Al–Sc Bonded Complexes: Synthesis, Structure, and Reaction with Benzene in the Presence of Alkyl Halide

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ABSTRACT: An alumanyl anion possessing a new skeleton with N,N'-bis(2,6-diisopropylphenyl)-1,3-propanediamine ligand was synthesized and characterized. Transmetalation of this Al anion with diaminoscandium chloride precursors afforded the corresponding Al–Sc complexes possessing an unprecedented Al–Sc bond. The Al–Sc complex having $Sc[N(SiMe_3)_2]$ unit underwent intramolecular C–H cleavage to form a bridged dinuclear complex with μ-hydrido and μ-methylene ligands. The Al–Sc complex having $Sc(N^iPr_2)_2$ unit reacted with benzene in the presence of alkyl bromide to furnish a 1,4-dialuminated cyclohexadiene product with a concomitant formation of alkyl-alkyl coupled product. Although the latter product seems to form through the radical mechanism, DFT calculations revealed an ionic mechanism involving the following four steps: (1) C–Br bond cleavage through cooperative participation of both the Al and Sc centers, (2) C–C bond formation by a nucleophilic attack of the resulting alkyl-Al intermediate, (3) addition of Al anion moiety to benzene mediated by scandium center to form anionic Meisenheimer type intermediate, (4) subsequent reaction of the resulting Meisenheimer intermediate with bromoalumane intermediate to form dialuminated cyclohexadiene product. Such bimetallic reaction pathways to react with alkyl bromide and benzene would provide new insight into the chemistry of metal-metal bonded compounds.

The chemistry of unsupported metal-metal bond between two metal atoms has traditionally been a fascinating field to chemists because of its continuous contribution to both novel bonding patterns and reactivity.[1] Among metal-metal bonded compounds, transition metal (TM)[2] complexes having a three-coordinate X-type aluminum ligand, which would exhibit Lewis acidity due to a vacant p-orbital on the Al atom, have emerged since the 1990s. However, examples of TM–alumanyl complexes possessing a tricoordinated aluminum center are still limited so far (Figure 1). Salt elimination between a transition metal nucleophile and electrophilic aluminum gave Al–Fe heterometallic complexes **A** and **B** which were structurally authenticated by X-ray crystallography [Figure 1(a)].[3] Elimination of alkanes was also shown to be an effective method to prepare Al–Ir complexes **C** and **D** [Figure 1(b)].[4] Recently, new synthetic methods to construct Al–TM bond using neutral/anionic Al(I) reagent have been reported. Mixing copper chloride with a newly prepared neutral Al(I) species led to a formation of Al–Cu complex **E** through oxidative addition of Cu–Cl bond to Al(I) center [Figure 1(c)].[5] Inspired by the transmetalation reactions of the recently developed Al-anions[6] with group 1, 2, and 12 metal salts,[6d, 6f, 7] reactions of three-coordinate Al anions with TM-halides were also demonstrated to afford Al–TM complexes **F** and **G** possessing a three-coordinate X-type Al ligand [Figure 1(c)].[8,9] It should be noted that **G** is the sole example of early-metal–Al complex so far, however, the reactivity of **G** has not been studied due to its unavailability in a large scale and its instability in solution at room temperature. Thus, the reactivity of early-metal–Al complexes has not been reported.

Herein, we report the synthesis of Al–Sc(NSiMe₃)₂ and Al–Sc(N^iPr)₂ complexes featuring an unprecedented Al–Sc bond from an Al anion having a new skeleton. The former underwent intramolecular C–H cleavage and the latter reacted with alkyl bromide to

form dialuminated cyclohexadiene. Detailed DFT calculations revealed that the reaction proceeds through a two-step process: (1) Lewis-base-assisted nucleophilic substitution of alkyl bromide with Al anion moiety (2) subsequent nucleophilic attack of Al anion moiety to benzene to form Sc-stabilized Meisenheimer complex which can undergo nucleophilic substitution of bromoalumane generated in the step (1).
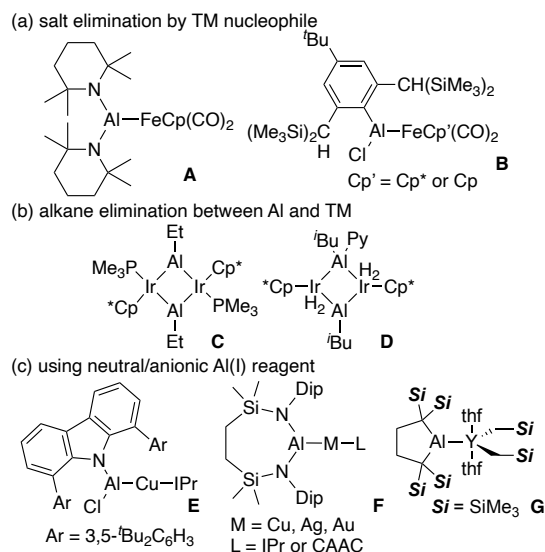

Figure 1. Transition metal complexes having three-coordinate X-type Al ligand(s) prepared by (a) salt elimination, (b) alkane elimination, and (c) reaction of neutral/anionic Al(I) reagent.

The synthesis of aluminum anion **3** on a gram scale is illustrated in Scheme 1. Treatment of bis(amide) **1** with one equivalent of AlI₃

gave an iodide-bridged dimer **2** in 68% yield. Reduction of **2** with Na/K alloy (1:2, 8 equiv. as K) in toluene afforded potassium salt of Al anion **3** as yellow crystalline solids in 58% yield. It should be noted that the synthesis of **3** could be conducted on gram scale. The ^{1}H and ^{13}C NMR spectra of **3** indicated its D_{2h} symmetrical structure in solution. A single-crystal X-ray diffraction analysis showed that **3** possesses a dimeric structure (Figure 2), which is similar to those of previously reported Al anions.[6d-g] Addition of [2.2.2]cryptand to a solution of **3** afforded the corresponding separated ion pair **4**,[6h, 6j, 10] which similarly exhibited a D_{2h} symmetrical pattern in its ^{1}H and ^{13}C NMR spectra. Crystal structure of **4** showed a well-separated interatomic distance of 7.656(2) Å between Al1 and K1 atoms (Figure 2). It should be noted that the Al–N distances in the separated ion pair **4** [1.849(4) and 1.880(4) Å] are essentially identical to those of the dimeric contact ion pair **3**, indicating the separation of ion pair did not alter the electronic structure of diamino-substituted Al anion.

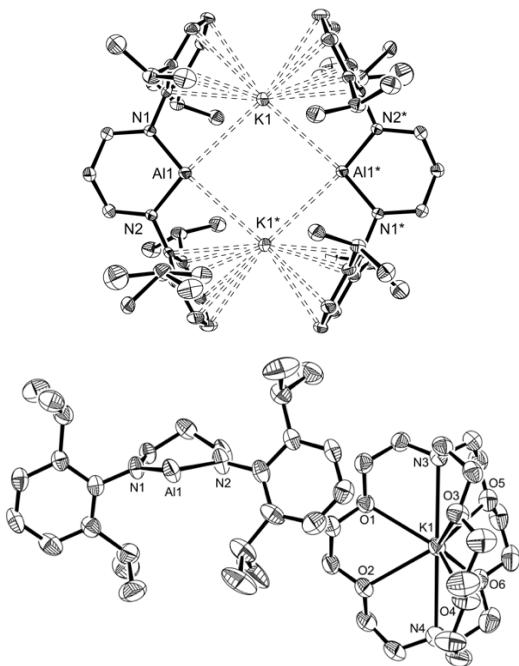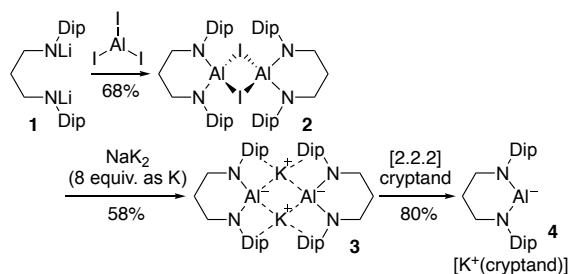**Scheme 1. Synthesis of aluminum anions 3 and 4.**

Figure 2. Molecular structures of **3** (top) and **4** (bottom). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms and one of two independent molecules (for **3**) are omitted for clarity.

The reaction of **3** with N(SiMe$_3$)$_2$- and N^{i}Pr$_2$-ligated scandium chloride at –35 °C furnished the corresponding Al–Sc complexes **5** and **6** as pale-yellow and colorless crystalline solids, respectively (Scheme 2). It should be noted that the reaction of **3** with the cationic complex [Sc(CH$_2$SiMe$_3$)$_2$(THF)$_3$]$^+$[BPh$_4$]$^-$ resulted in the formation of a complicated mixture. The ^{1}H NMR spectra of **5** and **6** exhibited magnetically equivalent four SiMe$_3$ and ^{i}Pr groups on N atoms, indicating rapid rotation about the Al–Sc and Sc–N bonds in

solution. Single-crystal X-ray diffraction analysis revealed a three-coordinate Al atom bearing the first Al–Sc bond [**5**: Al–Sc 3.0395(5) Å, **6**: 3.018(1), 2.976(1) Å], which are longer than the sum of their covalent radii (2.74 Å) (Figure 3).[11] Such a long Al–M bond was also observed in the previously reported Al–Y complex,[8a] suggesting the ionic character of the Al–Sc bond. This flexible nature of ionic Al–Sc bond also deviates the planarity of the three-coordinate Al center [**5**: $\Sigma\angle$Al 358.55°, **6**: $\Sigma\angle$Al 359.79°, 359.8°]. The Al–N bond lengths in **5** and **6** [**5**: Al–N 1.841(2), 1.834(1) Å, **6**: 1.832(3), 1.835(3), 1.831(3), 1.831(3) Å] are slightly shorter than those of **3** and **4**, indicating that the electronic character of the Al center in **5** and **6** would be similar to those of Al(I) center in **3** and **4**. Last but not least, it should be emphasized that the Sc1–N4–Si4 angle of 107.76(8)° is smaller than 120°, an ideal angle of the trigonal nitrogen atom, suggesting that the proximal Si4–CH$_3$ bond would donate electrons to stabilize a highly Lewis acidic scandium center.

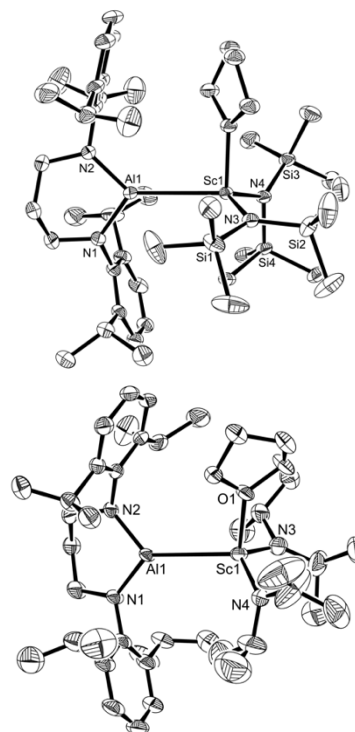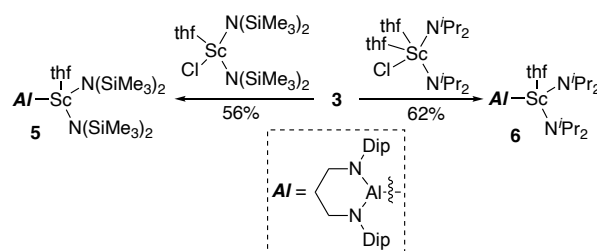**Scheme 2. Synthesis of Al–Sc complexes 5 and 6.**

Figure 3. Molecular structures of **5** (top) and **6** (bottom). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms, one of two independent molecules (for **6**), and co-crystallized solvent molecules are omitted for clarity.

To understand the electronic character of **5** and **6**, DFT calculations were conducted at B3LYP/LANL2DZ (for Sc)/6-31+G(d) (for others) level of theory. It should be noted that the optimized structures of **5** and **6** involve a completely planar Al atom, indicating the slight pyramidalization of the Al atoms in the solid state would

be caused by a crystal packing effect and the flexible nature of the ionic Al–Sc bond. LUMO/LUMO+1 of **5** and LUMO/LUMO+2 of **6** correspond to "bonding" vacant orbitals, consisting of vacant 3p orbitals of the Al atom and vacant 3d orbital of the Sc atom. This overlapping of two vacant atomic orbitals significantly lowers the energy level of this molecular orbital as we previously reported for diborane(4),[12] alumaborane,[13] B–Au complex,[14] and Al–Y complex.[8a] It should be emphasized that the lone pairs on the nitrogen atoms of the diamino ligand on the Al atom mainly contributed to HOMO. While HOMO−1 corresponds to Al–Sc bonding molecular orbital (MO) in both cases. This is in contrast to the previously reported alkyl-substituted Al–Y complex that possesses the Al–Y bonding MO as HOMO due to the lack of electronegative N atoms. The Si–N bonds are close to donate electron density to the Sc atom in **5**, as supported by NBO calculations with the second order perturbation energy (SOPE) of ca. 18 kcal/mol.
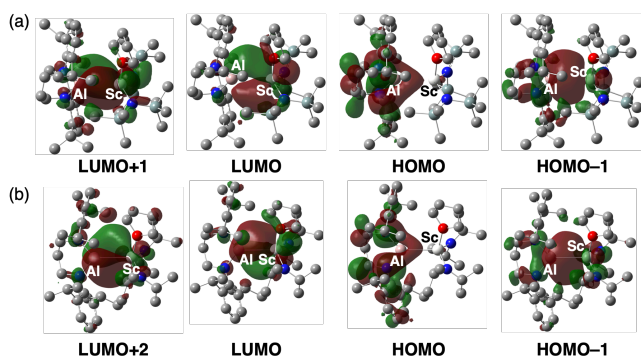

Figure 4. Characteristic molecular orbitals of (a) **5** and (b) **6** calculated at B3LYP/LANL2DZ (for Sc)/6-31+G(d) (for others) level of theory.

Although compound **5** is stable in a solid state at –35 °C, leaving benzene solution of **5** led to a gradual decomposition with a color change from pale-yellow to colorless (Scheme 3). Monitoring by ^{1}H NMR confirmed a complete consumption of **5** and a generation of a new compound within 12 h at room temperature. The ^{1}H NMR spectrum of the resulting compound exhibited many signals, indicating the broken symmetry of the compound. X-ray diffraction analysis revealed a CH$_2$- and H-bridged dinuclear structure of **7** (Figure 5). The 3c-2e bonding character of the bridging CH$_2$ and hydride was supported by NBO analysis (SOPE: Al–H to Sc: 35.18, CH$_2$ to Al: 37.01, CH$_2$ to Sc: 15.62 kcal/mol). Although the Al–Sc interatomic distances of 3.039(1) and 3.054(1) Å in **7** are similar to those of Al–Sc complexes **5** and **6**, the Al center in **7** should be considered to adopt a tetracoordinate aluminate structure without bonding interaction between Al and Sc atoms as confirmed by AIM analysis (see SI). Reflecting the restricted motion of SiMe$_2$ moiety due to the existence of the bridging CH$_2$ group, ^{1}H NMR spectrum of **7** displayed a pair of doublet signals for diastereotopic CH$_2$ and two distinct SiMe groups in high filed, although no signal for bridging hydride was detected probably due to direct coupling with quadrupolar [27]Al nucleus. The proximity between Si4–CH$_3$ bond and the Sc center (*vide supra*) would contribute to this C–H cleaving reactivity of the Al–Sc bond. The difference in electronegativity between aluminum and scandium (Pauling, Al: 1.61, Sc: 1.36) implies a Al$^{\delta-}$–Sc$^{\delta+}$ polarization on the Al–Sc bond and the resulting Al(I) character would induce the oxidative addition of one of C–H bonds on TMS group. Thus, the reactivity of Al–early transition metal bond toward

C–H bond would be distinguished from those of Al–late transition metal bond.

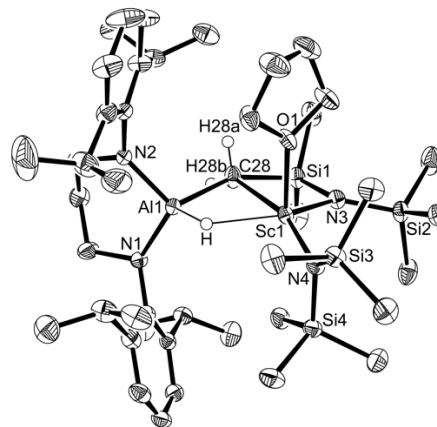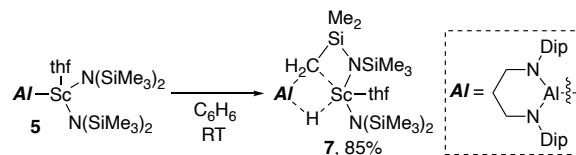**Scheme 3. Thermal decomposition of Al–Sc complex 5.**

Figure 5. Molecular structure of **7**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms omitted.

Treatment of **6** with one equivalent of Ph$_2$CHBr in benzene rapidly induced a color change from colorless to brown [Scheme 4(a)]. The ^{1}H NMR spectrum of the crude reaction mixture and X-ray crystallographic analysis revealed the formation of dialuminated cyclohexadiene **8** and a concomitant formation of Ph$_2$CH–CHPh$_2$ (**9**).[15] Distinguished C–C and C=C bonds in the central cyclohexadiene ring in **8** demonstrated the dearomatization of the benzene ring during the reaction. Similar 1,4-dialuminated cyclohexadiene structures were reported by reaction of benzene with a transient Al=Al bonded compound,[16] or by reduction of NHC-coordinated (ferrocenyl)Al diiodide.[17] The ^{1}H NMR spectrum of **8** in THF-d_8 exhibits the magnetic inequivalence of geminal protons of three CH$_2$ groups, indicating that Al–O and Al–C bonds are not cleaved in solution. The reaction of **6** with other alkyl bromides, such as PhCH$_2$Br, (*p*-tol)$_2$CHBr, bromocyclohexane, 1-bromoadamantane, and ^{n}BuBr, also produced **8** as judged by NMR spectroscopy (37-52%, see SI). Since we considered the formation of **8** and **9** could be explained with radical mechanism, involving the formation of Al-centered radical and [Ph$_2$CH]· radical intermediates, some control experiments were conducted [Scheme 4(b)(c)]. Treatment of Al-anion **3** with Ar$_2$CHBr (Ar = Ph, *p*-tol) did not give any **8**, but afforded alkyl-alkyl coupled products **9** and **10**[18] were detected by the ^{1}H NMR spectrum. Heating a solution of **6** in C$_6$H$_6$ led to the decomposition of **6** without the formation of **8**. Replacement of solvent to toluene-d_8 for the reaction of **6** with Ph$_2$CHBr furnished THF-coordinated bromoalumane **11-thf**, which was separately synthesized and isolated, and **9**. Additionally, the reaction of **6** with **11-thf** did not afford dialuminated cyclohexadiene **8**. These results indicated the following things: (1) The Al–Sc bond is required to form **8**; (2) The coexistence of benzene and alkyl bromide is required to form **8**; (3) The introduction of methyl group to benzene substrate shuts off the dialumination; (4) Formation of **9** is independent of the formation of **8**; (5) Al–Br **11** is NOT the intermediate for the formation of **8**.

Scheme 4. The reaction of 6 with alkyl bromide and control experiments for mechanistic study.
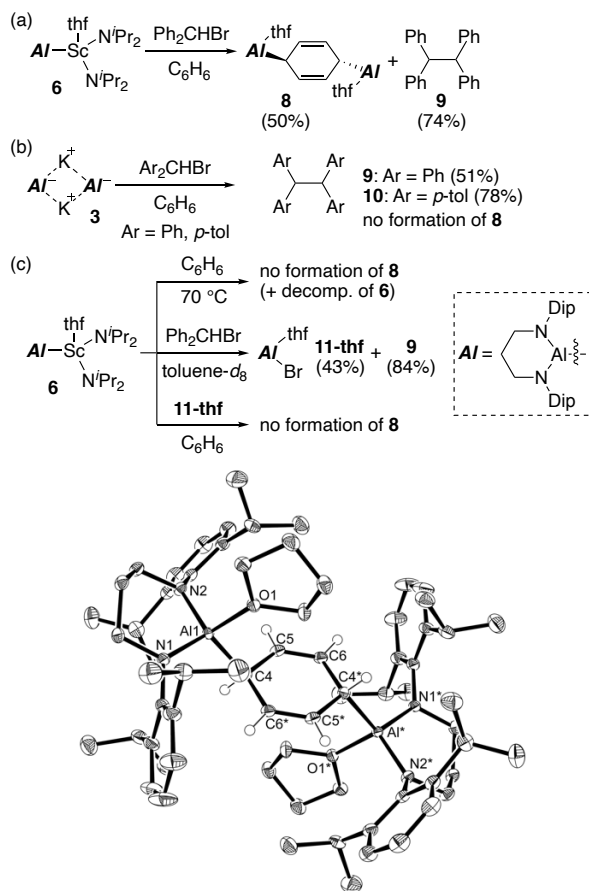
Figure 6. Molecular structure of **8**. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms omitted.

To shed light on the reaction mechanism for the formation of **8** from the reaction of **6** with Ph₂CHBr, DFT calculations were performed with a model complex **6'** possessing simplified substituents at the ωB97XD/def2tzvp (for Sc and Al)/6-31G(d) (for others) level of theory. A schematic illustration of the revealed mechanism is summarized in Scheme 5. Coordination of the bromine atom in Ph₂CHBr to the Sc atom in **6'** furnishes the intermediate **12'**, where the bromide strongly coordinates to the Sc atom as judged by NBO analysis (SOPE: 193 kcal/mol). Coordination of the N atom to the Al atom, nucleophilic attack of the Al atom in **13'** using Al–Sc bonding electrons, and cleavage of C–Br bond in **12'** proceed to form Al-alkyl intermediate **13'**, having a new Al–C bond. Coordination of the second equivalent of Ph₂CHBr to the Al atom releases a neutral BrSc(NMe₂)₂(thf) (**14'**) to give **15'**. The CHPh₂ group in **15'** dissociates to form an ion pair **16'**, which subsequently undergoes the formation of a C–C bond to produce **9** and aluminum bromide **11'**. During the conversion from **6'** to **11'**, the highest activation energy of 23.3 kcal/mol was recorded at **TS₁₆'-₁₁'** (vs **13'**), which is consistent with the room-temperature reaction (see SI for detailed energy profile). On the other hand, **6'** can also react with benzene to form benzene-coordinated Sc complex **17'** with a concomitant 1,2-shift of THF from Sc to Al atom. The "Al anion" moiety in **17'** attacks a carbon atom in the Sc-coordinated benzene to afford an Al-substituted (η^5-pentadienyl)scandium intermediate **18'** via Al–C bond formation, which is in contrast to the hydride-eliminating S_NAr-type reactivity of the previously reported potassium salt of Al anion.[19]

Thus, **18'** can be considered as Sc-stabilized Meisenheimer intermediate, also suggested by NBO analysis (SOPE: 15.49-28.97 kcal/mol). Upon interaction between **18'** and aluminum bromide **11'**, which was generated in the earlier part of the reaction, results in the formation of **19'**. The resulting loosely bound cationic Sc atom to pentadienyl ligand in **19'** captures bromide to form dialuminated cyclohexadiene **20'**. Subsequent dissociation of BrSc(NMe₂)₂ and THF ligand transfer from **13'** gives the final products **8'**. In this process for conversion from **6'** to **8'**, the highest activation energy of 16.3 kcal/mol was recorded at **TS₂₀'-₂₁'**, which was lower than that for the conversion of **6'** to **11'**, suggesting the formation of **9** is the rate-determining step. Thus, this analysis provides new insight into the reactivity of Al-early metal heterobimetallic compounds.

Scheme 5. The proposed ionic mechanism for the formation of 8 based on DFT calculations.
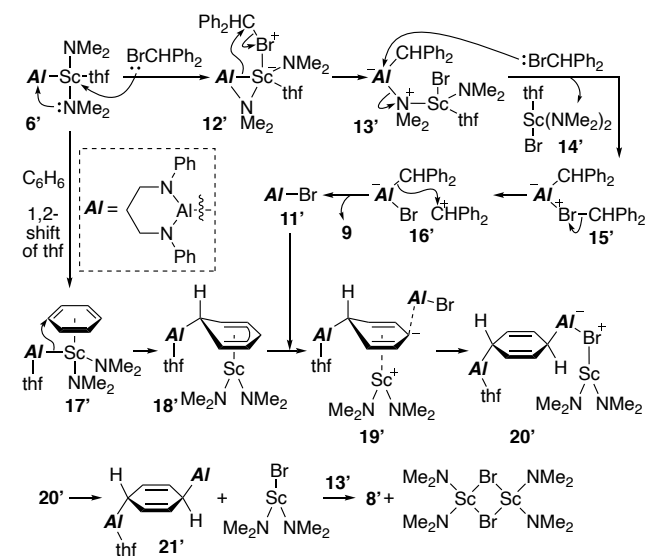
In conclusion, we synthesized two Al–Sc complexes by means of the newly prepared Al-anion possessing a 1,3-propanediamine ligand. The Al–Sc[N(Me₃Si)₂]₂ complex underwent intramolecular C–H bond cleavage and the Al–Sc(NⁱPr₂)₂ complex reacted with benzene in the presence of alkyl halide to give dialuminated cyclohexadiene. The latter reaction was analyzed by DFT calculations to provide information about the two-step process involving activation of alkyl bromide and benzene, respectively, to indicate the cooperative role of Al and Sc atoms.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Experimental and computational details (PDF)
Crystallographic data for **2-8, 11-thf** (CIF)
DFT coordinates (XYZ)

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Notes

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TS for Sc-induced
substitution

Sc-stabilized
Meisenheimer
intermediate