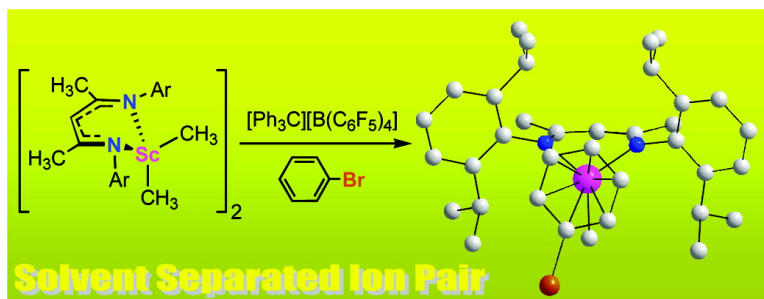


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## Cationic Organoscandium $\beta$ -Diketiminato Chemistry: Arene Exchange Kinetics in Solvent Separated Ion Pairs

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It is well established that early transition metal organometallic ion pairs with weakly coordinating anions are the active species in olefin polymerization processes.<sup>1</sup> Increasingly, it is becoming apparent that subtle interplay between cation/anion interactions and solvent effects has a significant impact on ion pair dynamics, which in turn profoundly influence the activity and selectivity of a given catalyst system.<sup>2</sup> While these effects have been studied experimentally and computationally in some detail for metallocene<sup>3</sup> and constrained geometry catalysts families,<sup>4</sup> some controversy remains concerning the relative importance of contact ion pairs (CIP) versus solvent separated ion pairs (SSIP) in the initiation and propagation steps of a polymerization reaction.<sup>5</sup> Of the two classes of ion pair, the CIPs are the more well understood from a structural and dynamic perspective. SSIPs formed in relevant nonpolar solvents are more ephemeral species, with few experimentally well-characterized examples in the literature.<sup>6</sup>

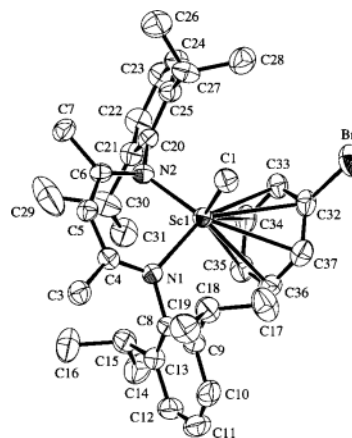
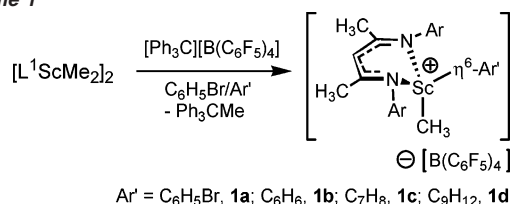
Recently, we reported a family of base-free dialkyl organoscandium complexes supported by bulky  $\beta$ -diketiminato ligands incorporating 2,6-diisopropylphenyl groups on nitrogen, and either Me ( $L^1$ ) or  $t$ Bu ( $L^2$ ) substituents in the 2,4 positions of the ligand backbone.<sup>7</sup> Activation of the monomeric  $t$ Bu-substituted dimethyl compound  $L^2ScMe_2$  with  $B(C_6F_5)_3$  gave a well-defined CIP which was highly active for ethylene polymerization.<sup>8</sup> Here we describe the activation chemistry of the less sterically encumbered scandium dimethyl derivative supported by  $L^1$ , which gives rise to stable SSIPs in arene solvents, providing the opportunity to probe solvent exchange processes in these rare species.

Previously, the compounds  $L^1ScCl_2$  and  $L^1ScMe_2$  were only available as THF adducts,<sup>7</sup> but we have subsequently discovered that prolonged exposure of  $L^1ScCl_2 \cdot THF$  to  $10^{-4}$  Torr at 130 °C removes the base completely. Alkylation of the resulting oligomeric  $[L^1ScCl_2]_n$  with MeLi in toluene cleanly affords the base-free dimethyl derivative  $[L^1ScMe_2]_2$  in 90% yield. The dimethyl compound is dimeric in the solid state, but, in solution, the terminal and bridging methyl groups are not distinguishable by NMR spectroscopy, suggesting a rapid dimer/monomer equilibrium or an intramolecular exchange process. In any event, reaction of  $[L^1ScMe_2]_2$  with common activators yields products consistent with reaction through a monomeric organoscandium compound.

For example, reaction with 1 equiv of  $B(C_6F_5)_3$ <sup>9</sup> at 240 K showed the formation of the expected CIP  $[L^1ScMe]^+[MeB(C_6F_5)_3]^-$ . Upon warming to 270 K, however, rapid  $C_6F_5$  transfer from the borate counterion to the metal center, along with production of  $MeB(C_6F_5)_2$ , was observed.<sup>10</sup> Addition of a second equivalent of borane results in abstraction of the remaining methyl group and formation of the CIP  $[L^1Sc-C_6F_5][MeB(C_6F_5)_3]$ . Evidently, the lower steric impact of  $L^1$  versus  $L^2$  reduces the barrier for  $C_6F_5$  back-transfer because we do not observe this in the  $[L^2ScMe][MeB(C_6F_5)_3]$  CIP.<sup>8</sup>

By contrast, activation of  $[L^1ScMe_2]_2$  in  $d_5$ -bromobenzene with 1 equiv of the trityl borate activator,  $[CPh_3][B(C_6F_5)_4]$ ,<sup>11</sup> cleanly produces an ion pair (**1a**) which shows no evidence for  $C_6F_5$  transfer

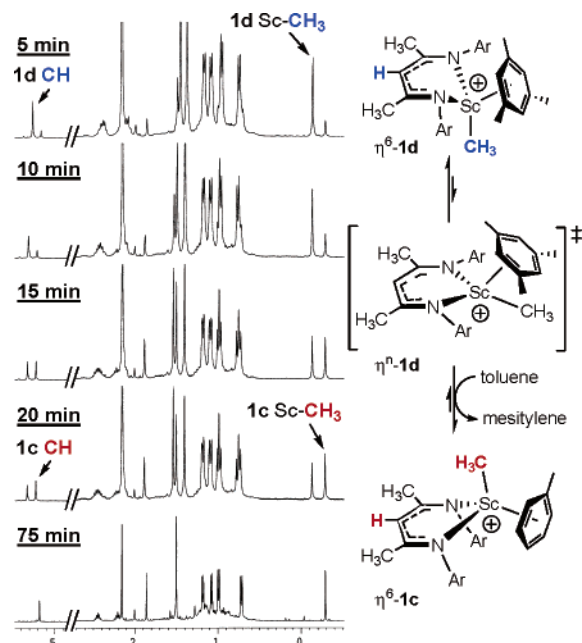
Scheme 1



**Figure 1.** Molecular structure of **1a** (counterion omitted for clarity). Selected bond distances (Å) and angles (deg): Sc(1)–N(1), 2.100(4); Sc(1)–N(2), 2.105(4); Sc(1)–C(1), 2.162(5); Sc(1)–C(32), 2.842(4); Sc(1)–C(33), 2.767(4); Sc(1)–C(34), 2.682(4); Sc(1)–C(35), 2.640(4); Sc(1)–C(36), 2.715(4); Sc(1)–C(37), 2.802(5); N(1)–Sc(1)–N(2), 90.79(14); N(1)–Sc(1)–C(1), 105.22(16); N(2)–Sc(1)–C(1), 105.23(16).

even at elevated temperatures (Scheme 1). X-ray crystallography reveals that in **1a** the bromobenzene solvent, surprisingly, coordinates the cationic Sc center in an  $\eta^6$  bonding mode (Figure 1). Usually, haloarenes coordinate in an  $\eta^1$  fashion via the halogen to  $d^0$  metals;<sup>12</sup> the preference for  $\eta^6$  hapticity here demonstrates the high electrophilicity and steric openness of these cations. Although the aromatic fragment is  $\eta^6$  bound, steric interactions invoke significant ring tilting (Sc–C<sub>arene</sub> = 2.640(4)–2.842(4) Å).<sup>13</sup> There are no close contacts ( $\leq 4.9$  Å) between the borate anion and the metal center.

The <sup>1</sup>H NMR spectra for SSIP **1a** at various temperatures exhibit a pattern consistent with rapid exchange between free and bound arene. Indeed, upon addition of more basic arenes to **1a**, the bromobenzene is displaced to give new SSIPs **1b–d** (Scheme 1).<sup>14</sup> X-ray crystallography shows that the toluene adduct **1c** is essentially isostructural with **1a**,<sup>15</sup> but the increased basicity of toluene<sup>16</sup> leads to  $C_s$  symmetry in the <sup>1</sup>H NMR spectrum at ambient temperatures. Upfield shifted resonances for the  $\eta^6$  toluene are observed at 6.81, 6.66, 6.39, and 1.85 ppm in  $C_6D_5Br$ . Addition of excess  $d_8$ -toluene to this sample of **1c** results in the disappearance of the signals for coordinated toluene over the course of 5 min, indicating exchange with free toluene. Competition experiments show that the order of



**Figure 2.** Representative series of  $^1\text{H}$  NMR spectra (300 MHz, 270 K,  $\text{C}_6\text{D}_5\text{Br}$ ) for the arene exchange of **1d** to **1c** (left). Proposed mechanism of exchange (right).

arene coordination is  $\text{C}_6\text{H}_5\text{Br} \ll \text{C}_6\text{H}_6$  (**1b**) <  $\text{C}_9\text{H}_{12}$  (**1d**) <  $\text{C}_7\text{H}_8$ , showing that steric factors come into play on incorporation of more than one methyl group in the arene.

At low temperatures, it is possible to quantitatively monitor the displacement of mesitylene from **1d** by toluene to give **1c** under pseudo-first-order conditions by  $^1\text{H}$  NMR spectroscopy (Figure 2). The reaction was followed at various temperatures, and an Eyring plot allowed for extraction of the activation parameters ( $\Delta H^\ddagger = 21.4(6) \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = 6(1) \text{ cal mol}^{-1} \text{ K}^{-1}$ ) which are quite close to those found for ion pair reorganization processes in metallocenium and constrained geometry cations partnered with the  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  anion.<sup>17</sup> Assessment of the rate using varying amounts of toluene (still pseudo-first-order) at the same temperature (261 K) indicates there is no dependence on [toluene]; in fact, at very high [toluene], the rate is slightly depressed, probably because the dielectric constant of the medium has changed significantly under these conditions. Although  $\Delta S^\ddagger$  is not large enough to support a fully dissociative mechanism, it is slightly positive; in combination with the lack of [toluene] dependence, a mechanism involving partial slippage of the outgoing  $\eta^6$  arene to a lower hapticity mode before displacement by the more basic toluene (Figure 2) is consistent with our results.

Thermodynamic parameters for arene exchange in cationic  $d^0$  complexes of relevance to olefin polymerization have not been reported to date; indeed, previous examples do not undergo arene exchange readily.<sup>6</sup> It has been previously noted that toluene has a dampening effect on olefin polymerization activity in lower coordinate, sterically open catalysts,<sup>18</sup> and these results provide a

concrete explanation for this observation. Indeed, preliminary studies using mesitylene complex **1d** as a catalyst show that there is significant polymerization activity when the experiment is conducted in bromobenzene whereas activity is negligible when carried out in more coordinating toluene. Thus, while ethylene is able to displace mesitylene, which has a barrier similar to that of the coordinating anion  $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ , it cannot compete with toluene for the active site, and activity is nullified.

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**Supporting Information Available:** Experimental details, tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic parameters for **1a** and **1c** (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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