Cationic Organoscanium β-Diketiminato Chemistry: Arene Exchange Kinetics in Solvent Separated Ion Pairs
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Received February 14, 2003; E-mail: wpiers@ucalgary.ca

Published on Web 04/18/2003

It is well established that early transition metal organometallic ion pairs with weakly coordinating anions are the active species in olefin polymerization processes.1 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.2 While these effects have been studied experimentally and computationally in some detail for metalloocene3 and constrained geometry catalyst families,4 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.5 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.6

Recently, we reported a family of base-free dialkyl organoscan­dium complexes supported by bulky β-diketiminato ligands incorporating 2,6-diisopropylphenyl groups on nitrogen, and either Me (L1) or Bu (L2) substituents in the 2,4 positions of the ligand backbone.7 Activation of the monomeric ‘Bu-substituted dimethyl compound L2ScMe2 with B(C6F5)3 gave a well-defined CIP which was highly active for ethylene polymerization.5 Here we describe the activation chemistry of the less sterically encumbered scandium dimethyl derivative supported by L1, which gives rise to stable SSIPs in arene solvents, providing the opportunity to probe solvent exchange processes in these rare species.

Previously, the compounds L1ScCl2 and L1ScMe2 were only available as THF adducts,7 but we have subsequently discovered that prolonged exposure of L1ScCl2:THF to 10–4 Torr at 130 °C removes the base completely. Alkylation of the resulting oligomeric [L1ScCl]n with MeLi in toluene cleanly affords the base-free dimethyl derivative [L1ScMe]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 [L1ScMe]2 with common activators yields products consistent with reaction through a monomeric organoscadnium complex.

For example, reaction with 1 equiv of B(C6F5)3 at 240 K showed that in the 1H NMR spectrum at ambient temperatures.

**Scheme 1**

![Scheme 1](image)

**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(10), 105.22(16); N(2)–Sc(1)–C(10), 105.23(16).
arene coordination is C₆H₅Br ≪ C₆H₆ (1b) < C₉H₁₂ (1d) < C₇H₈, 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 ¹H NMR spectroscopy (Figure 2). The reaction was followed at various temperatures, and an Eyring plot allowed for extraction of the activation parameters (ΔH° = 21.4(6) kcal mol⁻¹ and ΔS° = 6(1) cal mol⁻¹ K⁻¹) which are quite close to those found for ion pair reorganization processes in metalloccenium and constrained geometry cations partnered with the [B(C₆F₅)₄]⁻ anion.¹⁷ 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 ΔS° 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 η⁵ 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 d⁰ complexes of relevance to olefin polymerization have not been reported to date; indeed, previous examples do not undergo arene exchange readily.⁶ It has been previously noted that toluene has a dampening effect on olefin polymerization activity in lower coordinate, sterically open catalysts,¹⁸ 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 toluene for the active site, and activity is nullified.

Acknowledgment. This work is dedicated to Prof. Hans H. Brintlinger for his outstanding contributions to organometallic chemistry. Financial support for this work came from the NSERC of Canada in the form of a Discovery Grant and an E. W. R. Steacie Fellowship to W.E.P. (2001–2003), and scholarship support to P.G.H. (PGS-A and PGS-B). P.G.H. also thanks the Alberta Heritage Foundation for a Steinhauer Award and the Sir Izaak Walton Killam Foundation for a Fellowship.

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.

References

(14) While arene exchange in d⁰ metals is rare, several studies involving d⁰ metals exist, see for leading references: Telayg, T. G.; Stewart, K. J. J. Am. Chem. Soc. 1986, 108, 6977.
(15) See Supporting Information for details.

Figure 2. Representative series of ¹H NMR spectra (300 MHz, 270 K, C₆D₅Br) for the arene exchange of 1d to 1c (left). Proposed mechanism of exchange (right).