Efficient Ethylene Polymerization

Homogeneous Ethylene-Polymerization Catalysts Based on Alkyl Cations of the Rare-Earth Metals: Are Dicationic Mono(alkyl) Complexes the Active Species?**

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Cationic alkyl complexes of Group 4 metals, for example, alkyl zirconocenium ions, currently play a pivotal role as single-site catalysts in homogeneous olefin-polymerization reactions.[1] The first cationic alkyl rare earth metal complex $[La(\eta^5\text{-}C_5Me_5)\{CH(SiMe_3)_2\}(thf)_x]^+[BPh_4]^-$ ($x = 0$ or 3) was reported in 1992,[2a] and since then, there has only been one report with evidence that such a complex, a scandium dimethyl cation, polymerizes ethylene.[2b] A number of cationic alkyl complexes of the rare-earth metals $[Ln(L)R]^+$ supported by monoanionic ancillary noncyclopentadienyl ligands L, such as the amido-functionalized triazacyclononane,[3] β-diketiminate,[4] or benzamidinate[5] were surmised to also catalyze ethylene polymerization. We reported that the thermally sensitive tris(trimethylsilylmethyl) complexes $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Lu, Y)[6] can be transformed into robust monocationic bis(alkyl) complexes $[Ln(CH_2SiMe_3)_2(thf)_x]^+$ by the reaction with BPh_3.[7] Herein we report that the tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(thf)_2]$ without any ancillary ligand L can act as precursors for highly active catalysts for homogeneous ethylene polymerization. There is evidence that the active species are the dications $[Ln(CH_2SiMe_3)(solv)_z]^{2+}$, which are formed by the protonolysis of $[Ln(CH_2SiMe_3)_3(thf)_2]$ via the dialkyl monocations $[Ln(CH_2SiMe_3)_2(solv)_y]^+$.

Toluene solutions of the alkyl complexes $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Tm, Er, Y, Ho, Dy, Tb) efficiently catalyze ethylene polymerization upon activation with the Brønsted acid $[NMe_2HPh][B(C_6F_5)_4]$ in the presence of $Al\textit{i}Bu_3$. After short run times (10 min) at 5 bar of ethylene pressure, linear polyethylenes with molecular weights $\bar{M}_n = 3500\text{–}45\,000$ and polydispersities $\bar{M}_w/\bar{M}_n = 2\text{–}6$ were produced with activities up to 899 $kg\,mol^{-1}\,h^{-1}\,bar^{-1}$ (Table 1). As illustrated in Figure 1, the catalyst performance can be adjusted by the choice of the rare-earth metal as the activity is well correlated

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Table 1: Ethylene polymerization with $[Ln(CH_2SiMe_3)_3(thf)_2]$ as catalyst precursor.[a]

Ln	R[b] [Å]	Yield [g]	Activity [kg mol^{-1} h^{-1} bar^{-1}]	$\bar{M}_n$ [g mol^{-1}]	$\bar{M}_w/\bar{M}_n$	T_m [°C]
Sc[c]	0.89	0.03	1	–	–	–
Lu[c]	1.00	traces	–	–	–	–
Yb	1.01	–	–	–	–	–
Tm	1.02	0.76	183	22033	4.1	136.7
Er	1.03	0.85	205	13430	5.3	134.7
Y[d]	1.04	0.91	272	14150	2.9	135.5
Ho	1.04	1.15	275	44847 3446[e]	1.7 1.8	132.5
Dy	1.05	3.51	842	3652	3.6	126.3
Tb	1.06	3.74	899	3816	2.9	126.3

[a] $[NMe_2HPh][B(C_6F_5)_4]$ as activator in the presence of $AliBu_3$. Conditions: 5 μmol Ln; B:Ln = 5:1, Al:Ln = 200:1, T = 25 °C, p = 5 bar, t = 10 min, V = 30 mL (toluene). [b] Effective ionic radius of Ln^{3+} for $CN = 6$, see reference [8]. [c] t = 60 min. [d] t = 8 min. [e] Bimodal molecular weight distribution.

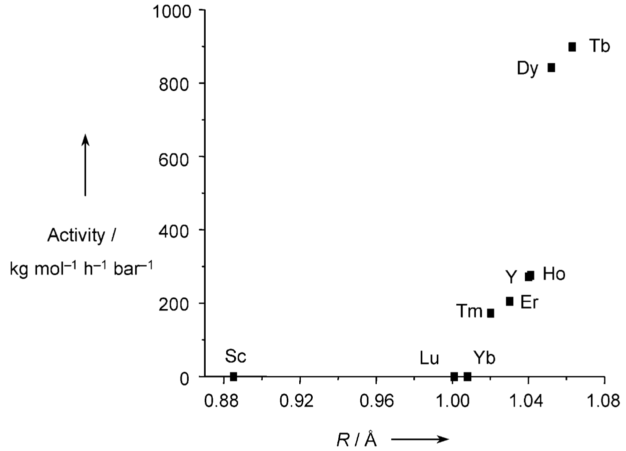
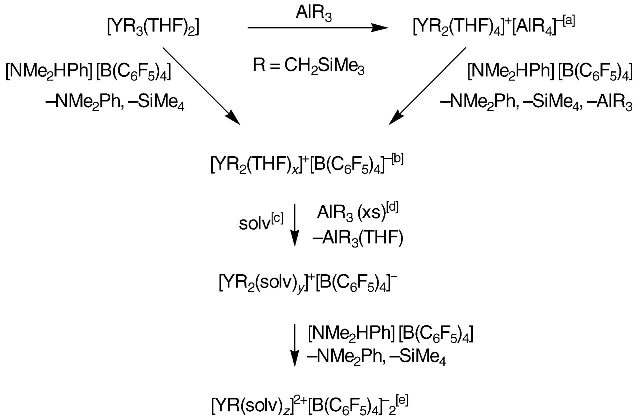


Figure 1. Plot of the polymerization activity versus the effective ionic radius R of the trivalent rare earth metal for coordination number $CN = 6$.



Scheme 1. Activation of $[Y(CH_2SiMe_3)_3(thf)_2]$ with $[NMe_2HPh][B(C_6F_5)_4]$ in the presence of $Al(CH_2SiMe_3)_3$; [a] isolated, [b] analogous complex isolated as $[Y(CH_2SiMe_3)_2(thf)_4]^+[BPh_4]^-$, [c] solv = toluene in polymerization experiments, the exchange of THF by toluene is postulated,[11] [d] xs = excess, [e] analogous complex isolated as $[Y(CH_2SiMe_3)(thf)_5]^{2+}[BPh_4]^-{}_2$.

with the effective ionic radius[8] of the rare-earth metal. For the smaller elements scandium, lutetium, and ytterbium, no significant activity was observed, whereas thulium produced polyethylene with 183 kg mol^{-1} h^{-1} bar^{-1}. For terbium, the element with the largest radius within the series examined, an activity of 899 kg mol^{-1} h^{-1} bar^{-1} was found, corroborating that rare-earth metal alkyl cations are the active species.[9] Although the active species initially appeared to be the monocationic bis(alkyl) complex $[Ln(CH_2SiMe_3)_2(solv)_y]^+[B(C_6F_5)_4]^-$ (Scheme 1), with aluminum alkyl acting as scavenger for THF, two findings cast doubts on this hypothesis. 1) Why is an excess of $[NMe_2HPh][B(C_6F_5)_4]$ necessary to activate the catalyst precursor?[10] 2) Why does the choice of the aluminum alkyl have a significant influence on the polymerization results?[11] We therefore studied the following (Scheme 1) as model reactions for the activation steps: 1) The reaction of $[Y(CH_2SiMe_3)_3(thf)_2]$ with excess $[NMe_2HPh][BPh_4]$. 2) The reactivity of $[Y(CH_2SiMe_3)_3(thf)_2]$ towards the aluminum alkyl $Al(CH_2SiMe_3)_3$. For these preparative-scale and NMR-tube experiments, the use of the polar solvents pyridine or THF was required, as oils form from aromatic hydrocarbons such as toluene, benzene, or bromobenzene. To avoid ring opening polymerization of THF, the use of $[BPh_4]^-$ instead of $[B(C_6F_5)_4]^-$ as the counter anion was required when THF was used as solvent.

When a THF solution containing the yttrium tris(alkyl) $[Y(CH_2SiMe_3)_3(thf)_2]$ and three equivalents of $[NMe_2HPh][BPh_4]$ was stirred for 24 h at 25 °C, colorless microcrystals of the thermally robust dicationic alkyl complex $[Y(CH_2SiMe_3)(thf)_5]^{2+}[BPh_4]^-{}_2$ were isolated in virtually quantitative yield.[12] In [D$_5$]pyridine, the methylene protons at yttrium appear as a doublet at $\delta = 0.73$ ppm with $^2J(Y,H) = 3.3$ Hz in the corresponding ^{1}H NMR, while the ^{13}C NMR spectrum exhibits a doublet for the YCH_2 group at $\delta = 44.5$ with $^1J(Y,C) = 44.9$ Hz. The ^{89}Y NMR resonance of $[Y(CH_2SiMe_3)(thf)_5]^{2+}[BPh_4]^-{}_2$ in [D$_8$]THF at $\delta = 409.2$ is shifted to a significantly higher field compared with that for the corresponding monocations $[Y(CH_2SiMe_3)_2(thf)_4]^+[Al(CH_2SiMe_3)_4]^-$ ($\delta = 666.4$,), $[Y(CH_2SiMe_3)_2(thf)_4]^+[BPh_4]^-$ ($\delta = 660.0$) or the neutral analogue $[Y(CH_2SiMe_3)_3(thf)_2]$ ($\delta = 882.7$).

The reaction of $[Y(CH_2SiMe_3)_3(thf)_2]$ in THF with more than two equivalents $[NMe_2HPh][BPh_4]$ to give the dication $[Y(CH_2SiMe_3)(thf)_5]^{2+}[BPh_4]^-{}_2$ as the exclusive yttrium-containing species suggests that the activation of the tris(alkyl) precursors $[Ln(CH_2SiMe_3)_3(thf)_2]$ in toluene with $[NMe_2HPh][B(C_6F_5)_4]$ generates dications $[Ln(CH_2SiMe_3)(solv)_z]^{2+}$ as the active species.[13] When the tris(aluminate) $[Y\{(\mu\text{-}Me_2)(AlMe_2)\}_3]$[14] was treated with excess $[NEt_3H][BPh_4]$ in THF, the ion triple $[Y(CH_3)(THF)_6]^{2+}[BPh_4]^-{}_2$ was obtained in crystalline form [Eq. (1)].[15] The resonance of the methyl

$$[Y\{(\mu\text{-}Me_2)(AlMe_2)\}_3] \xrightarrow[\text{THF}]{2\,[NEt_3H][BPh_4]} [Y(CH_3)(thf)_6]^{2+}[BPh_4]_2^- + 2\,NEt_3 + 2\,CH_4 + 3\,AlMe_3 \qquad (1)$$

group at the yttrium appears as a doublet in [D$_5$]pyridine at $\delta = 0.69$ with $^2J(Y,H) = 2.1$ Hz. The ^{13}C NMR spectrum exhibits a doublet for the YCH_3 group at $\delta = 32.8$ with $^{1}J(Y,C) = 53.6$ Hz, while the ^{89}Y-NMR resonance appears at $\delta = 433.2$.

Single crystals $[Y(CH_3)(thf)_6]^{2+}[BPh_4]^{-}_2$ suitable for X-ray structure analysis were grown from a supersaturated THF solution.[15b] The cationic portion of the ion triple $[Y(CH_3)(thf)_6]^{2+}[BPh_4]^{-}_2$ is shown in Figure 2, which illustrates the pentagonal bipyramidal coordination geometry around the yttrium center with the methyl group in the apical position. The Y–C bond length of 2.418(3) Å is comparable with those found for the ion pair $[Y(CH_2SiMe_3)_2(thf)_4]^{+}[Al(CH_2SiMe_3)_4]^{-}$ (2.384(6) and 2.411(6) Å),[16] while the Y–O bond lengths of $[Y(CH_3)(thf)_6]^{2+}[BPh_4]^{-}_2$ (2.352(3)–2.427(3) Å) are similar to those found for Y–O(THF) bond lengths at monocationic yttrium centers.[17]

Table 2: Ethylene polymerization with yttrium catalyst precursors.[a]

Precursor[b]	Aluminum alkyl	Yield [g]	Activity [kg mol^{-1} h^{-1} bar^{-1}]	$\bar{M}_n$ [g mol^{-1}]	$\bar{M}_w/\bar{M}_n$	T_m [°C]
$[YR_3(thf)_2]$	$AlEt_3$	0.11	27	–	–	128.3
$[YR_3(thf)_2]$	Al*n*Oct$_3$	0.43	103	–	–	136.7
$[YR_3(thf)_2]$[c]	Al*i*Bu$_3$	0.91	272	14150	2.9	135.5
$[YR_3(thf)_2]$	Al*i*Bu$_2$H	1.67	401	59730	1.7	130.2
				3030[d]	2.3	
$[YR_3(thf)_2]$[e]	AlR_3	1.53	1840	110990	2.9	138.0
$[YR_2(thf)_4]^{+}[AlR_4]^{-}$[e,f]	AlR_3	1.13	1351	215599	2.4	141.6
$[YR_3(thf)_2]$	MAO[g]	1.41	339	–	–	133.1

[a] $[NMe_2HPh][B(C_6F_5)_4]$ as activator in the presence of aluminum alkyl. Conditions: 5 μmol Y, B:Y = 5:1, Al:Y = 200:1, $T = 25$ °C, $p = 5$ bar, $t = 10$ min, $V = 30$ mL (toluene) [b] $R = CH_2SiMe_3$. [c] $t = 8$ min. [d] Bimodal molecular weight distribution. [e] $t = 2$ min. [f] Al:Y = 100:1. [g] Methylaluminoxane.

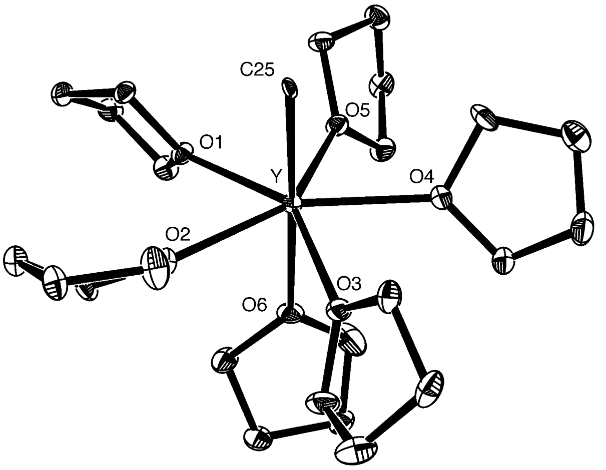


Figure 2. Molecular structure of the cationic portion of $[Y(CH_3)(thf)_6]^{2+}[BPh_4]^{-}_2$. Thermal ellipsoids are drawn at the 30% probability level, hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Y-O1 2.352(3), Y-O2 2.426(3), Y-O3 2.355(3), Y-O4 2.427(3), Y-O5 2.377(3), Y-O6 2.427(3), Y-C25 2.418(3); C25-Y-O6 176.5(1).

The nature of the aluminum alkyl compounds was found to have a remarkable influence on both the activity of the catalyst system $[Y(CH_2SiMe_3)_3(thf)_2]/[NMe_2HPh][B(C_6F_5)_4]$ as well as the molecular weight $\bar{M}_n$. From Table 2 it is apparent that the steric bulk of the alkyl group at the aluminum center is critical with respect to the activity: only traces of polyethylene were obtained with $AlMe_3$, whereas the use of $Al(CH_2SiMe_3)_3$ gave high molecular weight polyethylene ($\bar{M}_n = 110990$) with an outstanding activity of 1840 kg mol^{-1} h^{-1} bar^{-1}.[18]

Equimolar amounts of $[Y(CH_2SiMe_3)_3(thf)_2]$ and $Al(CH_2SiMe_3)_3$[19] were found to form the ion pair $[Y(CH_2SiMe_3)_2(thf)_x]^{+}[Al(CH_2SiMe_3)_4]^{-}$ in C_6D_6 and in $[D_8]$THF, which was isolated in 75% yield as the thermally stable ion pair $[Y(CH_2SiMe_3)_2(thf)_4]^{+}[Al(CH_2SiMe_3)_4]^{-}$. In the ^{1}H NMR spectrum of the product in $[D_8]$THF, the resonance of the methylene protons at the aluminate center was recorded at $\delta = -1.28$ ppm as a broad multiplet owing to $^{2}J(Al,H)$ coupling, whereas the methylene protons at the cationic yttrium appear as a doublet at $\delta = -0.73$ with $^{2}J(Y,H) = 3.1$ Hz. The ^{13}C NMR spectrum exhibits a doublet for the YCH_2 group at $\delta = 37.2$ with $^{1}J(Y,C) = 42.1$ Hz.

Single crystals of $[Y(CH_2SiMe_3)_2(thf)_4]^{+}[Al(CH_2SiMe_3)_4]^{-}$ suitable for X-ray structure analysis were obtained from pentane/THF.[15b] The cationic portion of the ion pair $[Y(CH_2SiMe_3)_2(thf)_4]^{+}[Al(CH_2SiMe_3)_4]^{-}$ is shown in Figure 3, which illustrates the distorted octahedral-coordination geom-

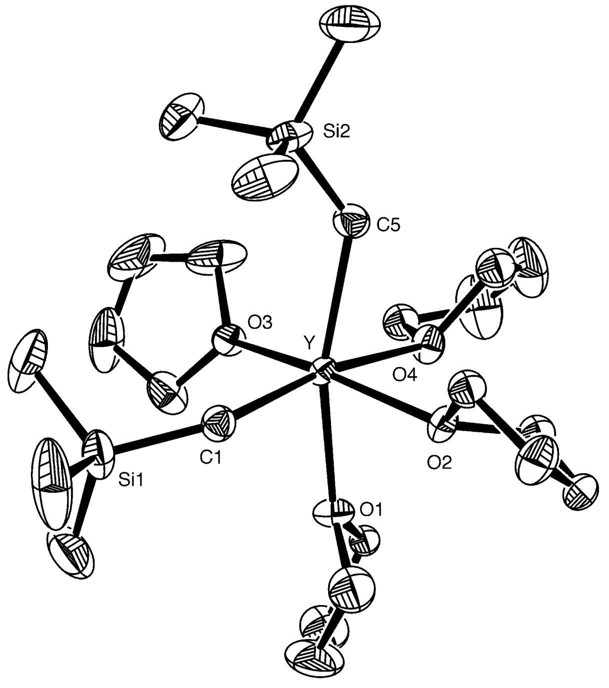


Figure 3. Molecular structure of the cationic portion of $[Y(CH_2SiMe_3)_2(thf)_4]^{+}[Al(CH_2SiMe_3)_4]^{-}$. Thermal ellipsoids are drawn at the 20% probability level, hydrogen atoms are omitted for clarity. Selected distances [Å^{-1}] and angles [°]: Y-O1 2.448(4), Y-O2 2.354(4), Y-O3 2.354(4), Y-O4 2.479(4), Y-C1 2.384(6), Y-C5 2.411(6); O1-Y-C5 163.7(2), O2-Y-O3 165.3(1), O4-Y-C1 171.0 (2).

etry around the yttrium center with the two alkyl groups arranged in a *cis* fashion.[20] The formation of alkyl aluminates of the rare-earth metals as ion pairs is unprecedented. So far, only complexes containing bridging alkyl groups such as $[Y\{(\mu\text{-}Me_2)(AlMe_2)\}_3]$[14] were reported for the trivalent rare earth metals. When $[Y(CH_2SiMe_3)_2(thf)_4]^+[Al(CH_2SiMe_3)_4]^-$ was activated with $[NMe_2HPh][B(C_6F_5)_4]$ for ethylene polymerization, similar results as for $[Y(CH_2SiMe_3)_3(thf)_2]$ were obtained (1351 versus 1840 kg mol^{-1} h^{-1} bar^{-1}), thus indicating that $[Y(CH_2SiMe_3)_2(thf)_4]^+[Al(CH_2SiMe_3)_4]^-$ is converted into a dication (Table 2).[21]

In conclusion, we have demonstrated that the easily accessible tris(alkyl) complexes of the rare-earth metals $[Ln(CH_2SiMe_3)_3(thf)_2]$ are precursors for highly active catalysts for ethylene polymerization and that an alkyl dication $[Ln(CH_2SiMe_3)(solv)_z]^{2+}$, formed via the dialkyl monocation $[Ln(CH_2SiMe_3)_2(solv)_y]^+$, is most probably the active species.

Experimental Section

$[Y(CH_2SiMe_3)_2(thf)_4]^+[BPh_4]^-$: A slurry of $[Y(CH_2SiMe_3)_3(thf)_2]$ (200 mg, 404 µmol) and $[NEt_3H][BPh_4]$ (170 mg, 404 µmol) was stirred in THF (20 mL) at −78 °C. The reaction mixture was allowed to slowly warm up to ambient temperature and stirred for 24 h to give a colorless clear solution. After the volatile fractions were removed in vacuo, the resultant colorless solid was washed with Et_2O (2 × 20 mL) and dried under vacuum to give colorless microcrystals (135 mg, 38 %). ^{1}H NMR (400 MHz, $[D_8]$THF, 25 °C, TMS): $\delta = -0.78$ (d, $^2J(Y,H) = 3.3$ Hz, 2 × 2 H; YCH_2SiCH_3), −0.06 (s, 2 × 9 H; YCH_2SiCH_3), 1.76 (m, 4 × 4 H; β-CH_2, THF), 3.60 (m, 4 × 4 H; α-CH_2, THF), 6.74 (t, $^3J(H,H) = 7.0$ Hz, 4 H; 4-Ph), 6.87 (t, $^3J(H,H) = 7.3$ Hz, 2 × 4 H; 3-Ph), 7.28 ppm (br, 2 × 4 H; 2-Ph). ^{13}C NMR (101 MHz, $[D_5]$pyridine, 25 °C, TMS): $\delta = 4.5$ (YCH_2SiCH_3), 25.8 (β-CH_2, THF), 30.9 (dt, $^1J(Y,C) = 36.5$ Hz, $^1J(C,H) = 97.2$ Hz; YCH_2SiCH_3), 67.8 (α-CH_2, THF), 122.3 (4-Ph), 126.2 (3-Ph), 137.2 (2-Ph), 165.0 ppm (q, $^1J(B,C) = 49.3$ Hz; 1-Ph). $^{11}B\{^1H\}$ NMR (128 MHz, $[D_8]$THF, 25 °C, $BF_3 \cdot Et_2O$): $\delta = -6.6$ ppm. ^{89}Y NMR (20 MHz, $[D_8]$THF, 25 °C, YCl_3): $\delta = 660.0$ ppm. Elemental analysis calcd (%) for $C_{48}H_{74}BO_4Si_2Y$: C 66.19, H 8.56, Y 10.21; found: C 65.91, H 8.44, Y 9.74.

$[Y(CH_2SiMe_3)(thf)_5]^{2+}[BPh_4]^-_2$: A solution of $[Y(CH_2SiMe_3)_3(thf)_2]$ (300 mg, 606 µmol) in THF (60 mL) was added to neat $[NMe_2HPh][BPh_4]$ (802 mg, 1818 µmol) at −78 °C. The reaction mixture was stirred at ambient temperature for 24 h to give a brownish solution. The solution was filtered, the volatile fractions were removed by evaporation, and the residue was washed with pentane (60 mL) gave a colorless powder of $[Y(CH_2SiMe_3)(thf)_5]^{2+}[BPh_4]^-_2$ (661 mg, 99 %). ^{1}H NMR (400 MHz, $[D_5]$pyridine, 25 °C, TMS): $\delta = 0.17$ (s, 9 H; YCH_2SiCH_3), 0.73 (d, $^2J(Y,H) = 3.3$ Hz, 2 H; YCH_2SiCH_3), 1.62 (m, 5 × 4 H; β-CH_2, THF), 3.66 (m, 5 × 4 H; α-CH_2, THF), 7.10 (t, $^3J(H,H) = 7.3$ Hz, 2 × 4 H; 4-Ph), 7.27 (t, $^3J(H,H) = 7.3$ Hz, 2 × 8 H; 3-Ph), 8.06 ppm (br, 2 × 8 H; 2-Ph). ^{13}C NMR (101 MHz, $[D_5]$pyridine, 25 °C, TMS): $\delta = 4.0$ (YCH_2SiCH_3), 25.9 (β-CH_2, THF), 44.5 (dt, $^1J(Y,C) = 44.9$ Hz, $^1J(C,H) = 93.8$ Hz; YCH_2SiCH_3), 67.9 (α-CH_2, THF), 122.4 (4-Ph), 126.2 (3-Ph), 137.1 (2-Ph), 165.0 ppm (q, $^1J(B,C) = 49.2$ Hz; 1-Ph). $^{11}B\{^1H\}$ NMR (128 MHz, $[D_8]$THF, 25 °C, $BF_3 \cdot Et_2O$): $\delta = -6.7$ ppm. ^{89}Y NMR (20 MHz, $[D_8]$THF, 25 °C, YCl_3): $\delta = 409.2$ ppm. Elemental analysis calcd (%) for $C_{72}H_{91}B_2O_5SiY$: C, 73.59; H, 7.81; Y, 7.57; found: C, 74.62; H, 8.37; Y, 7.16.

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[15] a) NMR data for $[Y(CH_3)(thf)_6]^{2+}[BPh_4]^-_2$: ^{1}H NMR (400 MHz, $[D_5]$pyridine, 25 °C, TMS): $\delta = 0.69$ (d, $^2J(Y,H) = 2.1$ Hz, 3 H; YCH_3), 1.63 (m, 4 × 4 H; β-CH_2, THF), 3.67 (m, 4 × 4 H; α-CH_2, THF), 7.10 (t, $^3J(H,H) = 7.0$ Hz, 2 × 4 H; 4-Ph), 7.26 (t, $^3J(H,H) = 7.4$ Hz, 2 × 8 H; 3-Ph), 8.04 ppm (br, 2 × 8 H; 2-Ph). ^{13}C NMR (101 MHz, $[D_5]$pyridine, 25 °C, TMS): $\delta = 27.6$ (β-CH_2, THF), 32.8 (dq, $^1J(Y,C) = 53.6$ Hz, $^1J(C,H) = 105.5$ Hz; YCH_3), 69.7 (α-CH_2, THF), 124.2 (4-Ph), 128.0 (3-Ph), 139.0 (2-Ph), 166.8 ppm (q, $^1J(B,C) = 49.2$ Hz; 1-Ph). $^{11}B\{^1H\}$-NMR (128 MHz, $[D_8]$THF, 25 °C, $BF_3 \cdot Et_2O$): $\delta = -4.7$ ppm. ^{89}Y-NMR (20 MHz, $[D_5]$pyridine, 25 °C, YCl_3): $\delta = 433.2$ ppm. Elemental analysis calcd (%) for $C_{77}H_{99}B_2O_7Y$: C 74.16, H 8.00; found: C 73.27, H 7.22;

b) CCDC-216055 ($[Y(CH_3)(THF)_6]^{2+}[BPh_4]^-{}_2$) CCDC-216054 ($[Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[16] For pertinent Y–C bond lengths, see: K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228–243.

[17] Y-O(THF) bond distances at monocationic yttrium centers: a) $[YCl(OtBu)(thf)_5]^+[BPh_4]^-\cdot THF$: Y-O = 2.405(5), 2.411(5), 2.391(5), 2.422(5), 2.408(5) Å, see: W. J. Evans, J. M. Olofson, J. W. Ziller, *J. Am. Chem. Soc.* **1990**, *112*, 2308–2314; b) $[YCl_2(thf)_5]^+[YCl_4(thf)_2]^-$: Y-O = 2.391(7), 2.368(5), 2.382(6) Å, see: P. Sobota, J. Utko, S. Szafert, *Inorg. Chem.* **1994**, *33*, 5203–5206; c) $[YCl_2(thf)_5]^+[C_2B_9H_{12}]^-$: Y-O = 2.378(8), 2.377(7), 2.396(8), 2.401(7), 2.309(7) Å, see: K. Chiu, Z. Zhang, T. C. W. Mak, Z. Xie, *J. Organomet. Chem.* **2000**, *614*, 107–112; d) $[Y(CH_2SiMe_3)_2(thf)_4]^+[Al(CH_2SiMe_3)_4]^-$: Y-O = 2 × 2.354(4), 2.448(4), 2.479(4) Å, this work.

[18] Not surprisingly, ethylene was also polymerized when methylaluminoxane was used instead of aluminum trialkyl; see Table 2.

[19] Because of its inertness towards $[NMe_2HPh][B(C_6F_5)_4]$, we selected $Al(CH_2SiMe_3)_3$ for our investigations. For $Al(CH_2SiMe_3)_3$, neither formation of aluminum alkyl cation, see reference [9], nor decomposition under ligand redistribution was observed. $AliBu_3$ was reported to react with $[NMe_2HPh][B(C_6F_5)_4]$ in C_6D_6 under forcing conditions to produce a mixture of $BiBu_3$, $Al(C_6F_5)_3$ and $AliBu(C_6F_5)_2$, see: C. Götz, A. Rau, G. Luft, *J. Mol. Catal. A* **2002**, *184*, 95–110.

[20] Higher coordination numbers 7 and 8 were reported for cationic alkyl complexes of lutetium, see reference [7].

[21] The monocation $[Y(CH_2SiMe_3)_2(thf)_x]^+[Al(CH_2SiMe_3)_4]^-$ does not polymerize ethylene unless activated with excess of $[NMe_2HPh][B(C_6F_5)_4]$. In $[D_8]$THF it reacts with one equivalent of $[NMe_2HPh][BPh_4]$, to form $SiMe_4$, NMe_2Ph, $Al(CH_2SiMe_3)_3$, and $[Y(CH_2SiMe_3)_2([D_8]thf)_x]^+[BPh_4]^-$. A similar reaction between $[Sm(\eta^5\text{-}C_5Me_5)_2(AlMe_4)]_2$ and $[Ph_3C][B(C_6F_5)_4]$ was reported to give $[Sm(\eta^5\text{-}C_5Me_5)_2][B(C_6F_5)_4]$, Ph_3CMe, and $AlMe_3$, see: S. Kaita, Z. Hou, M. Nishiura, Y. Doi, J. Kurazumi, A. C. Horiuchi, Y. Wakatsuki, *Macromol. Rapid Commun.* **2003**, *24*, 179–184.