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Chromium complexes coordinated with chelating disiloxane-1,3-diamido ligands as catalyst precursors for ethylene polymerization

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Abstract

Reaction of $\mathrm{CrCl_2}$ with 0.5 equivalents of $\mathrm{Li_4[(N^tBuSiMe_2)_2O]_2}$ (**1**) gave a new chromium(II) complex, $\mathrm{Cr_2[(N^tBuSiMe_2)_2O]_2}$ (**2**). Similar reaction of $\mathrm{CrCl_3}$ with **1** yielded the corresponding chromium(III) complex, $\mathrm{Cr_2[(N^tBuSiMe_2)_2O]_3}$ (**3**). The dinuclear structure of **3** was revealed by X-ray crystallography, in which the disiloxanediamido ligand can be regarded as an *N*,*N*-bidentate ligand. The complexes **2** and **3** showed relatively high catalytic activities for ethylene polymerization upon activation with diethylaluminum chloride.

Keywords: Chromium; Disiloxane-1,3-diamido; Diethylaluminum chloride; Ethylene polymerization

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1. Introduction

The Phillips catalysts, inorganic chromium catalysts supported on silica, are commercially used for ethylene polymerization [1–3]. In spite of their commercial importance, the active species have not been fully established due to its heterogeneity. Recently soluble organochromium complexes have been found, which catalyze the ethylene polymerization efficiently [4–11]. In particular, chromium complexes having *ansa*-Cp-amino type ligands have been found to show the highest activity among the homogeneous chromium catalysts [11]. Cp-free chromium complex catalysts have also been attracting much interest [12–17]. Recently, *N*,*N*-, *N*,*N*,*N*-, and *N*,*O*-chelating ligands were reported to be good for chromium catalysts [18–22]. This encouraged us to study the chromium complexes having disiloxane-1,3-diamido ligands, which have been found to act as *N*,*O*,*N*-tridentate ligands in Group 4 metal complexes [23]. In this paper, we report the syntheses, structures, and ethylene polymerization activities of new divalent and trivalent chromium complexes with chelating disiloxanediamido ligands.

2. Results and discussion

1,3-Bis(*t*-butylamino)disiloxane was synthesized according to the literature [23]. Lithiation of the diaminodisiloxane gave the corresponding lithium salt, $\mathrm{Li_4[(N^tBuSiMe_2)_2O]_2}$ (**1**), quantitatively (Eq. (1)). The structure of **1** was revealed by X-ray crystallography to have dimeric structure in which each nitrogen atom of the ligand was doubly bridged by lithium (Fig. 1). The selected bond distances and angles are listed in Table 1.

The reaction of $\mathrm{CrCl_2}$ with 0.5 equivalents of **1** afforded a divalent chromium complex, $\mathrm{Cr_2[(N^tBuSiMe_2)_2O]_2}$ (**2**), as a green powder in 18% yield (Eq. (2)). Mass spectrum of **2** indicated that it has dimeric structure. Taking into account that chromium amide complexes tend to have three- or four-coordinated structure [24,25], we are assuming the structure of **2** as shown in Eq. (2). We also tried to synthesize monochlorochromium(III) complex, $\mathrm{CrCl[(N^tBuSiMe_2)_2O]}$, from the 2:1 reaction of $\mathrm{CrCl_3}$ with **1** in $\mathrm{Et_2O}$. However, we could not isolate the monochloro complex, and obtained a

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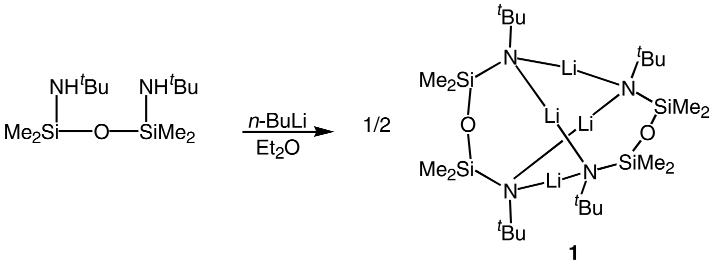
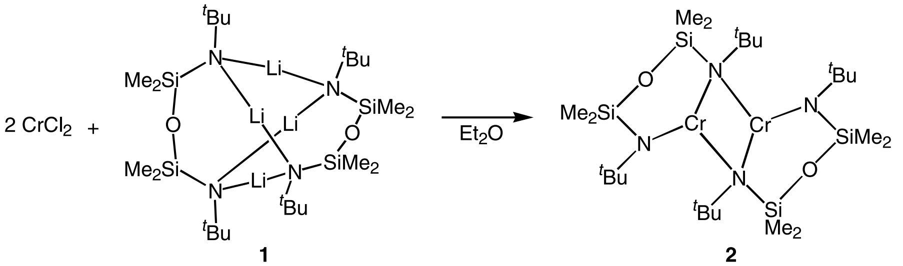
Cl-free complex, $Cr_2[(N^tBuSiMe_2)_2O]_3$ (**3**), as blue–green crystals in 26% yield (Eq. (3)). This may come from poor solubility of $CrCl_3$ in Et_2O. The reaction of THF–soluble $CrCl_3(THF)_3$ with **1** in THF gave a complicated mixture.

The molecular structure of **3** determined by X-ray crystallography is shown in Fig. 2. The selected bond distances and angles are listed in Table 2. Complex **3** has dinuclear structure in which one disiloxanediamido ligand is bridging two $Cr[(N^tBuSiMe_2)_2O]$ moieties. The O2 atom in the bridging ligand is located on the crystallographic center of symmetry. The sum of the angles around the chromium center (358.6°) indicates that the chromium has trigonal planar structure. The Cr–N distances of **3** (av. 1.884 Å) are similar to those of $Cr[N(C_6H_3Me_2\text{-}3,5)(adamantyl)]_3$ (av. 1.868 Å) [24], and slightly shorter than those of Cr(2,2,6,6,-tetramethylpiperidinyl)$_3$ (av. 1.916 Å) [24], and of $(\eta^5\text{-}Me_4C_5SiMe_2\text{-}\eta^1\text{-}N^tBu)Cr(CH_2SiMe_3)$ (1.920(4) Å) [9]. The sums of the angles around N1, N2, and N3 in **3** are 359.9, 359.9, and 360.0°, respectively, indicating sp^2 hybridization of nitrogen atoms and π donation from nitrogen to chromium. The Cr(1)–O(1) distance (2.685(3) Å) is far longer than the typical Cr^{III}–O coordination bonds (e.g. 2.143 Å in $(Ph)_2$nacnac-$CrCl_2(THF)_2$ [18]). Thus, in sharp contrast to the zirconium analogues [23], the disiloxanediamido ligand can be better described as an *N*,*N*-bidentate ligand than as an *N*,*O*,*N*-tridentate ligand in the chromium complex **3**.



(1)



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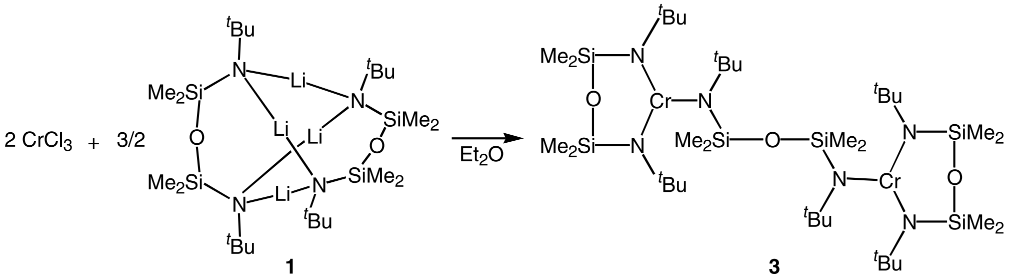

(3)

This should come from the lower Lewis acidity of chromium than that of zirconium.

2.1. Polymerization of ethylene

The catalytic activity of these complexes for ethylene polymerization was studied in toluene at room temperature.

The complex **2** itself showed no activity for ethylene polymerization without cocatalyst. Addition of modified methylaluminoxane (MMAO) or diethylaluminum chloride (DEAC) was found to be quite effective in the activation of **2**, while a system composed of **2** and triisobutylaluminum (TIBAL) did not polymerize ethylene under the same condition (Table 3). The catalytic activities of the **2**–DEAC system exhibit strong dependence on an [Al]/[Cr] ratio, and the highest activity (3.4×10^3 g mol^{-1} h^{-1} atm) was observed at an [Al]/[Cr] ratio of 100 (Table 4).

Similarly, complex **3** showed no activity without a cocatalyst, and could be activated by the addition of cocatalysts including TIBAL as well as MMAO and DEAC. Among these three cocatalysts, DEAC was also most effective for the activation of **3** (Table 5). The **3**–DEAC system was most active at [Al]/[Cr] = 25 and at room temperature to show activity of 2.3×10^4 g mol^{-1} h^{-1} atm (Tables 6 and 7), although it is yet two

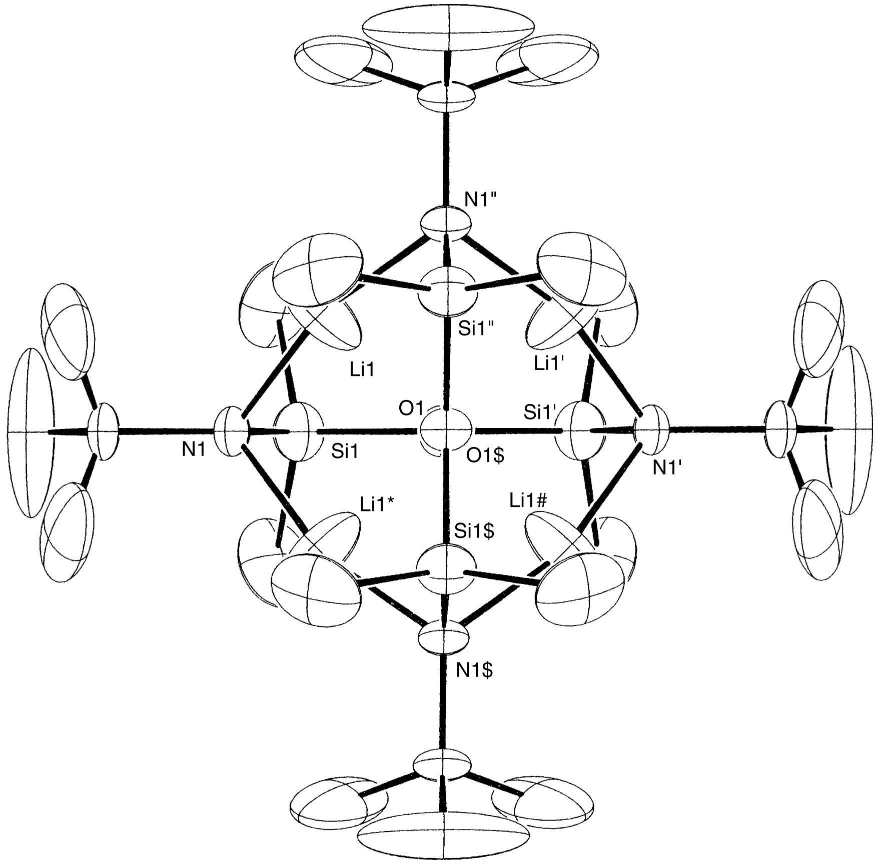

Fig. 1. Molecular structure of $Li_4[(N^tBuSiMe_2)_2O]_2$ (**1**).

orders of magnitude lower than those of the most active *ansa*-Cp-amino type complexes [11]. The trivalent complex **3** was found to be more active than the corresponding divalent complex **2**, suggesting that the active species in these systems might be tri- or higher valent species. In all cases, melting points typical for the linear polyethylene were observed.

The resulting polyethylenes obtained with complexes **2** and **3** based catalysts have very broad molecular weight distribution indicating that several kinds of active species were generated in these systems. We speculate that the some of the Cr–N bonds of **2** and **3** must be cleaved on the activation with aluminum reagents to generate a variety of active species such as neutral or cationic alkylchromium species having one or two Cr–N bonds. This may be responsible for the broad molecular weight distribution of the resulting polyethylene in these systems. The molecular weights of the resulting polymers obtained with complex **3** tend to decrease with increasing amounts of DEAC (Table 6). We are assuming that the active species having two Cr–N bonds produce high molecular weight polyethylene and that the low molecular weight polymers were produced by the species with one Cr–N bond.

For comparison, we also investigated the ethylene polymerization activity of a tris(amido)chromium complex, $Cr[N(SiMe_3)_2]_3$ (**4**) [26], under the similar condition. The complex **4**–DEAC system showed the activity of 2.8×10^3 g mol^{-1} h^{-1} atm, about ten times lower than that of **3**. This indicates that the disiloxane-bridged structure of the chelating ligand in **3** is essential for high activity, although Cr–O interaction is very weak (vide supra). Thus, the chelating disiloxane-1,3-diamido ligand was demonstrated to be effective for homogeneous chromium-based polymerization catalyst.

3. Conclusion

We prepared new types of divalent and trivalent chromium complexes having disiloxane-1,3-diamido

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

Bond distances			
Si(1)–O(1)	1.670(3)	Si(1)–N(1)	1.653(6)
N(1)–Li(1)	1.935(5)	N(1)–Li(1)*	1.935(5)
Bond angles			
O(1)–Si(1)–N(1)	99.3(3)	Si(1)–O(1)–Si(1)′	142.7(4)
N(1)–Li(1)–N(1)″	163(1)	Li(1)–N(1)–Li(1)*	90(1)
Si(1)–N(1)–Li(1)	101.2(3)	Si(1)–N(1)–Li(1)*	101.2(3)

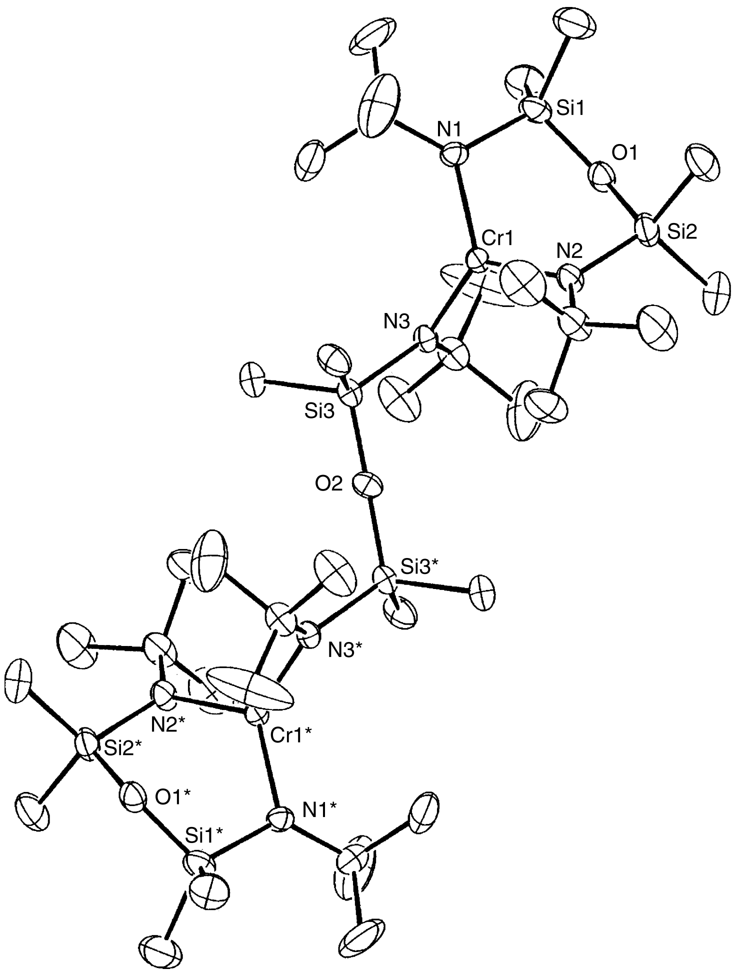

Fig. 2. Molecular structure of $Cr_2[(N^tBuSiMe_2)_2O]_3$ (**3**).

ligands, $Cr_2[(N^tBuSiMe_2)_2O]_2$ (**2**) and $Cr_2[(N^tBuSiMe_2)_2O]_3$ (**3**). The dinuclear structure of **3** was revealed by X-ray crystallography, in which the disiloxanediamido ligand is acting as an *N*,*N*-bidentate ligand. The complex **3** system showed moderate activity for ethylene polymerization, thus, the chelating disiloxane-1,3-diamido ligand was demonstrated to be effective for homogeneous chromium-based polymerization catalyst.

4. Experimental

4.1. General considerations

Because of air and moisture sensitivity of organochromium compounds, all the manipulations were carried out under a dry argon atmosphere, using standard Schlenk techniques. Solvents such as tetrahydrofuran, *n*-hexane, and diethylether were distilled from Na–K alloy–benzophenone under argon. Toluene was purified by distillation from sodium–benzophenone under argon. All solvents were stored over sodium. ^{1}H-NMR spectra were measured on a JEOL JNM-LA400 (400 MHz) spectrometer, and chemical shifts were calibrated by using residual signals of chloroform (δ 7.24 ppm) in chloroform-*d*, and Me_2SO (δ 2.49 ppm) in Me_2SO-d_6. The characterizations of

Table 2
Selected bond distances (Å) and angles (°) of **3**

Bond distances			
Cr(1)–N(1)	1.879(3)	Cr(1)–N(2)	1.890(3)
Cr(1)–N(3)	1.883(3)	Si(1)–O(1)	1.635(3)
Si(1)–N(1)	1.731(4)	Si(2)–O(1)	1.656(3)
Si(2)–N(2)	1.725(4)	Si(3)–O(2)	1.637(1)
Si(3)–N(3)	1.734(3)		
Bond angles			
N(1)–Cr(1)–N(2)	114.5(2)	N(1)–Cr(1)–N(3)	121.4(1)
N(2)–Cr(1)–N(3)	122.7(2)	Cr(1)–N(1)–Si(1)	108.6(2)
Cr(1)–N(1)–C(1)	126.9(3)	Si(1)–N(1)–C(1)	124.4(3)
Cr(1)–N(2)–Si(2)	108.4(2)	Cr(1)–N(2)–C(9)	125.6(3)
Si(2)–N(2)–C(9)	125.9(3)	Cr(1)–N(3)–Si(3)	121.5(2)
Cr(1)–N(3)–C(13)	117.9(3)	Si(3)–N(3)–C(13)	120.6(3)
O(1)–Si(1)–N(1)	102.4(2)	O(1)–Si(2)–N(2)	102.4(2)
O(2)–Si(3)–N(3)	112.9(1)	Si(1)–O(1)–Si(2)	137.8(2)
Si(3)–O(2)–Si(3)*	180.00		

Table 3
Polymerization of ethylene catalyzed by **2** [a]

Cocatalyst	Activity (g mol^{-1} h^{-1} atm)	M_w [b]	M_w/M_n [b]	T_m (°C)
None	0	–	–	–
MMAO	1.5×10^2	3.6×10^5	63	n.d.
TIBAL	0	–	–	–
DEAC	3.4×10^3	4.1×10^5	193	126.6

[a] In toluene (30 ml), at r.t., 0.1 MPa ethylene, [Al]/[Cr] = 100.
[b] Determined by GPC.

Table 4
Polymerization of ethylene catalyzed by **2**–DEAC [a]

[Al]/[Cr]	Activity (g mol^{-1} h^{-1} atm)	M_w [b]	M_w/M_n [b]	T_m (°C)
0	0	–	–	–
10	9.3×10^2	3.6×10^5	117	125.3
20	1.9×10^3	4.4×10^5	122	n.d.
50	3.3×10^3	5.8×10^5	124	128.0
100	3.4×10^3	4.1×10^5	193	126.6
200	2.0×10^3	n.d.	n.d.	n.d.
500	9.2×10^2	3.1×10^5	106	127.5
1000	5.7×10^1	0.6×10^4	3.1	n.d.

[a] In toluene (30 ml), at r.t., 0.1 MPa ethylene.
[b] Determined by GPC.

Table 5
Polymerization of ethylene catalyzed by **3** [a]

Cocatalyst	Activity (g mol^{-1} h^{-1} atm)	M_w [b]	M_w/M_n [b]	T_m (°C)
None	0	–	–	–
MMAO	1.8×10^3	6.6×10^5	140	131.1
TIBAL	2.9×10^2	2.5×10^5	35	n.d.
DEAC	1.2×10^4	7.0×10^5	92	128.1

[a] In toluene (30 ml), at r.t., 0.1 MPa ethylene, [Al]/[Cr] = 100.
[b] Determined by GPC.

Table 6
Polymerization of ethylene catalyzed by **3**–DEAC [a]

[Al]/[Cr]	Activity (g mol^{-1} h^{-1} atm)	M_w [b]	M_w/M_n [b]	T_m (°C)
0	0	–	–	–
10	1.6×10^4	1.2×10^6	79	132.6
25	2.3×10^4	9.6×10^5	60	131.6
50	1.4×10^4	1.1×10^6	98	131.7
100	1.2×10^4	7.0×10^5	92	128.1
200	1.2×10^4	8.8×10^5	129	128.7
500	1.3×10^4	2.1×10^5	121	126.3

[a] In toluene (30 ml), at r.t., 0.1 MPa ethylene.
[b] Determined by GPC.

chromium complexes were carried out with elemental analyses on a Perkin–Elmer 2400 series ll CHN–O analyzer after sealing the sample in the tin foil under argon and with mass spectra (JEOL JMS-SX102A Mass spectrometer). For X-ray analysis, all the diffraction data measurements were made on a Rigaku AFC-7R diffractometer with graphite-monochromatized Mo–K_α radiation. As the complexes are all very air-sensitive, crystals were sealed in thin-walled glass capillary tubes under argon atmosphere. The X-ray data were collected at 23 °C using $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0°. The data were corrected for conventional absorption, Lorentz and polarization effect. The crystal structures were solved by the direct method and were expanded by the successive Fouier syntheses. The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares methods, while the hydrogen atoms were fixed at their standard geometries and were not refined. All the calculations were performed by the use of TEXSAN crystallographic software package. The gel-permeation chromatography (GPC) measurements for polyethylene were carried out using a Waters 150C model equipped with Shodex-HT806M. The GPC curve was calibrated with standard polystyrene. 1,2,4-Trichlorobenzene was used as the eluent at 140 °C.

4.2. Preparation of 1,1,3,3-tetramethyl-1,3-di-tert-butylamino-disiloxane

1,1,3,3-Tetramethyl-1,3-dichlorodisiloxane (Tokyo Kasei Co. Ltd.) (20 g, 98.4 mmol) in *n*-hexane (150 ml) was added to the solution of *tert*-butylamine (Kanto Chemical) (42 ml, 400 mmol) in *n*-hexane (300 ml) via syringe at 0 °C. When the reaction temperature was raised from 0 °C to room tempearture (r.t.), the reaction mixture turns to white slurry. The slurry was stirred at ambient temperature overnight. The suspension was centrifuged, and the supernatant was collected. After removal of the solvent and excess *tert*-butylamine, the crude product (22.79 g, 82.4 mmol, 83.7%) was distillated under reduced pressure (b.p. 84–88 °C/8 mmHg) to give the title compound as a colorless liquid in 69% yield (18.77 g, 67.9 mmol). ^{1}H-NMR (400 MHz, $CDC1_3$): δ 0.07 (s, 12H), 0.93 (br, 2H), 1.17 (s, 18H).

Table 7
Polymerization of ethylene catalyzed by **3**–DEAC [a]

Temperature (°C)	Activity (g mol^{-1} h^{-1} atm)	M_w [b]	M_w/M_n [b]	T_m (°C)
60	3.9×10^1	n.d.	n.d.	n.d.
r.t.	2.3×10^4	9.6×10^5	60	131.6
0	1.6×10^3	1.2×10^6	76	128.8
−78	0	–	–	–

[a] In toluene (30 ml), 0.1 MPa ethylene, [Al]/[Cr] = 25.
[b] Determined by GPC.

Table 8
Crystal data and data collection parameters

Complex	**1**	**3**
Empirical formula	$C_{24}H_{60}O_2N_4Li_4Si_4$	$C_{36}H_{90}O_3N_6Si_6Cr_2$
Formula weight	576.86	927.65
Temperature (°C)	23	23
Crystal system	Tetragonal	Triclinic
Space group	$P4_2/nmc$ (no. 137)	$P\bar{1}$(no. 2)
a (Å)	13.131(2)	10.365(2)
b (Å)	–	16.215(3)
c (Å)	11.080(3)	8.863(2)
α (°)	90	96.15(2)
β (°)	90	111.91(2)
γ (°)	90	79.49(2)
V (Å^3)	1910.5(6)	1357.6(5)
Z	2	1
Radiation	Mo–K$_\alpha$	Mo–K$_\alpha$
Absorption coefficient (cm^{-1})	1.78	5.68
Crystal size (mm)	$0.7\times0.4\times0.2$	$0.5\times0.3\times0.2$
Scan mode	$\omega-2\theta$	ω–2θ
Scan speed (° min^{-1})	16	16
Scan width (°)	$1.47+0.30\tan\theta$	$1.05+0.30\tan\theta$
$2\theta_{max}$ (°)	55	55
Unique data [$I>3\sigma(I)$]	652	4303
Variables	52	241
R	0.080	0.064
R_w	0.084	0.064
Goodness-of-fit	6.49	3.93

*4.3. Preparation of [O(SiMe$_2$N^{t}BuLi)$_2$]$_2$ (**1**)*

^{n}BuLi (Kanto Chemical) (20.3 ml, 31.7 mmol) in hexane was added at 0 °C via syringe to 1,1,3,3-tetramethyl-1,3-di-*tert*-butylamino-disiloxane (4.382 g, 15.84 mmol) in Et$_2$O (80 ml) to precipitate the product as colorless microcrystals in quantitative yield.

*4.4. Preparation of [O(SiMe$_2$^{t}BuN)$_2$]$_2$Cr$_2$ (**2**)*

^{n}BuLi (Kanto Chemical) (20.3 ml, 31.7 mmol) in hexane was added at 0 °C via syringe to a solution of 1,1,3,3-tetramethyl-1,3-di-*tert*-butylamino-disiloxane (4.38 g, 15.8 mmol) in Et$_2$O (100 ml). The mixture was allowed to warm to r.t., and stirred there overnight. At 0 °C, the solution containing lithium reagent (100 ml, 15.8 mmol) was added to a suspension of CrC1$_2$ (Aldrich) (2.226 g, 18. 1 mmol) in Et$_2$O (100 ml) via syringe. The mixture was allowed to reach r.t., and stirred overnight. The suspension was centrifuged, and the supernatant was collected. After the removal of Et$_2$O, the dark-green crude product was recrystallized from *n*-hexane to give **2** as a green powder. The yield was 18% (0.93 g, 2.85 mmol). Anal. Calc. for $C_{12}H_{30}CrON_2Si_2$: C, 44.13; H, 9.26; N, 8.58. Found: C, 44.59; H, 8.97; N, 7.78%. MS (EI) *m*/*z* 652 [M$^+$, 40], 188 (^{t}BuNSiMe$_2$OSiMe, 100).

*4.5. Preparation of O(SiMe$_2$^{t}BuN)$_2$CrN^{t}BuSiMe$_2$OSiMe$_2$^{t}BuNCr(^{t}BuNSiMe$_2$)$_2$O (**3**)*

^{n}BuLi (Kanto Chemical) (15.7 ml, 25.0 mmol) in hexane was added at 0 °C via syringe to 1,1,3,3-tetramethyl-1,3-di-*tert*-butylaminodisiloxane (3.45 g, 12.5 mmol) in Et$_2$O (100 ml). The mixture was allowed to warm to r.t., and stirred there overnight. At 0 °C, the Et$_2$O solution containing lithium reagent (104 ml, 11.2 mmol) was added to a suspension of CrC1$_3$ (Aldrich) (1.77 g, 11.2 mmol) in Et$_2$O (100 ml) via syringe. The mixture was allowed to reach r.t., and stirred overnight. The suspension was centrifuged, and the supernatant was collected. The dark-green solution was recrystallized from Et$_2$O to give blue–green plate. The yield was 26% (1.068 g, 2.95 mmol). Anal. Calc. for $C_{36}H_{90}Cr_2O_3N_6Si_6$: C, 39.81; H, 8.35; N, 7.74. Found: C, 41.03; H, 9.44; N, 7.30%. MS (EI) *m*/*z* 723 [M$^+$ − ^{t}BuNSiMe$_2$OSiMe$_2$, 3], 188 (^{t}BuNSiMe$_2$OSiMe, 100).

*4.6. Crystallographic study of **1** and **3***

The crystals of **1** and **3** 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$_\alpha$ radiation. Three standard reflections were chosen and monitored every 150 reflections. Measured non-equivalent reflections with $I>3.0\sigma(I)$ were used for the structure determination. Empirical absorption correction was carried out based on an azimuthal scan.

The structures of **1** and **3** were solved by the direct methods [27]. In the final refinement cycle (full-matrix), hydrogen atom coordinates were included at idealized positions, and the hydrogen atoms were given the same temperature factor as that of the carbon atom to which they were bonded. All calculations were performed using the TEXSAN crystallographic software package. All the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were not refined.

The pertinent details of data collection and the final cell dimensions for **1** and **3** are given in Table 8.

4.7. Polymerization of ethylene with chromium complexes

A mixture of Cr complex (0.01–0.075 mmol) and distilled toluene (30 ml) was added to MMAO (Tosoh Akzo Co.) or DEAC, TIBAL (Ethyl Corporations). The mixture solution was degassed and the polymerization started by introducting ethylene at 1 atm. The polymerization mixture was quenched with large amount of methanol containing a small amount of hydrochloric acid. The precipitates were centrifuged, filtered, and dried in vacuo. The white solid was collected.

5. Supplementary material

Crystallographic data for the structural analysis of **1** and **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 165208 and 165209, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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