.39 (s, 1H, 3-C_6H_2O), 7.32 (t, 1H, *p′-Ph*C), 7.31 (s, 1H, 3′-C_6H_2O), 7.13 (s, 1H, 5-C_6H_2O), 6.91 (s, 1H, 5′-C_6H_2O), 2.30 (s, 3H, M−C*H*$_3$), 2.23 (s, 3H, *Me*), 2.07 (s, 3H, *Me′*), 1.48 (s, 9H, ^{t}*Bu*), 1.05 (s, 9H, ^{t}*Bu′*), 0.45 (s, 3H, M−C*H*$_3$). ^{1}H NMR (CD_2Cl_2, −90 °C, 500 MHz): δ 7.82 (dd, 2H, *o-Ph*C), 7.72 (dd, 2H, *o′-Ph*C), 7.61 (t, 2H, *m-Ph*C), 7.47 (t, 2H, *m′-Ph*C), 7.43 (t, 1H, *p-Ph*C), 7.37 (s, 1H, 3-C_6H_2O), 7.36 (t, 1H, *p′-Ph*C), 7.30 (s, 1H, 3′-C_6H_2O), 7.07 (s, 1H, 5-C_6H_2O), 6.84 (s, 1H, 5′-C_6H_2O), 2.23 (s, 3H, M−C*H*$_3$), 2.15 (s, 3H, *Me*), 1.86 (s, 3H, *Me′*), 1.37 (s, 9H, ^{t}*Bu*), 0.96 (s, 9H, ^{t}*Bu′*), 0.40 (s, 3H, M−C*H*$_3$). ^{13}C NMR (C_6D_6, 30 °C, 100 MHz): 208.5 (Ph*C*), 206.7 (Ph*C*), 167.5 (4-*C*$_6$H$_2$O), 165.0 (4′-*C*$_6$H$_2$O), 143.0, 142.0, 140.9 (6-*C*$_6$H$_2$O), 139.0 (6′-*C*$_6$H$_2$O), 132.2 (*o-Ph*C), 131.1 (3-*C*$_6$H$_2$O), 130.6 (5-*C*$_6$H$_2$O), 130.1 (*p′-Ph*C), 129.6 (5′-*C*$_6$H$_2$O), 129.0 (*o′-Ph*C), 128.2 (3′-*C*$_6$H$_2$O), 121.8, 120.6, 66.4 (M-*C*H$_3$), 60.7 (M-*C*H$_3$), 35.6 (*C*Me$_3$), 34.8 (*C*Me$_3$′), 29.8 (C*Me*$_3$), 29.4 (C*Me*$_3$′), 20.8 (*Me*), 20.6 (*Me′*). Anal. Calcd for $C_{38}H_{44}O_2S_1W_1$: C, 60.96; H, 5.92. Found: C, 61.10; H, 5.92.

Preparation of W(η^2-PhC≡CPh)[S(4-Me-6-^{t}BuC$_6$H$_2$O)$_2$]-(CH$_2$Ph)$_2$ (8). This complex was prepared and isolated in a manner similar to that for **5** as red crystals in 64% yield, mp 160 °C (dec). A numbering scheme of benzyl groups in **8** is shown in Chart 2. ^{1}H NMR (CD_2Cl_2, 30 °C, 500 MHz): δ 7.60 (s, 1H, 3-C_6H_2O), 7.44 (t, 2H, *m-Ph*C), 7.40 (s, 1H, 3′-C_6H_2O), 7.33 (t, 1H, *p-Ph*C), 7.30 (s, 1H, 5-C_6H_2O), 7.29−7.15 (m, 6H, *Ph*C + CH_2Ph'), 7.07 (t, 2H, *m*-CH_2Ph), 6.97 (s, 1H, 5′-C_6H_2O), 6.96−6.85 (m, 6H, *Ph*C + CH_2Ph'), 6.67 (d, 2H, *o*-CH_2Ph), 6.65 (t, 1H, *p-Ph*C), 5.00 (d, 1H, $^2J_{H^3H^4} = 11.0$ Hz, C*H*^{3} H^{4}Ph), 4.72 (d, 1H, $^2J_{H^4H^3} = 11.2$ Hz, C*H*^{4} H^{3}Ph), 4.11 (d, 1H, $^2J_{H^2H^1} = 10.1$

Chart 2



Hz, C*H*^{2} H^{1}Ph), 2.23 (s, 3H, *Me*), 1.93 (s, 3H, *Me′*), 1.83 (s, 9H, ^{t}*Bu*), 1.52 (d, 1H, $^{2}J_{H^1H^2}$ = 9.9 Hz, C*H*^{1} H^{2}Ph), 1.00 (s, 9H, ^{t}*Bu′*). ^{13}C NMR (CD_2Cl_2, 30 °C, 125 MHz): 208.1 (Ph*C*), 205.8 (Ph*C*), 165.4 (4-*C*$_6$H$_2$O), 164.3 (4′-*C*$_6$H$_2$O), 147.9−119.1 (*Ph*C + CH$_2$*Ph* + *C*$_6$H$_2$O), 96.9 (*C*H^{1}H^{2}Ph, $^{1}J_{CH^1}$ = 140, $^{1}J_{CH^2}$ = 120 Hz), 72.7 (*C*H^{3}H^{4}Ph, $^{1}J_{CH}$ = 125 Hz), 34.6 (*C*Me$_3$), 33.5 (*C*Me$_3$′), 29.4 (C*Me*$_3$), 28.1 (C*Me*$_3$′),19.7 (*Me*), 19.6 (*Me′*). CP/MAS (rotating 7.3 kHz): δ 212.3 (Ph*C*), 169.7−120.2 (*aromatics*), 103.5 (*C*H$_2$-Ph), 86.4 (*C*H$_2$Ph), 35.7 (*C*Me$_3$), 35.0 (*C*Me$_3$′), 31.6 (C*Me*$_3$), 30.6 (C*Me*$_3$′), 23.4 (*Me*), 20.1 (*Me′*) Anal. Calcd for $C_{50}H_{52}O_2S_1W_1$: C, 66.66; H, 5.82. Found: C, 66.58; H, 5.89.

α-H Elimination of 8. A solution of Mg(CH$_2$Ph)$_2$ (0.24 mmol, 1 equiv) in diethyl ether was added to a solution of W(η^{2}-PhC≡CPh)[S(4-Me-6-^{t} BuC$_6$H$_2$O)$_2$]Cl$_2$ (0.19 g, 0.24 mmol) in diethyl ether (30 mL) via syringe at −78 °C. After stirring for 20 min, the reaction mixture was allowed to warm to ambient temperature and stirred for 1 h. The color of the solution changed from dark purple to orange. All volatiles were removed under reduced pressure. The resulting residue was extracted with *n*-hexane (30 mL). The extract was evaporated to dryness and redissolved in toluene (25 mL). Heating the solution to 80 °C for 3 h followed by refluxing for 1 h resulted in a color change from red to dark brown. All volatiles were removed under reduced pressure. The resulting residue was extracted with *n*-hexane (30 mL). The solvent was removed under reduced pressure, and recrystallization from toluene (1 mL) and *n*-hexane (2 mL) cooled to −20 °C gave **9** and **9′** as brown microcrystals in 13% yield. Anal. Calcd for $C_{43}H_{44}O_2S_1W$: C, 63.86; H, 5.48. Found: C, 63.53; H, 5.64. ESI-MS for ^{184}W *m*/*z*: 841 [(M + O$_2$)$^-$].

Polymerization of Norbornene: General Procedures. To a solution of W(η^{2}-PhC≡CPh)[S(4-Me-6-^{t} BuC$_6$H$_2$O)$_2$](CH$_2$-SiMe$_3$)$_2$ (18 mg, 0.02 mmol) in benzene (1.0 mL) was added a solution of norbornene (100 equiv, 2 mmol) in benzene (2 M, 1 mL) at 30 °C. After the solution was stirred at 30 or 60 °C for a prescribed period, methanol (15 mL) was added to the resulting reddish viscous solution to precipitate a pale yellow polymer. The polymer was washed with methanol and then dried in vacuo.

GPC Analysis of the Poly(norbornene). For polymers obtained by using **6**, **7**, and **8** as catalysts, gel permeation chromatographic (GPC) analyses were carried out at 40 °C using a Shimadzu LC-10A liquid chromatograph system and a RID-10A differential refractometer, equipped with a Shodex KF-806L column. THF was used as the eluent at a flow rate of 0.8 mL/min, and sample concentrations of 0.5 mg/mL were applied. The GPC column was calibrated versus commercially available polystyrene standards (Aldrich). For polymers obtained by using other complexes as catalysts, GPC analyses were carried out using Tosoh TSKgel HXL-H and L columns connected to a Tosoh UV-8010 absorbance detector. Samples were prepared in THF (0.1−0.3% (w/v)) and were filtered through an Advantec DISMIC-25JP filter in order to remove particulates before injection. GPC columns were calibrated versus commercially available polystyrene standards (Polymer Laboratories Ltd.) whose molecular weight ranged from 500 to 2.15 × 10^{6}.

Crystallographic Data Collections and Structure Determination of 3b, 7, and 8. The crystals of **3b**, **7,** and **8** suitable for X-ray diffraction studies were sealed in glass capillaries under argon and then mounted on a Rigaku AFC-5R four-circle diffractometer for data collection using Mo Kα radiation. Relevant crystal and data statistics are summarized in Table 6. The unit cell parameters at 23 °C were determined by a least-squares fit to 2θ values of 25 strong higher reflections for all complexes. Three standard reflections were chosen and monitored every 150 reflections. Empirical absorption correction was carried out on the basis of an azimuthal scan. Every sample showed no significant intensity decay during the data collection. The structures of all complexes were solved by direct methods (SHELXS 86)[32] and refined by the full-matrix least-squares method. Measured nonequivalent reflections with $I > 3.0\sigma(I)$ were used for the structure determination. In the subsequent refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$, where $w^{-1} = \sigma^2(F_o) = [\sigma_c^2(F_o) + p^2/4(F_o^2)]$. The positions of all non-hydrogen atoms for complexes **3b**, **7**, and **8** were found from a difference Fourier electron density map and refined anisotropically. Hydrogen atoms for each complex were placed as follows: for **8** hydrogen atoms on the α-methylene carbons of the benzyl ligands were found from a difference Fourier syntheses and were refined isotropically, and the other hydrogen atoms were placed in calculated positions (d(C−H) = 0.95 Å) and constrained to ride on their respective carbon atoms. For **3b** and **7** all hydrogen atoms were placed in calculated positions (d(C−H) = 0.95 Å) and kept fixed. All calculations were performed using the TEXSAN crystallographic software package, and illustrations were drawn with ORTEP.

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Supporting Information Available: Tables of final positional parameters, final thermal parameters, and bond distances and angles for **3b**, **7**, and **8** together with their drawings with all numbering schemes of nonhydrogen atoms, and NMR spectra of **5** and **6.** This material is available free of charge via the Internet at http://pubs.acs.org.

OM9808965

(32) Sheldrick, G. M. *SHELXS86*: Program for the Solution of Crystal Structures; Universität Göttingen: Germany, 1986.