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Indenyl Abstraction versus Alkyl Abstraction of [(Indenyl)ScR_2(thf)] by [Ph_3C] [$B(C_6F_5)_4$]: Aspecific and Syndiospecific Styrene Polymerization

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The metallocene complex [Cp_2TiCl_2] (Cp = cyclopentadienyl) was investigated for olefin polymerization upon activation with AlR_3 or AlR_2Cl half a century ago, and showed low catalytic activity.[1] Nineteen years later, Sinn, Kaminsky, and co-workers found that the use of methylaluminoxane (MAO) as the activator greatly enhanced the activity of [Cp_2MR_2] (M = Ti and Zr) to olefin polymerization.[2] Subsequent mechanistic studies revealed that the active species in Group IV metallocene/MAO systems are cationic metallocene alkyls, which are generated through a reaction involving an alkyl abstraction of the neutral metallocene complexes by MAO.

An alternative route to access the cationic metallocene alkyl species is by employing a well-defined strong Lewis acid, such as $B(C_6F_5)_3$, to abstract the alkyl group of neutral metallocene alkyl complexes.[3] However, in some cases, the counterions [$R{-}B(C_6F_5)_3$]$^-$ form "tight" ion pairs with the highly electrophilic cations through R bridging and compete with coordination of the monomer, which results in a decrease in catalytic activity, especially in α-olefin polymerization.[3a,4] To overcome this problem, [Ph_3C][$B(C_6F_5)_4$], which contains a more weakly coordinating anion [$B(C_6F_5)_4$]$^-$, was developed as the activator. The [Ph_3C]$^+$ moiety is an excellent alkyl or hydride abstractor, forming the "innocent" byproduct $Ph_3C{-}R$, and the resulting "loose" ion pairing complexes [Cp_2MR]$^+$[$B(C_6F_5)_4$]$^-$ generally show higher activity for olefin polymerization.[3a,5] It was found that neutral rare-earth metal alkyl complexes could also be converted into the cationic species through alkyl abstraction, and the cationic species generated generally show much higher activity than the neutral ones.[6–10] For example, the [$Cp'ScR_2$(thf)]/[Ph_3C][$B(C_6F_5)_4$] (Cp′ = substituted cyclopentadienyl) systems exhibit good catalytic activities for syndiospecific polymerization of styrene,[11] syndiospecific copolymerization of styrene and ethylene (or isoprene),[11a,12] and alternating copolymerization of ethylene and norbornene,[13] producing some materials that have excellent properties. Recently, we prepared a series of mono(indenyl)–Sc–dialkyl complexes and studied their reactivity towards styrene polymerization with [Ph_3C][$B(C_6F_5)_4$] as the activator. The study revealed an interesting observation that [Ph_3C][$B(C_6F_5)_4$] abstract not only the alkyl ligand but also the π-bonded indenyl ligand, and the resulting two types of cationic species catalyze styrene polymerization to give syndiotactic polystyrene (sPS) and atactic PS (aPS), respectively. Herein we describe these results.

The first ligand precursors that were tried for preparing mono(indenyl)–Sc–dialkyl complexes were 1,3-bis(methyl)indene and 1,3-bis(isopropyl)indene.[14] However, the alkane elimination reactions of these two compounds with [$Sc(CH_2SiMe_3)_3(thf)_2$] did not occur at room temperature, and raising the reaction temperature caused the gradual decomposition of the Sc–trialkyl complexes, giving none of the desired complexes. In comparison with alkyl substituents, the $SiMe_3$ group is relatively electron withdrawing,[15] and we hoped that this property of the $SiMe_3$ substituent would promote the alkane elimination reaction of the related ligand precursor with [$Sc(CH_2SiMe_3)_3(thf)_2$]. Therefore, the ligand precursor 1,3-bis(trimethylsilyl)indene was prepared, and its reaction with [$Sc(CH_2SiMe_3)_3(thf)_2$] was investigated. To our delight, the reaction worked and the desired mono(indenyl)–Sc–dialkyl complex was produced. Subsequently, seven other ligand precursors with the $SiMe_3$ substituent were synthesized, and reactions of these ligand precursors with [$Sc(CH_2SiMe_3)_3(thf)_2$] all gave the mono(indenyl)–Sc–dialkyl complexes (Scheme 1). These Sc complexes were characterized by NMR spectroscopy (^{1}H, ^{13}C)

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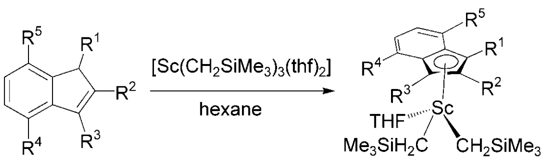


1: $R^1 = R^3 = SiMe_3$; $R^2 = R^4 = R^5 = H$
2: $R^1 = SiMe_3$; $R^2 = R^3 = R^4 = R^5 = H$
3: $R^1 = SiMe_3$; $R^2 = Me$, $R^3 = R^4 = R^5 = H$
4: $R^1 = SiMe_3$; $R^3 = Me$, $R^2 = R^4 = R^5 = H$
5: $R^1 = SiMe_3$; $R^3 = R^4 = R^5 = Me$, $R^2 = H$
6: $R^1 = SiMe_3$; $R^4 = R^5 = Me$, $R^2 = R^3 = H$
7: $R^1 = SiMe_2H$; $R^2 = R^3 = R^4 = R^5 = H$
8: $R^1 = R^3 = SiMe_3$; $R^2 = Me$, $R^4 = R^5 = H$

Scheme 1. Synthesis of the mono(indenyl)–Sc–dialkyl complexes.

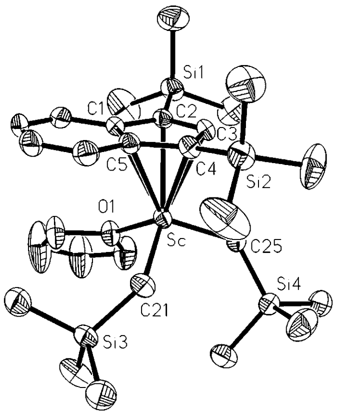


Figure 1. ORTEP view of **1**; thermal ellipsoids set at the 30 % probability level, hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Sc–C1 2.608(3), Sc–C2 2.549(3), Sc–C3 2.493(3), Sc–C4 2.538(3), Sc–C5 2.615(3), Sc–C21 2.191(3), Sc–C25 2.221(3), Sc–O 2.1616(19); C21–Sc–C25 106.10(11).

and elemental analysis. Single crystals of **1**, **4**, **6**, and **7** were grown from solutions in hexane, and the solid-state structures were determined by X-ray diffraction.[16] The structure of **1** is shown in Figure 1, whereas those of **4**, **6**, and **7** are given in the Supporting Information. The structural data indicate η^5 hapticity of the indenyl ligands in all of the complexes.

Upon activation with $[Ph_3C][B(C_6F_5)_4]$, most of these mono(indenyl)–Sc–dialkyl complexes showed good activities for styrene polymerization (Table 1),[17] and the activities are in the order of **5** < **6** ≈ **3** ≈ **7** < **4** < **2** < **8** ≈ **1**. The activity of **1** is up to 12 066 kg PS/mol Sc h (Table 1, entry 2), which is comparable to those of the most active transition-metal styrene polymerization catalysts.[11a,18] The $[(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)]/[Ph_3C][B(C_6F_5)_4]$ system has been reported for the highly syndiospecific styrene polymerization.[11a] Surprisingly, solvent extraction experiments and ^{13}C NMR spectroscopy indicated that mono(indenyl)–Sc–dialkyl/$[Ph_3C][B(C_6F_5)_4]$ systems produced not only highly sPS, but also aPS, or sPS and aPS mixtures. The microstructures of PS are greatly influenced by indenyl ligands. Complexes **1** and **8**, in which both the 1 and 3 positions of the indenyl ligands are substituted by bulky $SiMe_3$ groups, produced highly sPS (Table 1, entries 1, 2, and 10), whereas **2**, with the 1-$SiMe_3$ indenyl ligand, gave aPS (Table 1, entry 4). The other complexes **3**–**7** provided sPS and aPS mixtures, and among them the complexes with methyl groups at the 3 position of the indenyl ligands, **4** and **5**, have higher syndiospecific selectivity than those with H at the 3 position of indenyl ligands, **3**, **6**, and **7** (Table 1, entries 6 and 7 vs. 5, 8, and 9). GPC traces of the sPS produced by **1** and **8** show monomodal peaks, and the polymers are of high molecular weight (240 ~450 × 10^3) and narrow polydispersity (PDIs = 1.37). The aPS generated by **2** is also of narrow monomodal molecular weight distribution (PDI = 1.72), but the molecular weight is only 3.9 × 10^3. On the other hand, GPC traces display bimodal peaks for the polymers produced by **3**–**7**, in which the high molecular weight fractions are sPS, whereas the low molecular weight fractions are the aPS. Furthermore, the molecular weights and polydispersities of the two fractions are similar to those of the polymers produced by **1** (or **8**) and **2**, respectively, and the ratios of sPS to aPS are in agreement with those revealed by the solvent extraction experiments. These observations indicate that there are two

Table 1. Styrene polymerization catalyzed by mono(indenyl)–Sc–dialkyl/$[Ph_3C][B(C_6F_5)_4]$ systems.[a]

Entry	Complex	T [min]	Yield [%]	Activity[b]	sPS[c] [%]	aPS[d] [%]	High M_n fraction $M_n(10^3)$[e]	PDI	Low M_n fraction $M_n(10^3)$	PDI	T_m[f] [°C]
1	**1**	1	100	6033	>99	<1	247	1.37	–	–	271
2[g]	**1**	1	100	12 066	>99	<1	448	1.37	–	–	270
3[h]	**1**	3	0	–	–	–	–	–	–	–	–
4	**2**	3	100	2011	0	100	–	–	3.9	1.72	–
5	**3**	3	81	1634	17	83	581	1.51	4.4	1.80	270
6	**4**	3	100	2011	88	12	430	1.46	3.7	1.53	269
7	**5**	3	41	811	80	20	422	1.40	5.6	1.56	270
8	**6**	3	81	1634	37	63	301	1.27	4.6	1.70	265
9	**7**	3	88	1778	20	80	225	1.29	4.2	1.82	268
10	**8**	1	100	6033	>99	<1	437	1.37	–	–	270
11	**2**	1	89	5367	0	100	–	–	n.d.	n.d.	–
12	**4**	1	58	3500	86	14	n.d.	n.d.	n.d.	n.d.	n.d.
13[i]	ScR_3	3	75	1511	0	100	–	–	3.4	1.67	–
14[j]	**9**	30	42	13	0	100	–	–	6.4	1.66	–

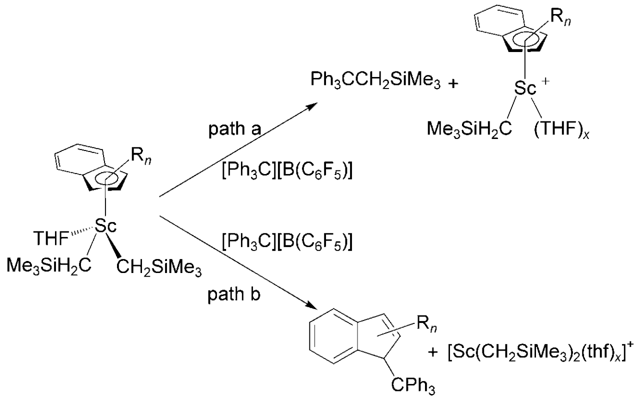
[a] Polymerization conditions: catalyst (18 μmol), 26 °C, Sc complex/$[Ph_3C][B(C_6F_5)_4]$ (1:1 mol/mol), monomer/Sc complex (1000:1 mol/mol), toluene/monomer (7:1 v/v). [b] kg PS/mol Ln h. [c] Percentage of polymers that are insoluble in 2-butanone at reflux. [d] Percentage of polymers that are soluble in 2-butanone at reflux. [e] Determined by GPC relative to the polystyrene standards. [f] Differential scanning calorimetry (DSC) analysis of the polymers that are insoluble in 2-butanone at reflux. [g] Monomer/Sc complex (2000:1 mol/mol). [h] Without $[Ph_3C][B(C_6F_5)_4]$. [i] $[Sc(CH_2SiMe_3)_3(thf)_2]/[Ph_3C][B(C_6F_5)_4]$ (1:2 mol/mol). [j] Monomer/Lu complex (150:1 mol/mol).

types of active species involved in the polymerizations: one for the syndiospecific polymerization and the other for the aspecific polymerization. The predominant active species is dependent on the ligands; the complexes with 1,3-substituted indenyl ligands have more tendency to form the active species for syndiospecific polymerization than other complexes. The formation of syndiotactic and atactic PS mixtures is common in organotitanium-complex-catalyzed styrene polymerization, and one explanation for this is the coexistence of several active species formed by different Ti oxidation states (2+, 3+, and 4+).[19] However, the Sc ion is generally in the 3+ oxidation state and it is very difficult to reduce. It is a generally held view that there is only one type of active species, $[Cp'ScR]^+$, generated from the $[Cp'ScR_2]/[Ph_3C][B(C_6F_5)_4]$ systems through alkyl abstraction.

We began to investigate the underlying reasons for the unusual styrene polymerization behavior mentioned above by studying the reactions of mono(indenyl)–Sc–dialkyl complexes with $[Ph_3C][B(C_6F_5)_4]$. The ^{1}H NMR spectra indicated that the addition of one equivalent of borate to **1** in C_6D_6 results in the rapid disappearance of **1** and the formation of the cationic mono(indenyl)–Sc–monoalkyl species $[(1,3\text{-}(SiMe_3)_2(C_9H_5)Sc(CH_2SiMe_3)(thf)_x][B(C_6F_5)_4]$ and $Ph_3CCH_2SiMe_3$; a similar observation has been noted for the reaction of $[(C_5Me_4SiMe_3)Sc(CH_2SiMe_3)_2(thf)]$ with $[Ph_3C][B(C_6F_5)_4]$.[11a] On the other hand, the reaction of **2** with $[Ph_3C][B(C_6F_5)_4]$ in C_6D_6 is completely different, giving not $Ph_3CCH_2SiMe_3$ but 1-Ph_3C-3-$SiMe_3$-indene. To further identify this product, 1-Ph_3C-3-$SiMe_3$-indene was prepared by treating **2** with $[Ph_3C][B(C_6F_5)_4]$ in toluene, and characterized by NMR (^{1}H, ^{13}C) spectroscopy and mass spectrometry. Moreover, ^{1}H NMR spectroscopic monitoring of the reaction of **6** with $[Ph_3C][B(C_6F_5)_4]$ in C_6D_6 showed the formation of $Ph_3CCH_2SiMe_3$ (minor product) and 1-Ph_3C-3-$SiMe_3$-4,7-$(Me)_2$-indene (major product); the latter was also obtained from the reaction in toluene and characterized by NMR (^{1}H, ^{13}C) spectroscopy and mass spectrometry.

The above investigations clearly show two types of reactions occurring between mono(indenyl)–Sc–dialkyl complexes and $[Ph_3C][B(C_6F_5)_4]$: alkyl and indenyl abstraction (Scheme 2), and the reaction type is dependent on the nature of indenyl ligand. The $[Ph_3C]^+$ moiety is best known for its excellent ability to abstract hydride and alkyl ligands, and so abstraction of the more strongly held η^5-indenyl observed here is really unexpected. We believe that this represents the first example of $[Ph_3C]^+$ abstracting a Cp-type π ligand rather than a σ-alkyl ligand.[20] A mono(indenyl)–Lu–dialkyl complex $[(1\text{-}SiMe_3C_9H_6)Lu(CH_2SiMe_3)_2(thf)]$ (**9**) was also prepared. It reacted with $[Ph_3C][B(C_6F_5)_4]$ to give only the indenyl abstraction products. The **9**/$[Ph_3C][B(C_6F_5)_4]$-catalyzed styrene polymerization produced low molecular weight aPS with a low activity of 13 kg PS/mol Lu h (Table 1, entry 14).

Indenyl abstraction results in the formation of $[Sc(CH_2SiMe_3)_2(thf)_n]^+$ species, which could be responsible for the formation of aPS. In this case, $[Sc(CH_2SiMe_3)_3(thf)_2]/[Ph_3C][B(C_6F_5)_4]$ was tested for styrene polymerization, which gave an atactic polymer ($M_n = 3.4\times10^3$; PDI = 1.68) very similar to that produced by **2**/$[Ph_3C][B(C_6F_5)_4]$ ($M_n = 3.9\times10^3$; PDI = 1.72). Increasing the steric bulk around the 3 position of the indenyl ligand can retard the indenyl abstraction process and subsequently benefit the alkyl abstraction process. Therefore, reaction of **6** with $[Ph_3C][B(C_6F_5)_4]$ produces not only Ph_3C-substituted indene, but also $Ph_3CCH_2SiMe_3$, and the **6** (or **3**)/$[Ph_3C][B(C_6F_5)_4]$ system catalyzes styrene polymerization to give a syndiotactic and atactic PS mixture. The most efficient way to repress the indenyl abstraction process is by introducing a non-hydrogen substitutent at the 3 position of the indenyl ligand, as can be seen from compounds **4** and **5**, in which the Me substituents at the 3 positions of the indenyl ligands give predominantly sPS mixtures, **1** and **8** that have greater steric bulk due to the $SiMe_3$ substituents, and hence, produce pure sPS.



Scheme 2. The two types of reactions between mono(indenyl)–Sc–dialkyl complexes and $[Ph_3C][B(C_6F_5)_4]$.

In summary, $[Ph_3C][B(C_6F_5)_4]$ is best known for its excellent hydride and alkyl abstraction properties, however, the present study on mono(indenyl)–Sc–dialkyl/$[Ph_3C][B(C_6F_5)_4]$ systems has found that $[Ph_3C][B(C_6F_5)_4]$ can abstract a π-bonded indenyl ligand rather than a σ-alkyl ligand. The abstraction pathway is influenced by the substituents on the indenyl ligands, and can be controlled by employing different indenyl ligands. For the styrene polymerization, two abstraction pathways, alkyl abstraction and indenyl abstraction, result in syndiospecific and aspecific styrene polymerization, respectively, and different types of polystyrene were produced by using Sc–dialkyl complexes with different indenyl ligands.

Experimental Section

Complex 1: 1,3-$(SiMe_3)_2C_9H_6$ (520 mg, 2.0 mmol) and $[Sc(CH_2SiMe_3)_3(thf)_2]$ (902 mg, 2.0 mmol) were mixed in hexane (20 mL). The reaction mixture was stirred at room temperature for one day, and then at 50 °C for a further 8 h. The reaction mixture was filtered, and evaporation of the resulting solution in vacuo gave a pale-yellow oil. Recrystallization of the oily residue from hexane at −35 °C afforded **1** as pale-yellow crystals (610 mg, 56 %). M. p. 82–84 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta =$

7.73 (q, 2H; Ind^4, Ind^7), 7.63 (s, 1H; Ind^2), 6.96 (q, 2H; Ind^5, Ind^6), 3.34 (br s, 4H; THF), 1.08 (br s, 4H; THF), 0.48 (s, 18H; Si*Me$_3$*), 0.27 (s, 18H; Si*Me$_3$*), 0.01 (d, ^2J(H,H) = 11.4 Hz, 2H; C*H$_2$*SiMe$_3$), −0.29 ppm (d, ^2J(H,H) = 11.1 Hz, 2H; C*H$_2$*SiMe$_3$); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ = 137.0, 136.6, 125.2, 122.0, 114.8 (s, 9C; Ind), 71.8 (s, 2C; THF), 45.5 (br s, 2C; *C*H$_2$SiMe$_3$), 24.6 (s, 2C; THF), 4.1(s, 6C; CH$_2$Si*Me$_3$*), 1.0 ppm (s, 6C; Si*Me$_3$*); elemental analysis calcd (%) for $C_{27}H_{53}Si_4OSc$: C 58.85, H 9.70; found: C 58.04, H 9.39.

A typical procedure for styrene polymerization: The mono(indenyl)–dialkyl–scandium complexes (18 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (18 μmol) were mixed in toluene (14 mL). The above reaction mixture was stirred at room temperature for 2 min, and then styrene (1.81 g, 18 mmol) was added under vigorous stirring. The reaction solution became very viscous after several seconds, and the polymerization was quenched with acidic methanol (2 mL). The reaction mixture was poured into methanol (50 mL) to precipitate the polymer. The resulting polymer was isolated, washed with methanol, and dried under vacuum for one day to give a constant weight.

For full experimental details see the Supporting Information.

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Keywords: borates · cations · polymerization · rare-earth metals · substituent effects

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[16] Crystal data for **1**: $C_{27}H_{53}OScSi_4$; $M_r = 551.01$; monoclinic; space group *P*21/*n*; $a = 10.1647(9)$, $b = 15.8130(15)$, $c = 22.023(2)$ Å; $\beta = 96.452(2)°$; $V = 3517.5(6)$ Å^3; $Z = 4$; $\mathrm{Mo}_{K\alpha}$, $\lambda = 0.71073$ Å; $T = 293(2)$ K; $R = 0.0562$; $wR = 0.1245$ for 3894 unique reflections with $I > 2\sigma(I)$. Crystal data for **4**: $C_{25}H_{47}OScSi_3$; $M_r = 492.86$; monoclinic; space group *P*21/*c*; $a = 10.5487(12)$, $b = 15.8307(19)$, $c = 19.058(2)$ Å; $\beta = 92.224(2)°$; $V = 3180.2(7)$ Å^3; $Z = 4$; $\mathrm{Mo}_{K\alpha}$, $\lambda = 0.71073$ Å; $T = 293(2)$ K; $R = 0.0762$; $wR = 0.1941$ for 2076 unique reflections with $I > 2\sigma(I)$. Crystal data for **6**: $C_{26}H_{49}OScSi_3$; $M_r = 506.88$; monoclinic; space group *P*21/*c*; $a = 14.6377(8)$, $b = 21.5594(12)$, $c = 20.7491(11)$ Å; $\beta = 98.8010(10)°$; $V = 6470.9(6)$ Å^3; $Z = 8$; $\mathrm{Mo}_{K\alpha}$, $\lambda = 0.71073$ Å; $T = 293(2)$ K; $R = 0.0698$; $wR = 0.1711$ for 5840 unique reflections with $I > 2\sigma(I)$. Crystal data for **7**: $C_{23}H_{43}OScSi_3$; $M_r = 464.80$; monoclinic; space group *P*21/*c*; $a = 10.7689(17)$, $b = 18.381(3)$, $c = 15.372(3)$ Å; $\beta = 104.151(3)°$; $V = 2950.3(8)$ Å^3; $Z = 4$; $\mathrm{Mo}_{K\alpha}$, $\lambda = 0.71073$ Å; $T = 293(2)$ K; $R = 0.0629$; $wR = 0.1391$ for 3012 unique reflections with $I > 2\sigma(I)$. CCDC-701470, 701471, 701472, and 701473 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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