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Cycloaddition of Dialkylaluminum Anion toward Unsaturated Hydrocarbons in (1+2) and (1+4) Modes

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Abstract: The reactivity of dialkylaluminum anion (**1**) toward naphthalene, anthracene, diphenylacetylene, and (*E*)/(*Z*)-stilbenes is investigated. The compound **1** reacts with naphthalene and anthracene through (1+4) cyclization, affording Al-containing norbornadiene derivatives. In the reaction of **1** with diphenylacetylene and (*E*)/(*Z*)-stilbenes, (1+2) cyclization proceeded to form Al–C–C three-membered rings. Cyclization toward (*E*)- or (*Z*)-stilbenes solely gave a *trans*-cycloadduct. DFT calculations revealed that the cycloaddition of **1** with (*Z*)-stilbene proceeds via a single transition state with a carbanion character, which results in the selectivity toward the *trans*-cycloadduct.

Main group element compounds, especially in low oxidation state, have been known to undergo oxidative addition at the main group element center to give oxidized compounds.^[1] Among them, aluminum-containing molecules in the low oxidation state have been extensively studied in the last three decades,^[2] especially for dialumane derivatives having an Al–Al bond,^[3] oligomeric form of Al(I) species,^[4] and Al=Al doubly bonded compounds.^[3o-s, 5] While the parent monomeric halogenated Al(I) species "AlX" (X = Cl, Br) are unstable and only can be handled in matrices,^[6] isolation of monomeric and nucleophilic Al(I) species are still limited to a handful of examples (Figure 1), including CpAl(I) species **A**,^[7] nacnac-substituted species **B**,^[8] Al(I) hydride **C** stabilized by two CAAC ligands,^[9] diamino-Al anion **D**,^[10] and oxygen-stabilized diamino-Al anions **E**^[11] and **F**.^[12] We recently reported an alkyl-substituted alumanyl anion **1**,^[13] featuring strong basicity to deprotonate benzene at room temperature as an anionic aluminum nucleophile.

Some of these Al(I) compounds in Chart 1 reacted with unsaturated hydrocarbons to give the corresponding cycloadducts (Scheme 1). The nacnac-stabilized Al(I) species **B** underwent (1+2) cycloaddition with alkynes and alkenes to form Al-containing three-membered ring species **G**.^[14] The diamino-Al anion **D** cyclized with cyclooctatetraene to give **H** via (1+2) cycloaddition.^[10a] Similarly, the monomeric form of oxygen-stabilized Al anion **F** reacted with ethylene to form (1+2) cycloadduct **I**. On the other hand, **B** also reacted with a benzene complex of [nacnac-Ca]⁺ to furnish an alumanorbornadiene product **J**.^[15] The anionic bicyclic compound **H** rearranged to the (1+4) product **K** upon addition of 18-crown-6.^[10a] Thus, compounds **B** and **F** are examples of Al(I) compound which exhibit reactivity for two different modes of cycloaddition reaction. It should also be noted that there is no stereochemical information in these Al-containing cycloaddition reactions. Herein, we report dialkyl-substituted Al anion **1** undergoes oxidative cycloaddition in both (1+4) and (1+2) modes to give the corresponding Al-containing norbornadiene, cyclopropene, and cyclopropane compounds. From the structure of the products and DFT

calculations, a possible reaction mechanism for the cycloaddition reaction was proposed.

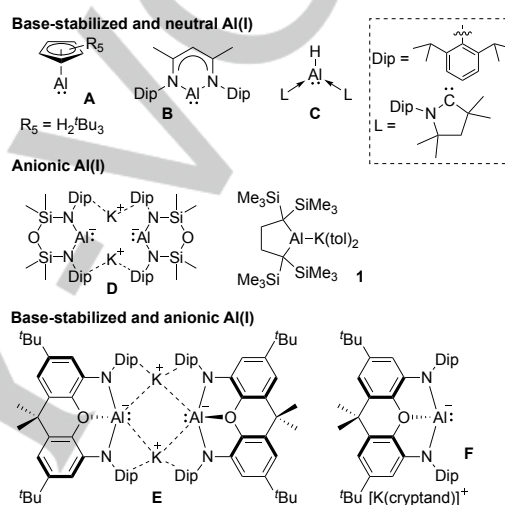
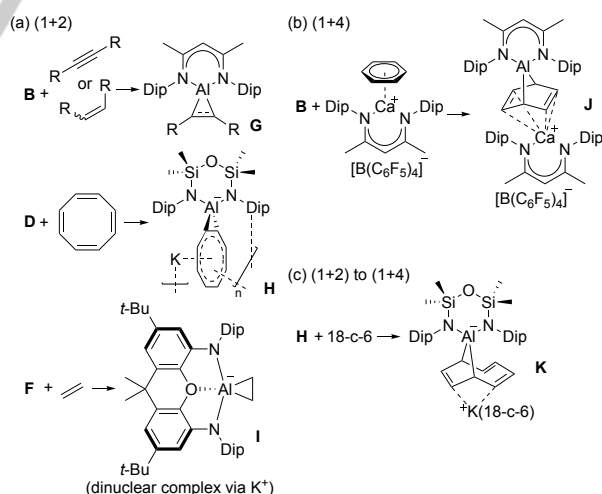


Figure 1. Isolated examples of monomeric Al(I) compounds.

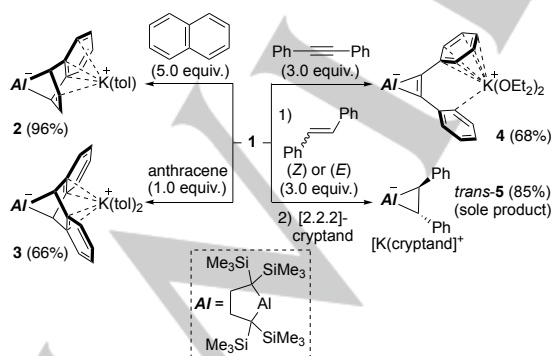


Scheme 1. Reactions of isolated monomeric Al(I) compounds with unsaturated hydrocarbons.

Reaction of **1** with unsaturated hydrocarbons furnished the corresponding (1+4) or (1+2) cycloaddition products (Scheme 2). The reaction of **1** with naphthalene at room temperature gave an aluminum-containing benzonorbornadiene derivative **2** as

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colorless crystals in 96% isolated yield, through (1+4) cyclization reaction. This is in contrast to that **F** reacted with naphthalene at 80 °C to form an isomeric mixture of (naphthyl)(hydrido)aluminane,^[12] and the isoelectronic dialkylsilylene (:Si[C(SiMe₃)₂CH₂]₂, **6**) bearing the same “helmet” substituents reacted with naphthalene to furnish mono- or bis-(1+2) adducts under the irradiation of visible light.^[16] Similarly, **1** was treated with anthracene to afford (1+4) cyclization product **3** as a colorless solid in 66% yield. The bicyclic structures of **2** and **3** was unambiguously confirmed by a single crystal X-ray diffraction analysis (Figure 2a,b). The ¹H NMR spectrum of **2** in THF-*d*₈ exhibited a C_s symmetrical pattern which is matched with the anionic part of the crystal structure of **2** with a characteristic multiplet signal of two bridgehead protons at δ 2.89 ppm which is correlated with a signal of alkenyl protons at δ 5.99 ppm. In the case of **3**, the ¹H NMR exhibited one singlet signal of magnetically equivalent four TMS groups and one signal of the bridgehead protons at δ 3.34 ppm, indicating the C_{2v}-symmetrical aluminadibenzonornbornadiene structure. The reaction of **1** with diphenylacetylene furnished a (1+2) cyclized product, aluminacyclopropene **4**, which was recrystallized from Et₂O. X-ray crystallographic analysis revealed a three-membered ring structure of **4** (Figure 2c). The resulting **4** exhibited carbanionic character, as confirmed by a hydrolysis to give (*Z*)-stilbene (see SI). The ¹H NMR spectrum of **4** suggested a C_{2v}-symmetrical structure of **4**, similar to the case of **3**. Cyclization of **1** also took place with (*Z*- or (*E*)-stilbenes to give the same single product (Fig S9), *trans*-diphenylaluminacyclopropane (*trans*-**5**), which was crystallized after complexation with [2.2.2]-cryptand. X-ray diffraction study unambiguously confirmed the *trans* stereochemistry of two phenyl substituents in *trans*-**5** (Figure 2d). Note that corresponding *cis* product was not observed by NMR measurements, indicating that the (1+2) cyclization of **1** with stilbenes took place in a stepwise manner to give a thermodynamically stable *trans* isomer (*vide infra*). It should be noted that the reaction of **1** with (*E*)-stilbene under the dark also proceeded to afford *trans*-**5**. In contrast, compound **1** did not react with cyclohexene, probably due to electron richness on the C=C double bond (*vide infra*). It has been reported that **6**^[17] did not react with (*Z*- and (*E*)-2-butenes at <10 °C under the dark but reacted with them at a slightly higher temperature or upon irradiation of visible light (>420 nm) to afford the corresponding stereoretained silacyclopropane derivatives.^{[18],[19]}



Scheme 2. Reaction of **1** with unsaturated hydrocarbons.

The single crystal X-ray diffraction analysis revealed characteristic structural parameters of **2**, **3**, **4**, and *trans*-**5** in comparison with those of reference compounds (Table 1). Compounds **2** and **3** are the first examples of anionic aluminanornbornadiene derivatives. Two newly formed Al–C(bridgehead) bonds of **2** and **3** [2: 2.1118(15), 2.1087(15) Å; 3: 2.1125(12), 2.1154(15) Å] are longer than those of the previously reported Al-incorporated bicyclic compounds (**L**,^[20] **J**,^[15] **K**^[10a]), reflecting the steric repulsion between four trimethylsilyl substituents and benzoannulated moiety in **2** and **3**. As a result, the C–Al–C angles in **2** and **3** [2: 75.10(6)°; 3: 75.21(6)°] are slightly smaller than those of reference compounds. Similar tendencies were found in the Al–C bonds and C–Al–C angles of **4** and *trans*-**5** in comparison with those of reference compounds (**G1-G6**,^[14] **H**^[10a]). One exception from these structural tendencies could be found in the structure of reference compound **M** probably due to the steric hindrance among bulky CH(SiMe₃)₂ substituents.^[21]

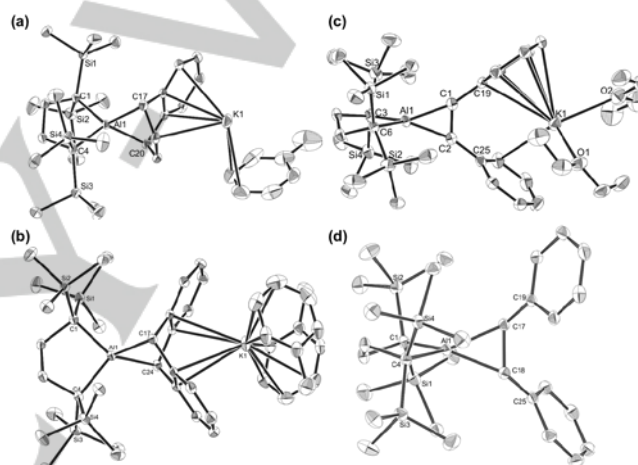


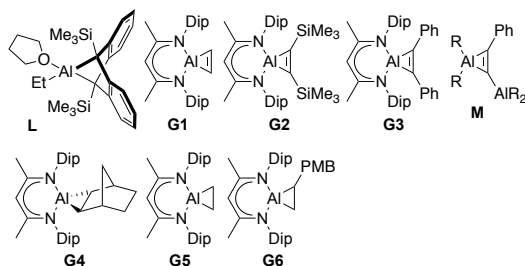
Figure 2. ORTEP drawings of (a) **2**, (b) **3**, (c) **4**, and (d) *trans*-**5** with 50% probability (hydrogen atoms, co-crystallized solvent molecules, and intermolecular interactions were omitted for clarity).

Table 1. Structural parameters (Å, °) of **2**, **3**, **4**, and *trans*-**5** with those of reference compounds.

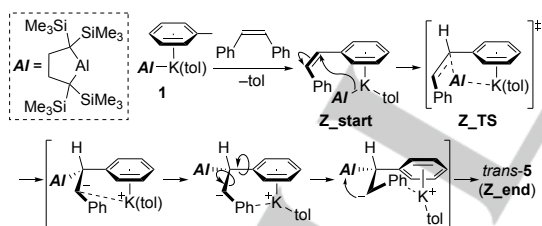
cpd	2	3	L	J	K
Al–C	2.1118(15) 2.1087(15)	2.1125(12) 2.1154(15)	2.059(4) 2.055(4)	2.060(3) 2.073(3)	2.025(3) 2.044(3)
C–Al–C	75.10(6)	75.21(6)	81.5(1)	77.2(1)	88.1(1)
cpd	4	G1	G2	G3	M
Al–C	1.945(3) 1.940(3)	1.885(2) 1.878(2)	1.899(3) 1.908(3)	1.889(3) 1.894(3) 1.887(3) 1.886(3)	2.052(3) 1.951(3)
C–Al–C	41.10(14)	42.30(7)	42.57(11)	42.02(14) 42.56(14)	37.6(1)
cpd	<i>trans</i> - 5	G4	G5	G6	H
Al–C	2.0178(18) 1.9953(19)	1.940(4) 1.948(3)	1.9209(18) 1.9163(19)	1.920(3) 1.924(3)	2.061(3) 2.071(3)

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C–Al–C 45.43(14) 49.35(17) 48.54(8) 48.78(12) 42.0(1)

Dip = 2,6-ⁱPr₂C₆H₃, R = CH(SiMe₃)₂, PMB = CH₂C₆H₄-4-OMe

To gain insights on the electronic character of transition structures for of the present cycloadditions, we performed DFT computations for the reactions of naphthalene, diphenylacetylene, and (*E*)-, and (*Z*)-stilbenes (See SI for details). Initial structures of these reactions were generated by replacing one of two toluene molecules in **1** with the reactant. In the reaction of naphthalene, a transition state was found to give a (1+2) cycloadduct, followed by a ring-expanding isomerization to (1+4) cycloadduct with a smaller energy barrier (Figures S12 and S13). This ring expansion seems to be similar to that in Scheme 1(c). Reactions of diphenylacetylene and (*E*)-stilbene take place in a concerted fashion to form the three-membered ring directly (Figures S14 and S15). In the reaction of (*Z*)-stilbene, a similar transition structure **Z_TS** was found to connect **Z_start** and **Z_end** (*trans*-5) (Scheme 3). The carbanionic nature of **Z_TS**, supported by Natural Population Analysis (Table S2), induced subsequent interaction between carbanion center and potassium, potassium shift from carbanion to phenyl group, rotation of two C–C bonds, and nucleophilic attack of carbanion center to the Al atom. Thus, the carbanionic character resulted from the nucleophilic attack of Al atom accounts for the *trans* selectivity in the formation of *trans*-5. Also, the reluctance of **1** toward cycloaddition with cyclohexene could be explained by the instability of carbanion species.



Scheme 1. Schematic mechanism based on DFT calculations for the formation of *trans*-5 from (*Z*)-stilbene.

In conclusion, we described reactivity of dialkylaluminum anion **1** toward unsaturated hydrocarbons such as naphthalene, anthracene, diphenylacetylene, and (*E*)-/(*Z*)-stilbenes. The former two reactions proceeded in (1+4) fashion to give Al-containing norbornadiene derivatives. The latter two reactions took place in (1+2) mode to give three-membered ring. Reaction of (*E*)-/(*Z*)-stilbenes solely furnished *trans*-product. DFT calculations suggested a carbanionic character of transition states explaining the selectivity toward *trans*-isomer.

Acknowledgements

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Keywords: aluminium • cycloaddition • low oxidation state • DFT calculations • aluminyl anion

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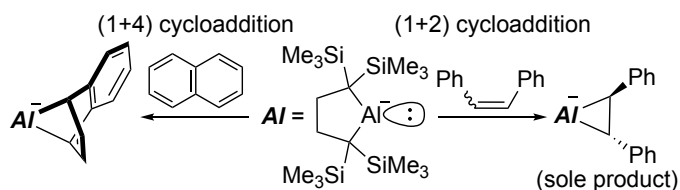
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The reactivity of dialkylaluminum anion (1) toward unsaturated hydrocarbons is investigated. Reaction with naphthalene and anthracene took place through (1+4) cyclization, while the reaction with diphenylacetylene and (*E*)/(*Z*)-stilbenes gave (1+2) cycloadducts. Cyclization toward (*E*)- or (*Z*)-stilbenes solely gave a *trans*-cycloadduct. DFT calculations revealed the selectivity toward the *trans*-cycloadduct.

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