Main-Group Chemistry

DOI: 10.1002/ange.201305228

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

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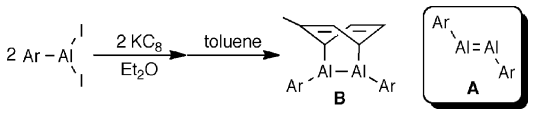
Dedicated to Professor Renji Okazaki on the occasion of his 76th birthday

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.

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[**] This work was partially supported by the JSPS KAKENHI (Nos. 22350017, 24550048, 24655028, and 24109013) and by the "Molecular Systems Research" project of RIKEN Advanced Science Institute. T.A. thanks the Kyoto Technoscience Center for the financial support. K.N. acknowledges the support by a Grant-in-Aid for JSPS Fellows from the Japan Society for the Promotion of Science (No. 252926). Synchrotron radiation experiments were performed at the BL38B1 of the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (Nos. 2012A1285, 2012B1194).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201305228.

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

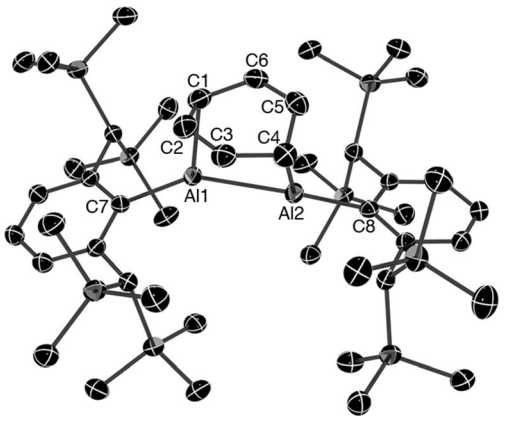
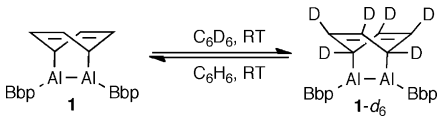


Figure 1. Molecular structure of **1** (30% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1–Al2 2.5552(19), Al1–C1 2.028(5), Al2–C4 2.020(5), Al1–C7 1.976(4), Al2–C8 1.965(4), C1–C2 1.488(7), C2–C3 1.355(7), C3–C4 1.453(7), C4–C5 1.480(7), C5–C6 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).

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**.

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

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

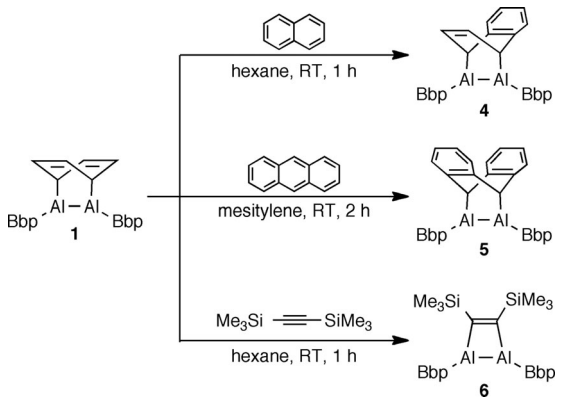


Scheme 3. Interconversion between **1** and [D_6]-**1**.

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.

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



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

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]

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

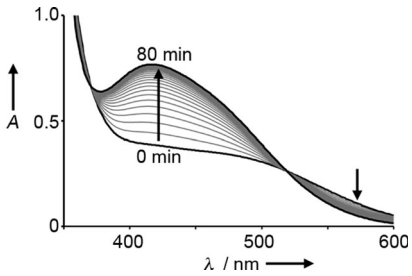


Figure 2. UV/Vis spectra of the mixture of **1** and naphthalene in *n*-hexane ([**1**] = 7.0×10^{-3} M, [naphthalene] = 9.7×10^{-3} M, 30 °C). Presence of a set of isosbestic points ($\lambda = 518$, 370 nm) indicates that the arene exchange occurred in a one-to-one fashion.

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.

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 $SiMe_4$. The ^{27}Al NMR spectra were recorded on a Bruker Avance-600 spectrometer and referenced against an external standard ($Al(NO_3)_3$ in 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 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, [D_{14}]methylcyclohexane, 20 °C): $\delta = 0.08$ (s, 72 H, Si(CH_3)$_3$), 1.14 (s, 4 H, CH(SiMe_3)$_2$), 4.69 (broad, 6 H, C_6H_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, [D_{14}]methylcyclohexane, −60 °C): $\delta = 0.05$ (s, 36 H, Si(CH_3)$_3$), 0.09 (s, 36 H, Si(CH_3)$_3$), 1.14 (broad, 4 H, CH(SiMe_3)$_2$), 2.54 (broad, 2 H, AlCH), 5.75 (broad, 4 H, C=CH), 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, [D_{14}]methylcyclohexane, −60 °C): $\delta = 0.2$ (Si(CH_3)), 1.0 (Si(CH_3)), 32.3 (CH(SiMe_3)$_2$), 42.6 (broad, AlCH), 122.3 (broad, C=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 [D_{14}]methylcyclohexane or 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, [D_{12}]cyclohexane): $\delta = 0.110$ (s, 72 H, Si(CH_3)$_3$), 1.19–1.60 (broad, 4 H, CH(SiMe_3)$_2$), 3.53 (*pseudo*-t, $^4J = 4.2$ Hz, 2 H, AlCH), 6.33 (*pseudo*-t, $^4J = 4.2$ Hz, 2 H, C=CH), 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, [D_{12}]cyclohexane): $\delta = 1.8$ (Si(CH_3)$_3$), 35.4 (broad, CH(SiMe_3)$_2$), 52.3 (AlCH), 123.0 (C=CH), 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 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 [$C_{50}H_{90}Al_2Si_8$ + H]: 969.4900; found: 969.4832 ([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, α = 67.8085(14), β = 70.2233(16), γ = 86.466(5)°, V = 2895.4(2) Å^3, Z = 2, μ(Mo $K\alpha$) = 0.243 mm^{-1}, 2.07° < θ < 25.50°, R_{int} = 0.0694, Completeness to θ_{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.

Received: June 18, 2013
Revised: July 27, 2103
Published online: August 28, 2013

Keywords: alkynes · aluminum · arenes · cycloaddition · structure elucidation

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