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Journal of Organometallic Chemistry 566 (1998) 111–116

Journal of Organometallic Chemistry

Polymerization of ethylene catalyzed by half-metallocene complexes of niobium, tantalum, and zirconium bearing *o*-xylylene or anthracene as an auxiliary ligand: molecular structure of $[Mg_2Cl_3(THF)_6][ZrCl_2(\eta^5\text{-}C_5Me_5)$ $(\eta\text{-}1\text{–}4\text{-anthracene})]$

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Received 25 February 1998; received in revised form 12 May 1998

Abstract

Polymerization of ethylene catalyzed by half-metallocene complexes of niobium and tantalum $MR_2(\eta^5\text{-}C_5Me_5)(L)$ (**1**: M = Ta, R = Cl, L = *o*-xylylene; **2**: M = Nb, R = Cl, L = *o*-xylylene; **3**: M = Ta, R = Cl, L = η-1–4-anthracene; **4**: M = Ta, R = CH_2Ph, L = η-1–4-anthracene) as well as by a new anthracene–zirconium complex $[Mg_2Cl_3(THF)_6][ZrCl_2(\eta^5\text{-}C_5Me_5)(\eta\text{-}1\text{–}4\text{-anthracene})]$ (**5**), whose structure was revealed by X-ray analysis, was studied and the results were compared with the reported results using 1,3-butadiene complexes of niobium and tantalum. The catalytic activity of niobium and tantalum complexes was found to be in the order of *o*-xylylene > butadiene ≫ anthracene, whereas the anthracene complex of zirconium **5** showed much lower activity and broad polydispersity.

Keywords: Tantalum; Zirconium; *o*-Xylylene; Anthracene; Polymerization; Ethylene

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1. Introduction

We have already reported that the conjugated diene complexes of niobium and tantalum are excellent catalyst precursors in the presence of an excess of MAO for the living polymerization of ethylene to give monodisperse polyethylene [1–3], and that the 1,3-butadiene complexes of tantalum catalyze the ring-opening metathesis polymerization (ROMP) of norbornene to give polynorbornene with high *cis*-content if a bulky $\eta^5\text{-}C_5Me_5$ (= Cp*) ligand was bound to the tantalum center [4]. Isoelectronic zirconium complexes bearing conjugated diene, $Zr(R)Cp^*(\eta^4\text{-}2,3\text{-dimethyl-}1,3\text{-butadiene})$ [5], aminoboratabenzene, $ZrCl_2Cp^*[C_5H_5BN(^iPr)_2]$ [6], and tribenzylidenemethane, $[ZrCp^*(\eta^4\text{-tribenzylidenemethane})Cl_2]^-$ [7], have proven to be unique catalysts for homologation and polymerization of alkenes. Recently we prepared *o*-xylylene and anthracene complexes of half-metallocene complexes of Group 5 metals as the alternative to η^4-1,3-butadiene complexes of Group 5 metals [8]. The spectral and structural data of the *o*-xylylene and anthracene complexes indicated that the electronic structures of η^4-*o*-xylylene and η^4-anthracene ligands are considerably deviated from the η^4-1,3-butadiene ligand. Actually when compared with the butadiene complexes, the *o*-xylylene complex has larger contribution of the $2\sigma\text{-}1\pi$; canonical form, whereas, in contrast, the anthracene complex have an increased contribution

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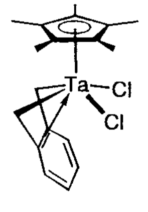
PII S0022-328X(98)00707-4

of 2π-η^4-diene canonical form. We accordingly anticipated that the contrary feature of *o*-xylylene and anthracene ligands could have a unique opportunity to control the catalytic behavior of Group 5 metal complexes. Herein we report systematic investigation on the catalytic behavior of the *o*-xylylene and anthracene complexes of niobium and tantalum together with an anionic anthracene complex of zirconium, which was prepared and crystallographically characterized, for the polymerization of ethylene.

2. Results and discussion

2.1. Preparation and characterization of an anionic anthracene–zirconium complex $[Mg_2Cl_3(THF)_6][Cp^*Zr(\eta^4\text{-}C_{14}H_{10})Cl_2]$ (5)

Our own research group and Teuben's group independently synthesized neutral Group 4 diene complexes of the general formula $MXCp^*(\eta^4\text{-diene})$ (M = Ti, Zr, Hf; X = Cl, alkyl) (Cp* = η^5-pentamethylcyclopentadienyl) by reduction of Cp^*MCl_3 with Na/Hg in the presence of 2,3-dimethylbutadiene [9] and by reaction of Cp^*MCl_3 with magnesium–diene adducts [10]. It is a new aspect of the diene complexes of Group 4 metals that neutral alkyl complexes catalyze the polymerization of ethylene [5] as well as 2-vinylpyridine [11]; it is also of interest that a neutral aminoboratabenzene complex, $ZrCl_2Cp^*[C_5H_5BN(^iPr)_2]$ [6] and an anionic tribenzylidenemethane complex, $[ZrCp^*(\eta^4\text{-tribenzylidenemethane})Cl_2]^-$ [7], catalyzed the polymerization of α-olefins. Thus we synthesized the corresponding anthracene complex of zirconium as an extension of 1,3-diene complexes of Group 4 metals [12–15]. The reaction of Cp^*ZrCl_3 with an equimolar amount of $Mg(anthracene)(THF)_3$ [16–22], gave an anionic η^4-anthracene complex of zirconium, $[Mg_2Cl_3(THF)_6]$ $[ZrCl_2Cp^*(\eta\text{-}1\text{-}4\text{-}C_{14}H_{10})]$ (**5**), as black crystals in 43% yield (Eq. 1). Complex **5** was highly air- and moisture-sensitive. The formulation of **5** was confirmed by NMR spectroscopy and elemental analysis along with the X-ray crystallographic study (vide infra). In the ^{1}H-NMR spectrum of **5** in THF-d_8, the 1,4-proton signals of the anthracene ligand were observed at δ 2.83, while a singlet signal due to 9,10-protons appeared at the normal aromatic region (δ 6.33) indicating that the anthracene ligand coordinates to the zirconium metal at C1–C4. The extents of sp^n hybridization of 1,4-carbons (δ 74.5, J_{C-H} = 148 Hz) and 2,3-carbons (δ 121.6, J_{C-H} = 165 Hz) of the anthracene ligand were calculated by using Newton's empirical law [23] to be n = 2.41 and 2.11, respectively, which were smaller than the corresponding neutral 1,3-butadiene complex, $ZrClCp^*(\eta^4\text{-}C_4H_6)$ (2.55 and 2.13) [9].



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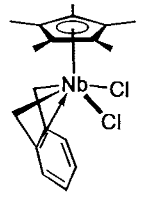

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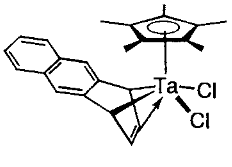

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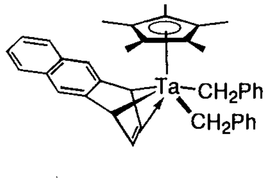

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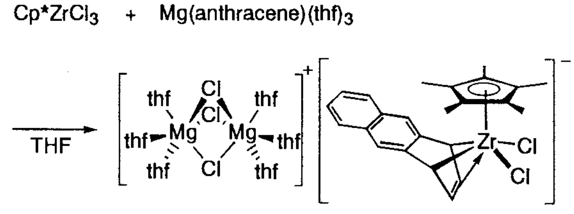


5

(1)

The molecular structure of an anionic part of **5** is shown in Fig. 1 and selected bond distances and angles are summarized in Table 1. In the anionic part of **5**, the zirconium center is best described as four legged piano-stool geometry where the Cp* is a capping ligand, the legs are two chloro ligands and the anthracene ligand occupying two sites as observed in a neutral tantalum complex **4** [8]. The anthracene ligand of **5** is bent away from the zirconium at C(1) and C(4); the dihedral angle between the planes defined by C(1)–C(2)–C(3)–C(4) and C(1)–C(4)–C(11)–C(12) is 135.7°, which is almost the same as that of **4** (133.9°), and hence the C(l)–Zr–C(4) and C(1)–C(2)–C(3)–C(4) planes in **5** make an acute dihedral angle of 86.5°. The C(1)–C(2) (1.45(1) Å), C(2)–C(3) (1.37(1) Å), and C(3)–C(4) (1.43(1) Å) distances of anthracene in **5** show a clear long-short-

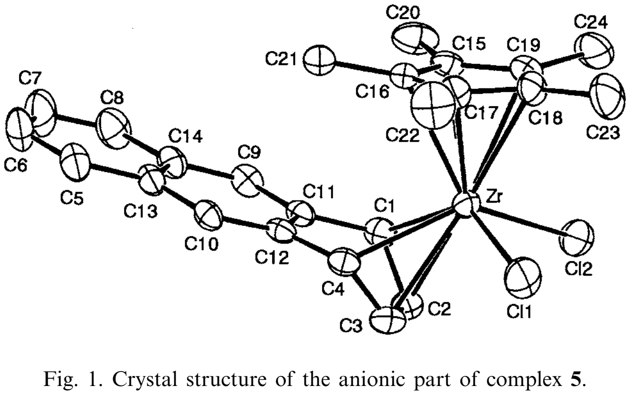


Fig. 1. Crystal structure of the anionic part of complex **5**.

Table 1
Selected bond distances (Å) and angles (°) of **5**

Bond distances (Å)			
Zr–Cl(1)	2.509(2)	Zr–Cl(2)	2.501(2)
Zr–C(1)	2.437(7)	Zr–C(2)	2.461(8)
Zr–C(3)	2.451(8)	Zr–C(4)	2.426(7)
Zr–C(15)	2.508(6)	Zr–C(16)	2.520(7)
Zr–C(17)	2.524(8)	Zr–C(18)	2.544(7)
Zr–C(19)	2.545(7)	C(1)–C(2)	1.45(1)
C(2)–C(3)	1.37(1)	C(3)–C(4)	1.43(1)
C(1)–C(11)	1.467(9)	C(4)–C(12)	1.462(9)
C(5)–C(6)	1.37(1)	C(5)–C(13)	1.399(9)
C(6)–C(7)	1.39(1)	C(7)–C(8)	1.34(1)
C(8)–C(14)	1.42(1)	C(9)–C(11)	1.361(9)
C(9)–C(14)	1.402(9)	C(10)–C(12)	1.362(8)
C(10)–C(13)	1.420(9)	C(11)–C(12)	1.423(8)
C(13)–C(14)	1.423(9)		
Bond angles (°)			
C(1)–Zr–C(2)	34.4(2)	C(1)–Zr–C(3)	58.3(3)
C(1)–Zr–C(4)	65.0(2)	C(2)–Zr–C(3)	32.4(2)
C(2)–Zr–C(4)	58.1(3)	C(3)–Zr–C(4)	34.1(2)
Zr–C(1)–C(2)	73.7(5)	Zr–C(2)–C(l)	71.9(4)
Zr–C(1)–C(1l)	110.6(5)	Zr–C(4)–C(3)	73.9(4)
Zr–C(3)–C(4)	72.0(4)	Zr–C(4)–C(12)	110.8(4)
C(1)–C(2)–C(3)	115.1(7)	C(2)–C(3)–C(4)	115.9(7)
C(2)–C(1)C(11)	114.9(6)	C(3)–C(4)–C(12)	114.1(7)
Cl(1)–Zr–Cl(2)	93.38(9)		

long bond alternation, indicating the contribution of 2σ-1π canonical form. The geometry of Zr defined by the Cp* ligand and the two chloro moieties is unexceptional. The cationic part of **5** has already been reported for $[Mg_2Cl_3(THF)_6][TiCl_3(tetraphenylcyclobutadiene)]$ [24].

2.2. Polymerization of ethylene catalyzed by the o-xylylene and anthracene complexes of niobium and tantalum and the anthracene complex of zirconium

We have already reported the living polymerization of ethylene using butadiene complexes of niobium and tantalum $MCl_2Cp^*(\eta^4\text{-}1,3\text{-butadiene})$ (**6**: M = Ta; **7**: M = Nb) [3]. *o*-Xylylene and anthracene are the other types of 4-electron ligand and thus we anticipated that *o*-xylylene and anthracene complexes of these Group 5 metals may have catalytic activity. The polymerization of ethylene using the *o*-xylylene and the anthracene complexes was carried out under the same conditions as that of the butadiene complexes [3] and the results are summarized in Table 2.

The tantalum *o*-xylylene complex **1** in the presence of 500 equivalents of MAO catalyzed the polymerization of ethylene, giving polyethylene (12.7 kg atm^{-1} h^{-1} [M] mol^{-1}) with narrow polydispersity (M_W/M_n = 1.47). The catalyst activity of **1** was twice as high and the molecular weight distribution of the polyethylene was much narrower compared to the data of the corresponding 1,3-butadiene complex **6** (activity: 5.9 kg atm^{-1} h^{-1} [M] mol^{-1} and $M_w/M_n = 2.04$). In sharp contrast, the anthracene complexes **3** and **4** did not show any catalytic activity, even though the anthracene complexes are isoelectronic to the 1,3-butadiene and *o*-xylylene complexes. Here the mode of combination of Cp* and an auxiliary ligand delicately affected the catalytic activity; in the order of *o*-xylylene > 1,3-butadiene ≫ anthracene. The **2**/MAO system was found to be more active than the niobium butadiene system, **7**/MAO, yielding polyethylene with a relatively narrow molecular weight distribution ($M_w/M_n = 1.64$). The activity of the niobium *o*-xylylene complex **2** was higher than the tantalum complex **1**, as found in the case of the butadiene complexes; **7** was much active than **6** [3].

It is interesting to compare structural features of the tantalum complexes: Table 3 shows the dihedral angle between cyclopentadienyl and C(1)–C(2)–C(3)–C(4) planes (θ^1) and that between M–C(1)–C(4) and C(1)–C(2)–C(3)–C(4) planes (θ^2). Both the θ^1 and θ^2 apparently increase in the order of *o*-xylylene > 1,3-butadiene > anthracene, and thus the *o*-xylylene complex is likely to have the most open space available for the approach of ethylene. Non activity of the anthracene complexes **3** and **4** for the polymerization may be due to the thermal instability under the polymerization condition. Thus, these findings may be attributed to delicate combination of the steric and electronic effects of the ligands on the tantalum center.

The anionic anthracene zirconium complex **5** in the presence of MAO showed low activity (4.9 kg atm^{-1} h^{-1} [M] mol^{-1}) for ethylene polymerization to give polyethylene with an extremely broad molecular weight distribution ($M_w/M_n = 15$), which corresponds to the reported fact that a neutral diene zirconium complex $Zr(R)Cp^*(\eta^4\text{-}2,3\text{-dimethyl-}1,3\text{-butadiene})$ catalyzed the homologation of α-olefin with ethylene, resulting in the high polydispersity [5] and an anionic complex $[ZrCp^*(\eta^4\text{-tribenzylidenemethane})Cl_2]^-$ catalyzed the ethylene polymerization to give a polymer with broad polydispersity [7]. Thus, we found that anthracene is inferior as an auxiliary ligand for the polymerization of ethylene.

3. Conclusion

We have revealed that the *o*-xylylene and anthracene ligands can vary the catalytic behavior of the mono(cyclopentadienyl)mono(butadiene)-type complexes of Group **4** and **5** metals. For ethylene polymerization, the activity of the Group **5** metal complexes follows the order of xylylene > butadiene ≫ anthracene. An anionic anthracene zirconium complex, $[Mg_2Cl_3(THF)_6][(\eta^5\text{-}C_5Me_5)Zr(\eta\text{-}1\text{–}4\text{-anthracene})Cl_2]$, was prepared and structurally characterized which showed low activity to give polyethylene with a broad molecular

Table 2
Polymerization of ethylene (1 atm) catalyzed by *o*-xylylene and anthracene complexes of niobium and tantalum and an anthracene complex of zirconium in comparison with the reported results using 1,3-butadiene complexes of niobium and tantalum

Run	complex	Time (h)	Activity (kg atm^{-1} h^{-1} [M] mol^{-1})	M$_n$/10^4	M$_w$/M$_n$	Reference
1	Cp*Ta(xy)Cl$_2$ (**1**)	3	12.7	2.1	1.47	This work
2	Cp*Ta(anth)Cl$_2$ (**3**)	6	No polymer	—	—	This work
3	Cp*Ta(anth)(CH$_2$Ph)$_2$ (**4**)	6	No polymer	—	—	This work
4	Cp*Ta(bd)Cl$_2$ (**6**)	6	5.9	2.0	2.04	[3]
5	Cp*Nb(xy)Cl$_2$ (**2**)	1	43.7	3.1	1.65	This work
6	Cp*Nb(bd)Cl$_2$ (**7**)	1	38.7	8.3	1.30	[3]
7	[Cp*Zr(anth)Cl$_2$]$^-$ (**5**)	6	4.9	1.5	15	This work

Abbreviation: Cp*, pentamethylcyclopentadienyl; anth, anthracene; xy, *o*-xylylene; bd, 1,3-butadiene.
In toluene, at 20°C, [M] = 1.44 mM, [Al]/[M] = 500.

weight distribution. Thus, the catalytic performance of the mono-Cp complexes can be effectively tuned by the selection of these diene type ligands [25].

4. Experimental section

4.1. General procedures

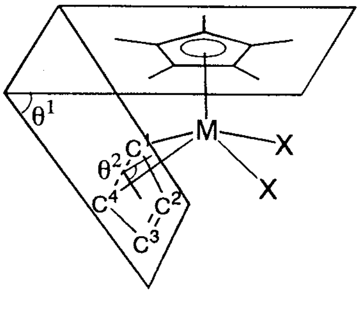
All manipulations involving air- and moisture-sensitive organometallic compounds were carried out using standard Schlenk techniques under argon. Complex Cp*ZrCl$_3$ [26], Mg(anthracene)(THF)$_3$ [16–22], complexes **1** [8], **2** [27], **3** [8], and **4** [8] were prepared according to the literature. Hexane, THF, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. THF-d$_8$ was distilled from Na/K alloy and thoroughly degassed by trap-to-trap distillation before use.

The ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra in THF-d$_8$ were measured on a JEOL JNM-GSX400 spectrometer. When THF-d$_8$ was used as the solvent, the spectra were referenced to the residual solvent protons at δ 3.6 in the ^{1}H-NMR spectra and to the solvent carbons at δ 67.4 (pentad for THF-d$_8$) in the ^{13}C-NMR spectra. Gel permeation chromatography (GPC) analysis was recorded by the use of Waters 150C equipped with a column AD80M/S (× 3) eluted with *o*-dichlorobenzene at 135°C. GPC columns were calibrated against commercially available polystyrene standards (Polymer Laboratories) which ranged in molecular weight from 500 to 1.11×10^6 M$_w$. Elemental analyses were performed at Elemental Analysis Center, Faculty of Science, Osaka University. All melting points of the complexes were measured in sealed tubes under argon and were not corrected.

Table 3
Comparison of the structural data of η^4-anthracene and η^4-diene complexes

Complexe	θ^1(°)^a	θ^2(°)^b	Reference
1	80.7	104.3	[27]
2	79.7	101.9	[27]
4	57.2	85.9	[8]
5	58.7	86.5	This work
CpTa(C$_4$H$_6$)Cl$_2$ (**8**)	71.9	94.9	[29]
Cp*Ta(C$_4$H$_6$)(CH$_2$Ph)$_2$ (**9**)	68.9	93.3	[4]

^{a} θ^1 denotes the dihedral angle between the cyclopentadienyl plane and the C(1)–C(2)–C(3)–C(4) plane.
^{b} θ^2 denotes the dibedral angle between the M–C(1)–C(4) and the C(1)–C(2)–C(3)–C(4) planes.



4.1.1. Preparation *[Mg$_2$Cl$_3$(THF)$_6$][ZrCl$_2$Cp*(η-1-4-anthracene] (5)*

A suspension of Mg(anthracene)(THF)$_3$ (0.60 mmol) in THF (2.50 ml) was added to a solution of ZrCl$_3$Cp* (198 mg, 0.59 mmol) in a mixture of THF (10 ml) and hexane (5 ml) via a syringe at − 78°C. The reaction mixture was slowly warmed to room temperature (r.t.) and then stirred overnight to give a black suspension. After removal of precipitates by centrifugation, hexane (10 ml) was layered over the solution. Standing it at r.t. for 5 days gave black prisms of **5** in 43% yield, m.p. > 300°C. ^{1}H-NMR (400 MHz, THF-d$_8$, 30°C): δ 7.16 (m, 2H, 5,8-H of anthracene), 6.80 (m, 2H, 6,7-H of anthracene), 6.33 (s, 2H, 9,10-H of anthracene), 6.20 (m, 2H, 2,3-H of anthracene), 2.83 (m, 2H, 1,4-H of anthracene), 1.78 (s, 15H, C$_5$Me$_5$): ^{13}C-NMR (100 MHz, THF-d$_8$, 30°C) δ 149.3 (s 11,12- or 13,14-C of anthracene), 133.6 (s 11,12- or 13,14-C of anthracene), 126.7 (d, $^1J_{C-H} = 160$ Hz, anthracene), 125.6 (d, $^1J_{C-H} = 156$ Hz, anthracene), 121.6 (d, $^1J_{C-H} = 165$ Hz, 2,3-H of anthracene), 120.8 (s, C_5Me$_5$), 113.6 (d, $^1J_{C-H} = 153$ Hz, anthracene), 74.5 (d, $^1J_{C-H} = 148$ Hz, 1,4-H of anthracene), 11.7 (q, $^1J_{C-H} = 126$ Hz, C_5Me_5). Anal. Calc. for $C_{44}H_{65}Cl_5Mg_2O_5Zr$: C, 53.32; H, 6.61. Found: C, 53.00; H, 6.73.

4.1.2. Polymerization of ethylene

To a suspension of **5** (12.2 mg, 1.14×10^{-5} mol) in toluene (10 ml) was added MAO (500 equivalents) via a syringe at −78°C. After the catalyst mixture was stirred at r.t. for 10 min, ethylene (atmospheric pressure) was introduced. After 6 h at r.t., the polymerization was quenched by addition of HCl–MeOH, and the activity was found to be 4.9 kg h^{-1} (mol of Zr)$^{-1}$. GPC analysis of this sample showed that the molecular weight (M_n) and the molecular weight distribution (M_w/M_n) was 1.5×10^4 and 15, respectively.

*4.1.3. Crystallographic data collections and structure determination of **5***

The crystals of **5** suitable for X-ray diffraction sealed in glass capillaries under argon atmosphere, were mounted on a Rigaku AFC-7R four-circle diffractometer for data collection using Mo–K_α radiation. Three standard reflections were chosen and monitored every 150 reflections. Over the course of data collection, the standards decreased by 6.3%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient, μ, for Mo–K_α radiation is 5.2 cm^{-1}. Empirical absorption correction based on azimuthal scans of several reflections was applied, resulting in transmission factors ranging from 0.88 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods (SHELXS86) [28] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were not refined but were given the same temperature factor as that of the carbon atoms to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 4074 observed reflections ($I > 3.00\sigma(I)$) and 559 variable parameters and converged (largest parameter shift was 0.00 times its S.D.) with unweighted and weighted agreement factors of: $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.047$, $R_W = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{\frac{1}{2}} = 0.047$. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. The pertinent detail of data collection and the final cell dimensions for **5** are given in Table 4.

Table 4
Crystal data and data collection parameters of **5**

Formula	$C_{48}H_{73}Cl_5Mg_2O_6Zr$
Formula weight	1063.20
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	12.424(4)
b (Å)	18.294(5)
c (Å)	12.414(6)
α (°)	94.33(3)
β (°)	93.05(4)
γ (°)	73.14(3)
V (Å^3)	2691(1)
Z	2
$D_{calc.}$ (g cm^{-3})	1.312
Radiation	Mo–K_α
Crystal size (mm)	$0.4 \times 0.3 \times 0.1$
Absorption coefficient (cm^{-1})	5.18
Scan mode	ω–2θ
Temperature (°C)	23
Scan speed (deg min^{-1})	16
Scan width (°)	$1.42 + 0.35\tan\theta$
2θmax (°)	55
Unique data [$I > 3\sigma(I)$]	4074
Number of variables	559
R	0.047
R_w	0.047
Goodness-of-fit F^2	1.65
Δ (e Å^{-3})	0.32 and −0.29

Acknowledgements

K. Mashima acknowledges the support by the Grant-in-Aid for Scientific Research on Priority Area (No. 09238103) from the Ministry of Education, Science, Sports and Culture, Japan and by the Asahi Glass Foundation. A. Nakamura is grateful for the financial support of the Ministry of Education, Science, Sports and Culture of Japan (Specially Promoted Research No. 06101004).

References

[1] K. Mashima, S. Fujikawa, A. Nakamura, J. Am. Chem. Soc. 115 (1993) 10990.
[2] K. Mashima, S. Fujikawa, H. Urata, E. Tanaka, A. Nakamura, J. Chem. Soc Chem. Commun. (1994) 1623.
[3] K. Mashima, S. Fujikawa, Y. Tanaka, et al., Organometallics 14 (1995) 2633.
[4] K. Mashima, Y. Tanaka, M. Kaidzu, A. Nakamura, Organometallics 15 (1996) 2431.
[5] B. Hessen, H.V.D. Heijden, J. Am. Chem. Soc. 118 (1996) 11670.
[6] G.H. Spies, R.J. Angelici, Organometallics 6 (1987) 1897.
[7] S. Luo, T.B. Rauchfuss, S.R. Wilson, J. Am. Chem. Soc. 114 (1992) 8515.
[8] K. Mashima, Y. Nakayama, M. Kaidzu, N. Ikushima, A. Nakamura, J. Organomet. Chem. (1997) in press.
[9] J. Blenkers, B. Hessen, F. van Bolhuis, A.J. Wagner, J.H. Teuben, Organometallics 6 (1987) 459.

[10] H. Yamamoto, H. Yasuda, K. Tatsumi, et al., Organometallics 8 (1989) 105.

[11] M.E.E. Meijer-Veldman, Y.Y. Tan, H.J. de Liefde Meijer, Polym. Commun. 26 (1985) 200.

[12] H. Yasuda, K. Tatsumi, A. Nakamura, Acc. Chem. Res. 18 (1985) 120.

[13] H. Yasuda, A. Nakamura, Angew. Chem. Int. Ed. Engl. 26 (1987) 723.

[14] G. Erker, C. Krüger, G. Müller, Adv. Organomet. Chem. 24 (1985) 1.

[15] J. Scholz, K.-H. Thiele, J. Organomet. Chem. 314 (1986) 7.

[16] B. Bogdanovic, N. Janke, H. Kinzelmann, U. Westeppe, Chem. Ber. 121 (1988) 33.

[17] B. Bogdanovic, S. Liao, M. Schwickardi, P. Sikorsky, B. Spliethoff, Angew. Chem. Int. Ed. Engl. 19 (1980) 818.

[18] B. Bogdanovic, S. Liao, R. Mynott, K. Schlichte, U. Westeppe, Chem. Ber. 117 (1984) 1378.

[19] B. Bogdanovic, Angew. Chem. Int. Ed. Engl. 24 (1985) 262.

[20] B. Bogdanovic, N. Janke, C. Krüger, R. Mynott, K. Schlichte, U. Westeppe, Angew. Chem. Int. Ed. Engl. 24 (1985) 960.

[21] T. Alonso, S. Harvey, P.C. Junk, C.L. Raston, B.W. Skelton, A.H. White, Organometallics 6 (1987) 2110.

[22] W.M. Brooks, C.L. Raston, R.E. Sue, F.J. Lincoln, J.J. McGinnity, Organometallics 10 (1991) 2098.

[23] M.D. Newton, J.M. Schulman, M.M. Manus, J. Am. Chem. Soc. 96 (1974) 17.

[24] M.E.E. Meijer-Veldman, J.L. de Boer, H.J. de Liefde Meijer, A.M.M. Schreurs, J. Kroon, A.L. Spec, J. Organomet. Chem. 269 (1984) 255.

[25] The activity of the tantalum-bis(benzyl) complexes $Ta(CH_2Ph)_2Cp^*(L)$ for ring-opening metathesis polymerization of norbornene was in the order of $L = $ anthracene $> L =$ butadiene $> L = o$-xylylene. The combination of a Cp* ligand and an auxiliary ligand, i.e. anthracene or butadiene, affords highly *cis*-polynorbornenes, while an *o*-xylylene complex yielded *trans*-polymers.

[26] J.H. Wengrovius, R.R. Schrock, J. Organomet. Chem. 205 (1981) 319.

[27] K. Mashima, M. Kaidzu, Y. Tanaka et al., (1998) submitted for publication.

[28] G.M. Sheldrick, SHELXS86, Program for the Solution of Crystal Structures, Universität Göttingen, 1986.

[29] H. Yasuda, K. Tatsumi, T. Okamoto, et al., J. Am. Chem. Soc. 107 (1985) 2410.