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Reactions of an Aluminum(I) Reagent with 1,2-, 1,3-, and 1,5-Dienes: Dearomatization, Reversibility, and a Pericyclic Mechanism

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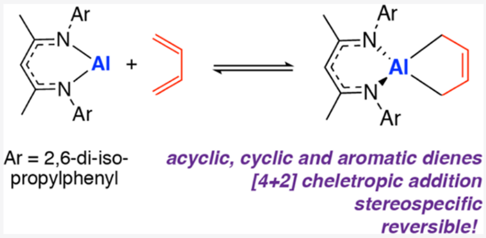

ABSTRACT: Addition of the aluminum(I) reagent [{(ArNCMe)$_2$CH}Al] (Ar = 2,6-di-iso-propylphenyl) to a series of cyclic and acyclic 1,2-, 1,3-, and 1,5-dienes is reported. In the case of 1,3-dienes, the reaction occurs by a pericyclic reaction mechanism, specifically a cheletropic cycloaddition, to form aluminocyclopentene-containing products. This mechanism has been examined by stereochemical experiments and DFT calculations. The stereochemical experiments show that the (4 + 1) cycloaddition follows a suprafacial topology, while calculations support a concerted albeit asynchronous pathway in which the transition state demonstrates aromatic character. Remarkably, the substrate scope of the (4 + 1) cycloaddition includes styene, 1,1-diphenylethylene, and anthracene. In these cases, the diene motif is either in part, or entirely, contained within an aromatic ring and reactions occur with dearomatisation of the substrate and can be reversible. In the case of 1,2-cyclononadiene or 1,5-cyclooctadiene, complementary reactivity is observed; the orthogonal nature of the C═C π-bonds (1,2-diene) and the homoconjugated system (1,5-diene) both disfavor a (4 + 1) cycloaddition. Rather, reaction pathways are determined by an initial (2 + 1) cycloaddition to form an aluminocyclopropane intermediate which can in turn undergo insertion of a further C═C π-bond, leading to complex organometallic products that incorporate fused hydrocarbon rings.

■ INTRODUCTION

In the past few years there has been fierce interest in reactivity studies of aluminum(I) compounds.[1−5] Aluminum is the most abundant metal in the Earth's crust. It is widely available, and its compounds typically display low toxicity. As such, it is an attractive target for the development of sustainable methods in synthesis and catalysis. The chemistry of aluminum compounds is still dominated by those in the +3-oxidation state. There is, however, a growing realization that both neutral and anionic aluminum compounds in the +1-oxidation state show some remarkable reactivity.[6−9] In some cases, the scope extends beyond the capabilities of even the most reactive transition-metal complexes.

In this contribution, we focus on reactions of aluminum(I) compounds with unsaturated and aromatic hydrocarbons. Contemporary work in this area has been foreshadowed by vapor deposition studies involving the co-condensation of aluminum atoms with ethylene, propene, or 1,3-butadiene at low temperature.[10−12] The deuterolysis products of these reactions support the formation of direct Al−C σ-bonds, while EPR spectroscopy of the organometallic products led the authors to speculate that these reactions may involve the formation of paramagnetic aluminocyclopropanes[10] and aluminocyclopentenes,[12] with the latter compound being derived from a cheletropic reaction of Al atoms with 1,3-butadiene.[12] Schnöckel's synthesis of AlCl allowed the first direct translation of this reactivity to aluminum(I) compounds. Addition of AlCl to but-2-yne forms a complex cluster,[13] while the reaction of AlCl and 2,3-dimethylbutadiene at low temperature leads to the formation of a stable cyclic oligomer. Both reactions provide unambiguous structural evidence for Al−C σ-bond formation.[14] A related cyclic dimer has been reported from the reaction of a terphenyl-stabilized gallium(I) compound with 2,3-dimethylbutadiene and has been proposed to derive from the dimerization of a metallocyclopentene intermediate.[15]

Based on the synthetic accessibility of a number of new aluminum(I) complexes, there have been some notable advances in this area in recent years. We have reported that **1**, originally reported by Roesky and co-workers,[16] reacts reversibly with alkenes to form aluminocyclopropanes by a (2 + 1) cycloaddition[17,18] and in a single instance nonreversibly with 1,3-cyclohexadiene to form a (4 + 1)[19] cycloaddition product (Figure 1).[20] Related reactions of **1** with alkynes are known to form aluminocyclopropenes.[21,22] Theoretical studies on **1** have led to the suggestion that this compound can undergo a (4 + 1) cycloaddition with benzene to form a high-

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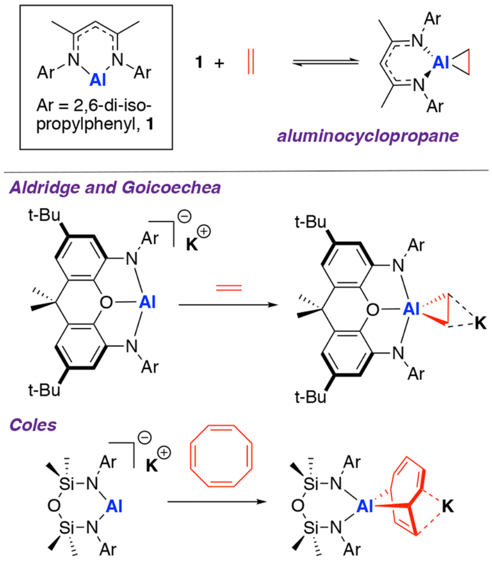


Figure 1. Reaction of selected aluminum(I) compounds with unsaturated hydrocarbons.

energy [2.2.1]aluminobicycloheptadiene moiety.[23] Although this reaction is endergonic, there is experimental support to suggest it is a tangible pathway. Harder and co-workers have shown that **1**, benzene, and a cationic calcium complex react to form a bimetallic product in which the dearomatized benzene unit is trapped between the two main group metals.[24] Coles and co-workers have reported an anionic aluminum(I) complex that reacts with 1,3,5,7-cyclooctatetrene (COT) to yield a reduced planar COT^{2-} complex which can isomerize to the nonplanar (4 + 1) cycloaddition product upon sequestration of the countercation.[25]

Reactions of aluminum(I) compounds with conjugated and aromatic hydrocarbons are not limited to just those involving the π-system. In the presence of either a palladium or calcium catalyst, **1** affects the C−H activation of benzene, toluene, and xylenes.[26−28] In the absence of catalyst **1** is also capable of allylic C−H activation.[17] Anionic aluminum(I) compounds have also been reported to affect the C−H activation of benzene in the absence of a catalyst.[29,30] Remarkably, for one of these systems sequestration of the potassium countercation generates an aluminum reagent capable of reversibly inserting into a C−C σ-bond of benzene, affecting its dearomatisation.[31]

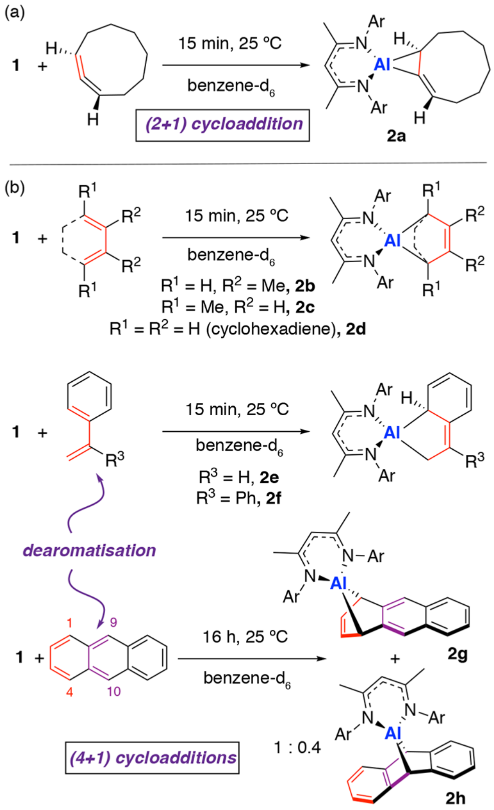
This emerging reactivity of low-valent group 13 compounds parallels that of group 14 reactive intermediates, which have been the subject of some detailed mechanistic analysis. For example, photochemically or thermally generated silylenes (R_2Si) react with 1,3-dienes to give either 2-vinylsiliranes or silacyclopentenes depending on the conditions of the experiment. There was originally some contention as to whether 2-vinylsiliranes are intermediates in the formation of silacyclopentenes. The weight of evidence now suggests that under thermal conditions the (2 + 1) addition of R_2Si to 1,3-dienes may be reversible, allowing equilibration to the more stable (4 + 1) product over time.[32−36] Expansion of the reactivity to germylenes (R_2Ge) and stannylenes (R_2Sn) generally results in higher selectivity for the (4 + 1) cycloaddition.[37] Stereochemical probe experiments involving stereopure 1,3-diene or bis(allene) substrates are consistent with these reactions being defined as cheletropic additions involving a pericyclic mechanism.[38−40] Calculations based on semiempirical (MNDO)[41] and DFT methods[42] support this concerted mechanism and the notion that the (2 + 1) cycloaddition may be reversible and lead to a kinetic product.

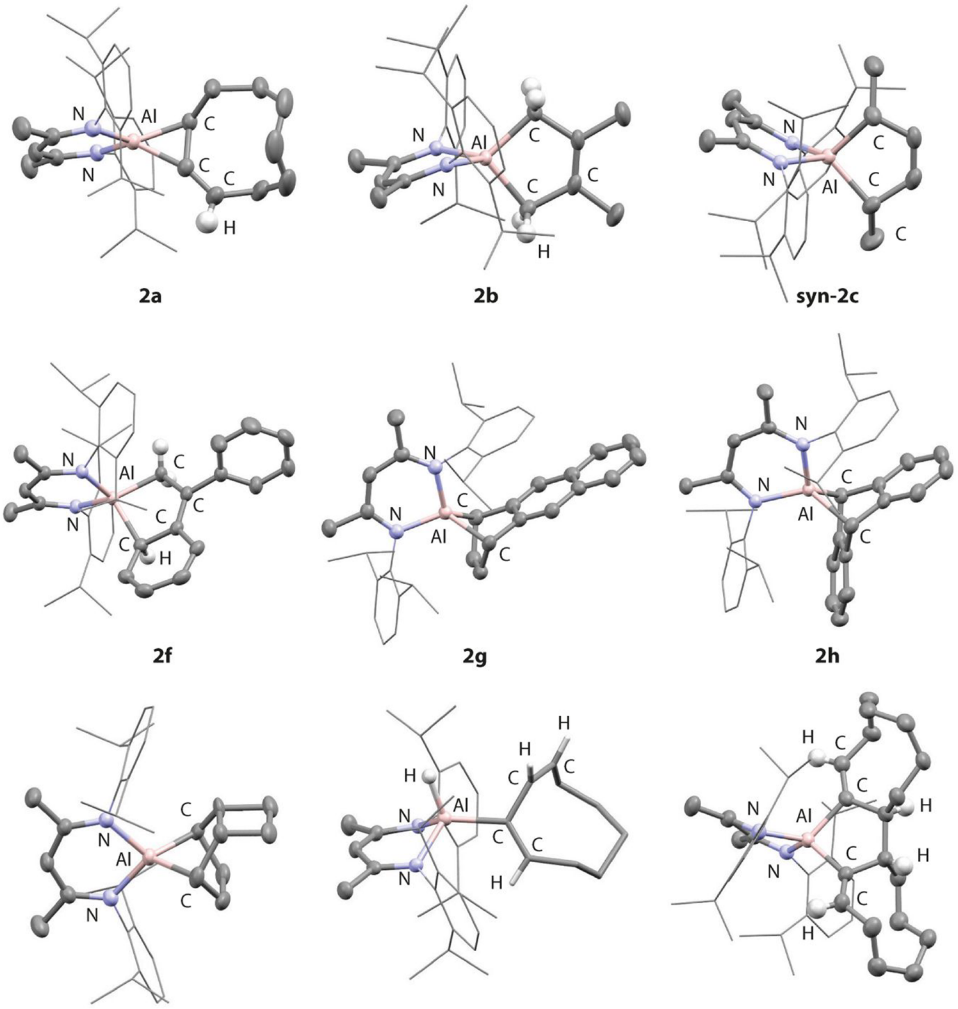
In this paper we expand the reactivity of **1** to 1,2- 1,3-, and 1,5-dienes along with π-extended aromatic systems. Through a combination of DFT studies and stereochemical probe experiments, we show that 1,3-dienes react with **1** by a cheletropic and pericyclic mechanism.

■ RESULTS AND DISCUSSION

1,2-Dienes. The reaction of **1** with 1,2-cyclononadiene in toluene or benzene solution proceeds rapidly to form metallocyclopropane **2a** at 25 °C as evidenced by an instant color change from orange to red on mixing the reagents (Scheme 1a, Figure 2). **2a** is the product of a formal (2 + 1) cycloaddition. It contains an aluminocyclopropane unit bearing an exocyclic alkene moiety as characterized by a diagnostic resonance for the vinylic proton at $\delta = 6.25$ (ddd, $^3J_{HH} = 10.1$, 5.7, $^4J_{HH} = 3.1$ Hz) ppm. Coupling is observed not only in the diastereotopic protons of the adjacent methylene group but also in the methine proton of the aluminocyclopropane itself. The exocyclic alkene group renders the aluminocyclopropane unit asymmetric, and this is clear in the single-crystal X-ray diffraction data. **2a** crystallizes with six independent molecules within the unit cell; the metrics of each are similar, and discussion is limited to a single molecule. The Al−C(sp^3) and Al−C(sp^2) bond lengths take values of 1.952(3) and 1.913(3) Å, respectively. The C(sp^2)−C(sp^3) bond length is 1.564(5) Å, while the C(sp^2)−Al−C(sp^3) angle is very acute at 47.7(1)°.

Scheme 1. Reaction of 1 with (a) 1,2-Cyclononadiene and (b) 1,3-Dienes, Styrene, 1,1-Diphenylethylene, and Anthracene





2a 2b syn-2c

2f 2g 2h

3 4a 4b

Figure 2. Structures from single-crystal X-ray diffraction data for **2a**, **2b**, **2f–h**, **3**, and **4a–b**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) from Single-Crystal X-ray Diffraction Data for 2a–c, 2f–h, 3, and 4a–b

	1[16]	2a[a]	2b	2c[b]	2f	2g[c]	2h	3[d]	4a	4b
Al—N	1.957(2)	1.889(2)	1.9051(14)	1.9089(15)	1.9029(17)	1.9053(18)	1.9108(12)	1.9260(17)	1.9111(18)	1.9381(16)
		1.887(2)	1.9236(15)	1.9344(15)	1.9120(17)	1.9089(18)	1.9134(12)	1.9252(16)	1.9081(17)	1.9212(17)
N–Al–N	89.86(8)	97.1(1)	96.09(6)	95.94(6)	96.96(7)	96.28(8)	97.02(5)	96.15(7)	95.16(8)	95.93(7)
Al–C(sp^3)		1.952(3)	1.9634(19)	1.985(2)	1.981(2)	2.047(2)	2.0495(15)	1.994(6)	–	–
			1.9737(17)	1.990(2)	2.013(2)	2.056(2)	2.0499(15)	2.018(5)		
Al–C(sp^2)		1.913(3)	–		–	–	–	–	1.964(2)	1.980(2)
										1.983(2)
C–Al–C		47.7(1)	94.10(8)	92.28(9)	89.03(9)	78.35(9)	78.15(6)	82.8(2)	–	91.37(8)
C=C		1.309(5)	1.336(3)	1.318(3)	1.357(3)	1.342(3)	–	n.r.	1.326(3)	1.331(3)
									1.323(5)	1.331(3)

[a] Molecule A, 1 of 6 in the asymmetric unit. [b] Cocrystallized 9:1 mixture of ***syn*-2C**/***anti*-2c.** [c] Cocrystallized 96:4 mixture of **2g**/**2h** with positional disorder of the anthracene unit. [d] Disordered across two sites.

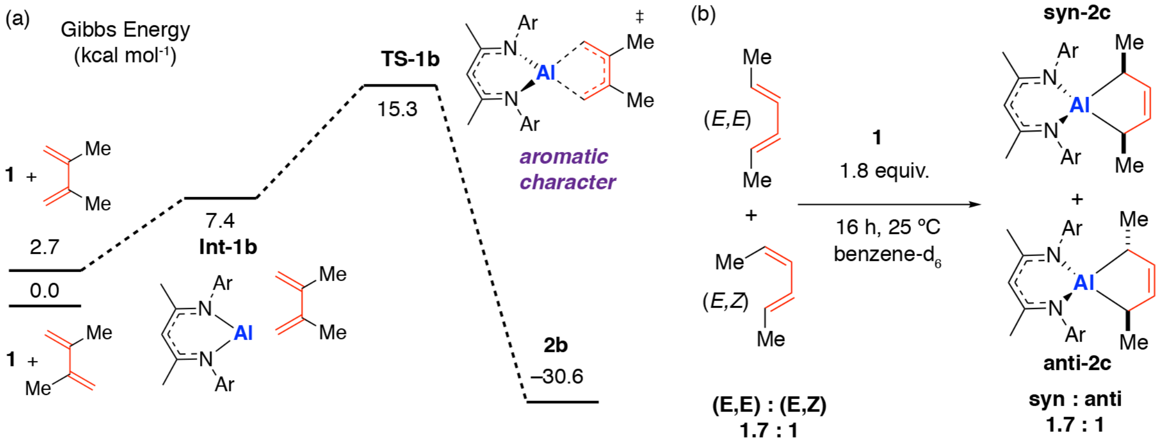


Figure 3. (a) Calculated mechanism for the concerted pericyclic reaction of **1** with 2,3-dimethylbutadiene to form **2b**. (b) Stereochemical probe experiments with a mixture of (*E*,*E*) and (*E*,*Z*)-2,4-hexadiene.

Despite the introduction of the exocyclic alkene moiety, these data fall within the range established for related compounds derived from alkenes.[17] The oxidative addition of **1** to this 1,2-diene parallels established reactivity between **1** and alkenes. The result is unsurprising; the orthogonal p-orbitals in the allene fragment mean it behaves like two isolated C═C *π*-systems.

1,3-Dienes and Dearomatisation. In contrast, **1** reacts with a number of 1,3-dienes by a (4 + 1) cycloaddition pathway. The reaction scope includes 2,3-dimethyl-1,3-butadiene (**2b**), 2,4-hexadiene (1.7:1 mixture of *E*,*E*:*E*,*Z* isomers, **2c**), 1,3-cyclohexadiene (**2d**),[20] styrene (**2e**), 1,1-diphenylethylene (**2f**), and anthracene (**2g**/**2h**). In the latter three cases, either part, or all, of the 1,3-diene fragment is contained within an aromatic ring system and the (4 + 1) cycloaddition occurs with a concurrent dearomatisation. Nevertheless, the scope includes both these aromatic systems in which the 1,3-diene motif is locked into a *s-cis* geometry and simpler open chain 1,3-dienes which are known to favor the *s-trans* conformation in solution (Scheme 1b, Figure 2).

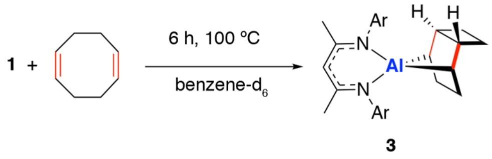
The (4 + 1) cycloaddition generates an aluminocyclopentene in which the aluminum atom forms part of a five-membered ring system. The reaction occurs with migration of C═C unsaturation within the hydrocarbon fragment, consistent with a concerted cheletropic process. In all cases, analysis of the solid-state data are consistent with the assignment of **2a**−**h** as aluminum(III) compounds. The Al−N bond lengths in this series range from 1.887(2) to 1.9236(15) Å and the N−Al−N bite angle varies from 96.09(6) to 97.1(1)° (Table 1). From the perspective of **1**, the reaction is an oxidative addition. Direct parallels can be drawn with the known cheletropic reaction of SO_2 with butadienes.[43]

In the case of **2e**−**2h**, **1** is a high enough energy species to effect the dearomatisation of a benzene ring. For example, the formation of **2e**−**f** occurs with dearomatisation due to the reactive 1,3-diene fragment forming part of a phenyl substituent. **2f** demonstrates a series of resonances in the ^{1}H NMR spectrum in benzene-d_6 at δ = 5.81 (m, 1H), 5.97 (m, 1H), 6.56 (dd, 1H, $^3J_{HH}$ = 9.6 Hz, $^3J_{HH}$ = 3.5 Hz), 6.61 (d, 1H, $^3J_{HH}$ = 9.6 Hz) ppm characteristic of the four proton spin system of the newly created 1,3-cyclohexadiene motif. There is a further characteristic high-field proton at δ = 2.65 (d, 1H, $^5J_{HH}$ = 8.4 Hz) ppm which can be assigned to the sp^3 methine heavily shielded and broadened due to the adjacent quadrupolar I = 5/2 aluminum atom. A related reaction of **1** with benzophenone was recently reported by Nikonov and co-workers.[44] The reaction of **1** with anthracene yields a 1:0.4 mixture of (4 + 1) cycloaddition products **2g** and **2h** formed from reaction at both the 1,4- and 9,10-positions of the hydrocarbon. Diagnostic resonances for the newly formed sp^3 centers could be observed in benzene-d_6 for **2g** and **2h** at δ = 3.81 (dd, $^3J_{H-H}$ = 4.7 Hz, 3.5 Hz) and 4.07 ppm, respectively. Prolonged heating results in the conversion of **2g** into the more thermodynamically stable product **2h**.

Compounds **2b**−**c** and **2f**−**h** were subject to single-crystal X-ray diffraction experiments (Figure 3). **2b** contains, at its core, an aluminocyclopentene. The five-membered ring allows expansion of the C−Al−C bond angle to 94.10(8)°, a value consistent with a tetrahedral geometry at aluminum. The Al−C(sp^3) bond lengths of 1.9634(19) and 1.9737(17) Å reveal a slight asymmetry to the ring system. The data are similar to a related 1,4-bis(trimethylsilyl)but-2-ene-1,4-diyl complex prepared through a salt-metathesis route.[45] The structure of **2c** as determined by single-crystal X-ray diffraction is very similar. **2c** forms as a 1.7:1 mixture of *syn*/*anti* isomers from the reaction of 1 with a 1.7:1 mixture of *E*,*E* and *E*,*Z*-2,4-hexadiene (see below for discussion of stereoselectivity). During the crystallization of **2c** the mixture is enriched in the major isomer and the single-crystal X-ray diffraction data were modeled as a 1:9 mixture of *anti*/*syn* isomers. The structures of **2f**−**h** reveal the dearomatisation of benzene rings. For example, in **2f** the aluminocyclopentene moiety incorporates a dearomatised phenyl group as evidenced by the formation of a sp^3-center and localized C—C and C═C bond lengths within the hydrocarbon ring. The Al−C(sp^3) bond lengths are asymmetric with the larger of 2.013(2) Å being that to the dearomatized system. Although this bond is long, it is still within the range established for a covalent Al−C *σ*-bond. The Al−C(sp^3) bond lengths of **2g** and **2h** are similarly elongated and range from 2.047(2) to 2.056(2) Å. In addition, the C−Al−C bond angles of **2f**−**h** are more acute than those in **2b**. Both trends are indicators of stretched Al−C bonds in the dearomatised compounds. The structure of **2g** was determined by a single-crystal X-ray diffraction experiment on a sample purified by fractional crystallization of a 1:0.4 mixture of **2g**/**2h**. Although **2g** crystallized preferentially, the sample is only enriched in **2g** and is not completely pure. The data were modeled as a 96:4 mixture of **2g**/**2h**, and the minor component **2h** could be observed in the ^{1}H NMR spectrum of the recrystallized material.

Formal (2 + 2 + 1) Cycloaddition of a 1,5-Diene. Attempts to expand the scope of reactivity to the non-conjugated diene, 1,5-cyclooctadiene, gave a remarkable ring-contraction product derived from reaction of both C=C *π*-bonds. Heating a mixture of two equivalents of 1,5-cyclooctadiene to a solution of **1** in benzene-d$_6$ at 100 °C for 6 h results in a characteristic color change from red-orange to bright yellow due to formation of **3** (Scheme 2). Recrystallization of the crude product by vapor diffusion of *n*-pentane into a concentrated toluene solution afforded **3** as bright yellow blocks. The fused ring-system is disordered over two sites in a ca. 80:20 ratio, and as such, the data should be treated with caution. The structure is reminiscent of **2d** previously reported by our group.[20] The average C—C bond length of the cyclobutane ring is 1.55 Å, while the average C−C−C angle approaches 90°. The protons of the cyclobutane resonate at δ = 1.21−1.27 (m, 2H), 2.19−2.25 (m, 2H), and 2.40 (m, 2H) ppm. The latter set of peaks are assigned to the bridgehead position. This ring contraction reaction of 1,5-cyclooctadiene presents similarities to known homo Diels−Alder cycloadditions.[46] While homo Diels−Alder [2 + 2 + 2] cycloadditions of homoconjugated dienes can occur under transition-metal catalysis or in the case of very reactive dienophiles without a catalyst,[47−49] cheletropic reactions with homoconjugated dienes are extremely rare.

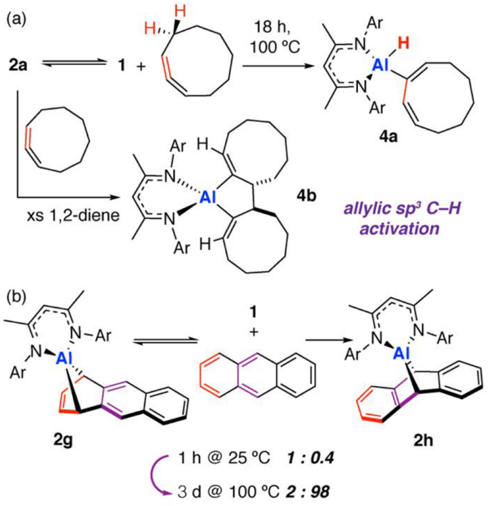
Scheme 2. Reaction of 1 with 1,5-Cyclooctadiene to Form 3



Reversibility. We have previously reported that (2 + 1) cycloadditions of **1** with alkenes can, in certain instances, be reversible.[17] The equilibria between **1** + alkene ← → aluminocyclopropane has been probed through variable temperature NMR spectroscopy and crossover experiments. The equilibria are of note as they represent reversible redox processes of a main group reagent, in this case involving interconversion between the +1 and +3 oxidation state of aluminum.

A series of reactions were conducted to investigate reversibility in the reaction of **1** with dienes. Heating samples of **2a** for 18 h at 100 °C in benzene-d$_6$ resulted in the formation of **4a**, the product of allylic sp^3 C−H activation (Scheme 3). We have previously concluded that the interconversion of related aluminocyclopropane and allylic C−H activation products occurs through a dissociative pathway involving reformation of **1**. Compound **4a** contains a 1,3-diene system metalated at the 2-position. In the solid-state, the Al−C(sp^2) bond length of 1.964(2) Å is similar to that found in **2a**. Although metalated dienes related to **4a** have proven remarkably adept in synthesis,[50,51] in part due to their ease of access from the hydroalumination of 1,3-diynes, there are limited examples of crystallographically characterized aluminum complexes of this type. Repeating this reaction in the presence of an excess (10 equiv) of 1,2-cyclononadiene results in the formation of **4b** in 1 h at 100 °C (Scheme 3). **4b** is derived from the insertion of 1,2-cyclononadiene into the Al−C(sp^3) bond of **2a**. **4b** contains a 2,5-dimetalated hexa-1,5-diene motif. The two hydrocarbon fragments are joined through a *trans*-fused ring junction. In the solid-state the Al−C(sp^2) bond lengths are 1.980(2) and 1.983(2) Å and are again reminiscent of those found in **2a** and **3**. Monitoring the reaction by ^{1}H NMR spectroscopy reveals that **4b** is formed in remarkably high selectivity. Despite the possible loss of selectivity across multiple selectivity determining events (see Scheme S4) **4b** is formed in 75% yield by NMR spectroscopy and in 65% isolated yield. 1,2-Cyclononadiene is known to undergo a symmetry allowed thermal [2 + 2] cycloaddition. Although this dimerization was observed to occur in parallel to the formation of **4b**, a control reaction between the dimerized hydrocarbon fragment and **1** did not result in the formation of **4b** (see Scheme S2). In combination, the experiments suggest that the formation of **2a** is reversible in the absence of additional substrate but undergoes insertion chemistry in the presence of exogeneous substrate.

Scheme 3. Reversibility in the Reactions of 1 with 1,2-Cyclononadiene and Anthracene



Although heating samples of **2b**−**d** in benzene-d$_6$ gave no evidence for reversibility in the (4 + 1) cycloaddition step, the ratio of **2g** and **2h** proved to be dependent on the reaction conditions. The data are consistent with an equilibrium between the two isomers being in operation at high temperatures. Hence, heating of 1:0.4 mixtures of **2g**/**2h** in benzene-d$_6$ to 100 °C for 3 days results in slow, but practically quantitative, equilibration to **2h**, ultimately to form a 2:98 mixture (Scheme 3). **2h** is the thermodynamic product of the reaction, and the implication is that at higher temperatures the (4 + 1) cycloaddition to form **2g** is reversible while that to form **2h** may be nonreversible. This hypothesis was confirmed by a crossover experiment between a 1:0.4 mixture of **2g**/**2h** and H$_2$ after 2 days between 80−100 °C; this reaction led to exclusive consumption of **2g** to form the aluminum(III) dihydride **1-H$_2$**. **2h** remained unreacted. A further crossover reaction with **2g**/**2h** and C$_6$F$_6$ led to the reformation of anthracene and a known C−F alumination compound; again **2h** remained unconsumed at the end of the reaction (compound **S1**, see Supporting Information for details). Similarly, heating samples of **2f** in the presence of an excess (10 equiv) of C$_6$F$_6$ at 100 °C showed complete conversion of **2f** to the same C−F aluminated product (Supporting

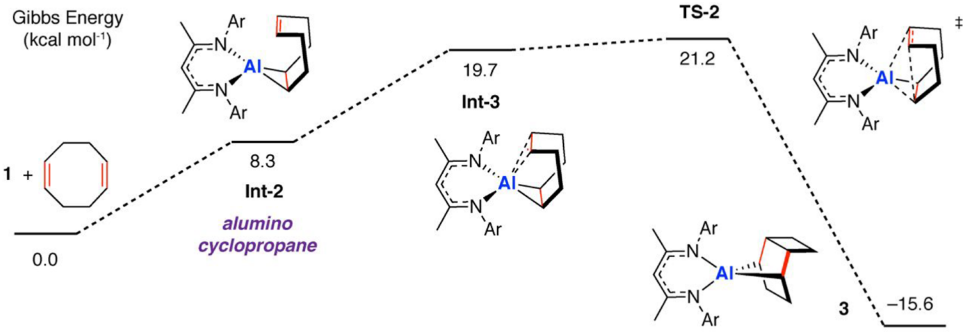


Figure 4. Calculated mechanism for stepwise reaction of **1** with 1,5-cyclooctadiene to form **3**.

Information). These experiments demonstrate the reversibility of the reaction between **1** and 1,1-diphenylethylene and anthracene.

A Pericyclic Mechanism. A series of DFT calculations and stereochemical probe experiments were conducted to gain insight into the reaction of **1** with 1,3- and 1,5-dienes. The potential energy surfaces for the reactions of **1** with 2,3-dimethylbutadiene, (*E*,*E*)-2,4-hexadiene, and anthracene were explored using DFT calculations (M06L, see SI for details). Dispersion effects were included via single point energy corrections and were modeled using Grimme's D3 correction. In all cases, concerted pathways were found in which a single transition state connects starting materials to products. In the case of anthracene two competitive pathways could be located for reaction at both the 1,4- and 9,10-positions of the aromatic hydrocarbon.

The (4 + 1) cycloadditions present high similarity to well-established cheletropic reactions. Cheletropic reactions are a subclass of pericyclic reactions. Pericyclic reactions themselves involve a cyclic array of overlapping orbitals. These concerted reactions are characterized by the cyclic nature and aromaticity of the transition state and follow strict stereochemical course as defined by the Woodward−Hoffmann rules. The reaction of **1** and 2,3-dimethylbutadiene was calculated to occur by isomerization of the diene from the *s-trans* to *s-cis* isomer prior to the cycloaddition ($\Delta G^{\circ}_{298\ \mathrm{K}}$ = +2.7 kcal mol^{-1}). Subsequent formation of **Int-1b**, an encounter complex of **1** and the diene, is endergonic ($\Delta G^{\circ}_{298\ \mathrm{K}}$ = +7.4 kcal mol^{-1}) and leads directly to **TS-1b** ($\Delta G^{\ddagger}_{298\ \mathrm{K}}$ = +15.3 kcal mol^{-1}). **TS-1b** is cyclic and concerted, albeit asynchronous. In **TS-1b**, the formation of the two Al−C σ-bonds, is accompanied by the disappearance of the two conjugated π-bonds and formation of the new π-bond, as would be expected for a pericyclic $[_{\pi}4_{s} + {}_{n}2_{s}]$ cheletropic cycloaddition (Figure 3a). The formation of the product **2b** is exergonic ($\Delta G^{\circ}_{298\ \mathrm{K}}$ = −30.6 kcal mol^{-1}), and the activation barrier for the reverse process is unlikely to be surmountable with any appreciable rate constant under the conditions of the reaction.

A similar reaction pathway was calculated for the reaction of **1** with (*E*,*E*)-2,4-hexadiene. Based on the orbital symmetry, the thermally allowed $[_{\pi}4_{s} + {}_{n}2_{s}]$ reaction pathway should involve suprafacial attack. The corresponding transition state, **TS-1c** ($\Delta G^{\ddagger}_{298\ \mathrm{K}}$ = +20.3 kcal mol^{-1}), reflects this and predicts exclusive formation of the *syn*-isomer of the product (Figure 3b). Related transition states could be located for the cheletropic reaction of **1** with both anthracene and benzene itself **TS-1g/h** and **TS-1i**, respectively (Supporting Information). To further substantiate the classification of the reaction as pericyclic, NICS(0) calculations were performed on these transition states.[52] These showed the transition states for the cheletropic reaction to be highly aromatic (NICS(0) = −10.6 to −14.3), while the corresponding aluminocyclopentene products **2b, 2c** were essentially nonaromatic (NICS(0) = −1.0 to −1.2).

Experimental support for a pericyclic mechanism was acquired from following the stereochemical course of the reaction of **1** with 2,4-hexadiene to form **2c**. A commercial sample (from Fluorochem) of 2,4-hexadiene was analyzed by ^{1}H NMR spectroscopy and confirmed as a 1:1.7 mixture of (*E*,*Z*)/(*E*,*E*) isomers. The least stable (*Z*,*Z*)-isomer could not be detected as part of the mixture. Reaction of the mixture of dienes with excess (1.8 equiv) **1** led to a 1:1.7 mixture of *anti*/*syn* **2c**. The experiment strongly suggests that reaction is stereospecific with the (*E*,*E*) isomer leading to *syn*-**2c** and the (*E*,*Z*) isomer leading to *anti*-**2c** (Figure 3c). Notably this ratio was not preserved when running the reaction with an excess of 2,4-hexadiene as **1** reacts with the (*E*,*Z*)-isomer at a faster rate than the (*E*,*E*)-isomer, and *anti*-**2c** was obtained preferentially. Subsequent heating of the product mixture at 100 °C for 3 days lead to no changes in the product ratio.

Curious as to whether a concerted process could also be in operation for the formation of the (2 + 2 + 1) cycloaddition product **3** from 1,5-COD, the reaction mechanism was studied by DFT calculations. In this instance the concerted pathway would have to involve a $[_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{n}2_{s}]$ cycloaddition due to the spatial separation of C═C π-systems. In some cases, related homo-Diels−Alder reactions have been shown to be concerted pericyclic cycloadditions.[53,54] In the current case, both concerted and stepwise pathways could be identified by DFT calculations (see Supporting Information). The stepwise pathway has the lowest energy barriers and is a more likely proposition than the concerted mechanism (Figure 4). Hence, reaction of **1** with a single alkene unit of 1,5-COD results in formation of aluminocyclopropane **Int-2** ($\Delta G^{\circ}_{298\ \mathrm{K}}$ = +8.3 kcal mol^{-1}). Approach of the second alkene unit to aluminum results in the formation of **Int-3** ($\Delta G^{\circ}_{298\ \mathrm{K}}$ = +19.7 kcal mol^{-1}). **Int-3** can form the tricyclic scaffold by insertion of the second alkene into the aluminocyclopropane moiety via **TS-2** ($\Delta G^{\ddagger}_{298\ \mathrm{K}}$ = +21.2 kcal mol^{-1}) forming **3** ($\Delta G^{\circ}_{298\ \mathrm{K}}$ = −15.6 kcal mol^{-1}) in an exergonic process with control of the stereochemistry of the *cis*-fused ring junction. The aluminocyclopropane intermediate is calculated to be unstable with respect to the starting materials and products. Experimentally no intermediates were observed during the formation of **3**. We were unable to locate a transition state for the (2 + 1) cycloaddition step in this reaction sequence and as such cannot unambiguously rule out the concerted $[_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{n}2_{s}]$ cycloaddition pathway.

■ CONCLUSIONS

In summary, we report the reactions of a monomeric aluminum(I) complex with a series of 1,2-, 1,3-, and 1,5-dienes. In the case of the nonconjugated dienes investigated to date, reactivity is defined by an initial (2 + 1) cycloaddition to form an aluminocyclopropane. Subsequent insertion of C═C unsaturation into the strained three-membered ring can lead to the formation of more complex organometallic products. In the case of 1,3-dienes a concerted (4 + 1) reaction occurs. This can proceed with the dearomatisation of the substrate due to the high-energy nature of the aluminum(I) reagent. Stereochemical probe experiments and DFT calculations are consistent with the (4 + 1) reaction being defined as a concerted pericyclic reaction, specifically a cheletropic reaction. The definition parallels that known for the addition of group 14 reactive intermediates to 1,3-dienes (e.g., silylenes, germylenes, and stannylenes). The experimental and theoretical realization of this reactivity in simple, well-defined molecular systems may be a useful step toward the design of catalytic cycles, especially given the potential for reversibility in the (4 + 1) cycloaddition step. Moreover, the new aluminocycles we report may be useful reactive organometallic building blocks in chemical synthesis, allowing easy access to complex ring systems from simple starting materials.[55]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03701.

Full details of the experiments and calculations (PDF)

Accession Codes

CCDC 1973313−1973321 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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