Main-Group Chemistry

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Synthesis of a Dialumene-Benzene Adduct and Its Reactivity as a Synthetic Equivalent of a Dialumene**

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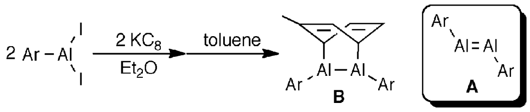
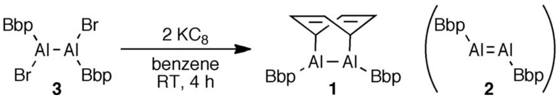
Dedicated to Professor Renji Okazaki on the occasion of his 76th birthday

Multiply bonded species involving heavier main-group elements have been extensively investigated,[1] whereas the chemistry of analogous species involving group 13 elements is still in its infancy.[2,3] Examples for isolable neutral heavier group 13 dimetallenes with the formula of R-M=M-R (M: Al, Ga, In, Tl) remain scarce for the homologues of gallium,[4] indium,[5] and thallium,[6] and have been unknown for aluminum so far.[7–9] In 2003, Power et al. reported the attempted synthesis of the 1,2-diaryldialumene **A** (Scheme 1).[10] Isolation of the compound **B** is likely interpreted in terms of the generation of **A** by the reduction of $ArAlI_2$ and subsequent trapping with toluene.[11,12]



Scheme 1. Formation of the dialumene-toluene adduct **B** and putative dialumene **A**. Ar = 2,6-$Dip_2C_6H_3$, Dip = 2,6-$(iPr)_2C_6H_3$.

Meanwhile, reactivities of dialumene-arene adducts such as **B** are interesting from the viewpoint of synthons for highly reactive dialumenes, since the adducts are expected to react with small molecules as an "Ar-Al=Al-Ar" building block along with elimination of the arene moiety as there is a gain in aromatic stabilization energies.[13,14] Herein, we report the synthesis and properties of the dialumene-benzene adduct **1** (Scheme 2). The reactivities of **1** have been investigated, and demonstrate the properties of **1** as a synthetic equivalent of a dialumene.



Scheme 2. Synthesis of dialumene-benzene adduct **1**. Bbp = 2,6-$[CH(SiMe_3)_2]_2C_6H_3$.

The dialumene-benzene adduct **1** was obtained quantitatively as air- and moisture-sensitive red crystals by the reduction of the 1,2-dibromodialumane **3** in benzene (Scheme 2).[15,16] The solid-state structure of **1** was determined by X-ray crystallographic analysis (Figure 1), thus showing its BbpAlAlBbp moiety bound to the benzene moiety at the 1,4-positions with the 7,8-dialumina-bicyclo[2.2.2]cycloocta-2,5-diene framework. The Al1−C1 [2.028(5) Å] and Al2−C4 [2.020(5) Å] bond lengths are larger than the Al−C(Bbp) distances [Al1−C7 1.976(4) Å, Al2−C8 (1.965(4) Å] and are close to the corresponding Al−C distances of **B** [2.0004(16), 2.0032(15) Å]. The C_6H_6 moiety is folded, and the sum of the internal bond angles (706°) is comparable to that for **B** (704°). Overall, the geometry of the $Al_2(C_6H_6)$ moiety of **1** is almost similar to the $Al_2(C_6H_5Me)$ moiety of **B**.

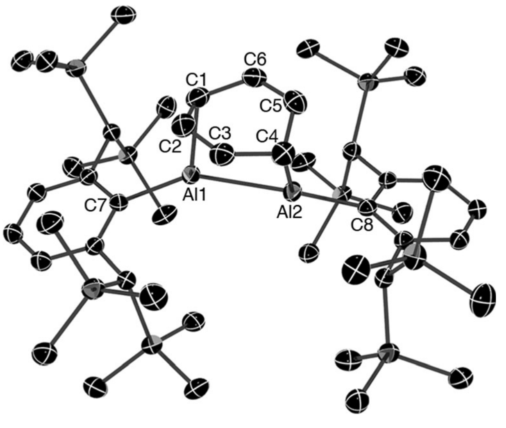


Figure 1. Molecular structure of **1** (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1–Al2 2.5552(19), Al1–C1 2.028(5), Al2–C4 2.020(5), Al1–C7 1.976(4), Al2–C8 1.965(4), C1–C2 1.488(7), C2–C3 1.355(7), C3–C4 1.453(7), C4–C5 1.480(7), C5–C6 1.314(7), C6–C1 1.479(7); C7-Al1-Al2 154.40(15), C8-Al2-Al1 150.01(14), C7-Al1-C1 116.9(2), C8-Al2-C4 118.4(2), C1-Al1-Al2 87.26(16), C4-Al2-Al1 89.95(16).

In the ^1H NMR spectra of **1** in $[D_{14}]$methylcyclohexane at room temperature, only a broadened signal was observed for

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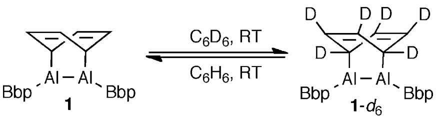
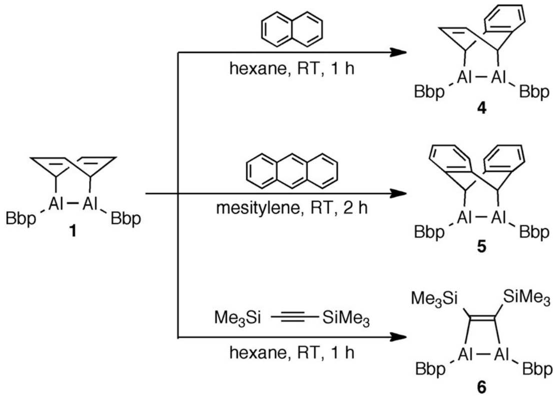
its C_6H_6 moiety, though two independent signals (protons on sp^3- and sp^2-carbon centers in 2:4 ratio) are expected to be observed. The protons of the C_6H_6 moiety of **1** would be rapidly exchanged inter- or intramolecularly with each other in solution at room temperature. At −60 °C, the ^{1}H NMR spectrum showed two broadened signals at $\delta = 2.54$ and 5.75 ppm, which are attributable to the protons on the sp^3- and sp^2-carbon atoms, respectively, of the C_6H_6 moiety. Similarly, the ^{13}C NMR spectrum recorded at −60 °C exhibited two signals at $\delta = 42.6$ and 122.3 ppm, which correspond to the sp^3- and sp^2-carbon atoms, respectively, of the C_6H_6 moiety. In C_6D_6 solution, the signal corresponding to the C_6H_6 moiety of **1** gradually disappeared along with the increase in the signal intensity of free C_6H_6, thus indicating the intermolecular exchange of the C_6H_6 moiety of **1** with the C_6D_6 solvent (Scheme 3). The spectral change was completed within 2 hours at room temperature. The adduct **1** was recovered by evaporation of the volatiles from the sample and re-dissolution of the residue in C_6H_6. The C_6H_6–C_6D_6 exchange rate in the dark is comparable to that under diffused indoor light, and thus photochemical processes may not be involved.



Scheme 3. Interconversion between **1** and [D$_6$]-**1**.

Intermolecular exchange of the C_6H_6 moiety of **1** with other aromatic compounds was investigated. Treatment of **1** with mesitylene gave an intractable mixture without any evidence for the generation of the expected arene-exchanged product, probably because of steric reasons. Reaction of **1** with toluene, a less hindered arene than mesitylene, afforded a single product, though the structure of the product could not be characterized. In contrast, naphthalene and anthracene, which have much higher diene characters compared to benzene, reacted with **1** to afford the expected arene-exchanged products (Scheme 4).[17] Upon addition of naphthalene, **1** was readily converted into the dialumene-naphthalene adduct **4** within 1 hour. Because of the difficulty in separating **4** from the remaining naphthalene, the yield of **4** was estimated as approximately 70 % by ^{1}H NMR analysis. Although the reaction of **1** with anthracene was very slow and did not go to completion in *n*-hexane, because of the low solubility of anthracene, a smooth reaction was observed in mesitylene, thus affording the dialumene-anthracene adduct **5** in 94 % yield. The structures of new arene-adducts **4** and **5** were determined by ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallographic analysis.

Reactions of **1** with alkenes and alkynes were also investigated to explore the scope of the exchange reactions. However, treatment of **1** with alkenes or alkynes, such as 3-hexene, cyclohexene, 2,3-dimethyl-1,3-butadiene, 3-hexyne, 1-hexyne, and phenylacetylene, gave complex mixtures, and the formation of the corresponding adducts of the dialumene **2** was not confirmed.[4f,18] Only in the case of bis(trimethylsilyl)acetylene, the C_6H_6 moiety of **1** was smoothly exchanged to afford the 1,2-dialuminacyclobutene **6** (Scheme 4).[19]



Scheme 4. Substitution reactions of the C_6H_6 moiety of **1**. The reactions were carried out in the dark.

To gain insight into the mechanism for the arene-exchange reactions, the reaction of **1** with naphthalene in *n*-hexane was monitored by UV/Vis spectroscopy. The UV/vis spectra of the mixture of **1** and naphthalene gradually changed with a set of isosbestic points ($\lambda = 518$, 370 nm), thus showing that any detectable intermediates are not involved (Figure 2). In addition, the conversion rate of **1** is almost independent from the concentration of naphthalene, and thus suggests that naphthalene may not participate in the rate-determining step. Additional in-depth kinetic studies and DFT calculations on the reaction mechanism are now under way.

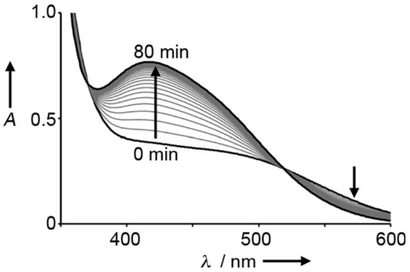


Figure 2. UV/Vis spectra of the mixture of **1** and naphthalene in *n*-hexane ($[\mathbf{1}] = 7.0 \times 10^{-3}$ M, [naphthalene] $= 9.7 \times 10^{-3}$ M, 30 °C). Presence of a set of isosbestic points ($\lambda = 518$, 370 nm) indicates that the arene exchange occurred in a one-to-one fashion.

In conclusion, the dialumene-benzene adduct **1** was obtained by the reduction of the 1,2-dibromodialumane **3** in benzene. The C_6H_6 moiety of **1** was readily exchanged with C_6D_6, naphthalene, anthracene, and bis(trimethylsilyl)acetylene at room temperature, thus affording the corresponding trapping products of dialumene **2**. It was demonstrated that **1** shows unique reactivity as a synthetic equivalent of **2** for applications in the development of new organoaluminum species.

Experimental Section

All the manipulations were performed under a dry argon atmosphere. Solvents were purified by the Ultimate Solvent System, Glass Contour Company[20] and by distillation from a potassium mirror. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-600 or a JEOL AL-300 spectrometer and referenced to $\mathrm{SiMe_4}$. The ^{27}Al NMR spectra were recorded on a Bruker Avance-600 spectrometer and referenced against an external standard ($\mathrm{Al(NO_3)_3}$ in $\mathrm{D_2O}$). UV/Vis spectra were recorded on a SHIMADZU UV-1700 UV-vis-NIR spectrometer equipped with a temperature controller. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF mass spectrometer equipped with an AMR DART-SVP ion source using He as an ionization gas. Melting points were determined on a Yanaco micro melting point apparatus and uncorrected.

1: Freshly prepared $\mathrm{KC_8}$ (5.5 mg, 0.040 mmol) was added to a benzene (6 mL) solution of **3** (20.2 mg, 0.020 mmol) at room temperature. The mixture was stirred for 4 h to give a dark red solution. After removal of volatiles, the residue was extracted with *n*-hexane and filtered. The filtrate was concentrated and stored at −35 °C for 1 d to afford **1** as red crystals (18.5 mg, 0.020 mmol, 100 %). m.p, 127 °C (dec); ^{1}H NMR (600 MHz, [$\mathrm{D_{14}}$]methylcyclohexane, 20 °C): $\delta = 0.08$ (s, 72 H, $\mathrm{Si(C}H_3)_3$), 1.14 (s, 4 H, $\mathrm{C}H\mathrm{(SiMe_3)_2}$), 4.69 (broad, 6 H, $\mathrm{C_6}H_6$), 6.60 (d, $^3J = 7.7$ Hz, 4 H, *m*-Bbp*H*), 6.95 ppm (t, $^3J = 7.7$ Hz, 2 H, *p*-Bbp*H*); ^{1}H NMR (600 MHz, [$\mathrm{D_{14}}$]methylcyclohexane, −60 °C): $\delta = 0.05$ (s, 36 H, $\mathrm{Si(C}H_3)_3$), 0.09 (s, 36 H, $\mathrm{Si(C}H_3)_3$), 1.14 (broad, 4 H, $\mathrm{C}H\mathrm{(SiMe_3)_2}$), 2.54 (broad, 2 H, $\mathrm{AlC}H$), 5.75 (broad, 4 H, $\mathrm{C{=}C}H$), 6.60 (d, $^3J = 7.2$ Hz, 4 H, *m*-Bbp*H*), 6.97 ppm (t, $^3J = 7.2$ Hz, 2 H, *p*-Bbp*H*); ^{13}C NMR (151 MHz, [$\mathrm{D_{14}}$]methylcyclohexane, −60 °C): $\delta = 0.2$ ($\mathrm{Si(}C\mathrm{H_3)}$), 1.0 ($\mathrm{Si(}C\mathrm{H_3)}$), 32.3 ($C\mathrm{H(SiMe_3)_2}$), 42.6 (broad, $\mathrm{Al}C\mathrm{H}$), 122.3 (broad, $C\mathrm{{=}CH}$), 122.6 (*m*-Bbp*C*), 128.0 (*p*-Bbp*C*), 146.8 (broad, *ipso*-Bbp*C*), 150.0 ppm (*o*-Bbp*C*); no signal was observed in the ^{27}Al NMR spectrum (in [$\mathrm{D_{14}}$]methylcyclohexane or $\mathrm{C_6D_6}$, measurement time: 2 days); UV/Vis (*n*-hexane): $\lambda_{\max} = 460$ nm ($\varepsilon = 410$).

4: Naphthalene (14.2 mg, 0.10 mmol) was added to a *n*-hexane (5 mL) solution of **1** (18.9 mg, 0.021 mmol) at room temperature, and the mixture was stirred in the dark for 1 h. Excess naphthalene was removed by sublimation, and the residue was recrystallized several times from *n*-hexane at −35 °C to afford orange crystals containing **4** and remaining naphthalene (19.5 mg, 0.014 mmol, ca. 70 %). The yield of **4** was estimated by the ^{1}H NMR spectrum of the orange crystals. m.p. 158 °C (dec.); ^{1}H NMR (300 MHz, [$\mathrm{D_{12}}$]cyclohexane): $\delta = 0.110$ (s, 72 H, $\mathrm{Si(C}H_3)_3$), 1.19–1.60 (broad, 4 H, $\mathrm{C}H\mathrm{(SiMe_3)_2}$), 3.53 (*pseudo*-t, $^4J = 4.2$ Hz, 2 H, $\mathrm{AlC}H$), 6.33 (*pseudo*-t, $^4J = 4.2$ Hz, 2 H, $\mathrm{C{=}C}H$), 6.67–6.74 (m, 8 H), 7.01 ppm (t, $^3J = 7.8$ Hz, 2 H, *p*-Bbp*H*); ^{13}C NMR (151 MHz, [$\mathrm{D_{12}}$]cyclohexane): $\delta = 1.8$ ($\mathrm{Si(}C\mathrm{H_3)_3}$), 35.4 (broad, $C\mathrm{H(SiMe_3)_2}$), 52.3 ($\mathrm{Al}C\mathrm{H}$), 123.0 ($\mathrm{C{=}}C\mathrm{H}$), 123.8 (*m*-Bbp*C*), 124.0 (*C*H) 124.7 (*C*H), 128.7 (*p*-Bbp*C*), 137.0 (*C*), 147.5 (*ipso*-Bbp*C*), 151.5 ppm (*o*-Bbp*C*); No signal was observed in the ^{27}Al NMR spectrum (in $\mathrm{C_6D_6}$, measurement time: 2 days); UV/Vis (*n*-hexane): $\lambda_{\max} = 410$ nm ($\varepsilon = 810$); HRMS (DART-TOF, positive-mode) *m/z* calcd for $[\mathrm{C_{50}H_{90}Al_2Si_8 + H}]$: 969.4900; found: 969.4832 ($[\mathrm{M+H}]^+$).

Crystal data for **1**: triclinic, space group $P\bar{1}$, −170 °C, $a = 13.3654(9)$, $b = 13.7655(5)$, $c = 18.1139(6)$ Å, $\alpha = 67.8085(14)$, $\beta = 70.2233(16)$, $\gamma = 86.466(5)°$, $V = 2895.4(2)$ Å^3, $Z = 2$, $\mu(\mathrm{Mo}\ K\alpha) = 0.243\ \mathrm{mm^{-1}}$, $2.07° < \theta < 25.50°$, $R_{\mathrm{int}} = 0.0694$, Completeness to $\theta_{\max}$ 98.3 %, 529 parameters refined, R_1 ($I > 2\sigma(I)$) = 0.0747, wR_2 (all data) = 0.1853, GOF = 1.113, largest diff. peak and hole 0.603 and −0.313 e Å^{-3}. CCDC 884389 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] Crystal structures of adducts **4**, **5**, and **6** are included in the Supporting Information. CCDC 885864 (**4**), CCDC 884401 (**5**), and CCDC 905842 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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