

## Unusually Stable Pyrazolate-Bridged Dialuminum Complexes Containing Bridging Methyl Groups

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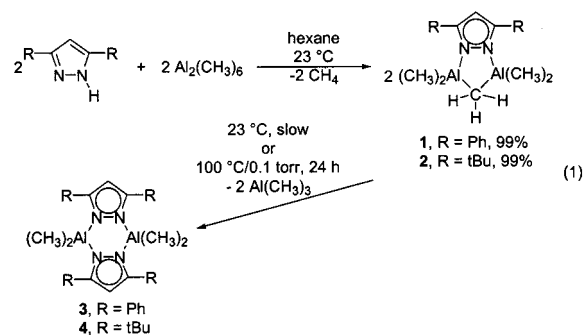
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Although it is widely appreciated that a methyl group can bridge between two aluminum(III) centers through 3-center-2-electron bonding,<sup>1</sup> there are only four structurally characterized examples: trimethylaluminum dimer,<sup>2</sup>  $\mu$ -diphenylamido- $\mu$ -methyl-tetramethyldialuminum,<sup>3</sup> bis( $\mu_2$ -methyl)-methyl-*N*-trimethyl-silyl-2,6-diisopropylanilinoaluminum,<sup>4</sup> and ( $\mu_2$ -methyl)-bis(*N,N*-diisopropylaminotroponiminato)methylaluminum tetrakis(pentafluorophenyl)borate.<sup>5</sup> In addition, several structurally characterized complexes have been documented in which a methyl group bridges between aluminum and a transition metal or lanthanide ion.<sup>6</sup> Recently, several groups have reported the use of linked diboron compounds as methide abstracting agents for use in single-site olefin polymerization catalysis.<sup>7–11</sup> It has been proposed that bidentate coordination of the abstracted alkyl group should stabilize the anion relative to an anion containing a single boron center,<sup>7</sup> leading to a more stable ion pair and higher polymerization activity. Therefore, factors that affect the formation and stability of alkyl-bridged complexes are of both fundamental and practical significance. With these considerations in mind, we report the synthesis, structure, reactivity, and molecular orbital calculations of several aluminum complexes containing bridging methyl groups in five-membered rings. These complexes are obtained upon treatment of bulky 3,5-disubstituted pyrazoles with excess trimethylaluminum. The bridging methyl groups in these complexes are more stable than those of trimethylaluminum dimer. The origin of this stability is described, and comments are made regarding the implications of these results.

Treatment of 3,5-diphenylpyrazole or 3,5-di-*tert*-butylpyrazole with excess trimethylaluminum (4 equiv) in hexane at ambient temperature resulted in the formation of the bridging methyl

complexes **1** and **2** after workup (99%; eq 1).<sup>12,13</sup> Complexes **1**



and **2** were identified by a combination of spectroscopic and analytical data. In particular, the <sup>1</sup>H NMR spectra of **1** and **2** at 23 °C showed sharp singlets for the bridging methyl resonances at  $\delta$  0.39 and 0.60 and for the terminal methyl resonances at  $\delta$  -0.62 and -0.30, respectively, in 1:4 ratios. Upon standing at room temperature, **1** and **2** underwent slow decomposition to the dimeric compounds **3** and **4**, with loss of trimethylaluminum. For example, after 3 weeks of standing at ambient temperature under argon **1** had undergone 4% decomposition to **3**. When **1** and **2** were stored at -20 °C under argon, no decomposition was observed over a period of four months. Pyrolysis of **1** at 100 °C/0.1 Torr for 24 h led to quantitative conversion to **3**. However, under the same conditions **2** only gave 10% conversion to **4** due to the high volatility of **2**, i.e., during the thermolysis **2** sublimed out of the heated zone faster than it decomposed to **4**.

The X-ray crystal structure of **1** was determined. Figure 1 shows a perspective view of **1** along with selected bond lengths and angles. The molecule occupies a crystallographic mirror plane containing C(1) and C(5). The two nitrogen atoms and two aluminum atoms lie in a plane, but the bridging methyl group is situated 0.9 Å above this plane. The aluminum–nitrogen bond length is 1.924(6) Å. The aluminum–carbon bond lengths are 1.945(7) and 1.948(8) Å for the terminal methyl groups and 2.144(10) Å for the bridging methyl group. The geometry about the aluminum centers is distorted tetrahedral. For comparison, crystallographically characterized aluminum complexes with bridging methyl groups have terminal aluminum–carbon bond lengths that range between 1.94 and 1.98 Å and bridging aluminum–carbon bond lengths between 2.12 and 2.177 Å.<sup>2–5</sup> The values for **1** fall within these ranges and are unexceptional. The aluminum–carbon–aluminum angles for bridging methyl groups within four-membered rings range between 74.7 and 78.9°. The related value for **1** (91.8(5)°) is larger due to the geometric constraints imposed by the five-membered ring.

The kinetics of exchange between the terminal and bridging methyl groups of **1** (0.20 M) was studied by <sup>1</sup>H NMR in toluene-*d*<sub>8</sub> between 38 and 79 °C. Details of these determinations are given in the Supporting Information. Eyring analysis of the exchange process gave  $\Delta H^\ddagger = 15.4 \pm 0.1$  kcal/mol,  $\Delta S^\ddagger = -3.2 \pm 0.1$  eu, and  $\Delta G^\ddagger_{(298)} = 16.4 \pm 0.1$  kcal/mol. Analysis of a 0.10 M solution of **1** in toluene-*d*<sub>8</sub> afforded rates and activation parameters that were identical within experimental error, suggesting that the exchange process is intramolecular. Rate constants for methyl exchange have been previously reported for trimethylaluminum dimer in cyclopentane.<sup>14,15</sup> Using these data,<sup>14</sup> the rate of terminal-bridging methyl exchange in **1** at 25 °C is

(12) If less trimethylaluminum was used, the dimeric complexes **3** and **4** were observed in varying proportions along with **1** and **2**. Use of  $\geq 4.0$  equiv of trimethylaluminum led to exclusive formation of **1** and **2**.

(13) Spectroscopic and analytical data for **1–4** are presented in the Supporting Information.

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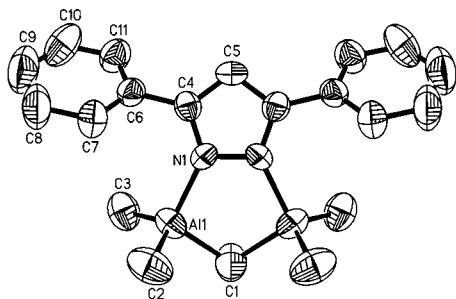
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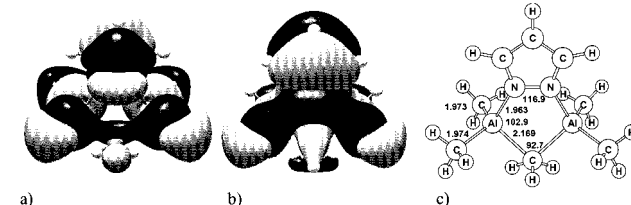
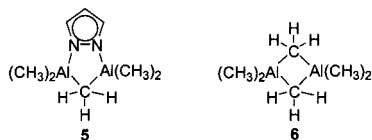
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**Figure 1.** Perspective view of **1**. Selected bond lengths (Å) and angles (deg): Al–N 1.924(6), Al–C(1) 2.144(10), Al–C(2) 1.948(8), Al–C(3) 1.945(7), N–Al–C(1) 102.1(4), N–Al–C(2) 111.1(3), N–Al–C(3) 108.7(3), C(1)–Al–C(2) 108.5(6), C(1)–Al–C(3) 103.2(5), C(2)–Al–C(3) 121.3(3), Al–C(1)–Al' 91.8(5).

calculated to be  $1.1 \times 10^4$  times slower than that for trimethylaluminum dimer at the same temperature.

To understand how the pyrazolato ligand affects the bonding between the aluminum atoms and the bridging methyl group, complex **5**, the trimethylaluminum dimer (**6**), and the transition



**Figure 2.** Computed structure of **5**, oriented with the bridging methyl out of the plane of the paper: (a) HOMO, showing minimization of antibonding interactions; (b) HOMO-2, showing the bonding interaction of the pyrazolato ligand with the  $\text{Al}_2(\text{CH}_3)_5$  fragment; and (c) B3LYP/6-311G(d) optimized structure.

1 kcal/mol. The computed  $\Delta H^\ddagger_{(298)}$  for methyl exchange in **5** by rotation about an aluminum–nitrogen bond is 16.4 kcal/mol, in excellent agreement with experiment. The dissociation enthalpy of **6** is 19.5 kcal/mol and corresponds to the breaking of two bridging aluminum–carbon bonds.<sup>19</sup> Thus, the bond strength of the bridging aluminum–carbon bond in **5** is about 6.6 kcal/mol stronger than that of the analogous bond in **6**. The extra stability of the bridging methyl bond in **5** arises from resonance with the pyrazolato ligand. Figure 2b shows a bonding interaction between the pyrazolato and  $\text{Al}_2\text{Me}_5$  moieties. The p orbital on the bridging carbon is tipped and overlaps well with the positive lobes of the aluminum p orbitals that are behind the plane of the page. Removal of a trimethylaluminum unit from **5** is endothermic by 35.4 kcal/mol, yielding  $(\eta^2\text{-pz})\text{Al}(\text{CH}_3)_2$  (the  $\eta^1$ -complex is 9.1 kcal/mol higher with a 0.5 kcal/mol barrier for conversion to the  $\eta^2$ -product).

This work demonstrates that the bridging methyl groups in **1** and **2** are stabilized substantially relative to the trimethylaluminum dimer. The increased stability of the bridging methyl groups in **1** and **2** originates from extended bonding interactions through the unsaturated five-membered heterocycle. Calculations suggest that the unusual nonplanar  $\text{Al}_2\text{N}_2\text{C}$  ring in **1** and **2** is a result of increased orbital overlap in the HOMO between the bridging methyl group and the aluminum–carbon p orbitals. Accordingly, the stability of an alkyl group bridging between two metal centers should be strongly affected by the nature of the other groups that are part of the metallacycle. In the present case, the pyrazolato bridge not only holds the dimethylaluminum groups in close proximity but also provides key extended orbital overlap with the bridging methyl group. Therefore aromatic and other unsaturated bridges are likely to be useful motifs in the construction of highly stable bridging alkyl complexes. The results described herein should be useful in the design of new bridging alkyl complexes and may contribute to new alkyl abstracting agents for use in olefin polymerization catalysis.

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**Supporting Information Available:** Synthetic procedures, analytical and spectroscopic data for **1–4**, kinetic data for **1** and **6**, and tables of Cartesian coordinates for **5**, **6**, and associated transition states (PDF). An X-ray crystallographic file for **1**, in CIF format is also available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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states for breaking an aluminum–carbon bond by rotation about an aluminum–nitrogen bond were optimized at the B3LYP/6-311G(d) level of density functional theory (DFT).<sup>16</sup> Dissociation of trimethylaluminum from **5** and **6** was also studied. Final barrier heights and binding energies were obtained from single-point MP2/6-311+G(2d,p),<sup>17</sup> since DFT has been shown to underbind bridge-bonded aluminum compounds.<sup>18</sup> As observed in **1**, the bridging methyl group in **5** is predicted to lie 0.66 Å out of the  $\text{Al}_2\text{N}_2$  plane. This nonplanarity can be interpreted as arising from minimization of antibonding interactions in the HOMO. When the bridging methyl group is in the  $\text{Al}_2\text{N}_2$  plane, the bridging carbon p orbital shown in Figure 2a is antibonding with respect to the aluminum p orbitals. Reversing the phase of the bridging carbon p orbital would result in a worse antibonding interaction with the pyrazolato ligand. However, a bonding interaction can be achieved by moving the methyl group out of the  $\text{Al}_2\text{N}_2$  plane. This is not a large effect, and stabilizes the molecule by less than

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