

## Reactivity of Cationic Organoaluminum Aminotroponimate Compounds with Unsaturated Substrates. Formation of Dinuclear Dicationic Aluminum Complexes

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Received July 22, 1999

Cationic organoaluminum compounds have drawn attention because of their potential applications as Lewis acids and as catalysts for the coordination polymerization of olefins.<sup>1</sup> Cationic aluminum alkyls containing bi- or tridentate *N*-chelating ligands including amidinates,<sup>2</sup> aminotroponimates,<sup>3</sup>  $\beta$ -diketiminates,<sup>4</sup> pyridyliminoamides,<sup>5</sup> and diethylenetriamides<sup>6</sup> have been synthesized recently, and several exhibit catalytic activity for ethylene polymerization. However, little is known about the reactivity properties of these species. Here we report that base-free ( $\text{Pr}_2\text{-ATI}(\text{AlR})^+$  cations ( $\text{B}(\text{C}_6\text{F}_5)_4^-$  salts; R = Et (**1a**), <sup>*i*</sup>Bu (**1b**), Pr (**1c**);  $\text{Pr}_2\text{-ATI} = N,N'$ -diisopropylaminotroponimate) undergo  $\beta$ -H transfer, insertion, and  $\sigma$ -bond metathesis reactions with acetone and *tert*-butyl acetylene, which in some cases lead to unique dinuclear dicationic Al species.

Compound **1a** reacts with 1 equiv of acetone to yield the acetone adduct **2a** (Scheme 1). The <sup>1</sup>H NMR spectrum of **2a** in  $\text{C}_6\text{D}_5\text{Cl}$  (23 °C) in the absence of excess acetone contains two doublets at ca.  $\delta$  1.0 for the isopropyl methyl groups consistent with  $C_s$  symmetry at Al, and a resonance for coordinated acetone ( $\delta$  2.02). However, in the presence of even a slight (4%) excess of acetone, the two isopropyl methyl doublets collapse to a single doublet indicative of time-averaged  $C_{2v}$  symmetry at Al due to intermolecular acetone exchange by an associative mechanism. Compound **2a** is slowly (3 d, 23 °C,  $\text{CD}_2\text{Cl}_2$ ) converted to the cationic isopropoxide complex **3** in quantitative yield by net  $\beta$ -H transfer with release of ethylene. Complexes **1b** and **1c** react with acetone in a similar manner; however, the corresponding intermediates **2b** and **2c** are less stable than **2a**, and are completely converted to **3** within 5 h at 23 °C in  $\text{C}_6\text{D}_5\text{Cl}$ . For comparison,  $\text{AlEt}_3$  reacts with diethyl ketone by competitive ketone insertion into the Al–Et bond,  $\beta$ -H transfer, and enolization; the product ratio depends on the  $\text{AlEt}_3/\text{ketone}$  ratio.<sup>7</sup> The monomeric Al alkyls ( $\text{BHT})_x\text{AlEt}_{3-x}$  ( $\text{BHT} = 2,6\text{-di-}i\text{-tert-butyl-4-methylphenoxide}$ ) react with enolizable ketones by enolization and subsequent aldol condensation.<sup>8</sup> No aldol condensation products are observed in the reactions of **1a–c** with 1 equiv of acetone.

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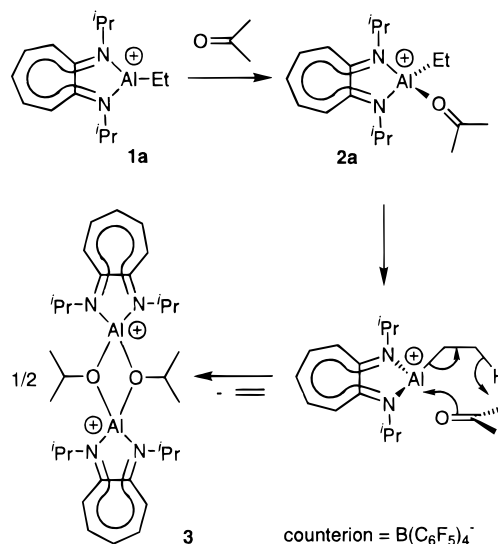
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### Scheme 1



Unlike **1a–c**, **3** is insoluble in  $\text{C}_6\text{H}_5\text{Cl}$  and only sparingly soluble in  $\text{CH}_2\text{Cl}_2$ . An X-ray crystallographic analysis established that **3** crystallizes from  $\text{CH}_2\text{Cl}_2$  as the complex salt  $\{(\text{Pr}_2\text{-ATI})\text{Al}(\mu\text{-O}^i\text{Pr})\}_2[\text{B}(\text{C}_6\text{F}_5)_4]_2 \cdot 2\text{CH}_2\text{Cl}_2$  (**3**·2 $\text{CH}_2\text{Cl}_2$ ). The structure of the dinuclear cation of **3** is shown in Figure 1. The planar  $\text{Al}_2\text{O}_2$  ring features an acute  $\text{O}(1)\text{–Al}(1)\text{–O}(1\text{A})$  angle ( $80.2(1)^\circ$ ) and an obtuse  $\text{Al}(1)\text{–O}(1)\text{–Al}(1\text{A})$  angle ( $99.8(1)^\circ$ ), and is nearly perpendicular to the ATI rings (angle between planes =  $93.2^\circ$ ). The Al–N bond distances ( $\text{Al}(1)\text{–N}(1)$  1.820(3) Å,  $\text{Al}(1)\text{–N}(2)$  1.832(3) Å) are ca. 0.05 Å shorter than those in the dinuclear monocation  $\{(\text{Pr}_2\text{-ATI})\text{Al}(\mu\text{-Me})\}_2^+$ ,<sup>3</sup> and ca. 0.09 Å shorter than those in neutral  $(\text{Pr}_2\text{-ATI})\text{AlMe}_2$ .<sup>9</sup> The Al–O bond distances ( $\text{Al}(1)\text{–O}(1)$  1.809(2) Å,  $\text{Al}(1)\text{–O}(1\text{A})$  1.817(3) Å) are similar to those in neutral aluminum  $\mu$ -OR compounds.<sup>10</sup> The geometry at the oxygens is pyramidal (sum of angles around  $\text{O}(1)$  =  $336.0^\circ$ ) rather than planar as normally observed in alkoxy-bridged aluminum compounds due to steric crowding between the  $\mu\text{-O}^i\text{Pr}$  and  $\text{N}^i\text{Pr}$  groups.<sup>10b–e</sup> The dinuclear structure of the cation explains the low solubility of **3**.

Compounds **1a–c** catalytically dimerize *tert*-butyl acetylene to the head-to-tail dimer 2-*tert*-butyl-5,5-dimethyl-1-hexen-3-yne (**4**,  $\text{C}_6\text{D}_5\text{Cl}$ , 23 °C, ca. 4 t.o./h, >90% selectivity for **4**) as shown in Scheme 2.<sup>11</sup> Support for the mechanism in Scheme 2 is provided by the following observations from NMR and GC-MS studies of stepwise reactions. (i) **1a** reacts with 1 equiv of  $^i\text{BuC}\equiv\text{CH}$  by  $\beta$ -H transfer to yield cationic vinyl compound **5** and ethylene quantitatively. **5** is stable in  $\text{C}_6\text{D}_5\text{Cl}$  solution at 23 °C in the absence of  $^i\text{BuC}\equiv\text{CH}$ . The trans stereochemistry is established by a vinyl  $^3J_{\text{HH}}$  value of 21 Hz.<sup>12</sup> (ii) **5** reacts with additional  $^i\text{BuC}\equiv\text{CH}$  by  $\sigma$ -bond metathesis to yield alkynyl complex **6** and

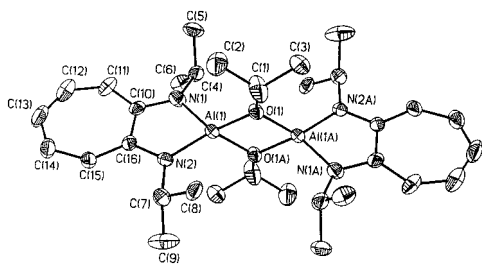
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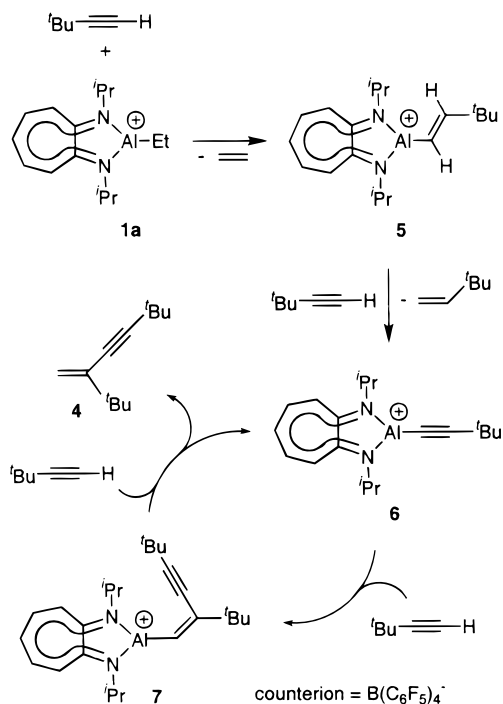
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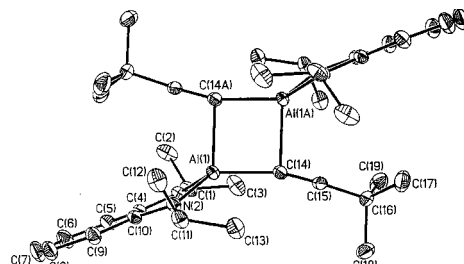
**Figure 1.** Structure of the  $\{(\text{Pr}_2\text{-ATI})\text{Al}(\mu\text{-O}'\text{Pr})\}_2^{2+}$  dication. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) not given in the text: Al(1)–Al(1A) 2.774(2), O(1)–C(1) 1.508(5); N(1)–Al(1)–N(2) 89.0(1), O(1)–Al(1)–O(1A) 80.2(1). Hydrogen atoms are omitted.

### Scheme 2



*tert*-butyl ethylene, followed by  $\text{tBuC}\equiv\text{CH}$  insertion to yield **7**. When **5** is reacted with 1 equiv of  $\text{tBuC}\equiv\text{CH}$ , a 4:1:1 mixture of **6**, **7**, and unreacted **5** is formed, indicating that the two reactions occur at similar rates. Removal of the volatiles from this reaction mixture followed by addition of  $\text{C}_6\text{H}_5\text{Cl}$  affords yellow crystalline **6** in 55% isolated yield. (iii) The reaction of **5** with excess  $\text{tBuC}\equiv\text{CH}$  results in catalytic formation of **4**. (iv) Isolated **6** is insoluble in  $\text{C}_6\text{D}_5\text{Cl}$ , but dissolves in the presence of excess  $\text{tBuC}\equiv\text{CH}$  yielding **7** with catalytic formation of **4**. (v) NMR spectra under catalytic conditions contain only signals for **7**, indicating that this species is the resting state of the catalytic cycle. The neutral bis-amidinate compound  $\{\text{PhC}(\text{NSiMe}_3)_2\}_2\text{AlH}$  and a variety of early transition metal species catalytically dimerize terminal alkynes by analogous mechanisms.<sup>13</sup> For comparison,  $\text{AlR}_3$  compounds normally react with terminal alkynes by  $\sigma$ -bond metathesis to give  $\text{R}_2\text{Al}-\text{C}\equiv\text{CR}'$  and  $\text{RH}$ , while insertion and  $\beta$ -H transfer reactions are less common.<sup>14</sup>

**6** crystallizes from  $\text{C}_6\text{H}_5\text{Cl}$  as the complex salt  $\{[(\text{Pr}_2\text{-ATI})\text{Al}(\mu\text{-C}\equiv\text{C}'\text{Bu})]\}_2[\text{B}(\text{C}_6\text{F}_5)_4]_2 \cdot 5\text{C}_6\text{H}_5\text{Cl}$ . The dinuclear dication of **6** (Figure 2) consists of two  $(\text{Pr}_2\text{-ATI})\text{Al}$  units linked by two unsymmetrical  $\sigma,\pi$ -alkynyl bridges. The short Al–C  $\sigma$ -bonds (Al(1)–C(14) 1.971(2) Å) are associated with a slightly bent Al–



**Figure 2.** Structure of the  $\{(\text{Pr}_2\text{-ATI})\text{Al}(\mu\text{-C}\equiv\text{C}'\text{Bu})\}_2^{2+}$  dication. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) not given in the text: Al(1)–N(1) 1.834(2), Al(1)–N(2) 1.837(2); N(1)–Al(1)–N(2) 88.86(7), C(14)–Al(1)–C(14A) 88.49(7), Al(1)–C(14)–Al(1A) 91.51(7). Hydrogen atoms are omitted.

$\text{C}\equiv\text{C}$  unit (Al(1)–C(14)–C(15) 163.6(2)°). The long Al–C bonds (Al(1)–C(14A) 2.151(2)°) are formed by donation of alkynyl  $\pi$ -electrons to an empty Al  $p$  orbital (Al(1A)–C(14)–C(15) 103.9(1)°).<sup>15</sup> The C(14)–C(15) bond (1.217(3) Å) retains triple bond character. The  $[\text{Al}_2\text{C}_2]$  plane is almost perpendicular to the ATI rings (angle between planes = 93.6°). Similar structures have been observed for neutral dinuclear aluminum compounds.<sup>15,16</sup> It is not known whether **6** observed by NMR in solution before crystallization is mononuclear or dinuclear.

These results show that (i)  $(\text{Pr}_2\text{-ATI})\text{AlR}^+$  complexes that contain  $\beta$ -hydrogens react with unsaturated substrates by  $\beta$ -H transfer, (ii)  $(\text{Pr}_2\text{-ATI})\text{Al}(\text{C}\equiv\text{CR})^+$  species catalyze terminal alkyne dimerization by an insertion/ $\sigma$ -bond metathesis process, and (iii)  $\{(\text{Pr}_2\text{-ATI})\text{AlX}\}_2^{2+}$  species form unique dinuclear dications when X is a potential bridging group such as  $-\text{OR}$  or  $-\text{C}\equiv\text{CR}$ .<sup>17,18</sup> The latter result suggests that  $(\text{Pr}_2\text{-ATI})\text{Al}(\text{alkenyl})^+$  and even  $(\text{Pr}_2\text{-ATI})\text{Al}(\text{alkyl})^+$  cations might adopt dinuclear structures.<sup>19</sup>

**Acknowledgment.** This work was supported by Department of Energy Grant DE-FG02-88ER13935 and Eastman Chemical Company.

**Supporting Information Available:** Synthetic procedures, characterization data for new compounds, and details of the X-ray structure determinations of **3** and **6** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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