ORGANOMETALLICS
Note
pubs.acs.org/Organometallics

Synthesis, Structure, and Properties of a Stable 1,2-Dibromodialumane(4) Bearing a Bulky Aryl Substituent

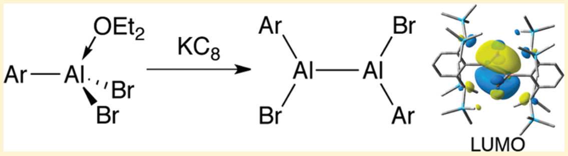
Tomohiro Agou,[†,‡] Koichi Nagata,[†] Heisuke Sakai,[§] Yukio Furukawa,[§] and Norihiro Tokitoh*[,†]

[†]Institute for Chemical Research and [‡]Kyoto University Pioneering Research Unit for Next Generation, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

[§]Department of Chemistry and Biochemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

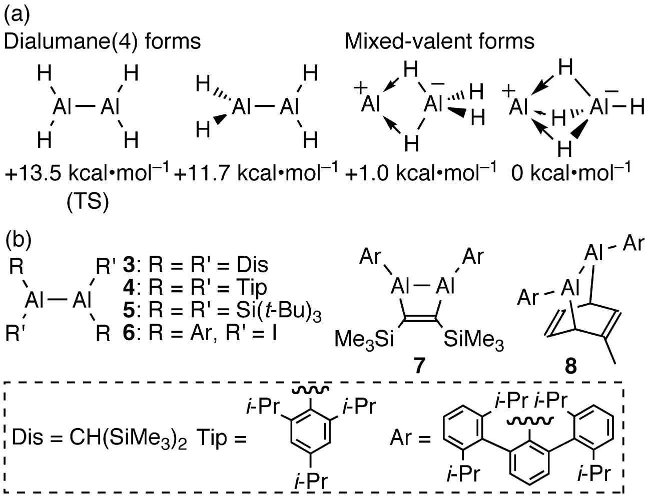
Supporting Information

ABSTRACT: The stable 1,2-dibromodialumane(4) Bbp(Br)Al–Al(Br)Bbp (**1**; Bbp = 2,6-bis[bis(trimethylsilyl)methyl]phenyl) was synthesized by the reduction of the corresponding dibromoalumane etherate $BbpAlBr_2 \cdot OEt_2$ (**2**). The structure and properties of **1** have been elucidated on the basis of the analyses of spectroscopic and crystallographic data and are supported by DFT calculations.



Despite their potential importance as reactive intermediates and promising building blocks for unique Al clusters, dialumanes(4) (>Al–Al<)[1] were long considered to be an elusive class of compounds.[2,3] Their fleetingness was explained on the basis of theoretical calculations for the structure of Al_2H_4 (Chart 1a), according to which initial isomerizations should trigger readily available thermal decomposition mechanisms. These in turn probably result in the formation of highly reactive mixed-valent forms.[4] Then, in 1988, Uhl demonstrated that it is possible to kinetically stabilize and isolate dialumane(4) **3** by the introduction of bulky substituents around the Al–Al moiety.[5] The bulky substituents suppress the aforementioned isomerizations as well as the subsequent decomposition and hence stabilize the dialumane(4) form. Since then, only a few examples of dialumanes(4) with the general formula $R_2Al{-}AlR_2$ (R = bulky substituents) free of Lewis base coordination have been synthesized and isolated (Chart 1b).[6,7] Recently, tetraorganyldialumanes(4) **7** and **8**, bearing only two bulky substituents on the Al–Al moiety, could be synthesized by trapping reactions of the transient dialumene ArAl═AlAr.[8] Although 1,2-dihalodialumanes(4) are expected to be potential building blocks for novel low-coordinated aluminum species,[8a,9−11] dialumanes(4) bearing halogen groups, as in the prototypical 1,2-dihalodialumane(4) R(X)Al–Al(X)R (X = halogen, R = bulky substituent), have not yet been systematically investigated. The lack of extensive studies is probably due to the difficulties arising from (i) the stabilization of the highly reactive X–Al–Al–X moiety and (ii) the necessary suppression of halogen atom migration and intermolecular reactions with external nucleophiles, resepctively.[12] Except for 1,2-diiododialumane(4) **6**,[8a] all halodialumanes(4) reported to date have been confined to those thermodynamically stabilized by coordination of Lewis bases to the Al–Al moiety.[11,13] A systematic investigation into halodialumanes(4) free of coordinated Lewis bases should significantly contribute to the understanding of the nature of functionalized alumane(4) derivatives. Here, we describe the synthesis, structure, and properties of the 1,2-dibromodialumane(4) Bbp(Br)Al–Al(Br)Bbp (**1**), which is the first example of a 1,2-dibromodialumane(4) without coordination of a Lewis base.

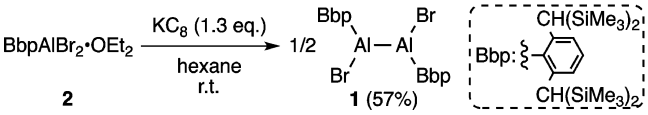
Chart 1. (a) Relative Energies of Al_2H_4 Isomers Calculated at the MP4/6-31G(d,p) Level of Theory and (b) Structurally Characterized Dialumanes(4) without Lewis Base Coordination



Dibromoalumane etherate **2** was prepared by the reaction of BbpLi[14] with $AlBr_3$ in Et_2O. The subsequent reduction with 1.3 equiv of potassium graphite (KC_8) in hexane at ambient temperature afforded 1,2-dibromodialumane(4) **1** as an air- and moisture-sensitive colorless solid in 57% yield (Scheme 1). In a vacuum-sealed tube, **1** sublimes above 232 °C without any sign

Received: March 21, 2012
Published: April 19, 2012

Scheme 1. Synthesis of 1,2-Dibromodialumane(4) 1



of decomposition, showing its impressive thermal stability. The ^{27}Al NMR spectrum of **1** in C_6D_6 did not exhibit any apparent signal, even after prolonged measurements (several days). We tentatively attribute the absence of any ^{27}Al NMR signals to the quadrupolar effects of the tricoordinated aluminum atoms.

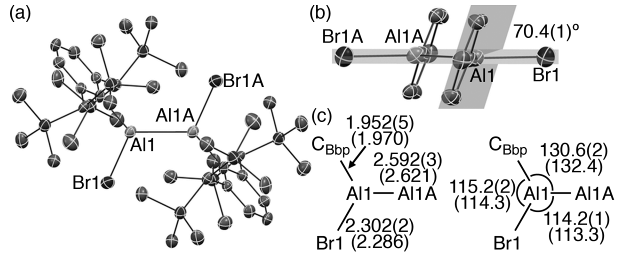


Figure 1. Molecular structure of **1**: (a) top view; (b) side view showing the dihedral angle between the least-squares plane of the aryl ring and the Al–Al plane (Dis groups are omitted). Thermal displacement ellipsoids are set at the 50% probability level, and hydrogen atoms are omitted. (c) Selected bond lengths (Å) and angles (deg). Structural parameters obtained from the DFT-optimized geometry of **1** are shown in parentheses (B3PW91/6-31G+G(2df)-[Al,Br]:6-31G(d)[Si,C,H]).

X-ray diffraction analysis on single crystals of **1**, obtained by recrystallization from toluene/hexane at −40 °C, revealed the molecular structure in the solid state (Figure 1). Dialumane(4) **1** has a crystallographic center of symmetry in the middle of the Al–Al bond, and the Al atoms exhibit a planar geometry (sum of the bond angles around the Al atom 360°). Therefore, the skeletal atoms of the Al–Al moiety in **1** (two C(*ipso*-Bbp), two Br, and two Al atoms) lie in the same plane, to which the aryl rings of the Bbp groups are orientated almost perpendicularly. The Al–Al bond length in **1** (2.592(3) Å) is shorter than those of the previously reported dialumane(4) derivatives bearing four carbon or silicon substituents (cf. **3**, 2.660(1) Å;[5a] **4**, 2.647(3) Å;[6a] **5**, 2.751(2) Å[6b]) and comparable to that of **6** (2.609(2) Å).[8a,15,16] The relatively short Al–Al bond length in 1,2-dihalodialumanes(4) **1** and **6** can be explained by the combination of two electronic effects of the halogen groups: (i) a relaxation of the electrostatic repulsion between the Al atoms due to n(X)→3p*(Al) electron donation[17] and (ii) an increase in the s character of the Al–Al bond as a result of the negative inductive effect of the halogen groups (Bent's rule).[18] The Al–C and Al–Br bond lengths in **1** are comparable to those in the dibromoalumane 2,4,6-(t-Bu)$_3C_6H_2AlBr_2$ (Al–C = 1.953(8) Å, Al–Br = 2.281(2) Å).[15,19] The experimentally obtained solid-state structure of **1** was reproduced in good agreement by the use of DFT calculations, as shown in Figure 1.[20]

The solid-state Raman spectrum of **1** (Figure 2) exhibited a signal at 453 cm^{-1}, which can be assigned to the Al–Al stretching vibration (cf. ν_{calcd} 451 cm^{-1}).[21] The higher Al–Al stretching frequency of **1** relative to that of **3** (373 cm^{-1})[5a] is indicative of an increase of the Al–Al bond strength, hence corroborating the contraction of the Al–Al bond. The natural bond orbital (NBO) analysis[22] for **1** revealed a high s character of the Al–Al bond (σ(Al–Al) = 0.7071(3s3p$^{0.51}$)Al + 0.7071(3s3p$^{0.51}$)Al), which is in accordance with the Al–Al bond contraction and the higher Al–Al stretching frequency. The NBO analysis furthermore suggested that the 4p(Br) → 3p*(Al) π-donations should both decrease the positive charge located on the Al atom (Al, +1.05 e; Br, −0.50 e) and enhance the stability of **1**, as is evident from the donor–acceptor stabilization energy, which was obtained from a second-order perturbation theory analysis (−29.63 kcal mol^{-1} for each Al–Br moiety).

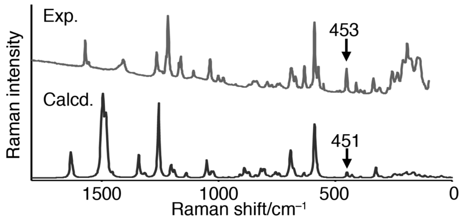


Figure 2. Raman spectra of **1**: (top) solid-state Raman spectrum of **1** (λ_{ex} 532 nm); (bottom) calculated Raman spectrum of **1** (HWHM = 4 cm^{-1}, without scaling).

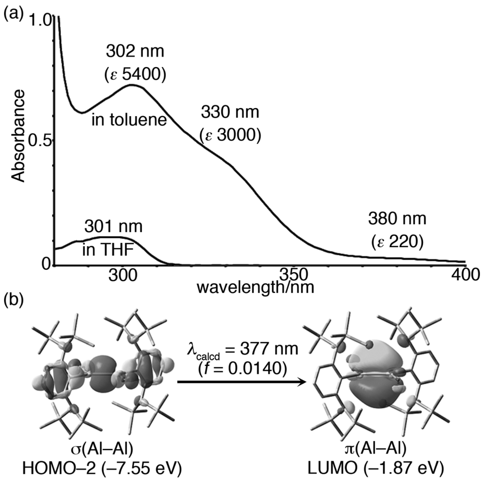
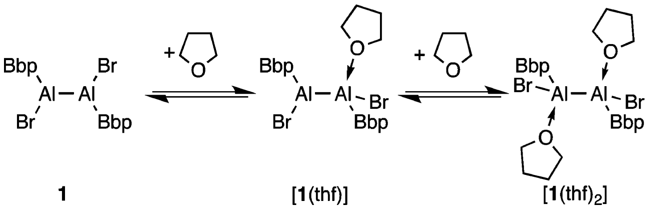


Figure 3. (a) UV–vis spectra of **1** in toluene and THF. (b) Frontier Kohn–Sham orbitals of **1** and the lowest energy transition (M062X/6-311+G(2df)[Al,Br]:6-31+G(d)[Si,C,H]). Hydrogen atoms are omitted for clarity.

The UV–vis spectrum of **1** in toluene showed one broad absorption band at λ_{max} 302 (ε = 5400), 330 (sh, ε = 3000) and 380 nm (sh, ε = 220 M^{-1} cm^{-1}) (Figure 3a). TD-DFT calculations for **1** suggested a correlation of the weak absorption at 380 nm to the σ(Al–Al) → π(Al–Al) electron transition (Figure 3b) and indicated the absorptions at shorter wavelengths (λ_{max} 302 and 330 nm) to be the result of a combination of several electron transitions from π(Bbp) orbitals to π*(Bbp) and σ*(Al–Br) orbitals.[23] The longest absorption wavelength of **1** is hypsochromically shifted with respect to those of **4** (λ_{max} 420 nm)[6a] and **5** (λ_{max} 525 nm).[6c,24] The UV–vis spectrum of **1** in THF (Figure 3a) was different from that in toluene. Only one weak absorption was observed at λ_{max} 301 nm, indicating the formation of THF adducts [**1**(thf)] and [**1**(thf)$_2$] (Scheme 2). The coordination of THF molecules to **1** should raise the π(Al–Al) orbital (LUMO) and increase the HOMO–LUMO energy gap, resulting in the hypsochromic shifts of the absorption. TD-DFT calculations on Me_2O adducts of the model dialumane Me(Br)Al–Al(Br)Me

Scheme 2. Plausible Coordination Equilibrium between 1 and THF



($\mathbf{1}_{\mathbf{Me}}$; λ_{calcd} 387 nm, f = 0.0103), [$\mathbf{1}_{\mathbf{Me}}$(OMe_2)] (λ_{calcd} 331 nm, f = 0.0268), and [$\mathbf{1}_{\mathbf{Me}}$(OMe_2)$_2$] (λ_{calcd} 291 nm, f = 0.0526) were able to reproduce the experimentally observed hypsochromic shift of the absorption maxima of **1** in THF in good agreement. Titration of **1** with THF in toluene indicated the stepwise formation of [**1**(thf)] and [**1**(thf)$_2$], and the ^{1}H NMR spectrum of a mixture of **1** and THF in C_6D_6 suggested a fast exchange of the coordinated THF molecules in solution (see the Supporting Information for details). Removal of all volatiles from this sample resulted in the quantitative recovery of **1**, indicating a complete reversibility of the THF coordination to the Al–Al moiety in **1**.

We have shown here the synthesis of the first 1,2-dibromodialumane(4) **1**, which is free of Lewis base coordination. Compound **1** is a thermally stable solid, and its molecular structure has been unambiguously assigned on the basis of its spectroscopic and crystallographic properties. The Al–Al bond in **1** is contracted relative to those of previously reported tetraorganyldialumane(4) derivatives and exhibits higher s character, which can be explained in terms of a combination of σ-withdrawing and π-donating effects of the bromine substituents. The reactivity of **1**, including substitution and reduction of the Al–Br moiety, is currently the subject of investigations in our laboratory, and results will be reported in due time.

EXPERIMENTAL SECTION

Synthesis of Bbp(Br)Al–Al(Br)Bbp (1). To a hexane (5 mL) solution of **2** (301 mg, 0.46 mmol) was gradually added freshly prepared KC_8 (80.8 mg, 0.60 mmol) at room temperature, and the mixture was stirred at room temperature for 2 h, concentrated under reduced pressure, and filtered though a Celite pad using hexane as the eluent. The filtrate was concentrated to 5 mL and stored at −30 °C to deposit **1** as colorless crystals (131 mg, 0.13 mmol, 57%). Sublimation point: 232 °C (in a vacuum-sealed tube). ^{1}H NMR (600 MHz, C_6D_6): δ 0.24 (s, 72H, Si(CH_3)$_3$), 1.31 (s, 4H, CH($SiMe_3$)$_2$), 6.76 (d, ^3J = 7.7 Hz, 4H, *m*-Ar*H*), 7.09 (t, ^3J = 7.7 Hz, 2H, *p*-Ar*H*). ^{13}C NMR (151 MHz, C_6D_6): δ 1.08 ($SiMe_3$), 38.54 ($CH(SiMe_3)_2$), 122.90 (*m*-*C*(Ar)), 130.31 (*p*-*C*(Ar)), 145.60 (broad, *ipso*-*C*(Ar), determined from HMBC measurments), 150.39 (*o*-*C*(Ar)). No signal was observed in the ^{27}Al NMR spectrum (even after several days). UV/vis (toluene): λ/nm (ε) 302 (5400), 330 (sh, 3000), 380 (sh, 220). The extremely high air and moisture sensitivity of **1** precluded the recording of satisfactory C,H,N analysis. The purity of **1** was accordingly confirmed by the ^{1}H and ^{13}C NMR spectra (see the Supporting Information).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving experimental procedures, analytical data for new compounds, computational results, the complete ref 20, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Tel: +81-774-38-3200. Fax: +81-774-38-3209. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by Grants-in-Aid for Scientific Research (B) (No. 22350017), Young Scientist (B) (No. 21750037), and the Global COE Program B09 from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Computational time was provided by the Super Computer System, Institute for Chemical Research, Kyoto University. This study was carried out with the FT-ICR-MS and the NMR spectrometer in the JURC at the Institute for Chemical Research, Kyoto University. The synchrotron radiation experiments were performed at the BL38B1 of the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2011B1296).

REFERENCES

(1) Although the name "alane" has been widely used for the parent trivalent aluminum (AlH_3), switching to the alternative name "alumane" has been advised by the recent IUPAC nomenclature recommendations. By following these recommendations and the borane nomenclature rules, the molecule $H_2Al–AlH_2$ should be named "dialumane(4)" rather than "dialane(4)".

(2) (a) Uhl, W.; Layh, M. In *The Group 13 Metals Aluminum, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*; Aldridge, S., Downs, A. J., Eds.; Wiley: Chichester, U.K., 2011; pp 246–284. (b) Linti, G.; Schnöckel, H.; Uhl, W.; Wiberg, N. In *Molecular Clusters of the Main Group Elements*; Driess, M., Nöth, H., Eds.; Wiley: Weinheim, Germany, 2004; pp 126–168.

(3) A parent dialumane(4) ($H_2Al–AlH_2$) stabilized by the coordination of an N-heterocyclic carbene has been reported recently: Bonyhady, S. J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. *Nature Chem.* **2010**, *2*, 865.

(4) (a) Lammertsma, K.; Güner, O. F.; Drewes, R. M.; Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1989**, *28*, 313. (b) Lammertsma, K.; Leszczyński, J. *J. Phys. Chem.* **1990**, *94*, 5543.

(5) (a) Uhl, W. *Z. Naturforsch.* **1988**, *43b*, 1113. (b) Uhl, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1386.

(6) (a) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983. (b) Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J. *Organometallics* **1998**, *17*, 5431. (c) Wiberg, N.; Blank, T.; Amelunxen, K.; Nöth, H.; Schnöckel, H.; Baum, E.; Purath, A.; Fenske, E. *Eur. J. Inorg. Chem.* **2002**, 341.

(7) The term "Lewis base free dialumanes(4)" is used for dialumane(4) derivatives in which both Al^{II} atoms are three-coordinated. By following this definition, dialumanes(4) containing multidentate ligands, such as (η^5-Cp*)(I)Al–Al(I)(η^5-Cp*), are not regarded as Lewis base free dialumane(4) derivatives.

(8) (a) Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 10784. (b) Cui, C.; Li, X.; Wang, C.; Zhang, J.; Cheng, J.; Zhu, X. *Angew. Chem., Int. Ed.* **2006**, *45*, 2245.

(9) 1,2-Diiododigallanes(4) have been used in the synthesis of the corresponding digallenes: Zhu, Z.; Fischer, R. C.; Ellis, B. D.; Rivard, E.; Merrill, W. A.; Olmstead, M. M.; Power, P. P.; Guo, J.-D.; Nagase, S.; Pu, L. *Chem. Eur. J.* **2009**, *15*, 5263.

(10) Dihalodigallium or dihalodiindium compounds have been utilized in the syntheses of gallium or indium clusters, respectively: (a) Wiberg, N.; Blank, T.; Westerhausen, M.; Schneiderbauer, S.; Schnöckel, H.; Krossing, I.; Schnepf, A. *Eur. J. Inorg. Chem.* **2002**, 351. (b) Uhl, W.; El-Hamdan, A. *Eur. J. Inorg. Chem.* **2004**, 969. (c) Uhl,

W.; Lawerenz, A.; Zemke, S. *Z. Anorg. Allg. Chem.* **2007**, *633*, 979. (e) Uhl, W.; El-Hamdan, A.; Schindler, K. P. *Eur. J. Inorg. Chem.* **2006**, 1817. (d) Uhl, W.; El-Hamdan, A.; Lawerenz, A. *Eur. J. Inorg. Chem.* **2005**, 1056.

(11) Minasian, S. G.; Arnold, J. *Chem. Commun.* **2008**, 4043.

(12) Structures of halodialumanes(4) have been recently investigated by theoretical calculations. (a) Compaan, K. R.; Wilke, J. J.; Schaefer, H. F., III *J. Am. Chem. Soc.* **2011**, *133*, 13387. (b) Szabó, A.; Kovàcs, A.; Frenking, G. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1803.

(13) (a) Klemp, C.; Üffing, C.; Baum, E.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1787. (b) Klimek, K. S.; Cui, C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **2000**, *19*, 3085. (c) Vollet, J.; Burger, R.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 6956. (d) Klemp, C.; Stößer, G.; Krossing, I.; Schnöckel, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 3691. (e) Ecker, A.; Baum, E.; Friesen, M. A.; Junker, M. A.; Üffing, C.; Köppe, R.; Schnöckel, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 513. (f) Mocker, M.; Robl, C.; Schnöckel, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 862.

(14) Agou, T.; Sugiyama, Y.; Sasamori, T.; Sakai, H.; Furukawa, Y.; Takagi, N.; Guo, J.-D.; Nagase, S.; Hashizume, D.; Tokitoh, N. *J. Am. Chem. Soc.* **2012**, *134*, 4120.

(15) The Al−Al, Al−Br, and Al−C bond lengths in **1** are in the ranges of those previously reported, respectively: Al−Al, 2.428−3.069 Å (mean 2.699 Å, median 2.685 Å); Al−Br, 2.195−2.749 Å (mean 2.337 Å, median 2.313 Å); Al−C, 1.811−2.458 Å (mean 2.016 Å, median 1.986 Å). These data were taken from the Cambridge Crystallographic Data Centre database.

(16) Lewis base free 1,2-dihalodigallanes(4) have reported to exhibit Ga−Ga bond contraction in comparison to those of the corresponding tetraorganyl digallanes(4): (a) Uhl, W.; El-Hamdan, A.; Geiseler, G.; Harms, K. *Z. Anorg. Allg. Chem.* **2004**, *630*, 821. (b) Uhl, W.; El-Hamdan, A.; Prött, M.; Spuhler, P.; Frenking, G. *Dalton Trans.* **2003**, 1360. (c) Cowly, A. H.; Decken, A.; Olazábal, C. A. *J. Organomet. Chem.* **1996**, *524*, 271. (d) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 2842. (e) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667.

(17) Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648.

(18) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

(19) Petrie, M. A.; Power, P. P.; Rasika Dias, H. V.; Ruhlandt-Senge, K.; Waggoner, K. M.; Wehmschulte, R. J. *Organometallics* **1993**, *12*, 1086.

(20) Frisch, M. J. et al. *Gaussian 09 (Revision C.01)*; Gaussian Inc., Wallingford, CT, 2010.

(21) Dennington, R.; Keith, T.; Millam, J. *GaussView (Version 5)*; Semichem Inc., Shawnee Mission, KS, 2009.

(22) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Weinhold, F. *NBO 5.0*; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001 (http://www.wisc.edu/~nbo5).

(23) (a) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215. (b) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157.

(24) Calculated transition energies for σ(Al−Al) → π(Al−Al) electron excitations of the model dialumanes(4) Me(Br)Al−Al(Br)Me ($\mathbf{1}_{\mathbf{Me}}$; λ_{calcd} 387 nm, f = 0.0103), $Me_2Al{-}AlMe_2$ (λ_{calcd} 417 nm, f = 0.0186), and $(H_3Si)_2Al{-}Al(SiH_3)_2$ (λ_{calcd} 442 nm, f = 0.0076) (B3PW91/6-31+G(d)) are in the same order as those experimentally observed for **1**, **4**, and **5**.