

### Three-Coordinate Cationic Aluminum Alkyl Complexes Incorporating $\beta$ -Diketiminato Ligands

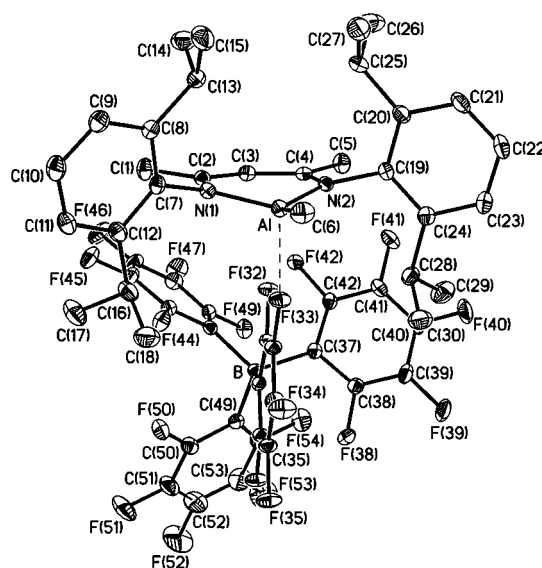
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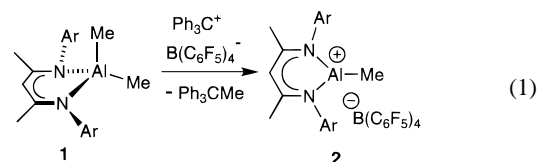
Low-coordinate cationic aluminum complexes are expected to be highly electrophilic and therefore are of interest for Lewis acid catalysis, olefin polymerization, and other potential applications.<sup>1</sup> Bochmann has reported that transient “R<sub>2</sub>Al<sup>+</sup>” (R = Me, <sup>t</sup>Bu) species can be generated in toluene-*d*<sub>8</sub> but abstract C<sub>6</sub>F<sub>5</sub><sup>-</sup> from B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> to form neutral Al and B complexes.<sup>2</sup> The bis-(cyclopentadienyl) aluminum cation in [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Al][MeB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] is more stable than AlR<sub>2</sub><sup>+</sup> alkyl species and has been exploited as an initiator for the cationic polymerization of isobutylene.<sup>3</sup> Nöth recently described the synthesis of [Al(NR<sub>2</sub>)<sub>2</sub>(L)][AlX<sub>4</sub>] salts (NR<sub>2</sub> = 2,2,6,6-tetramethylpiperidide; L = pyridine bases; X = Br, I) and concluded on the basis of <sup>27</sup>Al NMR, conductivity, and computational results that the Al cations have three-coordinate structures.<sup>4</sup> Several classes of four-coordinate Al cations have also been reported.<sup>5</sup> Here we describe three-coordinate, base-free aluminum alkyl cations that incorporate  $\beta$ -diketiminato ligands.

The reaction of {HC(CMeNAr)<sub>2</sub>}AlMe<sub>2</sub> (**1**, Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>-phenyl) with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in C<sub>6</sub>D<sub>6</sub> or C<sub>6</sub>D<sub>5</sub>Cl proceeds by methyl abstraction and yields [{HC(CMeNAr)<sub>2</sub>}AlMe][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**2**) and Ph<sub>3</sub>CMe (eq 1). Complex **2** is soluble in C<sub>6</sub>D<sub>5</sub>Cl, separates as a liquid clathrate (oil) from benzene, and was isolated as an off-white solid by the addition of hexanes to a liquid clathrate in benzene.<sup>6</sup> The addition of benzene/hexanes (1:10 by volume) to the isolated powder of **2**, gently heating to 50 °C for 2 days, and slowly cooling the mixture yielded **2**·benzene as colorless crystals. Complex **2** crystallizes as an ion pair in which the B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> anion binds weakly to the {HC(CMeNAr)<sub>2</sub>}AlMe<sup>+</sup> cation through a meta fluorine (Figure 1).<sup>7a</sup> The Al–F<sub>meta</sub> contact (Al–F(33), 2.151(1) Å) is significantly longer than typical terminal Al–F (~1.65 Å) and bridging Al–F–Al (~1.80 Å) bond distances.<sup>8</sup> Nevertheless, the Al–F(33) interaction results in lengthening of the C(33)–F(33) bond (1.394(2) Å) by 0.04 Å compared to the



**Figure 1.** Molecular structure of **2**. The hydrogen atoms have been omitted. Key bond distances (Å) and angles (deg) not given in text: Al–C(6) 1.905(2), N(1)–Al–N(2) 101.97(6), N(1)–Al–C(6) 125.97(8), N(2)–Al–C(6) 125.04(7).

average C–F bond length of the anion (1.350(6) Å). The geometry at Al is slightly distorted from planar to pyramidal: the sum of angles around Al is 353° and the Al is displaced from the N–N–CH<sub>3</sub> plane by 0.28 Å. The –85 °C <sup>1</sup>H NMR spectrum of **2** in CD<sub>2</sub>Cl<sub>2</sub> contains two doublets for the <sup>1</sup>Pr–Me groups, which is consistent with a C<sub>2v</sub>-symmetric structure and slow rotation around the N-aryl bonds. The –85 °C <sup>19</sup>F NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>) is not perturbed from that of free B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>.<sup>9</sup> These results indicate that B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> or CD<sub>2</sub>Cl<sub>2</sub> coordination to the {HC(CMeNAr)<sub>2</sub>}AlMe<sup>+</sup> cation, if present, is weak and labile under these conditions. The <sup>1</sup>H and <sup>19</sup>F NMR spectra of **2** are unchanged up to room temperature.



The reaction of **1** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> proceeds by methyl abstraction and yields [{HC(CMeNAr)<sub>2</sub>}AlMe][B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Me] (**3**, eq 2).

(7) (a) X-ray data for **2** benzene: triclinic, *P*1̄, *a* = 13.6005(7) Å, *b* = 14.6761(7) Å, *c* = 15.9556(8) Å,  $\alpha$  = 68.142(1)°,  $\beta$  = 82.499(1)°,  $\gamma$  = 75.838(1)°, *V* = 2863.2(2) Å<sup>3</sup>, *Z* = 2, *T* = 173(2) K, *D*<sub>calc</sub> = 1.411 g/cm<sup>3</sup>, *R*<sub>1</sub> = 0.0374, *wR*<sub>2</sub> = 0.0936 (*I* ≥ 2σ(*I*)). (b) X-ray data for **3**: triclinic, *P*1̄, *a* = 14.0700(7) Å, *b* = 16.6044(9) Å, *c* = 20.36(1) Å,  $\alpha$  = 99.262(1)°,  $\beta$  = 92.093(1)°,  $\gamma$  = 98.103(1)°, *V* = 4639.3(4) Å<sup>3</sup>, *Z* = 4, *T* = 173(2) K, *D*<sub>calc</sub> = 1.413 g/cm<sup>3</sup>, *R*<sub>1</sub> = 0.0368, *wR*<sub>2</sub> = 0.0898 (*I* ≥ 2σ(*I*)). All nonhydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. Software and sources of the scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI). Absorption corrections were applied using the program SADABS (Blessing, R. H. *Acta Crystallogr., Sect. A* 1995, 51, 33–38). Further details concerning the synthesis, characterization, and crystallographic analysis of **2**·benzene and **3** are given in the Supporting Information.

(8) (a) [(C<sub>5</sub>Me<sub>5</sub>)AlF<sub>2</sub>SiPh<sub>2</sub>]<sub>2</sub> contains Al–F–Al bridges (Al–F, 1.85 Å ave). Schulz, S.; Schoop, T.; Roesky, H. W.; Häming, L.; Steiner, A.; Irmer, R. H. *Angew. Chem., Int. Ed. Engl.* 1995, 34, 919. (b) [(Me<sub>3</sub>Si)<sub>3</sub>C]AlF<sub>2</sub> contains terminal Al–F bonds (Al–F, 1.67 Å ave) and bridging Al–F–Al interactions (Al–F, 1.80 Å ave). Schnitter, C.; Klimek, K.; Roesky, H. W.; Albers, T.; Schmidt, H.-G.; Röpken, C.; Parisini, E. *Organometallics* 1998, 17, 2249. (c) For a review of fluorocarbon coordination chemistry see: Plenio, H. *Chem. Rev.* 1997, 97, 3363.

(9) The <sup>19</sup>F NMR spectrum of **2** is identical to that of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]; see ref 1b.

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(1) (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* 1997, 119, 8125. (b) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* 1998, 120, 8277. (c) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* 1998, 120, 9384.

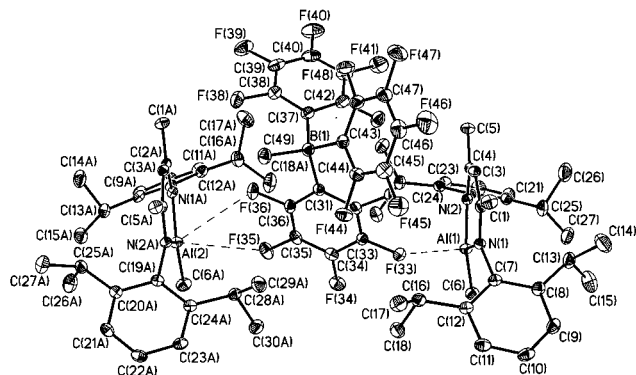
(2) Bochmann, M.; Sarsfield, M. J. *Organometallics* 1998, 17, 5908.

(3) (a) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* 1996, 35, 2226. (b) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* 1993, 32, 1655.

(4) Krossing, I.; Nöth, H.; Schwenk-Kircher, H. *Eur. J. Inorg. Chem.* 1998, 927, 7.

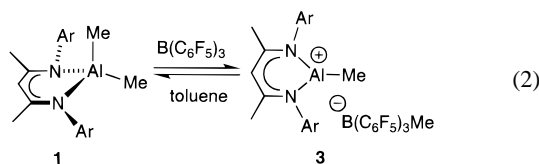
(5) (a) Coslédan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* 1999, 705. (b) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* 1998, 2523. (c) Atwood, D. A.; Jegier, J. *Inorg. Chem.* 1996, 35, 4277. (d) Emig, N.; Nguyen, N.; Krautscheid, H.; Réau, R.; Cazaux, J.-B.; Bertrand, G. *Organometallics* 1998, 17, 3599. (e) Atwood, D.; Jegier, J. *Chem. Commun.* 1996, 1507. (f) Uhl, W.; Wagner, J.; Fenske, D.; Baum, G. *Z. Anorg. Allg. Chem.* 1992, 612, 25. (g) Self, M. F.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* 1991, 10, 36. (h) Kynast, U.; Kelton, B. W.; White, A. H.; Henderson, M. J.; Raston, C. L. *J. Organomet. Chem.* 1990, 384, C1. (i) Engelhardt, L. M.; Kynast, U.; Raston, C. L.; White, A. H. *Angew. Chem., Int. Ed. Engl.* 1987, 26, 681. (j) Review: Atwood, D. A. *Coord. Chem. Rev.* 1998, 176, 407.

(6) Leading references to liquid clathrate phenomena: (a) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; pp 197–232. (b) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* 1999, 121, 5001.



**Figure 2.** Structure of the "triple ion" of **3**. The hydrogen atoms have been omitted. Key bond distances (Å) and angles (deg) not given in text: Al(1)–C(6) 1.902(2), Al(2)–C(6A) 1.907(2), N(1)–Al(1)–N(2) 103.18(6), N(1)–Al(1)–C(6) 126.62(7), N(2)–Al(1)–C(6) 125.20(7), N(1A)–Al(2)–N(2A) 102.86(6), N(1A)–Al(2)–C(6A) 128.37(7), N(2A)–Al(2)–C(6A) 128.46(7).

Compound **3** is soluble in  $C_6D_5Cl$ , benzene, and toluene and was isolated as a powder by the addition of hexanes to a solution of **3** in benzene, followed by filtration. Crystals of **3** were obtained by crystallization from toluene- $d_8$ .<sup>7b</sup> The asymmetric unit contains two cations and two anions which crystallize as a  $\{[HC(CMeNAr)_2]_2AlMe\}_2[B(C_6F_5)_3Me]^+$  "triple ion" (Figure 2) and a free  $B(C_6F_5)_3Me^-$  anion. One cation/anion pair (Al(1)/B(1)) within the triple ion interacts through a Al–F<sub>meta</sub> contact (Al(1)–F(33) = 2.275(1) Å) that is similar to that observed for **2**, and the C(33)–F(33) bond is correspondingly lengthened to 1.383(2) Å. The sum of the angles around Al(1) is 355°, and the displacement of Al(1) from the N–N–CH<sub>3</sub> plane is 0.24 Å. The Al(2) cation interacts with the B(1) anion by two very long Al–F contacts to ortho and meta fluorines of the same  $C_6F_5$  ring that interacts with Al(1). These Al–F distances are extremely long (Al(2)–F(35), 3.129(4) Å; Al(2)–F(36), 3.411(5) Å), and Al(2) is best regarded as a base-free, three-coordinate cation. The geometry at Al(2) is planar: the sum of the angles around Al(2) is 360° and the displacement of Al(2) from the N–N–CH<sub>3</sub> plane is only 0.06 Å. The closest Al–F contacts involving the B(2) borate anion are 4.97 Å (Al(1)) and 5.55 Å (Al(2)), and there are no Al–MeB contacts.



(10) Qian, B.; Ward, D. L.; Smith, M. R., III *Organometallics* **1998**, *17*, 3070.

(11) (a) Rahman, A. F. M. M.; Siddiqui, K. F.; Oliver, J. P. *Organometallics* **1982**, *1*, 881. (b) Healy, M. D.; Barron, A. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 921. (c) Barron, A. R.; Dobbs, K. D.; Franci, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 39. (d) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1997**, *119*, 8387–8388. (e) Petrie, M. A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 8704. (f) Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 2633. (g) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 3205. (h) Sheldrick, G. M.; Sheldrick, W. S. *J. Chem. Soc. (A)* **1969**, 2279. (i) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1699. (j) Petrie, M. A.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 1135. (k) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, *118*, 791. (l) Waggoner, K. M.; Ruhlandt-Senge, K.; Wehmschulte, R. J.; He, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2557. (m) Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *94*, 63.

(12) (a) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910. (b) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491. (c) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840.

(13) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(14) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

The  $-35$  °C NMR spectra of **3** in  $CD_2Cl_2$  contain  $\{[HC(CMeNAr)_2]AlMe^+\}$  resonances that are identical to those of **2** and  $B(C_6F_5)_3Me^-$  resonances that are very similar to those of  $[NBu_3Bz][B(C_6F_5)_3Me]$ . These results indicate that **3** exists as free or weakly ion-paired or solvated ions in  $CD_2Cl_2$  solution under those conditions. However, the behavior of **3** in toluene- $d_8$  is more complex. The  $-13$  °C  $^1H$  NMR spectrum of **3** in toluene- $d_8$  contains separate Al–Me ( $\delta$   $-0.83$ ) and B–Me ( $\delta$   $1.36$ ) resonances. The latter resonance is slightly shifted from that of  $[NBu_3Bz][B(C_6F_5)_3Me]$  ( $\delta$   $1.09$ ), probably due to ion-pairing effects. The Al–Me and B–Me resonances broaden and coalesce ( $23$  °C) as the temperature is raised, and at  $57$  °C, a single Al–Me/B–Me resonance is observed at  $\delta$   $-0.52$ , close to the position expected for **1**. Additionally, the  $^{19}F$  NMR spectrum changes significantly as the temperature is raised; in particular the  $p$ -F resonance broadens and shifts from  $\delta$   $-163.2$  at  $-3$  °C to  $\delta$   $-147.2$  at  $37$  °C. At  $62$  °C, the  $^{19}F$  NMR spectrum of **3** ( $\delta$   $-129.6$ ,  $-147.2$ ,  $-162.0$ ) is very similar to that of  $B(C_6F_5)_3$  ( $\delta$   $-129.2$ ,  $-142.9$ ,  $-160.7$ ) although the  $p$ -F resonance is still broadened. Concurrent with these changes, the  $^{11}B$  NMR resonance of **3** ( $\delta$   $-15.0$  at  $-58$  °C) broadens into the baseline as the temperature is raised, as expected for conversion of four-coordinate B to three-coordinate B. These spectral changes are reversible and show that **3** undergoes substantial reversion to **1** and  $B(C_6F_5)_3$  at higher temperatures, as indicated in eq 2. The observation of  $Me^-$  rather than  $C_6F_5^-$  transfer from  $B(C_6F_5)_3Me^-$  to  $\{[HC(CMeNAr)_2]AlMe^+\}$  is surprising given that Al–MeB interactions are not observed in the solid-state structure of **3** and similar compounds decompose by irreversible  $C_6F_5^-$  transfer.<sup>10</sup>

This work shows that three-coordinate aluminum alkyl complexes can be generated by alkyl abstraction from neutral dialkyl precursors by  $[Ph_3C][B(C_6F_5)_4]$  or  $B(C_6F_5)_3$ . The electronic properties and steric bulk of the  $\beta$ -diketiminato ligand contribute to the stability of the  $\{[HC(CMeNAr)_2]AlMe^+\}$  cation. The Al–N bond lengths of **2** (Al–N(1) 1.824(1), Al–N(2) 1.828(1) Å) and **3** (Al(1)–N(1) 1.822(1), Al(1)–N(2) 1.827(1), Al(2)–N(1A) 1.822(1), Al(2)–N(2A) 1.812(1) Å) are  $\sim 0.1$  Å shorter than those of **1** (Al(1)–N(1) 1.920(2), Al(1)–N(5) 1.942(2) Å),<sup>1c</sup> which is indicative of increased ionic interactions or N–Al  $\pi$ -bonding in the cationic species. The sterically demanding 2,6- $i$ -Pr<sub>2</sub>-phenyl groups disfavor the formation of dinuclear species and hinder exchange reactions with the anion. Similar strategies based on bulky alkoxide, amide, or alkyl ligands have been exploited in the synthesis of neutral three-coordinate aluminum complexes.<sup>11</sup> The electrophilic character of the  $\{[HC(CMeNAr)_2]AlMe^+\}$  cation is manifested by ion-pairing with the weakly nucleophilic  $B(C_6F_5)_4^-$  and  $B(C_6F_5)_3Me^-$  anions in the solid state. These Al–F–C interactions perturb the Al coordination geometry and lengthen the C–F bonds but appear to be weaker than the M–F interactions observed in transition metal salts of these anions.<sup>12</sup> For example, ion pairing in  $[(C_5Me_5)_2Zr][B(C_6F_5)_3H]$  (**4**) occurs through Zr–F contacts to meta and ortho fluorines of the anion (Zr–F<sub>ortho</sub> = 2.416(3), Zr–F<sub>meta</sub> = 2.534(3) Å).<sup>13</sup> These Zr–F contacts are  $\sim 10\%$  shorter than the Al–F contacts in **2** when corrected for the difference in ionic radii between Zr(IV) and Al(III).<sup>14</sup> Furthermore, the Zr–F interactions in **4** can be detected in toluene solution by  $^{19}F$  NMR below  $-30$  °C, whereas Al–F interactions are not detected for **2** and **3** in solution by  $^{19}F$  NMR. The difference in the solution behavior of **2** and **3** shows that, as for transition metal systems, the anion plays a key role in stabilizing cationic main group species. The reactivity of **2**, **3**, and related complexes will be discussed in a future report.<sup>1c</sup>

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**Supporting Information Available:** Synthetic procedures, characterization data for new compounds, and details of the X-ray structure determinations of **2** and **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.