Reversible Ethylene Cycloaddition Reactions of Cationic Aluminum β -Diketiminate Complexes

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We recently described several classes of aluminum dialkyl compounds $\{L-X\}AR_2$ that incorporate bidentate, monoanionic, nitrogen-based $L-X^{-1}$ ligands (Chart 1), including amidinates (I), guanidinates (II),² and aminotroponiminates (ATI, III).³ Reaction of {L-X}AlR₂ complexes with the "cationic activators" [HNMe₂-Ph][B(C₆F₅)₄], B(C₆F₅)₃, or [Ph₃C][B(C₆F₅)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 $\{L-X\}AIR_2$ 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 β -diketiminate ligands (VII) which form six-membered chlelate rings. Several β -diketiminate 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 β -diketiminate units have also been investigated.⁴⁻⁶ Here we describe new cationic β -diketiminate aluminum alkyl complexes and their remarkable reversible cycloaddition reactions with ethylene.7

The reaction of β -diketimine 1 (Ar = 2.6-ⁱPr₂-C₆H₂)⁸ with AlR₃ $(R = Me, Et, {}^{i}Bu)$ in hexanes yields 2-4 by alkane elimination (eq 1). The ¹H and ¹³C NMR spectra of 2-4 are consistent with time-averaged C_{2v} -symmetric structures and restricted rotation

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(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 well with those of Smith, et al. Qian, B.; Ward, D. L.; Smith, M. R., III. Organometallics **1998**, *17*, 3070.

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Chart 1



around the N-Ar bonds. The molecular structure of 2 was confirmed by X-ray crystallography.⁹ 2 exhibits distorted tetrahedral geometry at Al and contains a planar, delocalized, chelating β -diketiminate ligand. The N-Al-N angle (96.17(7)°) is larger than those in {ⁱPr₂-ATI}AlMe₂ (83.3(1)°) or (amidinate)AlMe₂ complexes (ca. 69°).^{1b,3b} The Al atom is displaced from the β -diketiminate 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 AlMe₂ signal is observed in the ¹H and ¹³C spectra.



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.^{1a,3a} 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_6D_5Cl results in β -hydride abstraction and formation of 1 equiv of Ph₃-CH, and affords the unusual bicyclic Al cation [$\{\eta^3-N,N,C HC(CMeNAr)_2(CH_2CH_2)$ AlEt][B(C₆F₅)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 ¹H and ¹³C NMR spectra of 5 are consistent with a C_s -symmetric structure, restricted rotation around the N-Ar

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⁽⁹⁾ X-ray data for **2**: crystal system monoclinic, space group $P2_i/n$, a = 13.467(3) Å, b = 19.510(6) Å, c = 12.718(3) Å, $\beta = 116.78(2)^{\circ}$, V = 2983.1(13) Å³, Z = 4, R1 = 0.0395, wR2 = 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)°.



bonds, and the presence of a single Al-Et group. The ¹H NMR spectrum contains broad resonances at δ 0.42 (2H) and 2.46 (2H), and the ¹³C NMR spectrum contains two triplets (δ –0.2, J_{CH} = 124 Hz; 27.6, J_{CH} = 140) for the AlCH₂CH₂C bridge. The ¹³C NMR methine (C_γ) resonance shifts from δ 98.3 (J_{CH} = 155) for **3** to δ 55.7 (J_{CH} = 139) for **5**, and the imine carbon resonance shifts from δ 170.7 for **3** to δ 189.2 for **5**. These results are consistent with conversion of the β -diketiminate ligand of **3** to a β -diketimine ligand in **5**. The structure of **5** was confirmed by a COSY spectrum which exhibited AlCH₂CH₂C/AlCH₂CH₂C correlations and C_γH/AlCH₂CH₂C correlations.

The reaction of **3** with 1 equiv of $[\text{HNMe}_2\text{Ph}][B(C_6F_5)_4]$ in CD₂Cl₂ generates the amine adduct [{HC(CMeNAr)₂}AlEt(NMe₂-Ph)][B(C₆F₅)₄] (**6**) and ethane (¹H NMR δ 0.88). NMR data establish that **6** has a *C*_s-symmetric structure with a plane of symmetry passing through the Et-Al-NMe₂Ph groups and bisecting the β -diketiminate ring. The ¹H and ¹³C NMR NMe₂Ph resonances are shifted from those of free NMe₂Ph, consistent with coordination of the amine to Al. Comparison of the ¹H and ¹³C NMR data for **6** to data for **2**–**5** indicates that the β -diketiminate structure is retained in **6**.

Remarkably, **5** undergoes cycloreversion and ethylene loss upon reaction with nucleophiles. The reaction of **5** with excess NMe₂-Ph in CD₂Cl₂ (<10 min, 23 °C) liberates ethylene (δ 5.4) and generates amine adduct **6**. The reaction of **5** with excess 2-butyne (<10 min, 23 °C) generates free ethylene and the 1,4 cycloaddition product **7**. NMR data establish that **7** has a bicyclic, *C_s*symmetric structure which is very similar to that of **5**. The ¹H NMR spectrum contains two singlets (δ 2.06 and 2.15) for the AlCMe=CMeC bridge. The ¹³C NMR resonances for the methine and imine carbons are very similar to those for **5**, indicating that **7** contains a tridentate, monoanionic diimine alkenyl ligand. **5** does not release ethylene in the solid state under vacuum but undergoes complete ethylene exchange (at the bridge site) with ethylene-*d*₄ (1 atm) in less than 10 min at 23 °C in CD₂Cl₂.

To intercept a cation of type **VI** prior to olefin cycloaddition, we investigated the reactivity of ^{*i*}Bu compound **4**. The reaction of **4** with $[Ph_3C][B(C_6F_5)_4]$ in C₆D₆ or C₆D₅Cl proceeds by β -hydride abstraction and yields [{HC(CMeNAr)_2}Al^{*i*}Bu][B(C_6F_5)_4]

(8), Ph₃CH, and polyisobutylene.¹⁰ Complex 8 was isolated as an off-white solid by addition of hexanes to a liquid clathrate of **8** in C₆H₆.^{3a} NMR data (23 °C) establish that the cation of **8** has a C_{2v} -symmetric structure, rotation around the N-Ar bonds is slow on the NMR time scale, and solvent coordination or ion pairing are weak and labile. These data are consistent with a monomeric cation structure in which the isobutyl group moves rapidly between the two available coordination sites or, less likely, a dinuclear dication structure with bridging isobutyl groups.^{3a} Further characterization of this interesting cation is in progress. 8 reacts with ethylene (1 atm, <10 min, 23 °C) to generate the 1,4 cycloaddition product $[\{\eta^3-N,N,C-HC(CMeNAr)_2(CH_2CH_2)\}$ - $Al^{i}Bu$ [B(C₆F₅)₄] (9). The ¹H and ¹³C NMR data for 9 are nearly identical to the data for 5. 9 does not release ethylene when exposed to dynamic vacuum but reacts rapidly (<10 min, 23 °C) with NMe₂Ph to yield [{HC(CMeNAr)₂}AlⁱBu(NMe₂Ph)][B(C₆F₅)₄] (10) and free ethylene. Amine adduct 10 is also formed by the reaction of 4 with 1 equiv of $[HNMe_2Ph][B(C_6F_5)_4]$.

Several Co, Rh, Fe, and Ru complexes of VIII (or related macrocyclic ligands that incorporate β -diketiminate units) undergo cycloaddition reactions with alkynes, strained alkenes, or nitriles that are related to the reactions described here.¹¹ Additionally, Pd, Rh, and Ir diketonate complexes undergo cycloaddition reactions with hexafluoro-2-butyne.¹² The present results are noteworthy because the unactivated olefin, ethylene, undergoes *reversible* cycloaddition to a cationic *main group* β -diketiminate complex. The 1,4 cycloaddition reactions of {HC(CMeNAr)₂}-AlR⁺ cations are promoted by the nucleophilic character of the β -diketiminate methine carbon,¹³ the electrophilic character of the 3-coordinate cationic Al center which can bind/activate the olefin or alkyne, and the puckered conformation of the {HC(CMeNAr)₂}-Al ring (cf. the structure of 2). We are currently investigating the mechanism of the cycloreversion reactions of 5 and 9 and other aspects of the chemistry of the novel cationic Al alkyls described here.14

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Supporting Information Available: Synthetic procedures, characterization data for new compounds, and details of the X-ray structure determination of 2 (20 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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