

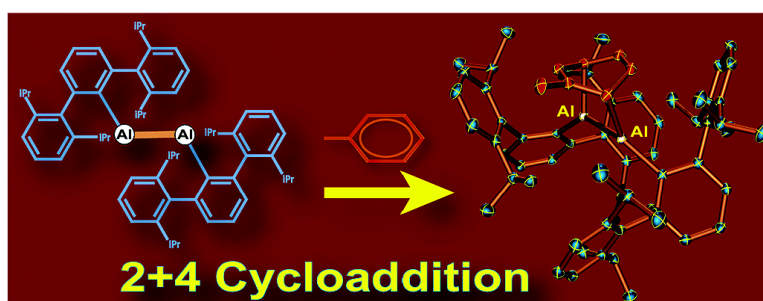
Communication

**The [2 + 4] Diels–Alder Cycloaddition Product of a Probable Dialuminene, Ar'AlAlAr' (Ar' = CH-2,6-Dipp; Dipp = CH-2,6-Pr), with Toluene**

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minum species.<sup>13</sup> The internal angles of the complexed toluene ring are narrowest at the Al-bound carbons C(1) and C(4) (109.4(1) and 109.4(1°)) and are in the range (120.8(1)–121.7(1°)) at C(2), C(3), C(5), and C(6). The C(1)–Al(1)–Al(2) and C(4)–Al(2)–Al(1) angles are close to 90°, and the external angles C(8)–Al(1)–Al(2) and C(38)–Al(2)–Al(1) involving the terphenyl ligands are wide at 142.18(5) and 141.08(5)°—probably as a result of steric repulsion. The aluminums are almost planar coordinated with angular sums of 359.25(6)° at Al(1) and 358.55(6)° at Al(2). The C(1)–Al(1)–Al(2)–C(4) torsion angle is only 24.5° which indicates the bulky substituents (Ar') are nearly cis with respect to each other.

There are a handful of reactions between unstable boron(I) or aluminum(I) monomers and unsaturated molecules. The first example was the reaction between BX (X = F,<sup>14a</sup> Cl<sup>14b</sup>) and acetylene to give 1,4-diboracyclohexadiene. Similarly, the reaction of AlCl with the alkynes, RC≡CR (R = Me, Et), gave the cage species, (AlCl·RC≡CR)<sub>4</sub>, which are dimers of substituted 1,4-dialuminacyclohexadiene.<sup>15</sup> In addition, the reaction of AlCl with 2,3-dimethylbutadiene (DMB) produced the cyclic hexamer (AlCl·DMB)<sub>6</sub>.<sup>16</sup> More recently, the formal [1 + 2] cycloaddition product formed from the potassium reduction of I<sub>2</sub>Al{DippN(Me)C}CH in the presence of RC≡CR; (R = Ph, or TMS) gave the aluminum cyclopropene analogue, HC{C(Me)DippN}Al(Ph)C=C(Ph).<sup>17</sup> However, none of these reactions afforded products with group 13–13 element bonds, and it is notable that concentrated toluene solutions of Ar'MMAR' (M = Ga, In, and Tl) display no trace of cycloaddition products. The relative inertness of the heavier “dimetalenes” toward [2 + 4] cycloadditions may be due to their ready dissociation in to monomeric Ar'M species in solution.<sup>5</sup>

Among heavier main group element compounds, the reactions which most resemble the addition of PhMe to **3** is the addition of unstable Me<sub>2</sub>SiSiMe<sub>2</sub> to aromatic molecules such as benzene, naphthalene, or anthracene to give disilabicyclo[2.2.2]octadiene derivatives with structures similar to that of **4**.<sup>18</sup> However, irradiation with UV (ca. 250 nm) regenerated the disilene by a photolytic [2 + 4] cycloreversion.<sup>19</sup> The analogous generation of Ar'AlAlAr' from **4** via photochemical methods is under investigation. In fact, future work may show that the chemistry of the lighter group 13 “dimetalenes”, RMMR (M = B and Al) will parallel that of the group 14 alkene analogues. Current work is focused on the isolation and characterization of an uncomplexed “dialuminene” and the examination of its reaction chemistry.

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**Supporting Information Available:** X-ray data (CIF) for **2** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (a) Under anaerobic and anhydrous conditions, Ar'AlI<sub>2</sub> (1.36 g, 2.0 mmol) was dissolved in Et<sub>2</sub>O (85 mL). The solution was added dropwise over 30 min to freshly synthesized KC<sub>8</sub> (0.54 g, 4.0 mmol) and stirred for 18 h. The deep red solution was allowed to settle (4 h) and was decanted from the graphite. The ether was removed under reduced pressure, and the dark red residue was extracted with toluene (15 mL). Overnight storage at ca. –30 °C afforded red crystals of **4** (0.2 g, 0.18 mmol). The supernatant liquid was removed from the crystals and further concentrated to 10 mL. Storage at –30 °C for 9 d gave **4** as red X-ray quality crystals. Yield: 0.19 g, 17%; mp = 103–107 °C (upon melting turned from red to pale yellow). Calcd. for C<sub>67</sub>H<sub>52</sub>Al: C = 85.49, H = 8.78. Found: C = 85.88, H = 8.03. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 0.964 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 0.985 (d, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 1.511 (s, 3H, Ph-CH<sub>3</sub>) 2.645 (m, C=C-CH), 2.745 (t, C=C-CH) <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2.909 (broad mult, 8H, CH(CH<sub>3</sub>)<sub>2</sub>), 5.907 (t, CH=CH) <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 6.771 (d, 4H, *m*-C<sub>6</sub>H<sub>3</sub>) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 7.081 (m, 10H, *m*-Dipp and *p*-C<sub>6</sub>H<sub>3</sub>), 7.197 (t, 4H, *p*-Dipp) <sup>3</sup>J<sub>HH</sub> = 7.5 Hz. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 74.46 MHz, 25 °C): δ 23.66 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.66 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.92 (CH(CH<sub>3</sub>)<sub>2</sub>), 123.75 (*m*-Dipp), 127.48 (*p*-C<sub>6</sub>H<sub>3</sub>), 128.97 (*m*-C<sub>6</sub>H<sub>3</sub>), 129.21 (*p*-Dipp), 141.93 (*i*-Dipp), 147.04 (*o*-Dipp), 147.14 (*o*-C<sub>6</sub>H<sub>3</sub>), 150.91 (*i*-C<sub>6</sub>H<sub>3</sub>). UV/vis (hexanes) λ<sub>max</sub> nm (ε mol<sup>-1</sup>·cm<sup>-1</sup>): 320 (3400); (b) Ar'AlI<sub>2</sub> (2.5 g, 3.69 mmol) was dissolved in Et<sub>2</sub>O (65 mL). The solution was added dropwise over 30 min to KC<sub>8</sub> (0.50 g, 3.69 mmol) at ca. –78 °C and stirred for 12 h. The red solution was decanted from the graphite. The ether was removed under reduced pressure, and the residue was washed with hexane (15 mL). The supernatant was removed from the pale yellow product. Yield: 0.81 g, 40%; mp = 226–229 °C. Calcd. for C<sub>30</sub>H<sub>37</sub>AlI: C = 65.33, H = 6.76. Found: C = 65.01, H = 7.01. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 0.987 (d, 24H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 1.151 (d, 24H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 3.012 (sept, 8H, CH(CH<sub>3</sub>)<sub>2</sub>) <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 7.09–7.06 (m, 6H, *m*-C<sub>6</sub>H<sub>3</sub>, *p*-C<sub>6</sub>H<sub>3</sub>), 7.146 (d, 8H, *m*-Dipp), 7.328 (t, 4H, *p*-Dipp) <sup>3</sup>J<sub>HH</sub> = 7.6 Hz. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 100.531 MHz, 25 °C): δ 25.25 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.52 (CH(CH<sub>3</sub>)<sub>2</sub>), 30.51 (CH(CH<sub>3</sub>)<sub>2</sub>), 124.16 (*m*-Dipp), *p*-C<sub>6</sub>H<sub>3</sub> (unobserved, probably obscured by C<sub>6</sub>D<sub>6</sub>), 129.87 (*m*-C<sub>6</sub>H<sub>3</sub>), 130.10 (*p*-Dipp), 139.59 (*i*-Dipp), 145.85 (*i*-C<sub>6</sub>H<sub>3</sub>), 146.93 (*o*-C<sub>6</sub>H<sub>3</sub>), 147.809 (*o*-Dipp).
- Crystal data for **2** at 90 K with Mo Kα (λ = 0.71073 Å) radiation: *a* = 13.5724(12) Å, *b* = 19.0587(17) Å, *c* = 15.5757(14) Å, α = 90°, β = 114.603(3)°, monoclinic, space group P2<sub>1</sub>/n, Z = 4, R<sub>1</sub> = 0.0426 for 5199 (*I* > 2σ(*I*)) data, wR<sub>2</sub> = 0.1245 for all (5731) data. Crystal data for **4** at 90 K with Mo Kα (λ = 0.71073 Å) radiation: *a* = 13.9134(15) Å, *b* = 13.9628(18) Å, *c* = 19.057(2) Å, α = 106.645(3)°, β = 107.171(4)°, γ = 91.862(5)°, triclinic, space group P1, Z = 2, R<sub>1</sub> = 0.0396 for 10326 (*I* > 2σ(*I*)) data, wR<sub>2</sub> = 0.1114 for all (13096) data.
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