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Synthesis of Dialkylscandium Complexes Supported by *β*-Diketiminato Ligands and Activation with Tris(pentafluorophenyl)borane

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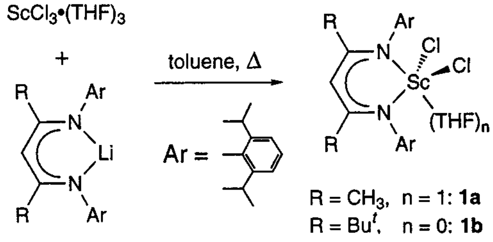
*Summary: Treatment of $ScCl_3\cdot THF_3$ with the lithium salts of the ligands ArNC(R)CHC(R)NAr, where Ar = 2,6-Pr^i-C_6H_3 and R = CH_3 and Bu^t, gives $LScCl_2\cdot n$THF derivatives (R = CH_3, n = 1, **1a**; R = Bu^t, n = 0, **1b**). These compounds can be derivatized by alkylation with methyllithium or benzylpotassium. The dibenzyl compound prepared from **1a**, when treated with $B(C_6F_5)_3$, gives an ion pair, **4**, in which the cationic scandium center is stabilized by a η^6-aryl interaction with the abstracted borate benzyl group.*

Nonmetallocene complexes of the early-transition-metal elements are of current interest as potentially novel olefin polymerization catalysts.[1] The flexibility of ligand design outside of the cyclopentadienyl paradigm has also allowed for the introduction of catalysts based on metals other than those of the traditional group 4, 5, and 6 triads, most notably the late-metal-based systems disclosed recently by Gibson[2] and Brookhart.[3] These examples make use of a general ligand environment first devised by McConville[4] in which two trigonal nitrogen donors are held in a chelating arrangement and the space around the metal center is sculpted by bulky aryl groups on the nitrogen atoms. A significant advantage to this ligand design is that neutral, monoanionic, and dianionic versions[1b] can be prepared and implemented depending on the available oxidation states of the metal in question.

The monoanionic *β*-diketiminato ligands, ArNC(R)CHC(R)NAr,[5] are ideal for use with metals in the +3 oxidation state and have recently been employed for early[6] and late[7] transition metals and group 13 main-group complexes.[8] These ligands have several attractive features, including the tunability possible in both Ar and R and variable bonding modes ranging from purely *σ* to a combination of *σ* and *π* donation depending on the steric environment and the electron demand at the bound metal.[6d] Our interest[9] in the chemistry of diorganoscandium complexes of general formula $LScR_2$,[10] coupled with the return to prominence of the *β*-diketiminato ligands, led us to prepare some examples of (*β*-diketiminato)ScR_2 complexes. In this communication, we detail those syntheses and present some preliminary reactivity data, including the generation and characterization of an organoscandium cation.

Lithium salts of the ligands ArNC(R)CHC(R)NAr, where Ar = 2,6-Pr^i-C_6H_3 and R = CH_3 and Bu^t, were prepared according to literature procedures.[6a] Reaction with $ScCl_3\cdot THF_3$ in toluene at high temperatures (85−100 °C) for extended periods (16−144 h) gave the dichloride derivatives **1a** and **1b** in good yields upon workup (eq 1). X-ray structural analysis[11] reveals **1a** to be monomeric with one THF molecule retained in the scandium's coordination sphere (Figure 1), which has a five-coordinate, distorted-trigonal-bipyramidal geometry. A symmetrical pattern for the ligand resonances



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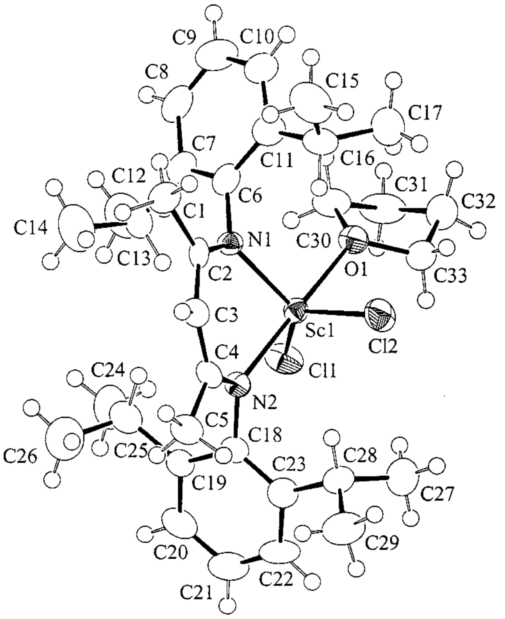
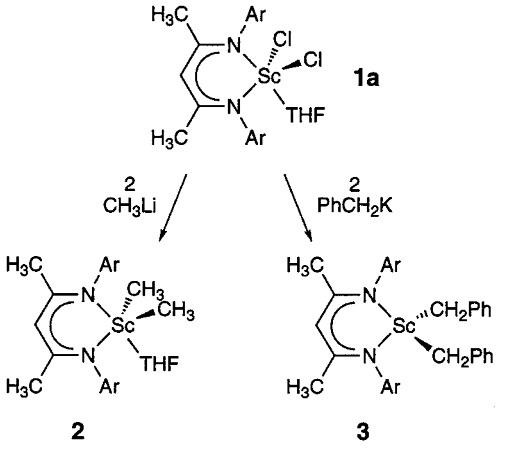


Figure 1. Molecular structure of **1a**. Selected bond lengths (Å): Sc(1)−N(1), 2.107(4); Sc(1)−N(2), 2.175(4); Sc(1)−O(1), 2.203(4); Sc(1)−Cl(1), 2.380(2); Sc(1)−Cl(2), 2.356(2); N(1)−C(2), 1.363(6); N(2)−C(4), 1.312(7); C(2)−C(3), 1.387(7); C(3)−C(4), 1.399(8). Selected bond angles (deg): N(1)−Sc(1)−N(2), 86.77(17); N(1)−Sc(1)−O(1), 95.82(16); N(2)−Sc(1)−O(1), 175.31(16); N(1)−Sc(1)−Cl(1), 123.79(13); N(1)−Sc(1)−Cl(2), 104.53(13); N(2)−Sc(1)−Cl(1), 92.33(12); N(2)−Sc(1)−Cl(2), 94.85(13); Sc(1)−N(1)−C(2), 122.4(3); Sc(1)−N(2)−C(4), 121.1(4).

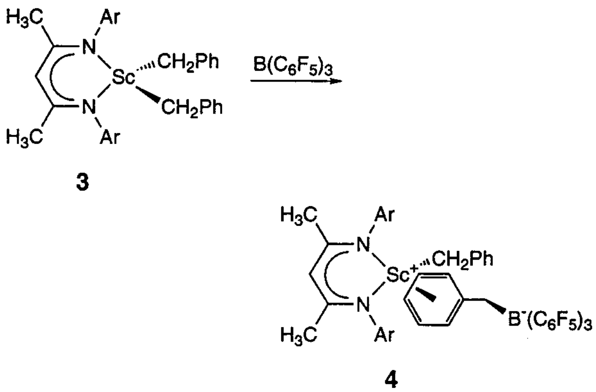
in the ^{1}H NMR spectrum of **1a** is observed, suggesting the compound is fluxional at room temperature. Attempts to thermally remove the THF under vacuum resulted primarily in decomposition.[12] In **1a**, the scandium center lies 0.694 Å out of the NC_3N plane, but the Sc−C(2,3,4) distances are quite long (3.062(6), 3.327(6), 3.066(6) Å, respectively) suggesting a negligible π contribution to the L−Sc bonding in this compound. Unlike **1a**, the dichloride derivative obtained from the Bu^t-substituted ancillary is devoid of THF. The bulkier Bu^t groups on the ligand backbone push the Ar moieties forward, relative to the methyl-substituted ancillary, forcing them to assume a more rigid configuration perpendicular to the N−Sc−N plane.[6b] This perturbation makes for a more sterically demanding ligand environment than in **1a**, accounting for the lack of THF coordination. Although the nuclearity of **1b** is unknown, its ready solubility in benzene is suggestive of a monomeric structure in solution.

Dichloride **1a** can be smoothly alkylated with conventional organolithium or potassium reagents (Scheme 1). Use of CH_3Li gives a THF-ligated dimethyl derivative (**2**), but incorporation of the more sterically demanding benzyl group using $PhCH_2K$ results in a THF-free dibenzyl compound (**3**). Although **3** is formally an eight-electron compound, normal values for the ^{13}C chemical shift of the benzyl C$_{ipso}$ atom[13] and the $^1J_{CH}$ coupling constant (121(1) Hz) suggest there is no multihapto bonding within the benzyl groups,[14] although a fluxional system cannot be ruled out in the absence of VT NMR studies.

Scheme 1



Neutral dialkyl compounds require activation via alkide abstraction with a strong electrophile in order to attain competency as an olefin polymerization mediator. Dibenzyl compound **3** reacts rapidly and cleanly with 1 equiv of $B(C_6F_5)_3$ to form an ion pair (**4**) in which the abstracted benzyl group remains closely associated with the scandium center through strong η^6-bonding[15] (eq 2). Four doublets in the ^{1}H NMR spectrum of **4** for the ligand Pr^i methyl groups indicate that the plane of symmetry in the molecule has been broken by a strong



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[11] Crystals of **1a** were grown from toluene/hexanes containing a few drops of THF: $C_{33}H_{49}N_2OCl_2Sc$, tetragonal, *I*1/*a* (No. 88), $a = 27.598(5)$ Å, $c = 17.567(5)$ Å, $V = 13380(3)$ Å^3, $Z = 16$, $D_{calcd} = 1.202$ g cm^{-3}, $2\theta_{max} = 50.1°$, Mo Kα radiation, $\lambda = 0.710$ 69 Å, $T = -103$ °C, 6399 measured reflections, 5792 unique, 2631 reflections with $I_{net} > 2.0\sigma(I_{net})$, $\mu = 4.05$ cm^{-1}, $R = 0.0652$, $R_w = 0.1777$, GOF = 7.37, 363 parameters.

[12] Protonated ligand was the major product isolated from this reaction.

[13] Three signals are observed in the C$_{ipso}$ region at 149.3, 143.2, and 142.2 ppm.

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ion–ion interaction. A doublet, triplet, triplet pattern (6.71, 6.34, and 6.15 ppm) for the *ortho*, *meta*, and *para* protons of the η^6-bound benzylic ring is characteristic of this moiety.[15]

The solution data are substantiated by an X-ray structural analysis[16] (Figure 2), which shows clearly the η^6-bonding of the abstracted benzyl group. Within this moiety, the average Sc(1)–carbon bond distance is 2.679(2) Å within a narrow range of 2.619–2.774(2) Å. For the benzyl group remaining on scandium, the Sc(1)–C(55)–C(56) angle of 117.1(4)° and the low $^1J_{CH}$ of 108(2) Hz[17] is indicative of normal η^1-bonding. The diketiminato ligand appears to be relatively more π-bound in this complex, compared to **1a**, as evidenced by the greater degree to which scandium lies out of the ligand plane (1.114 Å) and the shorter Sc(1)–C(1) and Sc(1)–C(3) distances of 2.835(2) and 2.787(2) Å, respectively. A stronger π component is to be expected for a more electrophilic, cationic scandium center. The N(1)–Sc(1)–N(2) angle of 94.79(7)° is significantly larger than the corresponding angle in **1a**.

The structure of **4** in solution is remarkably static. Heating samples to 90 °C resulted in no substantial change in the ^{1}H NMR spectrum. Furthermore, **4** was totally unreactive toward H_2 or ethylene, even at elevated temperatures. Evidently, the η^6-bound benzyl group is quite strongly attached in this system. It has been suggested by McConville that toluene binding to titanium cations in a similar ligand environment is responsible for suppressed activity of those systems in that solvent.[18] To this end, it is encouraging that a dimethylscandium complex free of THF can be obtained from **1b** and methyllithium. The reactivity of this base-free dimethyl complex toward standard and nonstandard activators is currently being explored in detail.

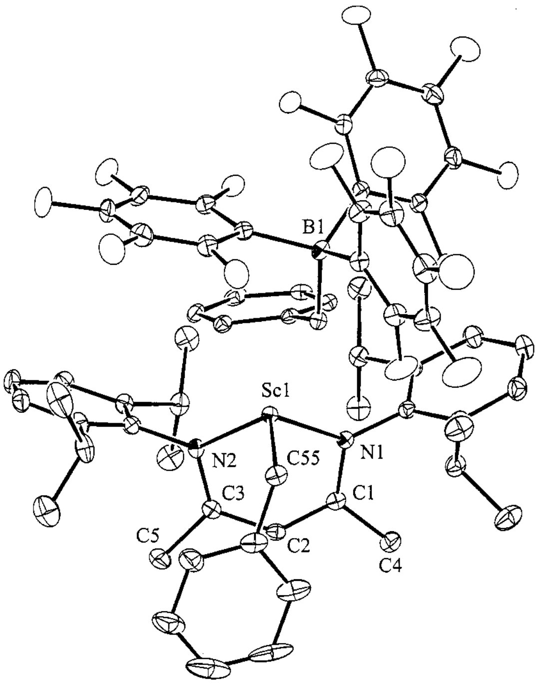

Figure 2. Molecular structure of **4**. Only one orientation of the disordered benzyl group[16] is shown for clarity. Selected bond lengths (Å): Sc(1)–N(1), 2.1143(11); Sc(1)–N(2), 2.0864(19); Sc(1)–C(1), 2.835(2); Sc(1)–C(2), 2.955(2); Sc(1)–C(3), 2.787(2); Sc(1)–C(55), 2.229(2); Sc(1)–C(30), 2.713(2); Sc(1)–(C31), 2.676(2); Sc(1)–C(32), 2.644(2); Sc(1)–C(33), 2.619(2), Sc(1)–C(34), 2.649(2); Sc(1)–C(35), 2.774(2); C(55)–C(56), 1.474(6); C(55)–C(56X), 1.508(11); C(35)–C(36), 1.482(3); C(36)–B(1), 1.679(3). Selected bond angles (deg): N(1)–Sc(1)–N(2), 94.79(7); N(1)–Sc(1)–C(55), 109.13(8); N(2)–Sc(1)–C(55), 110.33(8); Sc(1)–C(55)–C(56), 117.1(4); Sc(1)–C(55)–C(56X), 114.7(9); C(35)–C(36)–B(1), 115.71(19).

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Supporting Information Available: Text giving experimental details and characterization data for the compounds prepared in this paper and tables of crystal data, atomic coordinates and isotropic thermal parameters, and bond lengths and angles for compounds **1a** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystals of **4** were grown from benzene. A 2-fold disorder of the benzyl ligand attached to scandium in **4** was revealed in refinement. There are two orientations of the phenyl group with a common position for the methylene carbon. Crystal data: $C_{61}H_{55}N_2BF_{15}Sc{\cdot}C_6D_6$, monoclinic, $P2_1/c$, $a = 14.854(2)$ Å, $b = 10.9486(17)$ Å, $c = 37.357(6)$ Å, $\beta = 96.889(3)°$, $V = 6031.4(17)$ Å^3, $Z = 4$, $D_{calcd} = 1.367$ g cm^{-3}, $2\theta_{max} = 55.38°$, Mo Kα radiation, $\lambda = 0.710\,73$ Å, $T = 160(2)$ K, 10 575 measured reflections, 6442 with $I_{net} > 2.0\sigma(I_{net})$, $\mu = 2.11$ cm^{-1}, $R = 0.0461$, $R_w = 0.0919$, GOF = 0.875, 841 parameters.

(17) This value for $^1J_{CH}$ may point to an α-agostic interaction, although this question has not been probed further at this point.

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