

## Reversible Ethylene Cycloaddition Reactions of Cationic Aluminum $\beta$ -Diketiminato Complexes

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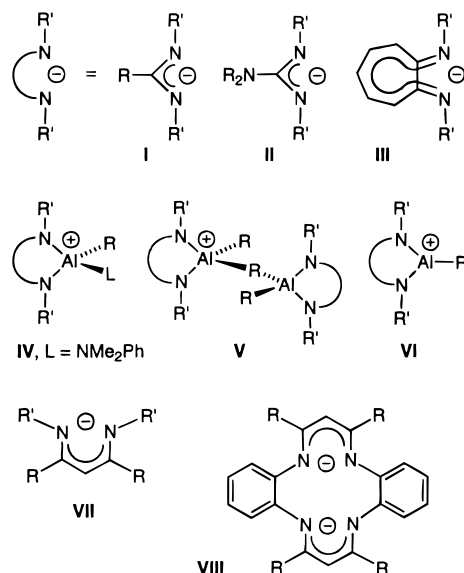
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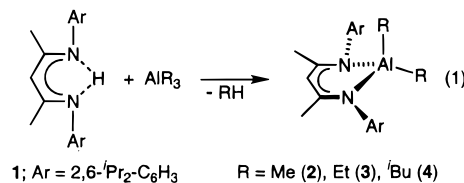
We recently described several classes of aluminum dialkyl compounds  $\{L-X\}AlR_2$  that incorporate bidentate, monoanionic, nitrogen-based  $L-X^-$  ligands (Chart 1), including amidinates (**I**),<sup>1</sup> guanidinates (**II**),<sup>2</sup> and aminotroponiminates (ATI, **III**).<sup>3</sup> Reaction of  $\{L-X\}AlR_2$  complexes with the "cationic activators"  $[HNMe_2-Ph][B(C_6F_5)_4]$ ,  $B(C_6F_5)_3$ , or  $[Ph_3C][B(C_6F_5)_4]$  yields cationic aluminum alkyls **IV–VI**. Species of type **VI**, with only weak solvent or counterion coordination, are of interest for catalytic applications such as olefin polymerization. Potential strategies for modifying the  $\{L-X\}AlR_2$  complexes to disfavor the formation of **IV** and **V** include (i) increasing the steric demand of the  $L-X^-$  ligands through incorporation of bulky R and R' substituents, (ii) using higher Al–R groups (R > Me) to minimize alkyl bridging, and (iii) increasing the chelate ring size to widen the N–Al–N angle (e.g., **III** vs **I** or **II**). To explore the latter theme we have investigated  $\beta$ -diketiminato ligands (**VII**) which form six-membered chelate rings. Several  $\beta$ -diketiminato complexes of s, d, and f block metals and tin have been described, and group 13 complexes of macrocyclic ligands (e.g., **VIII**) that incorporate  $\beta$ -diketiminato units have also been investigated.<sup>4–6</sup> Here we describe new cationic  $\beta$ -diketiminato aluminum alkyl complexes and their remarkable reversible cycloaddition reactions with ethylene.<sup>7</sup>

The reaction of  $\beta$ -diketimine **1** (Ar = 2,6-*i*-Pr<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sup>8</sup> with  $AlR_3$  (R = Me, Et, *i*Bu) in hexanes yields **2–4** by alkane elimination (eq 1). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2–4** are consistent with time-averaged *C*<sub>2v</sub>-symmetric structures and restricted rotation

Chart 1



around the N–Ar bonds. The molecular structure of **2** was confirmed by X-ray crystallography.<sup>9</sup> **2** exhibits distorted tetrahedral geometry at Al and contains a planar, delocalized, chelating  $\beta$ -diketiminato ligand. The N–Al–N angle (96.17(7)°) is larger than those in  $\{Pr_2-ATI\}AlMe_2$  (83.3(1)°) or (amidinate) $AlMe_2$  complexes (ca. 69°).<sup>1b,3b</sup> The Al atom is displaced from the  $\beta$ -diketiminato plane by 0.73 Å, giving rise to crystallographically distinct  $AlMe$  groups. However, exchange of the  $AlMe$  groups is fast on the NMR time scale (23 °C) as only one  $AlMe_2$  signal is observed in the <sup>1</sup>H and <sup>13</sup>C spectra.



(1) (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. (b) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, Jr., V. G., *Organometallics* **1997**, *16*, 5183. (c) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, in press.

(2) Aeilts, S.; Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 7, 3265.

(3) (a) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, in press. (b) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100.

(4) (a) Hitchcock, P. B.; Lappert, M. B.; Layh, M. *Chem. Commun.* **1998**, 201. (b) Hitchcock, P. B.; Lappert, M. B.; Tian, S. *J. Chem. Soc., Dalton Trans.* **1997**, 1945. (c) Hitchcock, P. B.; Lappert, M. B.; Layh, M.; Liu, D.-S.; Severn, J. R.; Shun, T. *Ann. Chim. Int. Ed.* **1996**, *92*, 186. (d) Hitchcock, P. B.; Lappert, M. F.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2637. (e) Hitchcock, P. B.; Lappert, M. B.; Liu, D.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 1699. (f) Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1968**, *7*, 1408. (g) McGeachin, S. G. *Can. J. Chem.* **1968**, *46*, 1903. (h) Mair, F. S.; Scully, D.; Edwards, A. J.; Raithby, P. R.; Snaith, R. *Polyhedron* **1995**, *14*, 2397. (i) Rahim, M.; Taylor, N. J.; Xin, S.; Collins, S. *Organometallics* **1998**, *17*, 1315.

(5) (a) Cannadine, J. C.; Errington, W.; Moore, P. Wallbridge, M. G. H.; Nield, E.; Fenn, D. J. *Organomet. Chem.* **1995**, *486*, 237. (b) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Gobran, H. R.; Atwood, J. L. *Inorg. Chem.* **1993**, *32*, 4671. (c) Atwood, D. A.; Atwood, V. O.; Cowley, A. H.; Atwood, J. L.; Roman, E. *Inorg. Chem.* **1992**, *31*, 3871. (d) Guillard, R.; Zrineh, A.; Tabard, A.; Courthaudon, L.; Han, B.; Ferhat, M.; Kadish, K. M. *J. Organomet. Chem.* **1991**, *401*, 227. (e) Kuroki, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1987**, *109*, 4737. (f) Goedken, V. L.; Ito, H.; Ito, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1453.

(6) Reviews of type **VIII** ligands: (a) Mountford, P. *Chem. Soc. Rev.* **1998**, *27*, 105. (b) Cotton, F. A.; Czuchajowska, J. *Polyhedron* **1990**, *9*, 2553.

(7) After submission of this manuscript, a paper by Smith, III et al. appeared which describes the synthesis and structural analysis of **2**. Our data for **2** agree well with those of Smith, et al. Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070.

(8) Feldman, J.; McLain, S. J.; Parthasarathy, A.; Marshall, W. J.; Calabrese, J. C.; Arthur, S. D. *Organometallics* **1997**, *16*, 1514.

In initial ethylene polymerization studies, it was found that treatment of **3** or **4** with 1 equiv of  $[Ph_3C][B(C_6F_5)_4]$  in toluene (23 or 100 °C; 75 psi ethylene), which was anticipated to generate cationic species of type **V** or **VI**, did not afford active catalysts. These results were surprising in light of previous observations of ethylene polymerization activity by cations of type **V** or **VI** containing amidinate or ATI ligands, generated in the same fashion.<sup>1a,3a</sup> The reactions of **3** and **4** with cationic activators were investigated further to determine the origin of this difference.

The reaction of **3** with 1 equiv of  $[Ph_3C][B(C_6F_5)_4]$  in *C*<sub>6</sub>D<sub>5</sub>Cl results in  $\beta$ -hydride abstraction and formation of 1 equiv of  $Ph_3CH$ , and affords the unusual bicyclic Al cation  $[\{\eta^3-N,N-C-HC(CMeNAr)_2(CH_2CH_2)\}AlEt^+][B(C_6F_5)_4]$  (**5**, Scheme 1). **5** is formally derived by 1,4 cycloaddition of ethylene to  $\{HC-(CMeNAr)_2\}AlEt^+$ , and contains a tridentate monoanionic diimine alkyl ligand. Analytically pure **5** can be isolated as a pale yellow solid by the addition of hexanes to the reaction mixture followed by filtration. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **5** are consistent with a *C*<sub>s</sub>-symmetric structure, restricted rotation around the N–Ar

(9) X-ray data for **2**: crystal system monoclinic, space group *P2<sub>1</sub>/n*, *a* = 13.467(3) Å, *b* = 19.510(6) Å, *c* = 12.718(3) Å,  $\beta$  = 116.78(2)°, *V* = 2983.1(13) Å<sup>3</sup>, *Z* = 4, *R*<sub>1</sub> = 0.0395, *wR*<sub>2</sub> = 0.0949, data/parameters = 5140/446. Key distances and angles: Al–N 1.920(2), 1.942(2) Å; Al–C 1.963(2), 1.971(2) Å; C–Al–C 117.4(1)°.

