

## Metalation-Resistant $\beta$ -Diketiminato Ligands for Thermally Robust Organoscandium Complexes

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Summary: A new ligand design for the widely used  $\beta$ -diketiminato framework implements a "remote steric bulk" strategy for the stabilization of low-coordinate, metalation-resistant organoscandium complexes. In comparison to standard ligands, substantial improvements in thermal stability for neutral dialkyl and cationic alkyl organoscandium complexes are observed.

Bulky  $\beta$ -diketiminato, or "nacnac", ligands have emerged as important ancillaries for metals from across the periodic table for a variety of applications.<sup>1</sup> One area of particularly high interest has been their use in stabilizing low-coordinate early transition metal complexes containing metal-alkyl, amido, and imido moieties.<sup>1,2</sup> The most commonly employed  $\beta$ -diketiminato ligands utilize N-aryl groups with *ortho*substitution (typically isopropyl groups) to provide steric bulk close to the metal center, with some fine-tuning available via modulation of the alkyl groups in the ligand backbone, **I**.

We have successfully deployed these ligands on group 3 metals scandium<sup>3</sup> and yttrium,<sup>4</sup> preparing low-coordinate bis-alkyls and well-defined alkyl cations<sup>5</sup> of moderate thermal stability. While workable under ambient conditions, these compounds are prone to metalative decomposition pathways, involving alkane elimination via  $\sigma$ -bond metathesis with a C-H bond of an *ortho*-isopropyl group from one of the N-aryl substituents. This has become particularly problematic

for further transformations requiring the application of heat<sup>6</sup> and has also impeded the isolation of base-free yttrium alkyl cations. Metalation has also been observed to be accelerated in the presence of Lewis acids.<sup>7</sup>

To circumvent this problem, we have reevaluated the  $\beta$ -diketiminato ligand design. The need to remove the offending C–H bonds from the vicinity of the metal's coordination sphere while maintaining the steric presence necessary for mononuclearity and low coordination numbers led us to consider a ligand with "remote steric bulk", using principles articulated and implemented by Wolczanski<sup>8</sup> and Stephan.<sup>9</sup> In this instance, relocation of the N-aryl substitution from the *ortho* to the *meta* positions, in concert with increasing their size, led us to consider ligands 1 and 2.

(11) Carey, D. T.; Cope-Eatough, E. K.; Vilaplana-Mafé, E.; Mair, F. S.; Pritchard, R. G.; Warren, J. E.; Woods, R. J. *Dalton Trans.* **2003**, 1083.

(12) See Supporting Information for details.

(13) Synthesis of [H(3,5-trip-C<sub>6</sub>H<sub>3</sub>)NC(Me)CHC(Me)N(3,5-trip-C<sub>6</sub>H<sub>3</sub>)] (2): A 100 mL round-bottom flask, fitted with a Dean–Stark condenser, was charged with 2,4-pentanedione (137 mg, 1.37 mmol), *p*-toluenesulfonic acid (260 mg, 1.37 mmol), and toluene (40 mL). This mixture was warmed to 60 °C for 30 min, after which time a solution of 3,5-bis(2,4,6-triisopropylphenyl)aniline (1.37 g, 2.76 mmol) in toluene (25 mL) was added via syringe. The reaction was refluxed overnight, removing water in the Dean–Stark when necessary, and the solvent volume in the reaction vessel was kept to 60–70 mL. After 24 h, 5 Å molecular sieves were added, and the reaction was refluxed or another 48 h. After cooling to room temperature, NEt<sub>3</sub> (160 mg, 1.6 mmol) was added and the solution stirred for 20 min. Upon removing the volatiles *in vacuo*, the yellow oily crude product was purified by column chromatography (using a basified silica column) and recrystallized in methanol to give a fine yellow powder of <sup>Hipt</sup>L<sub>Me</sub>H (1.05 g, 0.986 mmol, 72% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 12.90 (s, 1H, N··H··N), 7.01 (s, 8H, *m*-C<sub>6</sub>H<sub>2</sub>(trip)), 6.70 (d, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, 4H, *o*-C<sub>6</sub>H<sub>3</sub>), 6.60 (t, <sup>4</sup>J<sub>H-H</sub> = 1.4 Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 4.89 (s, 1H, CH), 2.90 (septet, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 4H, *p*-PrCH (trip)), 2.77 (septet, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 8H, *o*-<sup>1</sup>PrCH(trip)), 2.05 (s, 6H, CH<sub>3</sub>), 1.28 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, *p*-<sup>1</sup>PrCH<sub>3</sub>(trip)), 1.06 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, *o*-<sup>2</sup>Pr-CH<sub>3</sub>(trip)), 1.03 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, *o*-<sup>2</sup>Pr-CH<sub>3</sub>(trip)), 1.03 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, *o*-<sup>2</sup>Pr-CH<sub>3</sub>(trip)), 1.03 (d, <sup>3</sup>J<sub>H-H</sub> = 6.9 Hz, 24H, *o*-<sup>2</sup>Pr-CH<sub>3</sub>(trip)), 2.176 (Firso), 126.83 (*p*-C<sub>6</sub>H<sub>3</sub>), 122.05 (*o*-C<sub>6</sub>H<sub>3</sub>), 12.9.7 (*m*-C<sub>6</sub>H<sub>2</sub>(trip))), 21.46 (CH<sub>3</sub>). Anal. Calcd for C<sub>7</sub>7H<sub>106</sub>N<sub>2</sub>: C, 87.27; H, 10.08; N, 2.64. Found: C, 87.12; H, 10.14; N, 2.32.

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<sup>(1)</sup> Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. Chem. Rev. 2002, 102, 3031.

<sup>(2)</sup> For specific examples of Ti, Zr, V, and Cr complexes: (a) Budzelaar, P, H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485. (b) Basuli, F.; Huffman, J. C.; Mindiola, D. J. *Inorg. Chem.* **2003**, *42*, 8003. (c) Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. J. Am. Chem. Soc. **2003**, *126*, 6052. (d) Basuli, F.; Kilgore, U. J.; Hu, X.; Meyer, K.; Pink, M.; Huffman, J. C.; Mindiola, D. J. Angew. Chem., Int. Ed. **2004**, *43*, 3156. (e) Basuli, F; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. Chem. Commun. **2003**, 1554. (f) Basuli, F.; Kilgore, U. J.; Brown, D.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2004**, *23*, 6166. (g) Kakaliou, L.; Scanlon, W. J.; Qian, B.; Baek, S. W.; Smith, M.; Motry, D. H. *Inorg. Chem.* **1999**, *38*, 5964. (h) Rahim, M.; Taylor, N. J.; Smith, M. R.; Motry, D. H. *Organometallics* **1999**, *18*, 1693. (j) MacAdams, L. A.; Buffone, G. P.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. J. Am. Chem. Soc. **2005**, *127*, 1082.
(k) Kim, W.-K.; Fevola, M. J.; Liable-Sands, L. M.; Rheingold, A. L.; Theopold, K. H. *Organometallics* **1998**, *17*, 4541.

<sup>(3)</sup> Hayes, P. G.; Lee, L. W. M.; Knight, L. K.; Piers, W. E.; Parvez, M. Organometallics **2001**, *20*, 2533.

<sup>(4)</sup> Kenward, A. L.; Piers, W. E.; Parvez, W. E.; Hayes, P. G. Organometallics 2009, DOI: 10.1021/om 900082d.

 <sup>(5) (</sup>a) Hayes, P. G.; Piers, W. E.; McDonald, R. J. Am. Chem. Soc.
 2002, 124, 2132. (b) Hayes, P. G.; Piers, W. E.; Parvez, M. J. Am. Chem.
 Soc. 2003, 125, 5622. (c) Hayes, P. G.; Piers, W. E.; Parvez, M.
 Organometallics 2005, 24, 1173. (d) Hayes, P. G.; Piers, W. E.; Parvez, M.
 Chem.—Eur. J. 2007, 13, 2632.

<sup>(6) (</sup>a) Knight, L. K.; Piers, W. E.; Fleurat-Lessard, P.; McDonald, R.; Parvez, M. *Organometallics* **2004**, *23*, 2087. (b) Knight, L. K.; Piers, W. E.; McDonald, R. *Organometallics* **2006**, *25*, 3289. (c) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. Organometallics **2003**, *22*, 4705.

<sup>(7)</sup> Conroy, K. D.; Hayes, P. G.; Piers, W. E.; Parvez, M. Organometallics 2007, 26, 4464.

<sup>(8)</sup> Wolczanski, P. T. Polyhedron 1995, 14, 3335.

<sup>(9)</sup> Stephan, D. W. Organometallics 2005, 24, 2548.

<sup>(10)</sup> See Supporting Information for detailed preparation of terphenyl aniline  $H_2N$ -3,5-(2,4,6-*i*PrC<sub>6</sub>H<sub>2</sub>)C<sub>6</sub>H<sub>3</sub> via amination of a known aryl bromide: Yandulov, D. V.; Schrock, R. R.; Rheingold, A. L.; Ceccarelli, C.; Davis, W. M. *Inorg. Chem.* **2003**, *42*, 796.



Ligands 1 and 2 were prepared from 2,4-pentanedione and the appropriate anilines<sup>10</sup> via standard condensation methodology.<sup>2a,11,12</sup> Of particular interest, the terphenyl aniline utilized in the preparation of  $2^{13}$  was synthesized by first preparing the hexaisopropyl terphenyl bromide according to an established procedure<sup>14</sup> and then by direct amination with NH<sub>3</sub><sup>15</sup> (Scheme S1). Because of the more remote steric bulk, 1 and 2 can conveniently be affixed to scandium utilizing an alkane elimination protocol, whereas salt elimination/alkylation strategies were necessary with ligands I. Thus, dialkyl scandium complexes were accessible without having to resort to lithium salts of the ligands.

Scandium tris-alkyls  $Sc(CH_2SiMe_3)_3(THF)_2$  and  $Sc-(CH_2SiMe_2Ph)_3(THF)_2$  react with proteo-ligands 1 and 2 at room temperature, generating bis-alkyl complexes 3 and 4 (Scheme 1) with isolated yields ranging from 51% to 80%. The NMR spectra of isolated 3 and 4 reveal that no THF remains coordinated, and, unlike the scandium and yttrium complexes of ligand I, the <sup>1</sup>H NMR spectra are temperature invariant to -100 °C.



These variable-temperature NMR spectroscopic observations suggest that one of the consequences of the change in ligand structure is to allow the metal to lie in the plane of the ligand, favoring a  $C_{2\nu}$ , rather than  $C_s$ , symmetric groundstate structure. This is in line with the hypothesis that it is steric conflict between the *ortho* isopropyl groups of ligand I and the alkyl groups of a tetracoordinate metal complex that force the metal to adopt an out-of-plane stance in such complexes.<sup>2a,3</sup> Thus, in dialkyl scandium complexes of ligand I, the alkyl groups inhabit diastereotopic environments to alleviate steric interactions with the *ortho* isopropyl groups that are averaged on the NMR time scale. The assignment of  $C_{2\nu}$  symmetry to compounds 3 and 4 was confirmed by the X-ray



Figure 1. Thermal ellipsoid diagram (50%) of 3a. Selected bond distances (Å): Sc(1)-N(1), 2.1277(18); Sc(1)-N(2), 2.1279(17); Sc(1)-C(1), 2.215(2); Sc(1)-C(2), 2.210(2). Selected bond angles (deg): N(1)-Sc(1)-N(2), 83.06; C(1)-Sc(1)-C(2), 111.65 (8); Sc(1)-C(1)-Si(1), 123.33(10); Sc(1)-C(2)-Si(2), 121.11 (11). Selected dihedral angles (deg): C(4)-N(1)-C(8)-C(9), 82.6(3); C(6)-N(2)-C(22)-C(23), -56.5(3).



Figure 2. Thermal ellipsoid diagram (30%) of 4b. Selected bond distances (Å): Sc(1)-N(1), 2.127(4); Sc(1)-N(2), 2.122(4); Sc(1)-C(78), 2.201(4); Sc(1)-C(87), 2.202(5). Selected bond angles (deg): N(1)-Sc(1)-N(2), 84.96(14); C(78)-Sc(1)-C(87), 116.40(19). Selected dihedral angles (deg): C(2)-N(1)-C(6)-C(7), 77.0(6); C(4)-N(2)-C(42)-C(43), -82.0(6).

structural analysis of two of these complexes. Thermal ellipsoid diagrams of **3a** and **4b** are shown in Figures 1 and 2 respectively. In contrast to complexes of ligand **I**, in **3a** and **4b** 

<sup>(14)</sup> Yandulov, D. V.; Schrock, R. R. J. Am. Chem. Soc. 2002, 124, 6252.

<sup>(15)</sup> Surry, D. S.; Buchwald, S. L. J. Am. Chem. Soc. 2007, 129, 10354.



Scheme 3



the MR<sub>2</sub> group is nearly coplanar with the  $C_3N_2$  atoms of the ligand. In **3a**, the deviation of the scandium center from the  $C_3N_2Sc$  plane is 0.4896(3) Å, which is manifest in reduction of the N(1)-Sc(1)-N(2) angle by about 10° from those found in complexes of ligand **I**. In complex **4b**, the metal deviates only 0.224(3) Å from the  $C_3N_2Sc$  plane, providing further indication that redirection of the ligand bulk has reduced the steric confinements at the metal center.

Further inspection of the solid-state structures of **3** and **4** reveals that the "uprightness" of the N-aryl groups relative to the ligand plane differs from those found in complexes of ligands **I**, as exemplified by the dihedral angle C(2)-N(1)-C(6)-C(7) of 77.0(6) in **4b**. The N-aryl groups in **I** are much closer to perpendicular (89–99°). In spite of this, overall, ligands **1** and **2** provide impressive steric coverage about the scandium center, which, in concert with the bulky alkyl groups, renders these new complexes both monomeric and base free.

Scandium compounds **3** and **4** are *significantly* more thermally robust than the scandium bis-alkyls supported by ligands **I**. For example, while the complexes **I**-Sc- $(CH_2SiMe_3)_2$  and **I**-Sc $(CH_2SiMe_2Ph)_2$  begin to undergo metalation at 60 °C within 15 min,<sup>3</sup> the <sup>1</sup>H NMR spectra of **3** and **4** show no evidence of decomposition when heated to over 100 °C (see Figure S1, for example). When heated at 120 °C for over 5 h, signs of decomposition slowly begin to appear, although no well-defined metalation product could be identified by <sup>1</sup>H NMR spectroscopy.

Encouraged by the remarkable thermal stability of these complexes, we further explored their reactivity toward typical activating reagents, including  $[HNMe_2Ph][B(C_6F_5)_4]$  and  $[CPh_3][B(C_6F_5)_4]$ . The protonolysis of the bis-alkyls **4** with Brønstead acid  $[HNMe_2Ph][B(C_6F_5)_4]$  proceeded cleanly with the formation of new cationic complexes **5** and alkane liberation (Scheme 2). The product cations are subject to retention of the aniline produced in the reaction, as has commonly been

observed in early metal alkyl cations.<sup>16</sup> Interestingly, the chemical shifts of the coordinated aniline (7.24, 6.51, 6.49, 2.53 ppm in **5b**) are representative of  $\sigma$ -donation from the nitrogen lone pair. This N-based coordination contrasts recently characterized arene-based  $\pi$ -donation of coordinated NMe<sub>2</sub>Ph in  $\beta$ -diketiminato yttrium alkyl cations.<sup>4,17</sup>

In an NMR-scale reaction, treatment of bis-alkyl 4b with  $[CPh_3][B(C_6F_5)_4]$  cleanly afforded a new cationic product, 6 (Scheme 3). The <sup>1</sup>H NMR spectrum of 6 exhibits features representative of a  $C_{2\nu}$  symmetric complex, along with liberated Ph<sub>3</sub>CCH<sub>2</sub>SiMe<sub>2</sub>Ph. The <sup>11</sup>B NMR spectrum contains only one resonance at -16.5 ppm, typical for weakly coordinating perfluoroarylborate anions. The resonance at -7.9 ppm in the <sup>29</sup>Si NMR spectrum for the coordinated alkylsilane moiety is upfield of those observed in early metal complexes containing  $\beta$ -Si-C agostic interactions.<sup>18</sup> Furthermore, when this alkide abstraction is performed in nondeuterated solvent, there is no evidence of coordinated solvent, and this observation, along with the overall symmetric spectroscopic features, are in accord with 6 being a threecoordinate scandium alkyl cation. Despite several attempts, neither X-ray quality crystals nor a solid sample of 6 could be isolated. Similar to the neutral bis-alkyls, the scandium cations 5 and 6 supported by these redesigned  $\beta$ -diketiminate ligands

<sup>(16) (</sup>a) Horton, A. D.; de With, J. Organometallics **1997**, *16*, 5424. (b) Horton, A. D.; de With, J.; van der Linden, A.; van de Weg, H. Organometallics **1996**, *15*, 2672. (c) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F.; Peterson, J. L. Organometallics **1995**, *14*, 371. (d) Bei, Z.; Swenson, D. C.; Jordan, R. F. Organometallics **1997**, *16*, 3282. (e) Hollink, E.; Wei, P.; Stephan, D. W. Organometallics **2004**, *23*, 1562.

<sup>(17)</sup> Yu, N.; Nishiura, M.; Li, X.; Xi, Z.; Hou, Z. Chem. Asian J. 2008, 3, 1406.

<sup>(18) (</sup>a) Bolton, P. D.; Clot, E.; Adams, N.; Dubberley, S. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2006**, *25*, 2806. (b) Clot, E.; Eisenstein, O. *Struct. Bond.* **2004**, *113*, 1. (c) Tredget, C. S.; Clot, E.; Mountford, P. *Organometallics* **2008**, 27.

exhibit remarkable thermal stability. Over several days in room-temperature solution, there are no observable signs of decomposition, and heating to 80 °C overnight results in only slight decomposition (to protonated ligand and unidentifiable scandium-containing products).

The unparalleled thermal stability of these neutral and cationic scandium complexes verifies that in relocating the front-lying steric bulk in the  $\beta$ -diketiminato framework, we have implemented an effective ligand design strategy for preparing a metalation-resistant framework. These new complexes can now be subject to a previously unattainable thermal regime, and our ongoing studies are investigating reactions under these high-temperature conditions. Given the widespread use of  $\beta$ -diketiminato ligands I, these new

designs with remote steric bulk have substantial promise for stabilizing low-coordinate compounds of the early transition and main group metals.

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**Supporting Information Available:** Additional schemes and figures, experimental details, and crystallographic information files. This material is available free of charge via the Internet at http://pubs.acs.org.