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Scandium alkyl complex with phosphinimino-amine ligand: Synthesis, structure and catalysis on ethylene polymerization†

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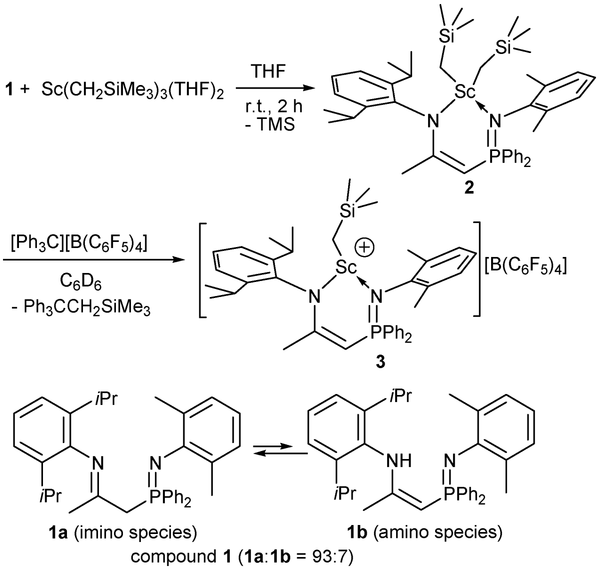
The THF-free scandium dialkyl complex LSc(CH_2SiMe_3)$_2$ (L = (2,6-*i*$Pr_2C_6H_3$)NC(Me)$CHPPh_2N$(2,6-$Me_2C_6H_3$)) bearing the phosphinimino-amine ligand was prepared, which under the activation of [Ph_3C][$B(C_6F_5)_4$] initiated the polymerization of ethylene with high activity.

Polyethylene is the largest volume synthetic polymer used in the world and has been almost applied in every aspect of our daily lives, such as packaging materials, pipes, textiles, *etc.* For the past half a century, polymerization of ethylene has remained one of the most attractive research subjects in both academic and industrial fields. During this period the development of catalysts plays a significant role in the great success of polyethylene, for instance the Ziegler–Natta catalysts, metallocene catalysts and post-metallocene catalysts which can produce polyethylene with versatile architectures.[1] Noteworthy is that these catalysts are mainly based on transition metals or late-transition metals,[2] comparatively those based on rare-earth metals have been explored less.[3] In fact, rare-earth metal complexes have exhibited distinguished catalytic activities towards the regio- and stereo-selective polymerization of conjugated dienes and polar monomers.[4] Therefore, to improve their catalytic activity towards the polymerization of ethylene *via* proper design of ligands is an obviously interesting and challenging project. Recently, rare-earth metal complexes bearing mono- and dicyclopentadienyl (Cp) ligands have been reported to show distinguished activities for the polymerization of ethylene.[5] In the meantime non-Cp ligands supported rare-earth metal complexes also attract increasing attention, because such ligands are easily prepared and swiftly modified by changing the substituents and backbone, which allow fine tuning of the electronics and sterics of complexes and their catalytic behaviour.[6] Of these non-Cp ligated complexes, the N-type amino and imino ligands stabilized rare-earth metal alkyl complexes[6a–6g] have exhibited moderate to high activities (10^4–10^6 g(PE) mol^{-1} h^{-1} bar^{-1}), respectively. Herein we report a new N-type ligand (**1**), phosphinimino-amine (2,6-*i*$Pr_2C_6H_3$)NHC(Me)$CHPPh_2N$(2,6-$Me_2C_6H_3$), where the "large" and "soft" phosphino moiety is introduced to the "nacnac" framework,[7] anticipated to increase the spatial bulkiness around the central metal and lower the electron density of the rare-earth metal center. Treatment of ligand **1** with scandium tris(alkyl)s gave solvent-free complex **2**,‡ LSc(CH_2SiMe_3)$_2$ (L = (2,6-*i*$Pr_2C_6H_3$)NC(Me)$CHPPh_2N$(2,6-$Me_2C_6H_3$)) *via* alkane elimination. **2** could be activated with [Ph_3C][$B(C_6F_5)_4$] to catalyze ethylene polymerization under mild conditions with a high catalytic activity up to 2 × 10^6 g(PE) mol^{-1} h^{-1} bar^{-1}.

Compound **1** was prepared according to the method reported previously by Stephan, which exists in imino (**1a**) and amino (**1b**) isomers in a ratio of 93 : 7.[8] Noteworthy was that only the amino isomer **1b** can directly react with rare-earth metal tris(alkyl)s through the alkyl abstraction by the amino proton (Scheme 1). Therefore the reaction between **1** and a slightly excess amount (1.2 equiv.) of Sc(CH_2SiMe_3)$_3$(THF)$_2$ was performed in benzene-d_6 at room temperature (1 h) and monitored by ^1H NMR spectroscopy. The result revealed that **1b** was consumed to generate complex **2** and the imino isomer **1a** shifted to **1b** gradually with the reaction going on. Thus, large scale preparation of complex **2** was carried out in THF at room temperature for 2 h and gave a moderate yield (58%). Colorless single crystals grew from a yellowish solution of mixed hexane and THF at −30 °C within several days. The ^1H NMR spectrum of **2** showed that the methylene protons of LSc(CH_2SiMe_3)$_2$ are inequivalent displaying interesting resonances of AB spin system in the upfield regions: δ 0.51 ppm and δ 0.32 ppm ($^2J_{HH}$ = 10.8 Hz).[9] THF resonances were not observed, suggesting that the THF molecule was eliminated from the central metal coordination sphere. It is known that isolation of rare-earth metal dialkyl complexes usually encounter salt-addition, dimerization or ligand redistribution *etc.* side reactions due to the highly active character of the



Scheme 1

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metal–carbon bonds and relatively less crowded steric environment of the molecules.[10] Therefore the successful isolation of solvent-free **2** was attributed to the more sterically bulky ligand **1**. The solid-state structure of complex **2** was determined by X-ray diffraction analysis to be a monomeric THF-free scandium dialkyl, in agreement with its solution-state structure (Fig. 1). The Sc^{3+} ion is chelated by a *N*,*N*-bidentate ligand and two *cis*-positioned alkyl groups, generating a four-coordinate tetrahedral geometry. The bond lengths of Sc–C(1) (2.237(2) Å) and Sc–C(2) (2.199(2) Å) and the bond angle of C(2)–Sc–C(1) (111.95(8)°) fall in the normal range observed in other scandium dialkyl complexes,[11] however, the bond angle of N(2)–Sc–N(1), 98.39(6)°, is, somewhat larger than that (such as 90.71(4)°) in the "nacnac" ligated scandium dialkyl complexes.[11a] In addition, the backbone of phosphinimino-amine is not co-planar compared to the generally planar "nacnac", suggesting that the introduction of the phosphino moiety increases the steric bulkiness.

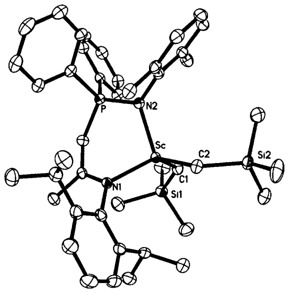

Fig. 1 Molecular structure of **2**. Thermal ellipsoids are set at 30% probability. (Hydrogen atoms omitted for clarity, unlabeled atoms are carbon). Selected bond lengths (Å) and angles (°): Sc–N(2) 2.1113(16), Sc–N(1) 2.1316(16), Sc–C(1) 2.237(2), Sc–C(2) 2.199(2); N(2)–Sc–N(1) 98.39(6), N(2)–Sc–C(2) 106.27(7), N(1)–Sc–C(1) 122.19(7), C(2)–Sc–C(1) 111.95(8).

Hessen reported that complex $[PhC(2,6\text{-}iPr_2C_6H_3N)_2]Y(CH_2SiMe_3)_2(THF)$ displayed a much higher catalytic activity for the polymerization of ethylene than its two-THF solvated counterpart.[6b] Therefore this non-solvated complex **2** was anticipated to polymerize ethylene with a high activity. Upon activation with an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ complex **2** indeed initiated the polymerization of ethylene. The selected polymerization results obtained under various conditions in toluene were listed in Table 1. Under the conditions of 1 bar ethylene atmosphere and room temperature (25 °C), with the polymerization time prolonging from 1 min to 10 min, the yield of polyethylene increased. Meanwhile, the molecular weight (M_w) increased correspondingly from 5.88 × 10^4 to 13.17 × 10^4, and the polydispersity (M_w/M_n) remained around 2.0. The catalytic activity of the system varied from 0.95 × 10^6 g(PE) mol^{-1} h^{-1} bar^{-1} up to 2 × 10^6 g(PE) mol^{-1} h^{-1} bar^{-1}, which was comparable to the best catalytic system based on rare-earth metals reported to date. In order to improve the activity, 50 equivalent of Al*i*Bu_3 was added into the above catalyst system. Unfortunately, a trace amount of polyethylene was isolated. When the activator was switched to $[PhNMe_2H][B(C_6F_5)_4]$, the polymerization was performed for 5 min to afford 0.38 g polyethylene with a decreased activity of 0.45 × 10^6 g(PE) mol^{-1} h^{-1} bar^{-1} (Table 1, run 6). When organoborane $B(C_6F_5)_3$ was used instead of $[Ph_3C][B(C_6F_5)_4]$, the polymerization became sluggish (0.05 × 10^6 g(PE) mol^{-1} h^{-1} bar^{-1}) (Table 1, run 7). As MAO was widely applied as an activator, we also attempted to employ MAO to replace $[Ph_3C][B(C_6F_5)_4]$, whereas, no polymerization was observed at all (Table 1, run 8), which was in contrast to the system composed of $[(2,6\text{-}iPr_2C_6H_3)NC(tBu)CHC(tBu)N(2,6\text{-}iPr_2C_6H_3)ScMe_2]$, in which MAO could efficiently increase the polymerization rate.[6g]

Table 1 Catalytic ethylene polymerization under various conditions[a]

Run	Time (min)	Yield (g)	Activity (10^6 g(PE) mol^{-1} h^{-1} bar^{-1})	M_w[g] (10^4)	M_w/M_n[g]
1	1	0.41	2.46	5.88	2.5
2	3	0.63	1.26	9.02	2.2
3	5	0.79	0.95	9.44	1.9
4[b]	10	1.11	0.66	13.17	2.3
5[c]	30	trace	—	—	—
6[d]	5	0.38	0.45	15.79	2.1
7[e]	30	0.24	0.05	8.44	2.2
8[f]	30	—	—	—	—

[a] *Conditions*: catalyst **2** 10 μmol, co-catalyst $[Ph_3C][B(C_6F_5)_4]$ 10 μmol, toluene 10 mL, 25 °C, ethylene pressure 1 bar. [b] Toluene 50 mL. [c] Co-catalyst $[Ph_3C][B(C_6F_5)_4]$ 10 μmol, Al*i*Bu_3 50 μmol. [d] Co-catalyst $[PhNMe_2H][B(C_6F_5)_4]$ 10 μmol. [e] Co-catalyst $B(C_6F_5)_3$ 10 μmol. [f] Co-catalyst MAO 3.0 mmol. [g] Determined by GPC in 1,2,4-trichlorobenzene *versus* polystyrene standard at 150 °C.

The characterization of active species for any polymerizations is an important topic, which facilitates further investigation of the mechanisms and modification of the catalytic performances of the existent catalyst systems and design of new ones. In order to investigate the actual initiating species of the present catalyst system, we tried to isolate the single crystal from the system but failed, unfortunately. However, monitoring the *in situ* reaction of complex **2** with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ in C_6D_6 by ^1H, ^{11}B, ^{19}F and ^{31}P NMR spectroscopy provided useful information about the generation of the active species.[12] In the ^1H NMR spectrum, compared with complex **2**, the disappearance of resonance signals of one $ScCH_2SiMe_3$ species could be observed and the chemical shifts of ligand remained almost unchanged; several signals arising from $Ph_3CCH_2SiMe_3$,[13] were similar to the product isolated from the reaction of Ph_3CCl with $LiCH_2SiMe_3$. Therefore the cationic monoalkyl species **3**, $[LScCH_2SiMe_3][B(C_6F_5)_4]$, was speculated to be generated.[6c,14] The ^{31}P signal of **3** (δ 21.13 ppm) shifted downfield compared with that of complex **2** (δ 16.00 ppm), owing to the cationic central metal of **3**. ^{11}B and ^{19}F NMR spectra of **3** remained similar in pattern to that of $[Ph_3C][B(C_6F_5)_4]$, suggesting that the anionic part of **3** was a non-coordinated anion $[B(C_6F_5)_4]^-$. This is different from the previously reported reaction between rare-earth metal alkyl complexes with organoborane in which the abstraction of a methyl group from a silicon moiety and a migration reaction giving cationic species $ScCH_2Si(Me_2)\text{-}CH_2SiMe_3$ takes place.[15]

In summary, the phosphinimino-amine ligand provides indeed a suitable coordination environment for the stability of the scandium dialkyl species. Upon activation with $[Ph_3C][B(C_6F_5)_4]$, this new scandium dialkyl complex can be converted into a cationic monoalkyl species which shows an up to 10^6 g(PE) mol^{-1} h^{-1} bar^{-1} catalytic activity for the polymerization of ethylene under mild conditions.

Acknowledgements

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Notes and references

‡ *Crystallographic data for* **2**: $C_{43}H_{62}N_2PScSi_2$, $M = 739.06$, monoclinic, space group $P2_1/c$, $a = 12.2513(7)$ Å, $b = 21.0117(12)$ Å, $c = 17.6635(10)$ Å, $\alpha = 90°$, $\beta = 107.6920(10)°$, $\gamma = 90°$, $V = 4331.9(4)$ Å^3, $t = -88$ °C, $Z = 4$, $D_c = 1.133$ g cm^{-3}, $\mu = 2.92$ cm^{-1}, $R_{int} = 0.0271$, GOF = 1.037, $R = 0.0438$, $R_w = 0.1064$, R (all data) = 0.0543, R_w (all data) = 0.1135, no. of reflections collected = 24125, no. of unique reflections = 8515. CCDC 780645.

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8 (*a*) J. D. Masuda, P. Wei and D. W. Stephan, *Dalton Trans.*, 2003, 3500; (*b*) *Selected NMR data* for **1**: ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, major isomer **1a**): δ 7.85 (m, 4H, *o*-PPh_2), 3.77 (d, $^2J_{P-H} = 14.0$ Hz, 2H, $PC\mathit{H}_2$), 2.78 (m, 2H, $C_6H_3(C\mathit{H}Me_2)_2$), 2.51 (s, 6H, $C_6H_3(C\mathit{H}_3)_2$), 1.62 (s, 3H, $NCC\mathit{H}_3$), 1.16 (quart, $^3J_{H-H} = 7.0$ Hz, 12H, $C_6H_3(CH(C\mathit{H}_3)_2)_2$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, 25 °C, major isomer **1a**):δ 165.30 (d, $^2J_{P-C} = 6.0$ Hz, 1C, $N\mathit{C}$), 45.62 (d, $J_{P-C} = 60.0$ Hz, 1C, $P\mathit{C}H_2$), 27.73 (s, 2C, $C_6H_3(\mathit{C}HMe_2)_2$), 24.75 (s, 1C, $NC\mathit{C}H_3$), 23.69 (s, 2C, $C_6H_3(CH(\mathit{C}H_3)_2)_2$), 23.31 (s, 2C, $C_6H_3(CH(\mathit{C}H_3)_2)_2$), 21.75 (s, 2C, $C_6H_3(\mathit{C}H_3)_2$) ppm. ^{31}P NMR (400 MHz, C_6D_6, 25 °C, H_3PO_4 was used as standard): δ −3.55, −15.48 ppm. Anal. Calcd for $C_{35}H_{41}N_2P$ (%): C, 80.73; H, 7.94; N, 5.38. Found: C, 80.94; H, 7.97; N, 5.36%.

9 *Selected NMR data* for **2** $LSc(CH_2SiMe_3)_2$: ^{1}H NMR (600 MH$_Z$, C_6D_6, 25 °C): δ 7.66 (br, 4H, *o*-PPh_2), 3.64 (m, 2H, $^3J_{H-H} = 6.6$ Hz $C\mathit{H}(CH_3)_2$), 3.21 (d, 1H, $^2J_{P-H} = 12.0$ Hz, $C\mathit{H}PPh_2$), 2.04 (s, 6H, $C_6H_3(C\mathit{H}_3)_2$), 1.87 (s, 3H, $CC\mathit{H}_3$), 1.42 (d, 6H, $^3J_{H-H} = 6.0$ Hz, $CH(C\mathit{H}_3)_2$), 1.38 (d, 6H, $^3J_{H-H} = 6.0$ Hz, $CH(C\mathit{H}_3)_2$), 0.51 and 0.32 (AB, 4H, $^2J_{H-H} = 10.8$ Hz, $C\mathit{H}_2SiMe_3$), 0.31 (s, 18H, $Si(C\mathit{H}_3)_3$) ppm. ^{13}C {^{1}H} NMR (150 MHz, C_6D_6, 25 °C):δ 175.04 (s, 1C, $N\mathit{C}$), 55.27 (d, $J_{P-C} = 127.5$ Hz, 1C, $\mathit{C}HP$), 44.31 (s, 1C, $\mathit{C}H_2SiMe_3$), 28.79 (s, 2C, $\mathit{C}H(CH_3)_2$), 25.60 (s, 4C, $CH(\mathit{C}H_3)_2$), 25.31 (s, 1C, $C\mathit{C}H_3$), 21.11 (s, 2C, $C_6H_3(\mathit{C}H_3)_2$), 3.68 (s, 1C, $Si(C\mathit{H}_3)_3$) ppm. ^{31}P NMR (400 MH$_Z$, C_6D_6, 25 °C, H_3PO_4 was used as standard)δ 16.0 ppm. Anal. Calcd for $C_{43}H_{62}N_2PScSi_2$ (%) C, 69.88; H, 8.46; N, 3.79. Found: C, 70.03; H, 8.48; N, 3.78.

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12 $[Ph_3C][B(C_6F_5)_4]$ (4.8 mg, 5.0 μmol) was dissolved in C_6D_6 (0.5 mL) and the resulting yellow solution was added to solution of **2** (3.8 mg, 5.0 μmol). The orange solution was formed and added to an NMR tube, sealed, and analyzed *in situ*. *Selected ^{1}H NMR data* for **3** $[LScCH_2SiMe_3][B(C_6F_5)_4]$: ^{1}H NMR (300 MH$_Z$, C_6D_6, 25 °C): δ 7.64 (br, 4H, *o*-PPh_2), 3.63 (m, 2H, $^3J_{H-H} = 6.9$ Hz $C\mathit{H}(CH_3)_2$), 3.19 (br, 1H, $C\mathit{H}PPh_2$), 2.03 (br, 6H, $C_6H_3(C\mathit{H}_3)_2$), 1.84 (br, 3H, $CC\mathit{H}_3$), 1.39 (quart, 12H, $^3J_{H-H} = 6.0$ Hz, $CH(C\mathit{H}_3)_2$), 0.51 (br, 2H, $C\mathit{H}_2SiMe_3$), 0.31 (br, 9H, $Si(C\mathit{H}_3)_3$) ppm. The ^{11}B NMR data for compound **3** and trityl borate were detected by Bruker AV300 spectrometer and $BF_3 \cdot Et_2O$ was used as external standard (0.00 ppm) in C_6D_6. The signal of **3** was at δ −16.62 ppm which changed little compared with that of trityl borate (δ −16.80 ppm). The ^{19}F NMR data for compound **3** and trityl borate were detected by Bruker AV300 spectrometer and $BF_3 \cdot Et_2O$ was used as external standard (0.00 ppm) in C_6D_6. The signals of **3** were at δ −56.01, −86.64 and −90.47 ppm which changed little compared with that of trityl borate (δ −56.16, −86.60 and −90.56 ppm). The ^{31}P NMR datum of **3** (δ 21.13 ppm) was detected by Bruker AV400 spectrometer and H_3PO_4 was used as external standard (0.00 ppm) in C_6D_6.

13 The formation of $Ph_3CCH_2SiMe_3$ was confirmed by the ^{1}H NMR spectrum of a sample prepared from Ph_3CCl and $LiCH_2SiMe_3$ in C_6D_6. Ph_3CCl (1.4 mg, 5.0μmol) was dissolved in C_6D_6 (0.5 mL) and the resulting yellow solution was added to solid $LiCH_2SiMe_3$ (0.5 mg, 5.0μmol). The light orange solution was added to an NMR tube, sealed, and analyzed *in situ* by Bruker AV300 spectrometer.

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