

Published on Web 08/16/2003

The [2 + 4] Diels–Alder Cycloadditon Product of a Probable Dialuminene, Ar'AlAlAr' (Ar' = C₆H₃- 2,6-Dipp₂; Dipp = C₆H₃-2,6-Prⁱ₂), with Toluene

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Heavier group 14 element alkene analogues (R_2MMR_2 ; M = Si^1 and $Ge^2_2 R = organo$ or related group) react with dienes to give cycloaddition products in a manner similar to the Diels-Alder reaction. In contrast, the unavailability of potentially double-bonded compounds RMMR (M = B-Tl) has prevented the analogous studies for group 13 species. Calculations for the hydrides HMMH $(M = Ga, In)^3$ and IR data on matrix-isolated species at low temperature,⁴ indicate a trans bent HMMH skeleton and weak M-M bonding (ca. 3 kcal mol⁻¹). The recently synthesized compounds Ar'MMAr' (M = Ga, ^{5a} In, ^{5b} and Tl; ^{5c} Ar' = C_6H_3 -2,6-Dipp₂, Dipp = C_6H_3 -2,6-Prⁱ₂) were also found to have a trans bent structure and M-M distances that were longer than single bonds. Moreover, they dissociated to Ar'M monomers in hydrocarbons at room temperature which is consistent with weak M-M bonding. Nonetheless, the "dialuminene" isomer, HAlAlH, was predicted to have a stronger M–M bond (ca. 10 kcal mol^{-1}) than its heavier congeners,⁶ and the Al–Al distance was calculated to be 2.613 Å, which is shorter than most Al-Al single bonds in the dialanes R₂-AlAlR₂.⁷ These data suggested the possibility of isolating an aluminum species of formula RAIAIR and the study of addition reactions to the Al-Al double bond. We now show that reaction of Ar'AlI₂ (1) with KC₈ afforded the 1,2-diiodoalane (2) and probably, the "dialuminene" (3) according to

$$\frac{2\operatorname{Ar'All}_{2} \xrightarrow{2\operatorname{KC}_{8}} I(\operatorname{Ar'})\operatorname{Al}-\operatorname{Al}(\operatorname{Ar'})I \xrightarrow{2\operatorname{KC}_{8}} \operatorname{Ar'Al}=\operatorname{AlAr'}_{3}}{2}$$

Thus far, the "dialuminene" 3 has not been isolated as a pure species but has been found to crystallize only from toluene. It reacts with this solvent to form the cycloaddition product 4 as shown by



Compound **3** was generated by the reduction of $Ar'AII_2$ with 2 equiv of KC₈ in Et₂O. Removal of the solvent and subsequent extraction into toluene, followed by separation of **2**, which is less soluble, and cooling in a ca. -30 °C freezer, afforded **4** as red crystals in 17% yield.^{8a} Compound **2**, an isolable intermediate en route to **3** can also be synthesized as a pale yellow solid in 40% yield from the reduction of **1** with 1 equiv of KC₈.^{8b} Yellow crystals of **2** were grown from C₆D₆ solution, and its structure (Figure 1)⁹ shows that **2** is a unique example of an unsolvated halogen-substituted dialane.¹⁰ It has a short Al–Al single bond 2.609(2) due to the contraction of the effective radius of Al by the iodine substituent. The large Ar' groups are orientated trans to each other, and the C–Al–Al angle is nearly 15° wider than the I–Al–Al angle.



Figure 1. Selected bond lengths (Å) and angles (deg) for **2**. H atoms are not shown. Al(1)-Al(1A) = 2.609(2), Al(1)-C(1) = 1.964(4), Al(1)-I(1) = 2.5020(12), C(1)-Al(1)-Al(1A) = 128.16(12), C(1)-Al(1)-I(1) = 118.25(11), I(1)-Al(1)-Al(1A) = 113.56(6).



Figure 2. Selected bond lengths (Å) and angles (deg) for **4**. H atoms are not shown. Al(1)–Al(2) = 2.5828(7), Al(1)–C(1) = 2.0004(16), Al(2)–C(4) = 2.0032(15), Al(1)–C(8) = 1.9946(15), Al(2)–C(38) = 1.9990-(15), C(2)–C(3) = 1.337(2), C(5)–C(6) = 1.344(2), C(1)–C(2) = 1.509(2), C(3)–C(4) = 1.503(2), C(4)–C(5) = 1.509(2), C(6)–C(1) = 1.496(2), C(1)–Al(1)–Al(2) = 91.95(5), C(4)–Al(2)–Al(1) = 93.45(5), C(8)–Al-(1)–Al(2) = 142.18(5), C(38)–Al(2)–Al(1) = 141.08(5).

The air- and moisture-sensitive 4 was characterized by ¹H and ¹³C NMR, and UV-vis. The ¹H NMR spectrum featured characteristic alkane and alkene hydrogen signals at 2.63-2.74 and 5.91 ppm that were indicative of localized C=C double bonding in a toluene that had undergone cycloaddition to Ar'AlAlAr'. Attempts to observe an ²⁷Al NMR signal were unsuccessful. The absence of a signal is probably a result of the unsymmetric aluminum environment which broadens the signal into the baseline.11 The 1H and ¹³C NMR data were confirmed by X-ray crystallography as shown in Figure 2. The respective bond lengths for C(2)-C(3) and C(5)-C(6) are 1.337(2) and 1.344(2) Å and are characteristic of C=C double bonding.¹² The other four ring C-C distances are in the range 1.496(2)-1.509(3) Å which indicated C-C single bonding between approximately sp² hybridized carbons.¹² The Al-(1)-Al(2) distance, 2.5828(7) Å, is shorter than that in 2 and is outside the known range (2.647(3)-2.751(2) Å) for Al-Al single bonds in three-coordinate R₂AlAlR₂ compounds.⁷ The Al(1)-C(1) and Al(2)-C(4) bond lengths are 2.0004(16) and 2.0032(15) Å which are typical for Al-C bond distances in trivalent organoaluminum species.¹³ 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,^{14a} Cl^{14b}) 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)₄, which are dimers of substituted 1,4-dialuminacyclohexadiene.¹⁵ In addition, the reaction of AlCl with 2,3-dimethylbutadiene (DMB) produced the cyclic hexamer (AlCl•DMB)₆.¹⁶ More recently, the formal [1 + 2] cycloaddition product formed from the potassium reduction of I₂Al[{DippN(Me)C}₂CH] in the presence of RC=CR; (R = Ph, or TMS) gave the aluminum

cyclopropene analogue, HC{C(Me)DippN}₂Al(Ph)C=C(Ph).¹⁷ 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 "dimetallenes" toward [2 + 4] cycloadditions may be due to their ready dissociation in to monomeric Ar'M species in solution.⁵

Among heavier main group element compounds, the reactions which most resemble the addition of PhMe to **3** is the addition of unstable Me₂SiSiMe₂ to aromatic molecules such as benzene, naphthalene, or anthracene to give disilabicyclo[2.2.2]octadiene derivatives with structures similar to that of **4**.¹⁸ However, irradiation with UV (ca. 250 nm) regenerated the disilene by a photolytic [2 + 4] cycloreversion.¹⁹ 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 "dimetallenes", 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.

Acknowledgment. We are grateful to the National Science Foundation (CHE-0096913) for financial support.

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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- (8) (a) Under anaerobic and anhydrous conditions, Ar'AlI₂ (1.36 g, 2.0 mmol) was dissolved in Et₂O (85 mL). The solution was added dropwise over 30 min to freshly synthesized KC8 (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 Supermatant fique was relative to the finite of the field was shown in the concentrated to 10 mL. Storage at $-30 \degree$ 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 C₆₇H₈₂Al₂: C = 85.49, H = 8.78. Found: C = 85.88, H = 8.03. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 0.964 (d, 12H, C) = 85.88. $^{-6.56}$, $^{-10.56}$, $^{-1$ 6.9 HZ, 2.909 (oroad muit, 8H, CH(CH₃)₂), 5.907 (t, CH=CH) ³/₃H_H = 7.2 Hz, 6.771 (d, 4H, m-C₆H₃) ³/₃H_H = 7.5 Hz, 7.081 (m, 10H, m-Dipp and p-C₆H₃), 7.197 (t, 4H, p-Dipp) ³/₃H_H = 7.5 Hz. ¹³C{¹H} NMR (C₆D₆, 74.46 MHz, 25 °C): δ 23.66 (CH(CH₃)₂), 25.66 (CH(CH₃)₂), 30.92 (CH(CH₃)₂), 123.75 (m-Dipp), 127.48 (p-C₆H₃), 128.97 (m-C₆H₃), 129.21 (p-Dipp), 141.93 (*i*-Dipp), 147.04 (*o*-Dipp), 147.14 (*o*-C₆H₃), 150.91 (*i*-C₆H₃). UV/vis (hexanes) λ_{max} nm (ϵ mol·L⁻¹·cm⁻¹): 320 (3400); (b) Ar'AlI₂ (2.5 g, 3.69 mmol) was dissolved in Et₂O (65 mL). The solution was added dropwise over 30 min to KC_8 (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 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 $C_{30}H_{37}AII: C = 65.33, H = 6.76.$ Found: C = 65.01, H = 7.01. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ 0.987 (d, 24H, o-CH(*CH*₃)₂) ³ $J_{HH} = 6.8$ Hz, 1.151 (d, 24H, o-CH(*CH*₃)₂) ³ $J_{HH} = 6.8$ Hz, 7.09–7.06 (m, 6H, m-C₄H₃, *n*-C₆H₃), 7.146 (d, 8H, m-Dipp), 7.328 (t, 4H, p-Dipp) ³ $J_{HH} = 7.6$ Hz. ¹³C{¹H} NMR (C₆ D_6 , 100.531 MHz, 25 °C): δ 25.25 (CH(*CH*₃)₂), 26.52 (CH(*CH*₃)₂), 20.51 (CH(*CH*₃)₂), 124 16 (m Dipp) and CH(*CH*₃)₂), 26.52 (CH(*CH*₃)₂), 20.51 (CH(*CH*₃)₂), 21.51 (CH(*CH*₃)₃), 21.51 (CH(*CH*₃)₃ $(^{0}_{0}D_{0})$ (100 $(CH(CH_{3})_{2})$, 124.16 (m-Dipp), p-C₆H₃ (unobserved, probably obscured by C₆D₆), 129.87 (m-C₆H₃), 130.10 (p-Dipp), 139.59 (i-Dipp), 145.85 (i-C₆H₃), 146.93 (o-C₆H₃), 147.809 (o-Dipp).
- (9) Crystal data for **2** at 90 K with Mo K α ($\lambda = 0.71073$ Å) radiation: a = 13.5724(12) Å, b = 19.0587(17) Å, c = 15.5757(14) Å, $\alpha = 90^{\circ} = \gamma$, $\beta = 114.603(3)^{\circ}$, monoclinic, space group P_2/n , Z = 4, $R_1 = 0.0426$ for 5199 ($I > 2\sigma(I)$) data, $wR_2 = 0.1245$ for all (5731) data. Crystal data for **4** at 90 K with Mo K α ($\lambda = 0.71073$ Å) radiation: a = 13.9134(15) Å, b = 13.9628(18) Å, c = 19.057(2) Å, $\alpha = 106.6.45(3)^{\circ}$, b = 107.171-(4° , $c = 91.862(5)^{\circ}$, triclinic, space group PI, Z = 2, $R_1 = 0.0396$ for 10326 ($I > 2\sigma(I)$) data, $wR_2 = 0.1114$ for all (13096) data.
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JA034478P