Synthesis of μ-Oxo Complexes of Group 4 Bridged-Metallocenes: A Convenient Separation of *meso* and *racemo* Isomers

Mina Koyama, Keisuke Kimura, Masato Nakano,† and Hiroshi Yamazaki*
Department of Applied Chemistry, Faculty of Science and Industry, Chuo University, Kasuga, Bunkyo-ku, Tokyo 112-8551
†*Chisso Petrochemical Corporation, Polymer Research Center, Ichihara-shi, Chiba 290-0058*

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Treatment of a 1:1 mixture of *meso* and *racemo* isomers of the group 4 bridged-metallocene dichlorides, $R_2A(R'_nC_5H_{4-n})_2MCl_2$ (R_2 = Me_2, $(CH_2)_4$; A = Si, Ge; R'= Me, *t*-Bu; M = Zr, Hf; n = 1-3) with 0.5 equivalent of amine afforded an μ-oxo complex arising from the *meso* isomer and left the *racemo* isomer intact, providing a convenient method of separation of the isomeric mixture.

Since the discovery of *isotactic* polymerization of propylene using the chiral ethylenebis(indenyl)zirconium dichloride / methylaluminoxane (MAO) system, much effort has been devoted to the synthesis of more active and more isospecific chiral group 4 metallocene catalysts in view of academic interest and industrial importance.[1] Now, it is well established that dimethylsilylene-bridged C_2-symmetric chiral bis(cyclopenadienyl) and bis(indenyl) zirconium complexes bearing methyl substituents next to the silylene bridge give fairly satisfactory results.[2] A problem in the synthesis of these complexes is concurrent formation of an achiral *meso* isomer which must be excluded during catalytic use. For example, the reaction of the dimethylsilylenebis(2,3,5-trimethylcyclopentadienyl) ligand with zirconium tetrachloride affords an 1:1 mixture of *racemo* and *meso* isomers. The procedure to remove the *meso* isomer from the mixture is tedious and usually the pure *racemo* isomer is isolated in low yield. Attempts to avoid or minimize the formation of the unnecessary *meso* isomer by introducing bulky substituents on the bridged Cp ligands and on the bridge moiety are partly successful in the synthesis of mono- and di-substituted bridged-metallocenes[3] but not for the tri-substituted ones. We wish to report here a novel method of separation of a mixture of *racemo* and *meso* isomers based on the different reactivity arising from the difference in the steric surroundings between them in which the substituents on the 3-position of the Cp rings are placed on different sides and the same side of the molecule, respectively.

It is well known that the treatment of the simple titanocene, zirconocene, and hafnocene dihalides with amines in the presence of water provides the corresponding μ-oxo complex (Eq.1).[4]

$$2(C_5H_5)_2MX_2 + 2R_2NH + H_2O \longrightarrow \mu\text{-}O\{(C_5H_5)_2MX\}_2 + 2R_2NH_2X \quad (1)$$

However, as far as we know, there is no report describing the formation of the μ-oxo complex from bridged-metallocenes. Preliminary examination of the reaction of the *meso* and *racemo* isomers of bridged-metallocenes with diethylamine suggested that only the *meso* isomers provided the corresponding μ-oxo complexes. We attempted to apply this reaction to the separation of the mixture of *meso* and *racemo* isomers of silylene and germylene bridged-zirconocene and hafnocene dichlorides [$Me_2Si(2,3,5\text{-}Me_3C_5H)_2ZrCl_2$ (**1**), $Me_2Ge(2,3,5\text{-}Me_3C_5H)_2ZrCl_2$ (**2**), $Me_2Ge(2,3,5\text{-}Me_3C_5H)_2HfCl_2$ (**3**), $(CH_2)_4Si(2,3,5\text{-}Me_3C_5H)_2ZrCl_2$ (**4**), $Me_2Ge(2,4\text{-}Me_2C_5H_2)_2ZrCl_2$ (**5**), $Me_2Si(3\text{-}t\text{-}BuC_5H_3)_2ZrCl_2$ (**6**)].

The solution of **1** (*meso* / *rac* = 1:1, 0.21 g) in moist toluene was treated with a 1/2 equivalent of diethylamine at -10 °C and then stored at room temperature for several hours. Disappearance of the *meso* isomer and appearance of a new complex were confirmed by the ^{1}H NMR spectrum. After concentration of the solution to almost dryness, the residue was resolved in a small amount of toluene and filtered to remove the resulting amine salt. The addition of hexane afforded colorless crystals of μ-$O\{Me_2Si(2,3,5\text{-}Me_3C_5H)_2ZrCl\}_2$ (**7**) (0.07 g, 70%). The ^{1}H NMR and elemental analyses suggested the formation of this complex. Treatment of **7** with an etheral solution of hydrogen chloride recovered the *meso* isomer of **1** quantitatively. Evacuation of the mother liquid and recrystallization of the residue from hexane gave almost pure *racemo* isomer in a reasonable yield(0.08 g, 76%). A wide variety of primary, secondary, and tertiary amines could be used for this procedure. Employment of an excess amount of amine resulted in decomposition of the *racemo* isomer and no sign of the formation of the μ-oxo complex from the *racemo* isomer was observed. The present method is widely applicable. However, it should be noted that this method is efficient only if the isomers under consideration have similar solubilities. Bridged trisubstituted metallocenes **2**, **3** and **4** were well suited for this method and the separation into their *meso* and *racemo* isomers was effected by the formation of the μ-oxo complexes, μ-$O\{Me_2Ge(2,3,5\text{-}Me_3C_5H)_2ZrCl\}_2$ (**8**), μ-$O\{Me_2Ge(2,3,5\text{-}Me_3C_5H)_2HfCl\}_2$ (**9**) and μ-$O\{(C_4H_8)Si\text{-}(2,3,5\text{-}Me_3C_5H)_2ZrCl\}_2$ (**10**), respectively. The μ-oxo complexes, μ-$O\{Me_2Ge(2,4\text{-}Me_2C_5H_2)_2ZrCl\}_2$ (**11**), and μ-$O\{Me_2Si(3\text{-}t\text{-}BuC_5H_3)_2ZrCl\}_2$ (**12**) were also obtained from the reaction of **5** and **6** with an amine. A similar μ-oxo complex bearing the Zr-Me moiety, μ-$O\{Me_2Si(2,3,5\text{-}Me_3C_5H)_2ZrMe\}_2$ (**13**) was prepared by prolonged stirring of $Me_2Si(2,3,5\text{-}Me_3C_5H)_2ZrMe_2$ in toluene. They were characterized by ^{1}H NMR[5] and elemental analyses.

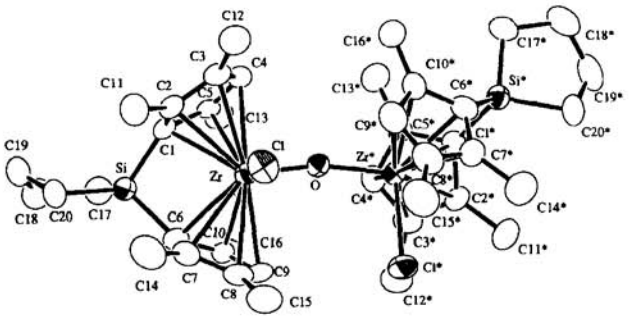

Figure 1. Molecular structure of complex **10**, showing atom-labeling scheme.

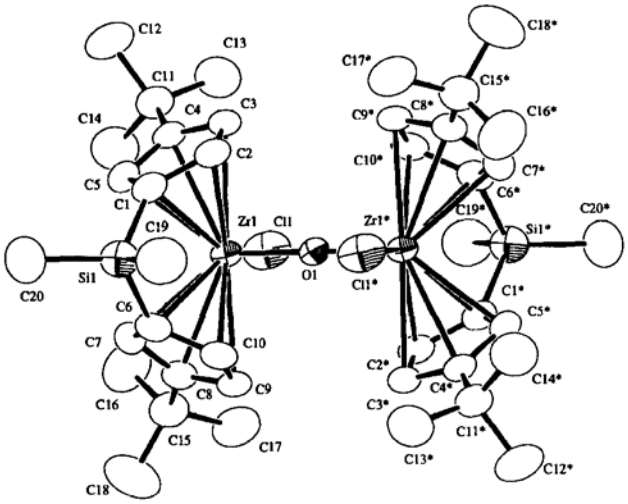

Figure 2. Molecular structure of complex **12**, showing atom-labeling scheme.

Table 1. Selected bond lengths (Å) and angles (°) of μ-O{$(C_5H_5)_2ZrCl$}$_2$, **10**, and **12**

	μ-O{$(C_5H_5)_2ZrCl$}$_2$	**10**	**12**
bond lengths (Å)			
Zr-O	1.94(1)	1.959(1)	1.9453(3)
	1.95(1)		1.9415(3)[b]
Zr-Cl	2.444(8)	2.451(2)	2.4368(8)
	2.459(8)		2.4360(8)[b]
Cp(cent)[a]-Zr	2.19	2.26	2.26
	2.20	2.26	2.26
	2.20		2.26[b]
	2.23		2.26[b]
bond angles (°)			
∠Zr-O-Zr	168.9(8)	159.6(3)	180.0
			180.0[b]
∠O-Zr-Cl	99.3(4)	99.4(1)	95.19(3)
	96.8(5)		93.40(2)[b]
∠Cp(cent)-Zr-Cp'(cent)	124.7	125.5	124.0
	132.0		123.3[b]

[a] Centroids of the Cp rings. [b] Another molecule in a unit cell.

Crystals of **10** and **12** suitable for X-ray structure determinations were obtained; the molecular structures are shown in Figures 1 and 2.[6] In **12**, there are two crystallographically independent molecules and only one of the two molecules is depicted in Figure 2. Selected bond lengths and angles for **10** and **12** are listed in Table 1, together with those of the known μ-O{$(C_5H_5)_2ZrCl$}$_2$.[4d] It is clearly shown that the Cl atom located between substituents on 3 and 3' positions is unreactive and remained intact.

References and Notes

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5 ^{1}H NMR ($CDCl_3$). **7**: δ 6.20 (s, 4 H, CpH), 2.42 (s, 12 H, CH_3), 2.20 (s, 12 H, CH_3), 1.99 (s, 12 H, CH_3), 1.10 (s, 6 H, CH_3), 0.97 (s, 6 H, CH_3). **8**: δ 6.17 (s, 4 H, CpH), 2.40 (s, 12 H, CH_3), 2.23 (s, 12 H, CH_3), 1.99 (s, 12 H, CH_3), 1.10 (s, 6 H, CH_3), 0.96 (s, 6 H, CH_3). **9**: δ 6.13 (s, 4 H, CpH), 2.48 (s, 12 H, CH_3), 2.20 (s, 12 H, CH_3), 1.83 (s, 12 H, CH_3), 1.10 (s, 6 H, CH_3), 0.97 (s, 6 H, CH_3). **10**: δ 6.21 (s, 4 H, CpH), 2.39 (s, 12 H, CH_3), 2.20 (s, 12 H, CH_3), 1.83 (s, 12 H, CH_3), 1.79-1.87 (m, 8H, CH_2), 1.59 (t, 4 H, CH_2), 1.43 (t, 4 H, CH_2). **11**: δ 6.23 (m, 4 H, CpH), 4.92 (m, 4 H, CpH), 2.34 (s, 12 H, CH_3), 2.29 (s, 12 H, CH_3), 1.09 (s, 6 H, CH_3), 0.63 (s, 6 H, CH_3). **12**: δ 6.31-6.32 (m, 4 H, CpH), 5.96-5.98 (m, 4 H, CpH), 5.47-5.49 (m, 4 H, CpH), 1.31 (s, 36 H, *t*-Bu), 0.73 (s, 6 H, CH_3), 0.72 (s, 6 H, CH_3).

6 Crystallographic data. **10**: $C_{40}H_{56}Cl_2Si_2Zr_2O$, Fw = 862.40; orthorhombic, space group *Pbcn* (# 60); a = 17.835(2) Å, b = 15.205(2) Å, c = 14.576(2) Å; V = 3592(1) Å^3; Z = 4; D_{calc} = 1.449 g·cm^{-3}; R = 0.038, Rw = 0.032 for 1634 reflection with $I > 3\sigma(I)$. **12**: $C_{40}H_{60}Cl_2Si_2Zr_2O$, Fw = 866.43; triclinic, space group $P\bar{1}$ (# 2); a = 14.882(2) Å, b = 15.620(2) Å, c = 10.142(2) Å, α = 100.78(1)°, β = 109.80(1)°, γ = 83.01(1)°; V = 2174.7(5) Å^3; Z = 2; D_{calc} = 1.323 g·cm^{-3}; R = 0.029, Rw = 0.023 for 7661 reflection with $I > 3\sigma(I)$.