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Cationic Scandium Methyl Complexes Supported by a β-Diketiminato ("Nacnac") Ligand Framework

Paul G. Hayes,[†] Warren E. Piers,*[,†] and Robert McDonald[‡]

Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary,
Alberta, Canada T2N 1N4, and X-ray Structure Laboratory, Department of Chemistry, University of Alberta,
Edmonton, Alberta, Canada T6G 2G2

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Alkyl cations of group 4 metals play a crucial role in olefin polymerization catalysis,[1] and the cationic nature of these species is critical to their productivity in this process. This is underscored by the fact that their neutral group 3 metal congeners are generally much less active catalysts.[2] While this has been recognized for some time, suitable ligand modifications to allow for generation of well-defined group 3 metal cations have been slow to develop. Nonetheless, there are a few recently reported systems for which cationic alkyl scandium[3] or yttrium[3c,4] complexes have been implicated spectroscopically and by higher polymerization activities.

We have recently reported a family of base-free β-diketiminato, "nacnac", supported dialkyl scandium complexes[5] and shown that one of the dibenzyl derivatives may be activated with $B(C_6F_5)_3$ to form an ion pair.[2a] The X-ray structure of this material shows that the $[PhCH_2B(C_6F_5)_3]^-$ counteranion is strongly η^6 coordinated to the cationic scandium center, a feature that is manifested in this ion pair's complete lack of reactivity toward olefins. Using a sterically more bulky nacnac donor with ^{t}Bu groups in the ligand backbone allows for the isolation of the THF-free dimethyl compound **1**; here we discuss this material's reactions with varying amounts of the activator $B(C_6F_5)_3$[6] and report the first structural characterization of a scandium methyl cation, along with a preliminary assessment of its solution dynamic behavior. In addition, we show that **1** has ethylene polymerization activities comparable to those of metallocenes under borane activation.

Dimethyl scandium compound **1** reacts with varying equivalencies of $B(C_6F_5)_3$ to form different ion pairs as shown in Scheme 1. Upon reaction with 0.5 equiv of borane, a μ-methyl dimer (**2**) is formed,[7] as indicated by a characteristic set of resonances for the terminal Sc-Me groups (−0.29 ppm, 6H) and the bridging Sc-Me-Sc group (0.10 ppm, $^1J_{CH}$ = 132(1) Hz, 3H). Dimer **2** could not be isolated as a well-behaved solid and slowly evolves CH_4 in bromobenzene solution,[7] yielding an as yet uncharacterized product. When **1** is treated with a full equivalent of $B(C_6F_5)_3$, however, a monomeric ion pair $[L^tBuScCH_3]^+[H_3CB(C_6F_5)_3]^-$, **3**, is produced in excellent isolated yield when precipitated from hexane.[8]

As a yellow crystalline solid, **3** is stable for long periods of time at −30 °C. Its solid-state structure is shown in Figure 1 along with selected metrical data. The scandium atom sits 1.232 Å out of the plane defined by the C_3N_2 ligand atoms (mean deviation from plane = 0.053 Å) mainly for steric reasons and not because of any bonding interactions with the ligand backbone CH moiety (Sc−C(5) = 2.773(6) Å).[5] The Sc-CH_3 group occupies the *endo* coordination site (pointing in toward the ligand) while the methylborate counteranion is situated in the sterically more open *exo* site. The methyl group is more closely associated with the boron atom (B−C(2) = 1.643(9) Å) than the scandium atom (Sc−C(2) = 2.703(6) Å), but is not linearly bridged between the two as is

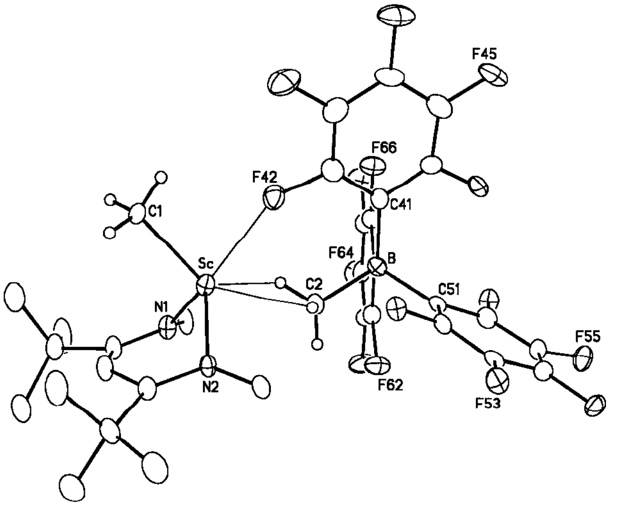
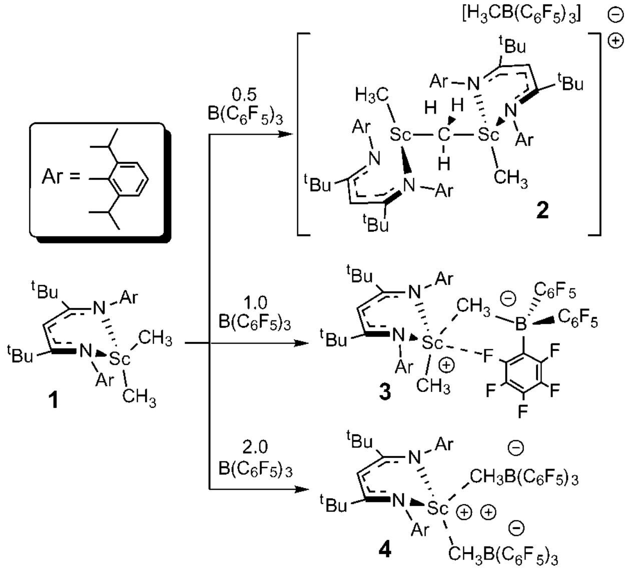


Figure 1. Molecular structure of ion pair **3**; aryl groups have been removed for clarity. Selected bond distances (Å): Sc−N(1), 2.060(5); Sc−N(2), 2.093(5); Sc−C(1), 2.221(5); Sc−C(2), 2.703(6); Sc−F(42), 2.390(4); B−C(2), 1.643(9). Selected bond angles (deg): N(1)−Sc−N(2), 95.06(19); Sc−C(2)−B, 138.72(18); Sc−F(42)−C(42), 153.7(4).

Scheme 1



[†] University of Calgary.
[‡] University of Alberta.

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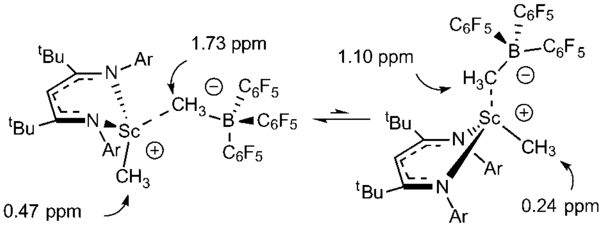
Scheme 2



3(Me*endo*) 2.2:1.0 **3(Me*exo*)**

commonly observed in metallocene structures[7] (Sc−C(2)−B = 138.72(18)°). The bending at this angle allows for a weak stabilizing interaction between an *ortho* fluorine group and the scandium center (Sc−F(42) = 2.390(4) Å); such a bonding mode for the $[H_3CB(C_6F_5)_3]^-$ anion has been observed previously in an yttrocene derivative.[9] In **3**, we could find no evidence for such a motif in solution by ^{19}F NMR spectroscopy.

Ion pair **3** exhibits complex dynamic behavior in solution. The ^1H NMR spectrum at room temperature is broad and essentially featureless, although signals for the bridging and terminal methyl groups can be identified at 1.40 and 0.28 ppm, respectively. These signals do not coalesce under any conditions, suggesting that borane dissociation[10] is a high barrier process in this system. When the sample is cooled to 213 K, the spectrum sharpens into a pattern consistent with the presence of two diastereomers (ratio 2.2:1.0) that differ in the *endo/exo* disposition of the terminal methyl group and the anion (Scheme 2). ROESY experiments show that the major diastereomer is the *endo*-Me, *exo*-anion isomer found in the solid state. Analysis of the NMR spectra at various temperatures reveals that exchange of the isomers occurs with a barrier of 12.4(5) kcal mol^{-1} at 263 K. Likely, these diastereomers interconvert via a ligand flipping mechanism similar to that proposed for the neutral dialkyl complexes,[5] although an associative ion pair reorganization process[11] via ion pair quadruples[12] may also be contributing to this exchange; further experiments are underway to unravel the details of this dynamic behavior more completely. Although stable as a solid for long periods, in solution **3** undergoes methane loss via metalation with a ligand isopropyl group[5] over the course of an hour at room temperature.

Although borane dissociation appears not to occur in these systems, we explored the possibility that excess free $B(C_6F_5)_3$ may catalyze the interconversion of the cationic diastereomers of **3**. Instead, we found that the second scandium methyl group can be abstracted to form the dicationic species **4** (Scheme 1) as an analytically pure white solid. This is indicated by the absence of an upfield $Sc-CH_3$ resonance in the ^1H NMR spectrum, and the appearance of signals for two diastereotopic $[MeB(C_6F_5)_3]^-$ anions in the ^1H, ^{11}B, and ^{19}F NMR spectra of the compound. We have observed high barriers to *endo*/*exo* group exchange in other sterically congested scandium nacnac compounds.[13] This double abstraction phenomenon has precedent in a non-Cp titanium-based system,[14] but unlike this system, compound **4** is moderately active for ethylene polymerization under ambient conditions (room temperature, 1 atm).

Compound **1** is an effective catalyst for ethylene polymerization under $B(C_6F_5)_3$, trityl borate, or PMAO-IP activation (Table 1) in a slurry batch reactor at 50 °C. Molecular weights are relatively high, and the polydispersities are consistent with a single site catalysis model. Activities are somewhat lower when the dichloride precursor is employed under MAO type activation, indicating that alkylation of the scandium center by organoaluminum reagents is slow. The activities in general, however, approach those observed for metallocene and other group 4 based catalysts, demonstrating that scandium cations can be highly effective catalysts. Notably, these activities are observed in the presence of the potentially coordinating solvent toluene,[3a,15] which was necessary to solubilize the catalyst.

Table 1. Ethylene Polymerization with **1** and Various Cocatalysts

E	cat.	CoCat	act.[a]	M_w ($\times 10^{-3}$)	M_w/M_n
1[b,c]	$LScCl_2$	PMAO-IP	9.9×10^4	1357	2.2
2[b,c]	1	PMAO-IP	1.2×10^6	1866	1.98
3[b,d]	1	$B(C_6F_5)_3$	3.0×10^5	1051	1.7
4[b,d]	1	TB[e]	4.8×10^5	851	2.48

[a] Activity in g PE/mol Sc•h. [b] Polymerization conditions: 50 °C, 300 psi, cyclohexane/toluene, [Sc] = 300 μM, stir rate = 2000 rpm. [c] Al/M = 20. [d] [Cocatalyst] = 315 μM, [PMAO-IP] = 1 mM as scavenger. [e] $[Ph_3C][B(C_6F_5)_4]$.

In summary, we have prepared a family of highly reactive organoscandium methyl cations supported by a bulky nacnac ligand and examined their solution and solid-state structures. These represent a new class of cationic organometallic compounds whose rich chemistry we are further exploring.

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Supporting Information Available: Experimental details, tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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