

Cationic scandium aminobenzyl complexes. Synthesis, structure and unprecedented catalysis of copolymerization of 1-hexene and dicyclopentadiene†

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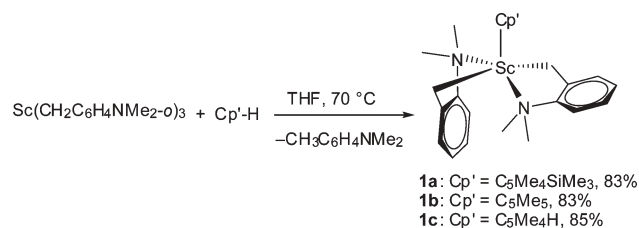
A structurally well-defined THF-free cationic half-sandwich scandium aminobenzyl complex serves as a novel catalyst for the first copolymerization of 1-hexene with dicyclopentadiene to give the random copolymers with a wide range of 1-hexene contents (32–70 mol%) unavailable previously.

Cationic rare earth metal alkyl complexes have received much current interest because of their unique catalytic activity in the polymerization and copolymerization of a variety of olefins.^{1,2} The alkyl ligands used for the cationic rare earth metal complexes reported so far in literature are commonly the η^1 -alkyl groups such as CH_2SiMe_3 ,^{2*a-i,3*} $\text{CH}(\text{SiMe}_3)_2$,⁴ Me ,^{2*k,5*} and CH_2Ph ,⁶ which usually require Lewis base ligands such as THF to stabilize the highly unsaturated Lewis-acidic metal centers. However, the coordination of a strong Lewis base ligand to the metal center of a catalyst could hamper the access of an olefin monomer to the active metal site and thus severely decreases its activity. In contrast with the η^1 -alkyl groups, *ortho-N,N*-dimethylaminobenzyl ($\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2$ -*o*) can serve as a bidentate ligand for rare earth metal ions by formation of chelating bonds *via* both the benzyl and the amino groups, and could therefore lead more easily to the formation of the external-Lewis-base-free complexes. In principle, if the benzyl unit could initiate insertion of an olefin monomer, such a THF-free cationic aminobenzyl complex would show higher catalytic activity than that of the THF-containing alkyl analogues, because the aminobenzyl group would eventually get away from the active metal center after the insertion of more olefin monomers. However, although aminobenzyl rare earth metal complexes have been known for a long time,⁷ such a cationic complex has not been reported previously, and the potential of an aminobenzyl–rare-earth-metal bond for the reaction with an olefin monomer has remained unexplored to date,⁸ as far as we are aware. We report herein the synthesis and structural characterization of the first cationic aminobenzyl–rare-earth-metal complex, $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)(\kappa^2\text{-F-C}_6\text{F}_5)\text{B}(\text{C}_6\text{F}_5)_3$, and demonstrate for the first time that the chelating aminobenzyl group can serve as an excellent scaffold for the stabilization of the external-Lewis-base-free rare earth polymerization

precatalysts and effect polymerization reactions which are difficult to achieve by other catalysts.

The acid–base reaction between the scandium tris(aminobenzyl) complex $\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_3$ ^{7*a*} and 1 equiv. of $\text{Cp}'\text{H}$ in THF at 70 °C afforded in high yields the corresponding mono(cyclopentadienyl)scandium bis(aminobenzyl) complexes $[\text{Cp}'\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)_2]$ ($\text{Cp}' = \text{C}_5\text{Me}_4\text{SiMe}_3$ (**1a**), C_5Me_5 (**1b**), $\text{C}_5\text{Me}_4\text{H}$ (**1c**)) (Scheme 1). An X-ray diffraction study showed that the two aminobenzyl ligands in **1a** are all bonded to the metal center in a chelating fashion *via* both the benzyl CH_2 carbon atom and the amino unit (Fig. 1(a)). No THF ligand was observed, although this complex was prepared in a THF solution.

Addition of 1 equiv. of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**A**) to **1a** in $\text{C}_6\text{D}_5\text{Cl}$ at 25 °C yielded quantitatively the cationic mono(aminobenzyl) complex $(\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)(\kappa^2\text{-F-C}_6\text{F}_5)\text{B}(\text{C}_6\text{F}_5)_3$ (**2a**) (Scheme 2) with release of Me_2NPh and $\text{Me}_2\text{NC}_6\text{H}_4\text{Me-2}$ as monitored by ¹H NMR. Layering hexane on a reaction mixture (concentrated to *ca.* 1 mL) of **1a** and **A** in $\text{C}_6\text{H}_5\text{Cl}$ at 25 °C afforded colorless single crystals of **2a**. An X-ray diffraction study‡ revealed that **2a** is a contact ion pair, in which the $[\text{B}(\text{C}_6\text{F}_5)_4]$ anion is coordinated to the metal center in a $\kappa^2\text{-F}$ -fashion with two adjacent (*ortho* and *meta*) F atoms (Sc-F1 2.436(2) Å, Sc-F2 2.308(2) Å) (Fig. 1(b)). Because of the higher electron deficiency of the cationic metal center in **2a**, the bond distances of the Sc–Cp' bonds in **2a** (av. 2.434(3) Å) are much shorter than those in the neutral precursor **1a** (av. 2.539(2) Å), and so are the Sc–benzyl (**2a**: 2.195(3) Å, **1a**: 2.288(2) Å) and Sc–amino (**2a**: 2.300(3) Å, **1a**: 2.470(2) Å) bond distances. Moreover, interactions between the Sc center and two phenyl atoms (*ipso* and *ortho*) of the benzyl group are also observed in **2a** (Sc-C2 2.570(3) Å, Sc-C3 2.643(3) Å), while such interactions were absent in **1a**. Therefore, the Sc–C1–phenyl(C2) angle in **2a** (86.5(2)°) is significantly smaller than those in **1a** (103.0(1) and 105.3(1)°). To our knowledge, **2a** represents the first example of a structurally characterized cationic aminobenzyl–rare-earth-metal complex, and



Scheme 1 Synthesis of THF-free half-sandwich scandium bis(aminobenzyl) complexes.

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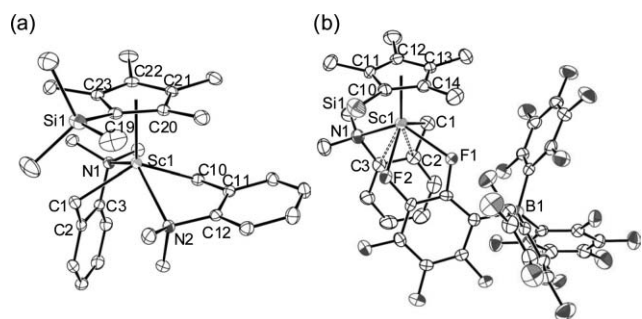
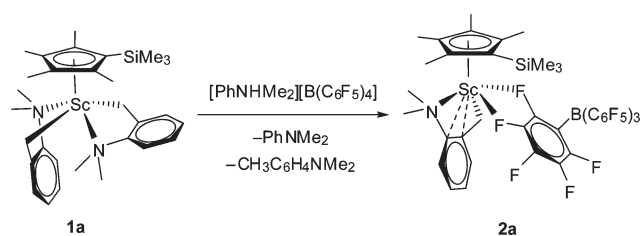


Fig. 1 ORTEP drawings of **1a** (a) and **2a** (b) with 30% thermal ellipsoids. The hydrogen atoms in **1a** and **2a** and the carbon atoms of the SiMe₃ group in **2a** are omitted for clarity. Selected bond lengths (Å) and angles (°): **1a**: Sc–C(1) 2.289(2), Sc–C(10) 2.287(2), Sc–N(1) 2.496(2), Sc–N(2) 2.443(2), Sc–Cp'(av.) 2.539(2); C(2)–C(1)–Sc(1) 103.0(1), C(11)–C(10)–Sc(1) 105.3(1); **2a**: Sc–C(1) 2.195(3), Sc–N(1) 2.300(3), Sc–F(1) 2.436(2), Sc–F(2) 2.308(2), Sc–C(2) 2.570(3), Sc–C(3) 2.643(3), Sc–Cp'(av.) 2.434(3); C(2)–C(1)–Sc(1) 86.5(2).



Scheme 2 Synthesis of a THF-free cationic half-sandwich scandium aminobenzyl complex.

also the first example of an external-Lewis-base-free cationic half-sandwich rare earth metal hydrocarbyl complex.^{5b,9}

In a C₆D₅Cl solution, the four C₆F₅ groups in **2a** showed one set of ¹⁹F NMR signals, suggesting that **2a** is highly fluxional, possibly due to the rapid dissociation and re-coordination of the [B(C₆F₅)₄] unit or the solvent molecule. This fluxionality was not fixed even at –45 °C, as shown by a variable-temperature ¹⁹F NMR study.

A preliminary study showed that the THF-free cationic aminobenzyl complex **2a** could initiate the polymerization of a variety of olefins such as ethylene, 1-hexene, styrene, norbornene (NB) and dicyclopentadiene (DCPD), demonstrating that even though in a chelating form, the dimethylaminobenzyl unit in **2a** is active enough for olefin insertion.¹⁰ More remarkably, **2a** could also copolymerize 1-hexene with norbornene and DCPD at room temperature to give the corresponding random copolymers. For these polymerization reactions, the use of the isolated cationic complex **2a** is not necessarily required. The 1 : 1 combination of **1a** with [PhNHMe₂H][B(C₆F₅)₄] (**A**) or [Ph₃C][B(C₆F₅)₄] (**B**) was also effective. Some representative results of the copolymerization of 1-hexene with DCPD are summarized in Table 1. It is noteworthy that the 1-hexene content in the copolymer products could be controlled in a broad range simply by changing the feed ratio of the co-monomers. For example, when the feed ratio of 1-hexene to DCPD was raised from 1 : 2 to 2 : 1, the 1-hexene content in the resulting copolymers increased from 38.4 to 70.0 mol% (Table 1, entries 7 and 10).

The copolymers all showed good solubility in THF and CHCl₃. The ¹³C NMR spectra suggest random distribution of the monomer moieties in the copolymer products (see ESI†). With respect to DCPD, the polymerization reaction took place only at the norbornene unit, while the cyclopentene C–C double bond remained unchanged, as shown by ¹H NMR. The GPC curves of the copolymers are all unimodal with moderate polydispersities (*M_w*/*M_n* = 1.55–1.87), consistent with the predominance of a homogeneous single-site catalytic species. The glass transition temperature (*T_g*) of the copolymers showed an almost linear correlation with the 1-hexene content (Fig. 2).

Selective polymerization or copolymerization of DCPD is usually difficult, because it requires a catalyst that is not only sufficiently active but can also distinguish the norbornene unit from the cyclopentene unit to prevent cross-linking side reactions.^{2f,11} This work represents the first example of copolymerization of an α-olefin with DCPD.

In summary, we have demonstrated that the bis(*ortho*-dimethylaminobenzyl) scandium complexes bearing mono(cyclopentadienyl)

Table 1 Copolymerization of 1-hexene and dicyclopentadiene by cationic half-sandwich scandium aminobenzyl complexes^a

Entry	Cat.	Act. ^b	H/mmol	DCPD/mmol	Yield/g	Act. ^c	H Cont. ^d /mol%	<i>M_n</i> ^e /10 ³	<i>M_w</i> / <i>M_n</i> ^e	<i>T_g</i> ^f /°C
1	2a	—	10.0	10.0	1.62	3.4	48.2	1.5	1.62	140
2	1a	A	10.0	10.0	1.40	2.9	46.1	1.5	1.55	152
3	1a	B	10.0	10.0	1.80	3.8	52.7	1.4	1.60	116
4	1b	B	10.0	10.0	1.37	2.9	40.9	1.6	1.55	176
5	1c	B	10.0	10.0	1.18	2.5	31.9	1.8	1.73	337
6	1a	B	20.0	—	1.50	3.1	100	3.5	1.70	–51
7	1a	B	13.3	6.7	1.67	3.5	70.0	1.3	1.68	9
8	1a	B	11.4	8.6	1.61	3.4	59.8	1.3	1.57	74
9	1a	B	8.6	11.4	1.82	3.8	44.1	1.7	1.70	177
10	1a	B	6.7	13.3	1.87	3.9	38.4	2.2	1.87	210
11	1a	B	—	20.0	0.24	0.5	0	—	—	359

^a Conditions: 40 μmol Sc complex, 40 μmol activator, 5 mL of toluene, 25 °C, 12 h. ^b Activator: **A** = [PhNHMe₂H][B(C₆F₅)₄], **B** = [Ph₃C][B(C₆F₅)₄]. ^c Activity in kg (copolymer) mol(Sc)^{–1} h^{–1}. ^d Determined by ¹³C NMR. ^e Determined by GPC in THF at 40 °C against polystyrene standard. ^f Measured by DSC.

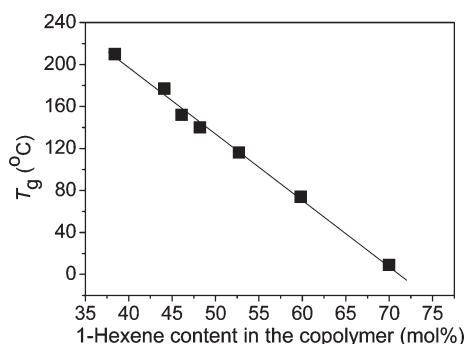


Fig. 2 Plot of 1-hexene content vs. T_g of the 1-hexene-DCPD copolymers obtained in Table 1 (entries 1–3, 7–10).

ligands (**1a–c**) can be easily prepared by reaction of the tris(aminobenzyl) scandium complexes with the corresponding cyclopentadiene ligands. Because of the intramolecular coordination of the amino group, external Lewis bases (such as THF) are not required for the stabilization of the highly Lewis-acidic metal center. This has enabled the isolation and structural characterization of the THF-free cationic aminobenzyl–scandium complex **2a**, the first example of an external-Lewis-base-free cationic half-sandwich rare earth metal hydrocarbyl complex. More remarkably, the aminobenzyl group in **2a**, even though in a chelating form, is active enough to initiate olefin polymerization. Because of the absence of an external Lewis base and the sufficient activity of the benzyl unit, **2a** or **1a**/[Ph₃C][B(C₆F₅)₄] showed unprecedented catalytic activity for the copolymerization of 1-hexene with DCPD to afford the copolymer materials unavailable previously. Studies on the aminobenzyl complexes with other ancillary ligands and other rare earth metals are in progress.

Notes and references

† Crystallographic data for **1a**: C₃₀H₄₅N₂ScSi, $M_w = 506.73$, $T = 173(2)$ K, triclinic, space group $P\bar{1}$, $a = 10.299(2)$, $b = 10.594(2)$, $c = 13.624(3)$ Å, $\alpha = 91.641(3)^\circ$, $\beta = 95.407(2)^\circ$, $\gamma = 106.911(2)^\circ$, $V = 1413.3(5)$ Å³, $Z = 2$, $D_c = 1.191$ Mg m⁻³, $\mu = 0.323$ mm⁻¹, reflections collected: 7426, independent reflections: 4888 ($R_{int} = 0.0235$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0399$, $wR_2 = 0.0879$, R indices (all data): $R_1 = 0.0559$, $wR_2 = 0.0928$; **2a**: C₄₅H₃₃BF₂₀N₂ScSi, $M_w = 1051.58$, $T = 173(2)$ K, orthorhombic, space group $Pna2_1/c$, $a = 17.823(4)$, $b = 10.479(3)$, $c = 23.866(6)$ Å, $V = 4457.2(19)$ Å³, $Z = 4$, $D_c = 1.567$ Mg m⁻³, $\mu = 0.311$ mm⁻¹, reflections collected: 22032, independent reflections: 7718 ($R_{int} = 0.0404$), Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0344$, $wR_2 = 0.0363$, R indices (all data): $R_1 = 0.0695$, $wR_2 = 0.0400$. CCDC 637040 (**1a**), 637041 (**1b**), 637042 (**1c**) and –637043 (**2a**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b708534f

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