


Cite this: *Dalton Trans.*, 2019, **48**, 4912

Synthesis and characterization of chromium complexes 2-Me₄CpC₆H₄CH₂(R)NHCrCl₂ and their catalytic properties in ethylene homo- and co-polymerization†

Tingting Song, Xin Tao, Xiaobo Tong, Ning Liu, Wei Gao, Xiaoyue Mu* and Ying Mu *

A series of new half-sandwich secondary amine-coordinated dichlorochromium complexes chelated by 2-(tetramethylcyclopentadienyl)benzylamine ligands, 2-Me₄CpC₆H₄CH₂(R)NHCrCl₂ [R = ⁱPr (**1**), Cy (**2**), Ph (**3**), 4-MePh (**4**), 2,6-Me₂Ph (**5**), 2,6-Et₂Ph (**6**)], have been synthesized from the reactions of CrCl₃(THF)₃ with the dilithium salts of the corresponding ligands in THF, followed by the addition of 1/2 eq. of H₂O to the reaction mixtures. The isolated yields of the chromium complexes were found to increase with the increase in the amount of H₂O introduced and reach the highest values (66–76%) when 1/2 eq. of H₂O is added. Attempts to isolate the 2-(tetramethylcyclopentadienyl)benzylamidochromium complexes, 2-Me₄CpC₆H₄CH₂(R)NCrCl, were not successful. The new dichlorochromium complexes were characterized by IR, ¹H NMR, EPR, and UV/Vis spectroscopy and elemental analyses, and the molecular structures of complexes **1**, **5** and **6** were determined by X-ray crystallography. The X-ray crystallographic analysis reveals that these chromium complexes possess a three-legged piano-stool geometry with the amine N atom in a mitered six-membered chelating ring and the two chloride atoms as the legs. Upon activation with AlR₃ and Ph₃CB(C₆F₅)₄, complexes **1–6** exhibit reasonable catalytic activity for ethylene polymerization and copolymerization with 1-hexene, producing polyethylenes with moderate to high molecular weights and poly(ethylene-co-1-hexene)s with moderate comonomer incorporation which are typical linear low-density polyethylenes (LLDPE). Complex **4** was found to show higher catalytic activity for ethylene homo- and co-polymerization than other complexes under similar conditions, while complex **3** produced poly(ethylene-co-1-hexene)s with the highest comonomer incorporation.

Received 30th January 2019,
Accepted 13th March 2019

DOI: 10.1039/c9dt00448c

rsc.li/dalton

Introduction

Chromium-based catalysts for olefin polymerization have attracted intensive research interest in the past decades,^{1–6} and a large amount of effort has been focused on two silica-supported systems: Phillips⁷ and Union Carbide⁸ systems (Cr/SiO₂). The first system is the most important chromium catalyst for the industrial production of polyolefins. In contrast to the homogeneous group 4 metal catalyst systems, a relatively small number of studies on chromium catalyst systems have been

reported so far due mainly to the paramagnetic nature of chromium complexes that makes the chromium catalyst systems difficult to study. Among the homogeneous Cr catalysts, a large number of Cp-based Cr(III) complexes bearing various ligands either bridged or unbridged to the Cp unit have been synthesized and studied.^{9–17} Of the monocyclopentadienyl Cr(III) complexes, the so called constrained-geometry monocyclopentadienyl Cr(III) complexes with a chelating side arm containing a nitrogen, oxygen, sulphur or phosphorus donor have attracted particular attention due to their structural features, and have been reported to be efficient catalyst precursors for ethylene homo- and co-polymerization. Some typical chromium complexes **a–m** of this category are listed in Chart 1.^{18–27}

We have previously synthesized a series of half-sandwich titanium(IV) complexes with 2-(tetramethylcyclopentadienyl)-benzyl-amido ligands^{28a} and half-sandwich scandium(III) complexes with imine-cyclopentadienyl ligands,^{28b} and found that the titanium(IV) complexes show very good catalytic performance for ethylene/1-hexene copolymerization while the scandium(III)

The State Key Laboratory for Supramolecular Structure and Materials, School of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, People's Republic of China. E-mail: xymu@jlu.edu.cn, ymu@jlu.edu.cn

† Electronic supplementary information (ESI) available: Crystal data and structure refinements, GPC traces, ¹³C NMR spectra for typical poly(ethylene-co-1-hexene) samples, UV/Vis spectra and NMR spectra. CCDC 1864417–1864419. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9dt00448c

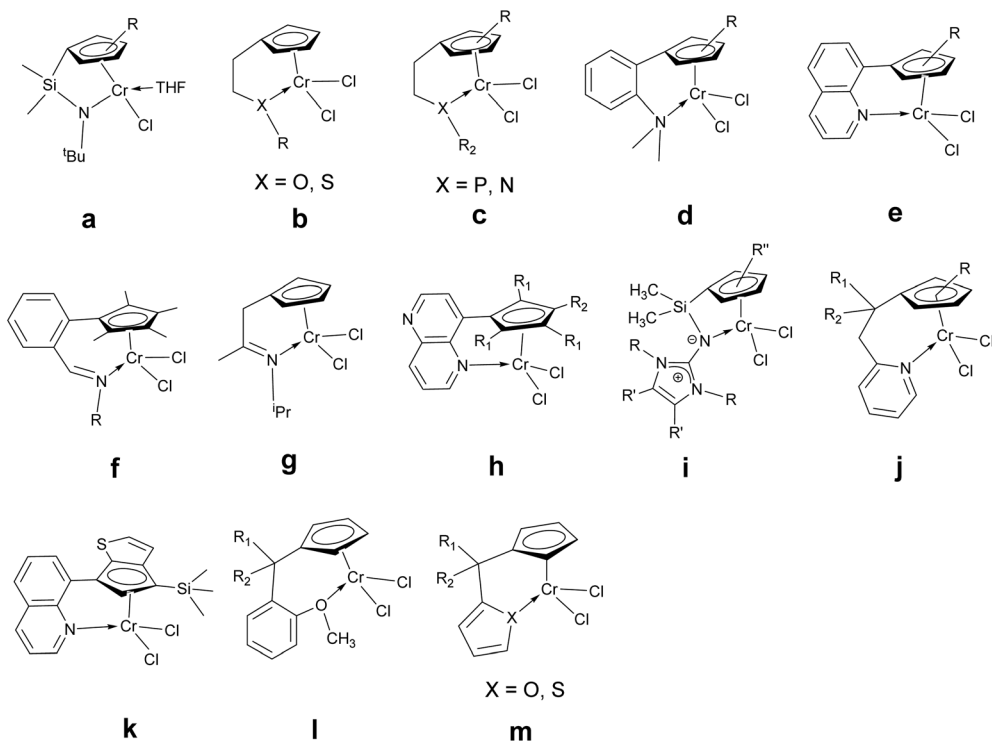


Chart 1 Some known constrained-geometry monocyclopentadienyl chromium complexes.

complexes exhibit moderate catalytic activity for propylene and 1-hexene polymerization. As a part of our research projects, we were interested in combining the 2-(tetramethylcyclopentadienyl)-benzylamido ligands with chromium(III) to prepare new half-sandwich Cr(III) complexes, 2-Me₄CpC₆H₄CH₂(R)NCRCl₂, and hoped these Cr(III) complexes would be converted to neutral olefin polymerization catalysts and show good catalytic performance for ethylene/1-hexene copolymerization upon activation with AlR₃ alone. To our surprise, the expected chromium complexes are hard to synthesize, and have not been obtained. Fortunately, after many tries, new amine-coordinated dichlorochromium complexes 2-Me₄CpC₆H₄CH₂(R)NHCrCl₂ were isolated from the reactions of the dilithium salts of the 2-(tetramethylcyclopentadienyl)-benzylamine ligands with CrCl₃(THF)₃ in THF followed by the addition of 1/2 eq. of H₂O. To our knowledge, no half-metallocene chromium complex with a coordinated secondary amine side-arm has been reported in the literature. We herein report the synthesis and characterization of these dichlorochromium complexes, 2-Me₄CpC₆H₄CH₂(R)NHCrCl₂ [R = ⁱPr (1), Cy (2), Ph (3), 4-MePh (4), 2,6-Me₂Ph (5), 2,6-Et₂Ph (6)] as well as their catalytic properties for ethylene polymerization and ethylene/1-hexene copolymerization.

Results and discussion

Synthesis of ligands and complexes

The free ligands 2-Me₄CpHC₆H₄CH₂(R)NH [R = ⁱPr (H₂L1), Cy (H₂L2), Ph (H₂L3), 4-MePh (H₂L4), 2,6-Me₂Ph (H₂L5), 2,6-Et₂Ph

(H₂L6)] were synthesized according to a published procedure.^{28a} Of them, H₂L1, H₂L2, and H₂L4 have been reported previously. These free ligands were synthesized in high yields (60–70%) from condensation reactions of 2-(tetramethylcyclopentadienyl)benzaldehyde with the corresponding amine derivatives followed by *in situ* reduction of the formed imine compounds with LiAlH₄. The new free ligands H₂L3, H₂L5 and H₂L6 were characterized by ¹H and ¹³C{¹H} NMR spectroscopy. On the basis of the ¹³C{¹H} NMR spectroscopy analysis, it can be found that these compounds exist in the form of two major isomers since two sets of signals for all carbon atoms in these compounds were found in their ¹³C{¹H} NMR spectra. The ¹H NMR spectra of these compounds are somewhat complicated due to the existence of two isomers and the C–H...N hydrogen bond interaction between the acidic H atom of the Cp ring and the nitrogen atom. The stability of the hydrogen bond in these compounds seems to be related to the steric bulk of the substituent on the amine N atom, so the complexity of the NMR signals of these compounds increases with the enlarging of the steric bulk of the substituent on the N atom in the order of H₂L3, H₂L5 and H₂L6 due to a dynamic process.

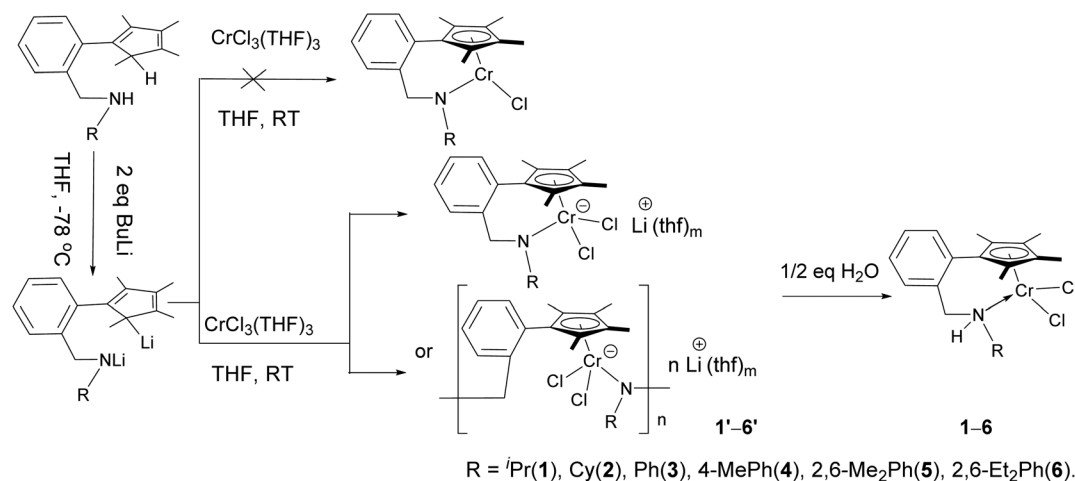
Treatment of the free ligands with 2 equiv. of *n*-butyllithium in THF at –78 °C leads to the formation of the corresponding dilithium salts of the ligands Li₂L1–Li₂L6, which was accompanied by a color change from colourless to reddish brown. The dichlorochromium complexes 1–6 were synthesized in high isolated yields (66–76%) by reactions of the corresponding dilithium salts of the ligands with 1 equiv. of CrCl₃(THF)₃ in THF at room temperature, followed by the

addition of 1/2 eq. of H₂O. During the reactions, the color of the reaction mixtures changes from purple to deep blue, indicating the formation of the complexes. We originally expected to synthesize the benzylamido Cr(III) complexes, 2-Me₄CpC₆H₄CH₂(R)NCRCl, by reactions of the dilithium salts of these ligands with 1 equiv. of CrCl₃(THF)₃ in THF under the same conditions. However, the dichlorochromium complexes, 2-Me₄CpC₆H₄CH₂(R)NHCrCl₂, instead of the expected monochlorochromium complexes, were always isolated in low yields from these reactions. We speculated that the starting material CrCl₃(THF)₃ might have absorbed a small amount of water due to long storage time, which led to the unexpected results. We therefore tried to synthesize the dichlorochromium complexes with 2 eq. of CrCl₃(THF)₃ as the starting material and the isolated yields of these complexes were indeed improved obviously. In order to further verify our conjecture, we repeated the synthesis experiments with newly dried CrCl₃(THF)₃ (treated with Me₃SiCl). However, the expected monochlorochromium complexes were still not obtained, and only some unidentifiable precipitates were formed. Attempts to grow single crystals of the obtained precipitates by recrystallization in different solvents were unsuccessful. Then, we tried to improve the yields of the dichlorochromium complexes by adding a certain amount of water into the reaction mixtures or the CrCl₃(THF)₃ starting material. It was found that the isolated yields of the dichlorochromium complexes increase with increasing amount of water and reach the highest values when 1/2 eq. is added in both cases. To our surprise, no oxygen-containing complex was obtained from these reactions. These results imply that the central chromium atom may prefer to form a mono- or multi-nuclear six-coordination species [2-Me₄CpC₆H₄CH₂NRCrCl₂]⁻ Li⁺(THF)_m or [2-Me₄CpC₆H₄CH₂NRCrCl₂]_n⁻ⁿ nLi⁺(THF)_m during the reactions and then be converted to the dichlorochromium complexes by hydrolysis as shown in Scheme 1. The obtained dichlorochromium complexes were found to be thermally stable under an inert atmosphere, but were air and moisture sensitive. These

complexes are fairly soluble in THF, soluble in toluene, but almost insoluble in common alkanes. All new complexes were characterized by means of IR, ¹H NMR, EPR, and UV/Vis spectroscopy and elemental analyses. The molecular structures of complexes 1, 5 and 6 were determined by X-ray diffraction. Suitable crystals for X-ray structural determination were obtained by recrystallization from *n*-hexane/THF mixed solvent systems. The IR spectra of complexes 1–6 show the N–H stretching vibration band at ν 3208 cm⁻¹ for 1, ν 3195 cm⁻¹ for 2, ν 3237 cm⁻¹ for 3, ν 3245 cm⁻¹ for 4, ν 3221 cm⁻¹ for 5 and ν 3217 cm⁻¹ for 6. The EPR spectroscopy analysis gives a *g* value of 3.86 for 1, 3.95 for 2, 4.01 for 3, 3.84 for 4, 3.90 for 5, and 3.95 for 6, indicative of the valence of Cr(III) in these complexes as these data are close to those of other trivalent chromium complexes (3.75–4.38).²⁹ Although the spectra of the complexes 1–6 all exhibit broadened paramagnetic spectral signatures and are not suitable for structural assignment, the ¹H NMR technique has been used to measure the magnetic moments of these complexes by the Evans method.³⁰ The obtained magnetic moments of 3.68–4.02 μ_B (3.87 μ_B theoretical) for these complexes are consistent with that of a d³ Cr(III) ion.

Crystal structures of complexes 1, 5 and 6

The molecular structures of complexes 1, 5 and 6 with the atom-numbering are shown in Fig. 1–3, and selected bond lengths and angles are listed in Table 1. Crystallographic data indicate that crystals of complexes 1 and 5 belong to the monoclinic system, with the *C2/c* space group for 1 and the *P2(1)/c* space group for 5, while complex 6 crystallizes in the orthorhombic system with the *Pna2(1)* space group. All three complexes possess a three-legged piano stool geometry with a distorted octahedral coordinating environment around the central chromium atom. As can be seen from their crystal structures, the coordination of the nitrogen atom to the central metal in these complexes builds a six-membered chelating ring in a vertical position to the cyclopentadienyl ring



Scheme 1 Synthetic route for complexes 1–6.

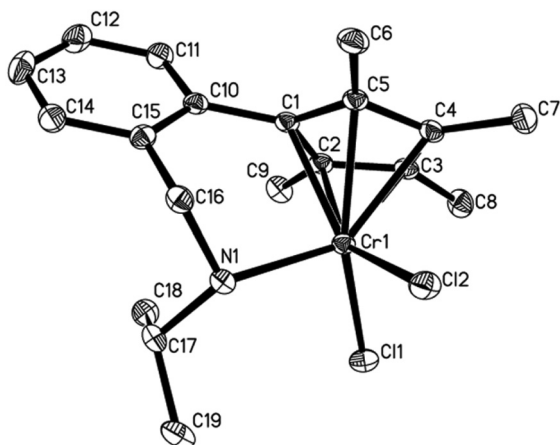


Fig. 1 Perspective view of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

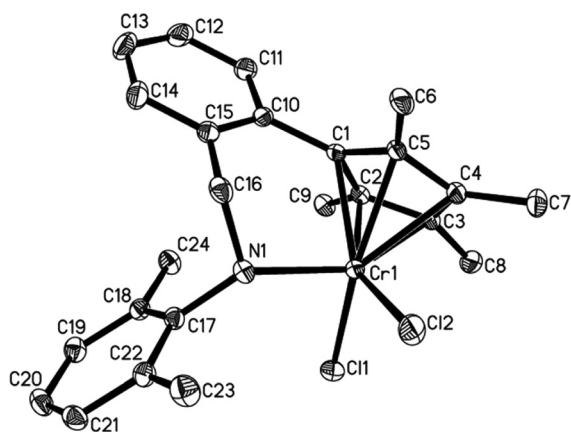


Fig. 2 Perspective view of **5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

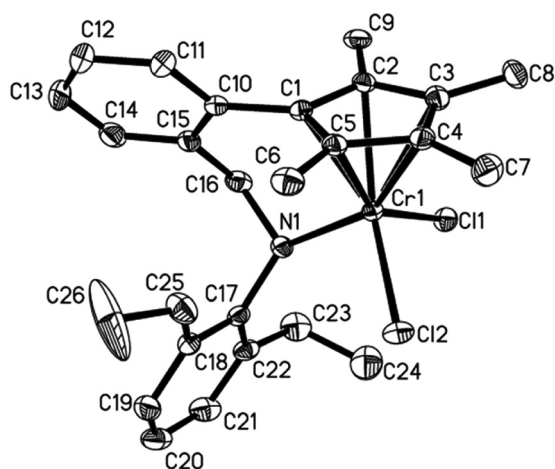


Fig. 3 Perspective view of **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) and bond angles (°) for complexes **1**, **5** and **6**

	1	5	6
Cr(1)–N(1)	2.139(2)	2.178(2)	2.187(3)
Cr(1)–Cl(1)	2.2963(8)	2.2870(8)	2.3178(9)
Cr(1)–Cl(2)	2.2946(8)	2.3156(8)	2.2858(11)
Cr(1)–CCp(range)	2.219(3)–2.271(3)	2.208(2)–2.270(3)	2.204(3)–2.267(4)
Cr(1)–C _{Cp} (av)	2.249(1)	2.239(7)	2.237(1)
Cr(1)–Cp(ct)	1.894	1.883	1.883
C(16)–N(1)	1.496(3)	1.511(3)	1.480(4)
C(17)–N(1)	1.517(4)	1.478(3)	1.511(5)
Cl(1)–Cr(1)–Cl(2)	98.89(3)	99.53(3)	99.75(4)
N(1)–Cr(1)–Cl(1)	98.83(7)	95.66(6)	96.99(9)
N(1)–Cr(1)–Cl(2)	88.09(7)	86.35(6)	85.75(8)
Cpct–Cr–N(1)	123.3	123.2	123.5
C(16)–N(1)–Cr(1)	108.79(16)	111.82(16)	110.3(2)
C(17)–N(1)–Cr(1)	126.32(17)	129.94(17)	132.0(2)
C(16)–N(1)–C(17)	111.2(2)	111.3(2)	111.4(3)
N(1)–C(16)–C(15)	114.2(2)	114.9(2)	116.4(3)
Cp∠Ph ^a	61.5	59.3	60.7

^a Angles between a cyclopentadienyl plane and an attached phenyl plane.

with the R group at the nitrogen atom being placed close to the metal center, which constructs a relatively crowded coordinating environment surrounding the central chromium atom. The Cr–N distances in complexes **1**, **5** and **6** are 2.139(2), 2.178(2), and 2.187(3) Å, respectively, being shorter than the corresponding Cr–N distances found in complex **d** (2.25 Å),²¹ but longer than those in complexes **e** (2.088 Å),²¹ **f** (2.128(5), 2.117(2), 2.131(2) Å),²² **i** (2.04 Å)²⁴ and **j** (2.108 Å),²⁵ while much longer than the one in **a** (1.920 Å),¹⁸ shown in Chart 1, indicating the coordination bond nature of the Cr–N bond in these complexes. The sums of the bond angles around N (346.3° for **1**, 353.1° for **5**, and 353.7° for **6**) are less than 360° as seen in the Cr complexes (nearly 360°) with a three coordinate N atom,^{16a,18,31} further confirming the presence of a coordinated –NHR group in these complexes. Complex **6** has the longest Cr–N bond distance among the complexes **1**, **5** and **6**, which is reasonable since the R group at the amine N atom in complex **6** is the biggest 2,6-diethylphenyl. The Cr–Cl bond distances (2.286–2.318 Å) in these complexes are in agreement with those observed for related amino-, pyridyl- or imino-functionalized cyclopentadienyl chromium dichloride complexes.^{20–22,25} The distances of Cr–Cp(ct) (ct = centroid) are close to each other for complexes **1**, **5** and **6** with the data of 1.883 Å for **5** and **6**, and 1.894 Å for **1**. Similarly, the Cr–C_{Cp}(av) (av = average) distances (2.249 Å for **1**, 2.239 Å for **5** and 2.237 Å for **6**) are also close to each other. The individual Cr–C_{Cp} bond distances range from 2.204 to 2.271 Å, with the Cr–C3 and Cr–C4 distances (2.270(3) and 2.271(3) Å for **1**, 2.252(3) and 2.270(3) Å for **5**, and 2.253(3) and 2.267(4) Å for **6**) being obviously longer than the remaining Cr–C_{Cp} bond lengths (average 2.2346 Å, 2.2253 Å, 2.2217 Å for **1**, **5**, and **6**, respectively), indicating that the central chromium atom is not located exactly below the center of the Cp ring due to the coordination of the amine N atom. The N–Cr–Cp(ct) angles of complexes **1** (123.3°), **5** (123.2°) and **6** (123.5°) are obviously larger than those observed in the known N functionalized chromium com-

plexes **c** (113.6°)²⁰ and **f** (118.7–120.6°),²² which is indicative of these complexes possessing a more crowded coordinating environment surrounding the central chromium atom than the reported similar complexes. A similar effect on the N–Cr–Cl angles (98.83(7) and 88.09(7)° for **1**, 95.66(6) and 86.35(6)° for **5**, 96.99(9) and 85.75(8)° for **6**) can also be observed. The Cr–N–C(17) angles (126.32° for **1**, 129.94° for **5**, and 132.0(2)° for **6**) are remarkably affected by the size of the R group. However, the influences from the bulkiness of the R group on the Cl–Cr–Cp(ct) (120.1 and 120.7° for **1**, 120.3 and 123.3° for **5**, 118.8 and 123.5° for **6**) and Cl–Cr–Cl (98.89° for **1**, 99.53° for **5**, and 99.75° for **6**) bond angles as well as the angles between the Cp ring and the attached phenyl ring (61.5° for **1**, 59.3° for **5** and 60.7° for **6**) are not obvious. These structural features may affect their catalytic performance by influencing the coordination of the olefin molecule to the central metal atom and insertion into the growing polymer chain, as well as the polymer chain termination processes.

Polymerization reactions

Ethylene polymerization reactions using complexes **1–6** as catalyst precursors under different conditions were examined, and the results are summarized in Table 2. Upon activation with AlR₃/Ph₃CB(C₆F₅)₄ (R = Me, Et and ⁱBu) or MAO, complexes **1–6** all exhibit moderate to high catalytic activity for the ethylene polymerization reaction. The highest catalytic activities [2.1 × 10⁶ g PE (mol Cr)^{−1} h^{−1} bar^{−1}] are slightly lower than those reported for most N-containing group functionalized cyclopentadienyl chromium complexes.^{21,24–26} Under similar conditions, the catalytic activity decreases in the order **4** > **3** > **2** > **1** > **5** > **6**, which indicates that the catalytic activity of these complexes is notably influenced by the nature of the R group on the amine N atom. For complexes **1–4**, the bulkier R group might be favorable for weakening the interaction between the

catalytically active cationic species and the anionic cocatalyst and therefore could increase the catalytic activity of the catalyst.^{28a} However, the steric effect of the R group is inverted for complexes **5** and **6**, and their catalytic activity decreases with the increase in the steric hindrance of the R group. It is possible that the R group in complexes **5** and **6** is so bulky that the coordination environment of the catalytically active center becomes congested for the coordination and insertion of ethylene. The unidentifiable precipitate **4'** obtained from the reaction of CrCl₃(THF)₃ with Li₂L**4** in THF was also tested as a catalyst for the ethylene polymerization reaction. The catalytic activity of **4'** was found to be slightly lower than that of complex **4** under similar conditions. These Cr complexes can be effectively activated with only a small amount of the AlR₃ cocatalyst, and their catalytic activity reaches the maximum with an Al/Cr molar ratio about 90. Similar results have previously been observed for chromium analogues.^{15,22,25,28a} To investigate the effect of the polymerization temperature on the catalytic activity of these catalyst systems, ethylene polymerization experiments with the **4**/AlEt₃/Ph₃CB(C₆F₅)₄ catalyst system were carried out at 30, 50, 70, and 90 °C (entries 4 and 10–12 in Table 2) with the highest catalytic activity being observed at 50 °C. This result is similar to those observed for other related half-metallocene chromium(III) catalyst systems.^{15,22,25,28a} When activated with MAO, complex **4** shows slightly lower catalytic activity than the **4**/AlEt₃/Ph₃CB(C₆F₅)₄ system for ethylene polymerization under similar conditions. The ethylene polymerization reaction with complex **4** as the catalyst and AlEt₃ alone as the cocatalyst was also examined and very low catalytic activity was observed. As reported with other catalyst systems, the molecular weight of the resulting polyethylene in the present system decreases with the increase in the Al/Cr molar ratio from 60 to 180 due to the increased probability of chain transfer from chromium to aluminum at

Table 2 Summary of polymerization of ethylene under various conditions^a

Entry	Cat	Activator	Al/Cr	Time (min)	T (°C)	Yield (g)	Activity ^b	M _n ^c (×10 ⁴)	T _m ^d (°C)
1	1	AlEt ₃	90	20	50	0.96	576	20.2	139.6
2	2	AlEt ₃	90	20	50	1.12	672	23.9	140.2
3	3	AlEt ₃	90	20	50	1.58	948	27.0	139.3
4	4	AlEt ₃	90	20	50	1.96	1176	38.7	138.9
5	5	AlEt ₃	90	20	50	0.21	126	53.1	140.4
6	6	AlEt ₃	90	20	50	0.15	90	60.1	139.5
7	4	AlEt ₃	180	20	50	0.78	468	20.6	138.2
8	4	AlEt ₃	120	20	50	1.87	1122	31.6	140.1
9	4	AlEt ₃	60	20	50	0.36	216	46.9	139.4
10	4	AlEt ₃	90	20	90	0.68	408	25.1	139.6
11	4	AlEt ₃	90	20	70	1.78	1068	32.3	140.1
12	4	AlEt ₃	90	20	30	0.95	570	44.7	140.7
13	4	AlEt ₃	90	10	50	1.79	2148	42.7	138.8
14	4	AlMe ₃	90	20	50	0.50	300	36.3	137.8
15	4	Al(ⁱ Bu) ₃	90	20	50	1.69	1014	40.3	141.1
16 ^e	4	AlEt ₃	90	20	50	0.26	156	38.1	139.1
17	4	MAO	1000	20	50	0.96	576	34.7	140.2
18	4'	AlEt ₃	90	20	50	1.88	1128	38.2	140.1

^a Polymerization conditions: Solvent 70 mL of toluene; catalyst, 1 × 10^{−6} mol; ethylene pressure, 5 bar; B/Cr molar ratio = 1.3 : 1. ^b Units of kg PE (mol Cr)^{−1} h^{−1} bar^{−1}. ^c Measured in decahydronaphthalene at 135 °C. ^d Determined by DSC at a heating rate of 10 °C min^{−1}. ^e No Ph₃CB(C₆F₅)₄ was used.

Table 3 Summary of copolymerization of ethylene/1-hexene under various conditions^a

Entry	Cat	1-Hexene (mol L ⁻¹)	Yield (g)	Activity ^b	1-Hexene content ^c (mol%)	M_w^d ($\times 10^4$)	M_w/M_n^d	T_m^e (°C)
19	1	0.5	0.59	354	0.47	6.48	2.68	130.1
20	1	1.0	0.88	528	0.98	6.18	2.27	124.9
21	1	1.5	0.73	438	1.39	6.02	2.80	130.5
22	2	0.5	1.85	1110	0.66	8.20	2.62	129.0
23	2	1.0	2.42	1452	1.29	7.10	2.69	129.5
24	2	1.5	2.31	1386	1.91	6.97	2.51	126.5
25	3	0.5	2.52	1512	2.05	12.22	2.08	127.7
26	3	1.0	2.78	1668	4.28	11.64	2.87	126.3
27	3	1.5	2.33	1398	5.97	7.58	2.41	122.1
28	4	0.5	2.88	1728	0.99	13.18	2.47	129.1
29	4	1.0	3.23	1938	1.89	13.08	2.54	126.1
30	4	1.5	2.6	1560	2.81	12.08	2.44	124.7
31	5	0.5	0.41	246	0.31	16.02	2.45	130.4
32	5	1.0	0.63	378	0.52	13.64	2.32	129.9
33	5	1.5	0.47	282	0.80	13.23	2.91	127.6
34	6	0.5	0.23	138	0.22	20.31	2.48	131.7
35	6	1.0	0.41	246	0.40	18.26	2.31	129.6
36	6	1.5	0.34	204	0.59	17.33	2.49	128.6
37	4'	0.5	2.72	1632	0.69	14.22	2.38	129.4
38	4'	1.0	3.01	1806	1.52	13.83	2.56	128.1
39	4'	1.5	2.41	1446	2.43	12.91	2.29	125.8

^a Polymerization conditions: Toluene + 1-hexene, total 70 mL; catalyst, 1×10^{-6} mol; Al/Ti molar ratio, 90; B/Ti molar ratio, 1.3; time, 20 min; temperature, 50 °C; ethylene pressure, 5 bar. ^b Units of kg polymer (mol Cr)⁻¹ h⁻¹ bar⁻¹. ^c Calculated on the basis of ¹³C NMR spectra. ^d Measured by GPC analysis. ^e Determined by DSC at a heating rate of 10 °C min⁻¹.

high Al/Cr molar ratios. The molecular weight of the resulting polyethylene was also found to be affected by the structure of the catalysts, and the polyethylene sample with the highest molecular weight was obtained with the bulkiest complex **6**. The polyethylene samples were also characterized by ¹³C NMR, which indicates that the resultant polyethylenes are linear with a characteristic resonance at 30.2 ppm. The melting points of the obtained polyethylenes range from 137.8 to 141.1 °C, which is typical for linear polyethylenes.^{22,27,28a}

Ethylene/1-hexene copolymerization reactions with the complexes **1–6** as catalyst precursors, activated with AlEt₃ and Ph₃CB(C₆F₅)₄, were also investigated and the results are summarized in Table 3. As mentioned above for the ethylene homopolymerization, the catalytic activity of these catalyst systems for the ethylene/1-hexene copolymerization under similar conditions also decreases in the order **4** > **3** > **2** > **1** > **5** > **6**. The precipitate **4'** was also investigated as the catalyst for the ethylene/1-hexene copolymerization reaction, and a lower catalytic activity than for complex **4** was observed under similar conditions. It was found that these catalytic systems demonstrate an obvious comonomer effect and their catalytic activities for most copolymerization reactions are higher than those observed for the ethylene homopolymerization reactions. The comonomer effect has been widely observed in ethylene/ α -olefin copolymerization reactions with various Cr-based catalyst systems.³² The resultant poly(ethylene-*co*-1-hexene)s were analyzed by ¹³C NMR, DSC and GPC. The DSC analysis of the copolymers shows their T_m values around 122.1–131.7 °C, which are lower than those of ethylene homopolymers (137.8–141.1 °C) produced under similar conditions. The comonomer content in the copolymers was calculated based on the ¹³C NMR analysis³³ and the data are listed in

Table 3. The copolymers obtained with these catalyst systems are typical linear low density polyethylenes with a comonomer content of 1–6 mol%. The comonomer incorporation ability of these catalysts was found to be evidently dependent on their structure and the copolymer with the highest (5.97 mol%, entry 27, Table 3) was obtained from the 3/AlEt₃/Ph₃CB(C₆F₅)₄ catalyst system. The GPC analysis reveals that the poly(ethylene-*co*-1-hexene)s produced by these catalysts possess relatively high molecular weights ($M_w = 6\text{--}20 \times 10^4$ g mol⁻¹) and the molecular weight distribution is basically unimodal and narrow.

Conclusions

A series of new half-sandwich amine-coordinated chromium(III) complexes, 2-Me₄CpC₆H₄CH₂(R)NHCrCl₂, have been synthesized in high yields from the reactions of the dilithium salts of the corresponding ligands with CrCl₃(THF)₃ followed by the addition of an adequate amount of H₂O. The isolated yields of the chromium complexes were found to be dependent on the amount of H₂O added into the reaction mixtures and the highest yields were obtained when 1/2 eq. of H₂O was added. X-ray crystallographic analysis indicates that these half-metallocene dichlorochromium complexes adopt a pseudo-octahedral coordination environment with the N coordinated to the Cr metal center. Upon activation with AlR₃/Ph₃CB(C₆F₅)₄, these complexes exhibit reasonable to high catalytic activity for ethylene homo- and co-polymerization with 1-hexene, producing polyethylenes with moderate to high molecular weights and poly(ethylene-*co*-1-hexene)s with moderate comonomer incorporation.

Experimental section

General methods and materials

All manipulations involving air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere (ultra-high purity) using either standard Schlenk techniques or glovebox techniques. Toluene, diethyl ether, THF and *n*-hexane were distilled under nitrogen in the presence of sodium and benzophenone. CH₂Cl₂ and 1-hexene were purified by distilling over calcium hydride before use. 2-(Tetramethylcyclopentadienyl)-benzylamido^{28a} and Ph₃CB(C₆F₅)₄ were prepared according to literature procedures. Polymerization grade ethylene was further purified by passing through columns of 5 Å molecular sieves and MnO. AlⁱBu₃, *n*-BuLi and LiAlH₄ were purchased from Aldrich. CrCl₃(THF)₃ was prepared by the standard method.³⁴ Elemental analyses were performed on a Varian EL microanalyzer. Infrared spectra were recorded using KBr disks with a Nicolet Avatar 360. The EPR spectra were recorded on a JEOL JES-FA200 EPR spectrometer. UV/Vis spectra have been recorded on a PerkinElmer Lambda 950 spectrophotometer. ¹H and ¹³C NMR spectra were recorded using a Bruker Avance III-400 NMR spectrometer. ¹³C NMR spectra of the copolymers were recorded on a Bruker Avance III-400 NMR spectrometer at 135 °C with *o*-C₆D₄Cl₂ as the solvent. The viscosity-averaged molecular weights of polyethylenes were measured in decahydronaphthalene at 135 °C by using a Ubbelohde viscometer according to the following equation: $[\eta] = 6.77 \times 10^{-4} M\eta^{0.67}$. The molecular weight and molecular weight distribution of the copolymer samples were measured on a PL-GPC 220 at 150 °C with 1,2,4-trichlorobenzene as the eluent. The melting points of the polymer were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 at a heating/cooling rate of 10 °C min⁻¹ from 35 to 160 °C and the data from the second heating scan were used.

Synthesis of 2-Me₄CpHC₆H₄CH₂(Ph)NH (H₂L3). Compound H₂L3 was synthesized in the same manner as reported previously with aniline (0.93 g, 10.0 mmol) as the starting material. The product (1.99 g, 6.56 mmol, 65.6%) was obtained as a colorless oily substance. ¹H NMR (CDCl₃, 400 MHz, 298 K): δ 7.52–6.56 (m, 9H, ArH), 4.47–4.17 (m, 2H, ArCH₂N), 3.99 (brs, 1H, NH), 3.20–2.73 (m, 1H, CpH), 1.94–1.01 (m, 12H, CpCH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz, 298 K): δ 148.34, 148.30, 141.46, 141.16, 140.66, 139.99, 139.30, 138.96, 138.25, 138.07, 136.76, 136.67, 133.64, 133.53, 130.40, 130.11, 129.25, 129.21, 129.19, 127.78, 127.25, 127.21, 126.94, 126.88, 117.30, 117.26, 112.91, 112.90 (ArC and CpC), 52.13, 51.82 (CpCH), 46.19, 46.09 (ArCH₂N), 14.61, 14.34, 12.73, 12.67, 11.96, 11.80, 11.37, 11.18 (CpCH₃) ppm. (Compound H₂L3 exists in the form of two major isomers).

Synthesis of 2-Me₄CpHC₆H₄CH₂((2,6-Me₂Ph)NH (H₂L5). Compound H₂L5 was synthesized in the same manner as reported previously with 2,6-dimethylaniline (1.21 g, 10.0 mmol) as the starting material. The product (2.50 g, 7.55 mmol, 75.5%) was obtained as a colorless oily substance. ¹H NMR (CDCl₃, 400 MHz, 298 K): δ 7.69–6.92 (m, 7H, ArH),

4.35–3.96 (m, 2H, ArCH₂N), 3.19 (brs, 1H, NH), 3.09–2.79 (m, 1H, CpH), 2.42–2.26 (m, 6H, ArCH₃), 1.97–1.04 (m, 12H, CpCH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz, 298 K): δ 146.39, 146.34, 141.27, 140.44, 138.73, 138.57, 136.97, 136.70, 136.31, 134.15, 133.96, 133.86, 130.47, 130.40, 130.20, 130.00, 129.96, 129.02, 128.91, 128.86, 128.83, 128.59, 127.34, 127.11, 127.04, 126.48, 122.43, 122.16 (ArC and CpC), 52.13, 51.87 (CpCH), 50.36, 49.84 (ArCH₂N), 18.83, 18.50, 18.41, 18.06 (ArCH₃), 14.35, 14.21, 12.58, 12.19, 11.88, 11.77, 11.39, 11.12 (CpCH₃) ppm. (Compound H₂L5 exists in the form of two major isomers).

Synthesis of 2-Me₄CpHC₆H₄CH₂((2,6-Et₂Ph)NH (H₂L6). Compound H₂L6 was synthesized in the same manner as reported previously with 2,6-diethylaniline (1.49 g, 10.0 mmol) as the starting material. The product (2.62 g, 7.28 mmol, 72.8%) was obtained as a colorless oily substance. ¹H NMR (CDCl₃, 400 MHz, 298 K): δ 7.76–6.98 (m, 7H, ArH), 4.27–3.81 (m, 2H, ArCH₂N), 3.07 (brs, 1H, NH), 2.78–2.70 (m, 1H, CpH), 2.67–2.57 (m, 4H, ArCH₂CH₃), 1.91–0.97 (m, 18H, ArCH₂CH₃ and CpCH₃) ppm. ¹³C{¹H} NMR (CDCl₃, 100 MHz, 298 K): δ 145.16, 145.09, 142.22, 141.59, 141.08, 140.30, 139.42, 138.92, 138.56, 138.31, 138.05, 137.60, 137.22, 136.81, 136.67, 134.00, 130.91, 130.33, 130.09, 128.61, 127.94, 127.55, 127.33, 127.02, 126.61, 126.05, 123.41, 123.01 (ArC and CpC), 52.92, 52.35 (CpCH), 52.06, 51.61 (ArCH₂N), 24.73, 24.35, 24.19, 23.99 (ArCH₂CH₃), 15.01 (ArCH₃), 14.32, 14.05, 13.10, 12.88, 12.48, 11.82, 11.33, 11.07 (CpCH₃) ppm. (Compound H₂L6 exists in the form of two major isomers).

Synthesis of complex 1. Path A: To a solution of free ligand H₂L1 (700 mg, 2.60 mmol) in 20 mL of THF was added dropwise a solution of *n*-BuLi (2.16 mL, 5.20 mmol) in *n*-hexane at –78 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The resulting solution was then added dropwise to a suspension of CrCl₃(THF)₃ (974 mg, 2.60 mmol) in 30 mL of THF at room temperature and the reaction mixture was stirred for 4 h. To the reaction mixture was added a solution of H₂O (1.30 mmol) in THF at room temperature, and an immediate color change from green to blue was observed. After the reaction mixture was stirred for further 1 h, after the solvent was removed under vacuum, the residue was extracted with 15 mL of toluene to remove the insoluble impurities. The pure product **1** was obtained by recrystallization from CH₂Cl₂/*n*-hexane (v/v = 1–2 : 10) as blue crystalline solids (671 mg, 66%). Elemental analyses: calcd for C₁₉H₂₆Cl₂CrN (391.32): C, 58.32; H, 6.70; N, 3.58. Found: C, 58.28; H, 6.58; N, 3.47. IR (KBr): 3208 (w), 2963 (s), 2922 (s), 2869 (m), 1625 (m), 1455 (s), 1380 (s), 1261 (w), 1171 (m), 1056 (m), 759 (m) and 533 (m) cm⁻¹. M.p. 146–147 °C. $\mu_{\text{eff}} = 3.71\mu_{\text{B}}$. UV-visible: λ_{max} (toluene) nm⁻¹ 481 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 643) and 617 (2642). **Path B:** To a solution of free ligand H₂L1 (700 mg, 2.60 mmol) in 20 mL of THF was added dropwise a solution of *n*-BuLi (2.16 mL, 5.20 mmol) in *n*-hexane at –78 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. In another Schlenk flask, to a suspension of CrCl₃(THF)₃ (974 mg, 2.60 mmol) in 30 mL of THF was added a solution of H₂O (1.30 mmol) in THF at room temperature and stirred for

1 h to allow the water to be absorbed by CrCl_3 . To the resulting suspension was then added dropwise the dilithium salt solution of the ligand. The reaction mixture was stirred for 4 h at room temperature, and the color of the reaction mixture changed from purple to dark blue during the reaction. After workup in the same way as mentioned in Path A, pure **1** was obtained as dark blue crystalline solids (620 mg, 61%).

Synthesis of complex 2. Complex **2** was synthesized in the same manner (path A) as complex **1** with compound $\text{H}_2\text{L2}$ (805 mg, 2.60 mmol), *n*-BuLi (5.20 mmol) and $\text{CrCl}_3(\text{THF})_3$ (974 mg, 2.60 mmol) as starting materials. Pure product **2** was obtained as dark blue crystalline solids (763 mg, 68%). Elemental analyses: calcd for $\text{C}_{22}\text{H}_{30}\text{Cl}_2\text{CrN}$ (431.39): C, 61.25; H, 7.01; N, 3.25. Found: C, 61.42; H, 6.95; N, 3.33. IR (KBr): 3195 (w), 2921 (s), 2854 (m), 1629 (w), 1449 (m), 1262 (m), 1098 (s), 1066 (s), 1047 (s), 1027 (s), 803 (m) and 587 (m) cm^{-1} . M.p. 150–151 °C. $\mu_{\text{eff}} = 3.68\mu_{\text{B}}$. UV-visible: $\lambda_{\text{max}}(\text{toluene}) \text{ nm}^{-1}$ 484 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 695) and 619 (2610).

Synthesis of complex 3. Complex **3** was synthesized in the same manner (path A) as complex **1** with compound $\text{H}_2\text{L3}$ (789 mg, 2.60 mmol), *n*-BuLi (5.20 mmol) and $\text{CrCl}_3(\text{THF})_3$ (974 mg, 2.60 mmol) as starting materials. Pure product **3** was obtained as dark blue crystalline solids (840 mg, 76%). Elemental analyses: calcd for $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{CrN}$ (425.34): C, 62.13; H, 5.69; N, 3.29. Found: C, 62.12; H, 5.25; N, 3.39. IR (KBr): 3237 (w), 3048 (w), 3023 (w), 2958 (s), 2916 (s), 2864 (s), 1602 (s), 1496 (s), 1477 (s), 1449 (s), 1378 (m), 1253 (w), 1185 (w), 1030 (m), 743 (s), 688 (m) and 522 (m) cm^{-1} . M.p. 153–154 °C. $\mu_{\text{eff}} = 3.99\mu_{\text{B}}$. UV-visible: $\lambda_{\text{max}}(\text{toluene}) \text{ nm}^{-1}$ 472 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 772) and 639 (2548).

Synthesis of complex 4. Complex **4** was synthesized in the same manner (path A) as complex **1** with compound $\text{H}_2\text{L4}$ (825 mg, 2.60 mmol), *n*-BuLi (5.20 mmol) and $\text{CrCl}_3(\text{THF})_3$ (974 mg, 2.60 mmol) as starting materials. Pure product **4** was obtained as dark blue crystalline solids (868 mg, 76%). Elemental analyses: calcd for $\text{C}_{23}\text{H}_{26}\text{Cl}_2\text{CrN}$ (439.36): C, 62.88; H, 5.96; N, 3.19. Found: C, 62.84; H, 5.88; N, 3.08. IR (KBr): 3245 (w), 2956 (s), 2918 (s), 2864 (s), 1616 (m), 1513 (m), 1445 (m), 1379 (m), 1266 (w), 1211 (w), 1115 (m), 1067 (m), 1040 (m), 1022 (m), 989 (m), 811 (m), 761 (m) and 541 (m) cm^{-1} . M.p. 152–154 °C. $\mu_{\text{eff}} = 4.02\mu_{\text{B}}$. UV-visible: $\lambda_{\text{max}}(\text{toluene}) \text{ nm}^{-1}$ 464 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 784) and 642 (2006).

Synthesis of complex 5. Complex **5** was synthesized in the same manner (path A) as complex **1** with compound $\text{H}_2\text{L5}$ (862 mg, 2.60 mmol), *n*-BuLi (5.20 mmol) and $\text{CrCl}_3(\text{THF})_3$ (974 mg, 2.60 mmol) as starting materials. Pure product **5** was obtained as dark blue crystalline solids (861 mg, 73%). Elemental analyses: calcd for $\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{CrN}$ (453.39): C, 63.58; H, 6.23; N, 3.09. Found: C, 63.91; H, 6.19; N, 3.03. IR (KBr): 3221 (w), 2960 (s), 2924 (s), 2866 (s), 1618 (m), 1454 (s), 1262 (w), 1164 (m), 1088 (s), 1024 (m), 772 (m), 640 (w) and 491 (w) cm^{-1} . M.p. 158–160 °C. $\mu_{\text{eff}} = 3.89\mu_{\text{B}}$. UV-visible: $\lambda_{\text{max}}(\text{toluene}) \text{ nm}^{-1}$ 504 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 466) and 646 (2065).

Synthesis of complex 6. Complex **6** was synthesized in the same manner (path A) as complex **1** with compound $\text{H}_2\text{L6}$ (935 mg, 2.60 mmol), *n*-BuLi (5.20 mmol) and $\text{CrCl}_3(\text{THF})_3$

(974 mg, 2.60 mmol) as starting materials. Pure product **6** was obtained as dark blue crystalline solids (926 mg, 74%). Elemental analyses: calcd for $\text{C}_{26}\text{H}_{32}\text{Cl}_2\text{CrN}$ (481.45): C, 64.86; H, 6.70; N, 2.91. Found: C, 64.98; H, 6.61; N, 2.86. IR (KBr): 3217 (w), 3055 (w), 2962 (s), 2925 (s), 2871 (s), 1603 (m), 1568 (m), 1450 (s), 1379 (m), 1202 (w), 1161 (w), 1106 (m), 802 (w), 755 (s) and 587 (m) cm^{-1} . M.p. 165–166 °C. $\mu_{\text{eff}} = 3.98\mu_{\text{B}}$. UV-visible: $\lambda_{\text{max}}(\text{toluene}) \text{ nm}^{-1}$ 505 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 692) and 651 (2080).

X-ray crystallographic studies. Single crystals of complexes **1**, **5**, and **6** suitable for X-ray analysis were obtained by recrystallization from a mixture of THF and hexane (*v/v* = 1–2 : 10). The crystals were mounted on glass fibers using an oil drop. Data obtained with the ω - 2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved using direct methods, and further refinements with full-matrix least squares on F^2 were obtained with the SHELXTL program package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages.³⁵

Polymerization reaction. The ethylene polymerization experiments were carried out as follows: a dry 250 mL steel autoclave with a magnetic stirrer was charged with 60 mL of toluene, thermostated at the desired temperature, and saturated with ethylene (1.0 atm). The polymerization reaction was started by the addition of a mixture of the catalyst and AlR_3 in toluene (5 mL) and a solution of $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ in toluene (5 mL) at the same time. The vessel was pressurized to 5 atm with ethylene immediately, and the pressure was maintained by continuous feeding of ethylene. The reaction mixture was stirred at the desired temperature for 20 min. The polymerization was then quenched by injecting acidified methanol containing HCl (3 M). The polymer was collected by filtration, washed with water and methanol, and dried to a constant weight under vacuum. For the ethylene/1-hexene copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

We are grateful for the financial support from the National Natural Science Foundation of China (51673078 and U1462111).

Notes and references

- (a) K. H. Theopold, *Acc. Chem. Res.*, 1990, **23**, 263; (b) K. H. Theopold, *Eur. J. Inorg. Chem.*, 1998, 15.

- 2 (a) M. A. Esteruelas, A. M. López, L. Méndez, M. Oliván and E. Oñate, *Organometallics*, 2003, **22**, 395; (b) B. L. Small, M. J. Carney, D. M. Holman, C. E. O'Rourke and J. Halfen, *Macromolecules*, 2004, **37**, 4375; (c) D.-H. Kwon, J. T. Fuller, U. J. Kilgore, O. L. Sydora, S. M. Bischof and D. H. Ess, *ACS Catal.*, 2018, **8**, 1138; (d) H. Lee and S. H. Hong, *Appl. Catal., A*, 2018, **560**, 21.
- 3 (a) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; (b) S. S. McGuinness, V. C. Gibson, D. F. Wass and J. W. Steed, *J. Am. Chem. Soc.*, 2003, **125**, 12716; (c) D. J. Jones, V. C. Gibson, S. M. Green, P. J. Maddox, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2005, **127**, 11037; (d) A. K. Tomov, J. J. Chirinos, R. J. Long, V. C. Gibson and M. R. Elsegood, *J. Am. Chem. Soc.*, 2006, **128**, 7704.
- 4 (a) F. Junges, M. C. A. Kuhn, A. H. D. P dos Santos, C. R. K. Rabello, C. M. Thomas, J.-F. Carpentier and O. L. Casagrande, *Organometallics*, 2007, **26**, 4010; (b) T. Gunasekara, J. Kim, A. Preston, D. K. Steelman, G. A. Medvedev, W. N. Delgass, O. L. Sydora, J. M. Caruthers and M. M. Abu-Omar, *ACS Catal.*, 2018, **8**, 6810; (c) N. A. Hirscher and T. Agapie, *Organometallics*, 2017, **36**, 4107; (d) H. Lee, Y. Joeb and H. Park, *Catal. Commun.*, 2019, **121**, 15.
- 5 (a) I. Vidyaratne, J. Scott, S. Gambarotta and R. Duchateau, *Organometallics*, 2007, **26**, 3201; (b) K. Albahily, D. Al-Baldawi, S. Gambarotta, E. Koc and R. Duchateau, *Organometallics*, 2008, **27**, 5943; (c) I. Vidyaratne, G. B. Nikiforov, S. I. Gorelsky, S. Gambarotta, R. Duchateau and I. Korobkov, *Angew. Chem., Int. Ed.*, 2009, **48**, 6552.
- 6 (a) D. S. McGuinness, *Organometallics*, 2009, **28**, 244; (b) P. Ai, A. A. Danopoulos and P. Braunstein, *Organometallics*, 2015, **34**, 4109; (c) J. D. Nobbs, A. K. Tomov, C. T. Young, A. J. P. White and G. J. P. Britovsek, *Catal. Sci. Technol.*, 2018, **8**, 1314; (d) M. Zhang, K. Wang and W. Sun, *Dalton Trans.*, 2009, 6354.
- 7 (a) J. P. Hogan and R. L. Banks, *US Pat*, 2825721, 1958; (b) J. P. Hogan, *J. Polym. Sci., Part A: Polym. Chem.*, 1970, **8**, 2637.
- 8 (a) G. L. Karapinka, *US Pat*, 3709853, 1973; (b) F. J. Karol, G. L. Karapinka, C. Wu, A. W. Dow, R. N. Johnson and W. L. Carrick, *J. Polym. Sci., Part A: Polym. Chem.*, 1972, **10**, 2621.
- 9 S. Derlin and W. Kaminsky, *Macromolecules*, 2008, **41**, 6280.
- 10 P. Fernández, H. Pritzkow, J. J. Carbó, P. Hofmann and M. Enders, *Organometallics*, 2007, **26**, 4402.
- 11 S. Mark, A. Kurek, R. Mülhaupt, R. Xu, G. Klatt, H. Köppel and M. Enders, *Angew. Chem., Int. Ed.*, 2010, **49**, 8751.
- 12 S. Mark, H. Wadepohl and M. Enders, *Beilstein J. Org. Chem.*, 2016, **12**, 1372.
- 13 M. Enders, P. Fernandez, S. Mihan and H. Pritzkow, *J. Organomet. Chem.*, 2003, **687**, 125.
- 14 M. Ronellenfitsch, H. Wadepohl and M. Enders, *Organometallics*, 2014, **33**, 5758.
- 15 (a) T. Xu, Y. Mu, W. Gao, J. Ni, L. Ye and Y. Tao, *J. Am. Chem. Soc.*, 2007, **129**, 2236; (b) M. Sun, Y. Liu, Q. Wu and L. Ye, *Organometallics*, 2011, **30**, 669; (c) M. Sun, Q. Wu, W. Gao and Y. Mu, *J. Organomet. Chem.*, 2015, **779**, 67.
- 16 (a) J. Liu, P. Tao, Y. Wang and Y. Li, *RSC Adv.*, 2014, **4**, 19433; (b) P. Tao, H. Mu, J. Liu and Y. Li, *J. Organomet. Chem.*, 2015, **798**, 422.
- 17 (a) Y. Huang and G. Jin, *Dalton Trans.*, 2009, 767; (b) Y. Huang, W. Yu and G. Jin, *Organometallics*, 2009, **28**, 4170.
- 18 Y. Liang, G. P. A. Yap, A. L. Rheingold and K. H. Theopold, *Organometallics*, 1996, **15**, 5284.
- 19 A. Döhring, J. Göhre, P. W. Jolly, B. Kryger, J. Rust and G. P. J. Verhovnik, *Organometallics*, 2000, **19**, 388.
- 20 (a) R. Emrich, O. Heinemann, P. W. Jolly, C. Krüger and G. P. J. Verhovnik, *Organometallics*, 1997, **16**, 1511; (b) A. Döhring, V. R. Jensen, P. W. Jolly, W. Thiel and J. C. Weber, *Organometallics*, 2001, **20**, 2234; (c) A. Döhring, V. R. Jensen, P. W. Jolly, W. Thiel and J. C. Weber, *Macromol. Symp.*, 2001, **173**, 117.
- 21 M. Enders, P. Fernandez, G. Ludwig and H. Pritzkow, *Organometallics*, 2001, **20**, 5005.
- 22 L. Zhang, W. Gao, X. Tao, Q. Wu, Y. Mu and L. Ye, *Organometallics*, 2010, **30**, 433.
- 23 D. Sieb, R. W. Baker, H. Wadepohl and M. Enders, *Organometallics*, 2012, **31**, 7368.
- 24 S. Randoll, P. G. Jones and M. Tamm, *Organometallics*, 2008, **27**, 3232.
- 25 H. Zhang, J. Ma, Y. Qian and J. Huang, *Organometallics*, 2004, **24**, 5681.
- 26 M. Ronellenfitsch, T. Gehrmann, H. Wadepohl and M. Enders, *Macromolecules*, 2017, **50**, 35.
- 27 R. Zhao, J. Ma, H. Zhang and J. Huang, *Molecules*, 2017, **22**, 856.
- 28 (a) X. Tao, Q. Wu, H. Huo, W. Gao and Y. Mu, *Organometallics*, 2013, **32**, 4185; (b) X. Tao, W. Gao, H. Huo and Y. Mu, *Organometallics*, 2013, **32**, 1287.
- 29 (a) I. Y. Skobelev, V. N. Panchenko, O. Y. Lyakin, K. P. Bryliakov, V. A. Zakharov and E. P. Talsi, *Organometallics*, 2010, **29**, 2943; (b) A. Brückner, J. K. Jabor, A. E. C. McConnell and P. B. Webb, *Organometallics*, 2008, **27**, 3849.
- 30 (a) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (b) J. Loliger and R. Scheffold, *J. Chem. Educ.*, 1972, **49**, 646; (c) S. K. Sur, *J. Magn. Reson.*, 1989, **82**, 169.
- 31 Y. Zhang, W. Yao, H. Li and Y. Mu, *Eur. J. Inorg. Chem.*, 2010, 3360.
- 32 M. P. McDaniel, E. D. Schwerdtfeger and M. D. Jensen, *J. Catal.*, 2014, **314**, 109.
- 33 J. C. Randall, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, 1989, **C29(2&3)**, 2034.
- 34 J.-H. So and P. Boudjouk, *Inorg. Chem.*, 1990, **29**, 1592.
- 35 *SMART and SAINT software packages*, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1996.