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Activation of Dihydrogen by Masked Doubly Bonded Aluminum Species

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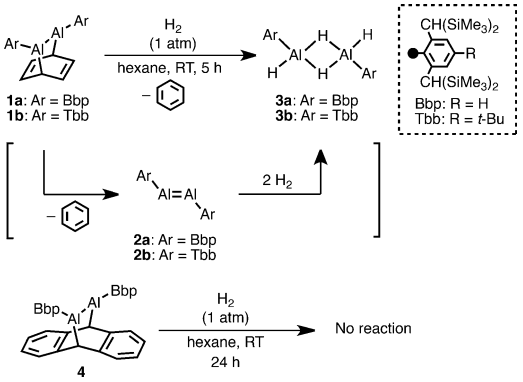
Dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday

Abstract: *Activation of dihydrogen by masked dialumenes (Al=Al doubly bonded species) is reported. Reactions of barrelene-type dialumanes, which have the reactivity as masked equivalents of 1,2-diaryldialumenes ArAl=AlAr, with H_2 afforded dihydroalumanes $ArAlH_2$ at room temperature (Ar: bulky aryl groups). These dihydroalumanes form hydrogen-bridged dimers $[ArHAl(\mu\text{-}H)]_2$ in the crystalline state, while a monomer–dimer equilibrium was suggested in solution. The 1,2-diaryldialumenes generated from the barrelene-type dialumanes are the putative active species in the cleavage of H_2.*

Activation of dihydrogen with transition-metal complexes is an important fundamental chemical transformation and has been extensively investigated for several decades.[1] In contrast, main-group element compounds had been considered as ineffective for the splitting of H_2 for a long time,[2] until the discoveries of the catalyst-free hydrogenation of heavier Group 14 dimetallynes[3] and of the frustrated Lewis pair (FLP)-catalyzed hydrogenation.[4] Thereafter, H_2 activation using multiply bonded and low-coordinate compounds of heavier main-group elements have been reported.[5] Among various heavier main-group elements, aluminum is a promising candidate as the key component of the H_2 activation reagents,[6] as shown by the recent reports on small-molecule activation with aluminum-based FLPs.[7]

Recently, we have reported the reactivity of barrelene-type dialumane **1** as the masked form of 1,2-diaryldialumene **2** (see Scheme 1).[8,9] At ambient temperature, **1** most certainly undergoes retro [2+4] cycloaddition to generate **2**, which can be trapped by various trapping reagents. These findings are indicative of the possibility of H_2 activation by using barrelene-type dialumanes **1**[10] as the masked forms of the corresponding dialumenes **2**.[11] Herein, we report the activation of H_2 with **1a** and **1b** under atmospheric pressure and at room temperature. A preliminary reactivity study of the hydrogen-activation products is also described.

When hexane solutions of **1a** and **1b** were exposed to an excess amount of H_2 under 1 atm and at room temperature, dihydroalumane dimers **3** were formed almost quantitatively (Scheme 1).[12] Compounds **3** were isolated as colorless,



Scheme 1. Reactions of dialumanes **1a**, **1b**, and **4** with H_2.

thermally stable solids (m.p. > 300 °C) in moderate yields (**3a**: 57%, **3b**: 80%). In contrast, structurally related dialumane **4**[9a] did not react with H_2 under similar reaction conditions. Unlike **1a**, compound **4** does not react with 1,2-bis(trimethylsilyl)acetylene to afford the trapping product **5** of the corresponding dialumene **2a** at room temperature (Scheme 2), indicating the lack of the reactivity of **4** as the masked form of dialumene **2a**. Considering these experimental results, dialumenes **2** generated from **1** are likely the active species in the H_2 activation (Scheme 1).

X-Ray diffraction analysis on single crystals of **3b** revealed its molecular structure (Figure 1),[13] thereby showing a centrosymmetric dimeric structure with the two aluminum atoms bridged by the hydrogen atoms. The aluminum-bound hydrogen atoms (H1 and H2) were found in the Fourier map and refined isotropically. The bridging Al–

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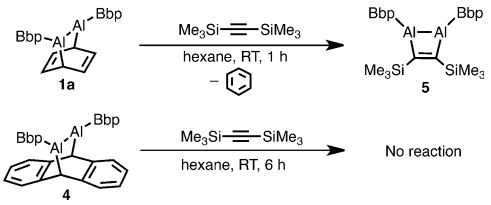


Scheme 2. Reactions of dialumanes **1a** and **4** with 1,2-bis(trimethylsilyl)acetylene.

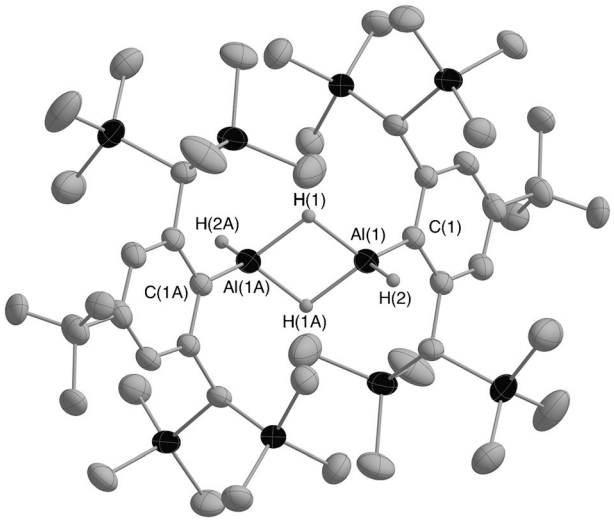
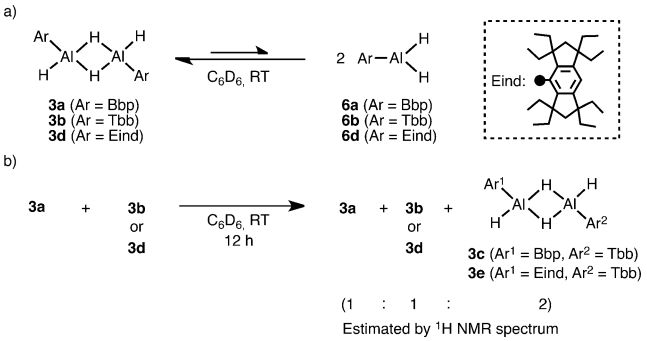


Figure 1. Molecular structure of dihydroalumane dimer **3b** with thermal ellipsoids set at 50% probability. Carbon-bound hydrogen atoms are omitted for clarity. Selected interatomic distances lengths [Å] and bond angles [°]: Al(1)···Al(1A) 2.632(1), Al(1)–H(1) 1.72(2), Al(1)–H(1A) 1.68(2), Al(1)–H(2) 1.60(2), Al(1)–C(1) 1.957(4); C(1)-Al(1)-Al(1A) 123.19(7), C(1)-Al(1)-H(1) 113.3(7), C(1)-Al(1)-H(2) 125.3(8), C(1)-Al(1)-H(1A) 116.9(7), Al(1A)-Al(1)-H(2) 111.5(8), H(1)-Al(1)-H(2) 110(1), H(1)-Al(1)-H(1A) 79(1), Al(1)-H(1)-Al(1A) 101(1).

H bond lengths (1.72(2) and 1.68(2) Å) and the terminal Al–H bond length (1.60(2) Å) are comparable to those of the dihydroalumane dimer $[Mes^*HAl(\mu\text{-}H)]_2$ (Al-$H_{bridging}$ 1.69(4) and 1.70(4) Å, Al-$H_{terminal}$ 1.50(4) Å, Mes* = 2,4,6-(*t*-Bu)$_3C_6H_2$).[14] The Al–Al distance (2.632(1) Å) is similar to that of the reported dihydroalumane dimer $[Mes^*HAl(\mu\text{-}H)]_2$ (2.652(2) Å). The solid-state ATR-IR spectra of **3a** and **3b** exhibited strong Al-$H_{terminal}$ vibrational absorptions (**3a**: 1870 cm^{-1}, **3b**: 1872 cm^{-1}) and Al-H-Al vibrational absorptions (**3a**: 1356 cm^{-1}, **3b**: 1358 cm^{-1}), which are comparable to those reported for $[Mes^*HAl(\mu\text{-}H)]_2$ (ν(Al-$H_{terminal}$) = 1888 cm^{-1}, ν(Al-H-Al) = 1345–1390 cm^{-1}).[14] Furthermore, these experimentally observed values were well reproduced by the theoretical calculations for the optimized structure of **3b** (ν(Al-$H_{terminal}$) = 1922 cm^{-1}, ν(Al-H-Al) = 1420 cm^{-1}),[15] indicating the hydrogen-bridged dimeric structures of **3a** and **3b** in the solid state as observed by the X-ray diffraction analysis of **3b**.[16]

At room temperature, the ^{1}H NMR spectra of **3a** and **3b** in C_6D_6 showed two broad signals (**3a**: δ_H = 4.49 and 4.88, **3b**: δ_H = 4.49 and 4.89) attributable to the aluminum-bound hydrides. These observed chemical shifts were comparable to those calculated for the optimized structure of **3b** ($\delta_{H(terminal)}$ = 5.32, $\delta_{H(bridging)}$ = 5.15),[15] indicating that the dimeric structures should be retained in solution at this temperature. Heating the solutions of **3a** and **3b** resulted in the broadening of the Al–H signals, and at 80 °C broad resonances were observed at δ = 4.46 and 4.42 ppm, respectively, suggesting an equilibrium between the dimers (**3a** and **3b**) and the monomers (**6a** and **6b**) in solution (Scheme 3a).



Scheme 3. a) Monomer–dimer equilibrium of the dihydroalumanes. b) Crossover experiments between **3a** and **3b**,**d**.

When a crossover experiment involving mixing **3a** and **3b** in 1:1 molar ratio was performed, the formation of a mixture of three dimers **3a**, **3b**, and **3c** in 1:1:2 molar ratio was observed (Scheme 3b), corroborating the monomer–dimer equilibrium at room temperature. Similarly, the crossover experiment involving **3b** and different type of dihydroalumane dimer $[(Eind)AlH(\mu\text{-}H)]_2$ (**3d**) (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacene-4-yl), which was obtained by the treatment of $[Li(OEt_2)]_2[(Eind)AlH_3]_2$ with chlorotrimethylsilane,[17,18] in 1:1 molar ratio also suggested the monomer–dimer equilibrium of these dihydroalumane dimers in solution.

In conclusion, we have reported the activation of dihydrogen by the dialumanes serving as masked-dialumene equivalents. The H_2 activation proceeded at 1 atm and at room temperature, yielding dihydroalumane derivatives. The dihydroalumanes form the hydrogen-bridged dimer in the solid state but dissociate to the monomer in solution. The H_2 activation mechanism and reactivity of dihydroalumane dimer[19] are currently under investigation and will be reported in due course.

Experimental Section

3a: A dark-red solution of **1a** (34.3 mg, 0.0373 mmol) in hexane (3 mL) was stirred at room temperature for 5 h under H_2 atmosphere to give a colorless solution. Storage of the solution at −35 °C afforded colorless crystals of **3a**. More crystals of **3a** were obtained by the concentration and cooling of the mother liquor (total: 18.1 mg, 0.0214 mmol, 57%). Sublimation point: 215 °C (in a vacuum-sealed tube). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): δ = 0.21 (s, 72 H, Si(C*H*)$_3$), 1.73 (s, 4 H, C*H*(SiMe$_3$)$_2$), 4.49 (s, $w_{1/2}$ ≈ 36 Hz, Al-*H*-Al), 4.88 (s, broad, $w_{1/2}$ ≈ 46 Hz, Al*H*$_{terminal}$), 6.85 (d, ^3J = 7.8 Hz, 4 H, *m*-Bbp(*H*)), 7.13 ppm (t, ^3J = 7.8 Hz, 2 H, *p*-Bbp(*H*)); ^{13}C NMR (151 MHz, C_6D_6, 25 °C): δ = 0.7 (Si*Me*$_3$), 36.7 (*C*H(SiMe$_3$)$_2$), 122.8 (*m*-*C*(Bbp)), 129.6 (*p*-*C*(Bbp)), 139.3 (*ipso*-*C*(Bbp), determined by the HMBC spectra),

152.5 ppm (*o*-*C*(Bbp)); No ^{27}Al NMR signal was observed after an overnight measurement; IR (ATR, solid state): $\nu = 1870\ cm^{-1}$ (Al-$H_{terminal}$), 1356 cm^{-1} (Al-$H_{bridging}$).

3b: A dark-red solution of **1b** (45.9 mg, 0.0445 mmol) in hexane (3 mL) was stirred at room temperature for 5 h under H_2 atmosphere to give a colorless solution. Storage of the solution at −35 °C afforded X-ray quality colorless crystals of **3b**. More crystals of **3b** were obtained by the concentration and cooling of the mother liquor (34.2 mg, 0.0357 mmol, 80 %). Sublimation point: 210 °C (in a vacuum-sealed tube). ^{1}H NMR (600 MHz, C_6D_6, 25 °C): $\delta = 0.25$ (s, 72 H, Si(C*H*$_3$)$_3$), 1.33 (s, 18 H, *t-Bu*), 1.76 (s, 4 H, C*H*(SiMe$_3$)$_2$), 4.49 (s, $w_{1/2} = 39$ Hz, Al-*H*-Al), 4.89 (s, broad, $w_{1/2} = 64$ Hz, Al$H_{terminal}$), 6.94 ppm (s, 4 H, *m*-Tbb(*H*)); ^{13}C NMR (151 MHz, C_6D_6, 25 °C): $\delta =$ 0.8 (Si*Me*$_3$), 31.3 (C(*C*H$_3$)$_3$), 34.5 (*C*(CH$_3$)$_3$), 36.4 (*C*H(SiMe$_3$)$_2$), 120.4 (*m*-*C*(Tbb)), 135.5 (*ipso*-*C*(Tbb), determined by the HMBC spectra), 151.9 (*p*-*C*(Tbb)), 152.0 ppm (*o*-*C*(Tbb)); No ^{27}Al NMR signal was observed after an overnight measurement; IR (ATR, solid state): $\nu =$ 1872 cm^{-1} (Al-$H_{terminal}$), 1358 cm^{-1} (Al-$H_{bridging}$).

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frequency calculations) or at the B3PW91/6-311 + G(2d,p) level of theory (for NMR chemical shift calculations by the gauge-independent atomic orbital (GIAO) method) by using the Gaussian 09 program package. The optimized structural parameters were close to those determined by the X-ray crystallographic analysis. Selected interatomic distances [Å] of the optimized structure of **3b**: Al–$H_{terminal}$ 1.591, Al–$H_{bridging}$ 1.749, 1.764, Al···Al 2.666. Gaussian 09, Revision D.01, M. J. Frisch, et al., Gaussian, Inc., Wallingford, CT, **2013**. See the Supporting Information for details.

[16] Owing to the poor crystal quality, the molecular structure of **3a** could not be determined with enough accuracy. However, a preliminary X-ray diffraction analysis on **3a** indicated a similar dimeric structure as observed for **3b**.

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[19] Treatment of dihydroalumane dimer **3b** with 4 equivalents of benzophenone led to the immediate disappearance of **3b** at room temperature. The ^{1}H NMR spectrum of the reaction mixture suggested the progress of the hydroalumination of benzophenone with **3b**. See the Supporting Information for details.

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