Reactions of an Aluminium(I) Reagent with 1,2-, 1,3- and 1,5-dienes: Dearomatisation, Reversibility, and a Pericyclic Mechanism

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Abstract:

The reactions of an aluminium(I) reagent with a series of 1,2-, 1,3- and 1,5-dienes are 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 interrogated 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 dienes that are either in part, or entirely, contained within aromatic rings. In these cases, reactions occur with dearomatisation of the substrate and can be reversible. In the case of 1,2- or 1,5-dienes complementary reactivity is observed; the orthogonal nature of the C=C π-bonds (1,2-diene) and the homoconjugated system (1,5-diene) both disfavour 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 aluminium(I) compounds.[1-4] Aluminium 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 aluminium compounds is still dominated by those in the +3-oxidation state. There is however a growing realisation that both neutral and anionic aluminium compounds in the +1-oxidation state show some remarkable reactivity.[5-8] 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 aluminium(I) compounds with unsaturated and aromatic hydrocarbons. Contemporary work in this area has been foreshadowed by vapour deposition studies involving the co-condensation of aluminium atoms with ethylene, propene or 1,3-butadiene at low temperature.[9-11] 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[9] and aluminocyclopentenes.[11] The latter compound being derived from a cheletropic reaction of Al atoms with 1,3-butadiene.[11] Schnöckel's synthesis of AlCl allowed the first direct translation of this reactivity to aluminium(I) compounds. Metal vapour deposition of AlCl and 2,3-dimethylbutadiene leads to the formation of a cyclic oligomer and provides unambiguous structural evidence for Al–C σ-bond formation.[12] A related cyclic dimer has been reported from the reaction of a terphenyl stabilised gallium(I) compound with 2,3-dimethylbutadiene and has been proposed to derive from the dimerization of a metallocyclopentene intermediate.[13]

Based on the synthetic accessibility of a number of new aluminium(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,[14] reacts reversibly with alkenes to form aluminocyclopropanes by a (2+1) cycloaddition,[15,16] and in a single instance non-reversibly with 1,3-cyclohexadiene to form a (4+1)[17] cycloaddition product (Figure 1).[18] Related reactions of **1** with alkynes are known to form aluminocyclopropenes.[19,20] Theoretical studies on **1**, have led to the suggestion that this compound can undergo a (4+1) cycloaddition with benzene to form a high-energy [2.2.1]aluminobicycloheptadiene moiety.[21] 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.[22] Coles and co-workers have reported, an anionic aluminium(I) complex that reacts with 1,3,5,7-cyclooctatetrene (COT) to yield a reduced planar COT^{2-} complex which can isomerise to the non-planar (4+1) cycloaddition product upon sequestration of the countercation.[23]

Reactions of aluminium(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** effects the C–H activation of benzene, toluene and xylenes.[24-26] In the absence of catalyst **1** is also capable of allylic C–H activation.[15] Anionic aluminium(I) compounds have also been reported to effect the C–H activation of benzene in the absence of a catalyst.[27,28] Remarkably, for one of these systems sequestration of the potassium countercation generates an aluminium reagent capable of reversibly inserting into a C–C σ-bond of benzene, effecting its dearomatisation.[29]

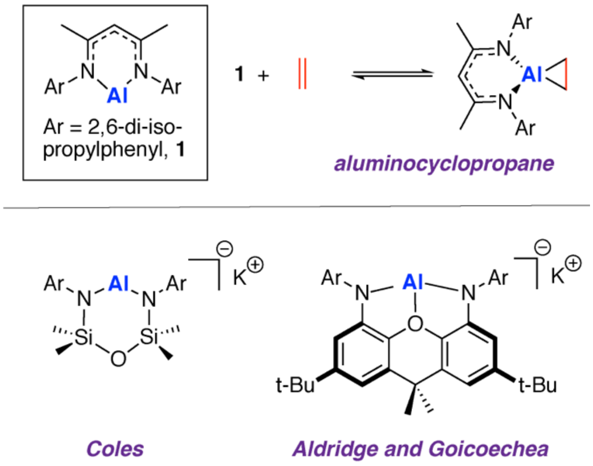


Figure 1. Reaction of selected aluminium(I) compounds with unsaturated hydrocarbons.

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 thermal 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.[30-34] Expansion of the reactivity to germylenes (R_2Ge) and stannylenes (R_2Sn) generally results in higher selectivity for the (4+1) cycloaddition.[35] 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.[36-38] Calculations based on semi-empirical (MNDO)[39] and DFT methods[40] 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-

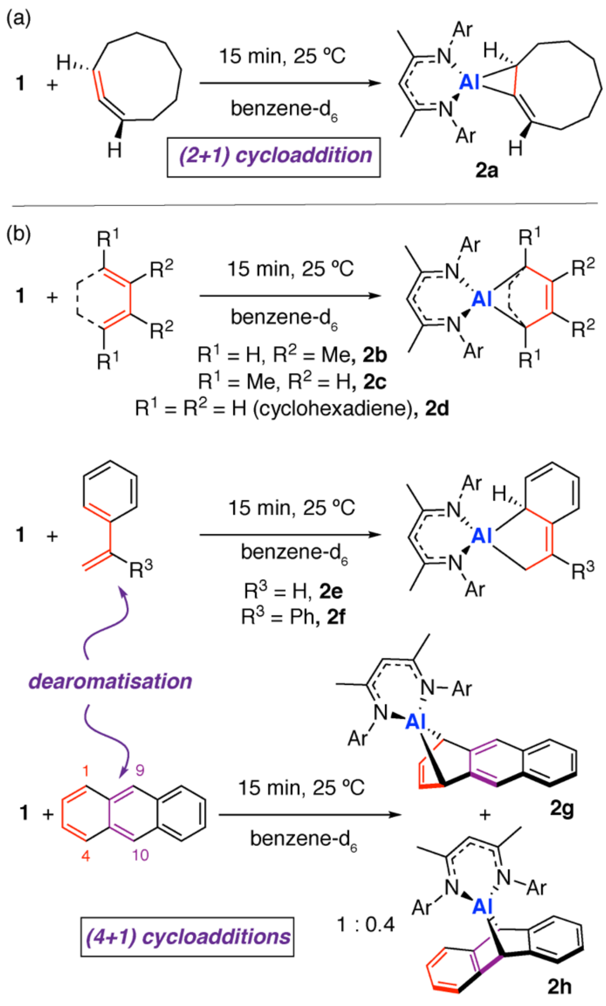
dienes react with **1** by a cheletropic and pericyclic mechanism. In certain cases, the reaction can lead to the dearomatisation of benzene rings and be reversible.

Results and Discussion

1,2-Dienes: The reaction of **1** with 1,2-cyclononadiene in toluene solution proceeds rapidly to form metallocyclopropane **2a** at 25 °C as evidenced by an instant colour change from orange to red on mixing the reagents (Scheme 1a). **2a** is the product of a formal (2+1) cycloaddition. It contains an aluminocyclopropane unit bearing an exocyclic alkene moiety as characterised 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 to not only the diastereotopic protons of the adjacent methylene group but also 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** crystallises with 6 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)°. Despite the introduction of the exocyclic alkene moiety, these data fall within the range established for related compounds derived from alkenes.[15] 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 (**2c**), 1,3-cyclohexadiene (**2d**),[18] 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 favour the *s*-trans configuration in solution (Scheme 1b).

The (4+1) cycloaddition generates an aluminocyclopentene in which the aluminium 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 aluminium(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.[41]



Scheme 1. Reaction of **1** with (a) 1,2-cyclononadiene and (b) 1,3-dienes, styrene, 1,1,-diphenylethylene and anthracene.

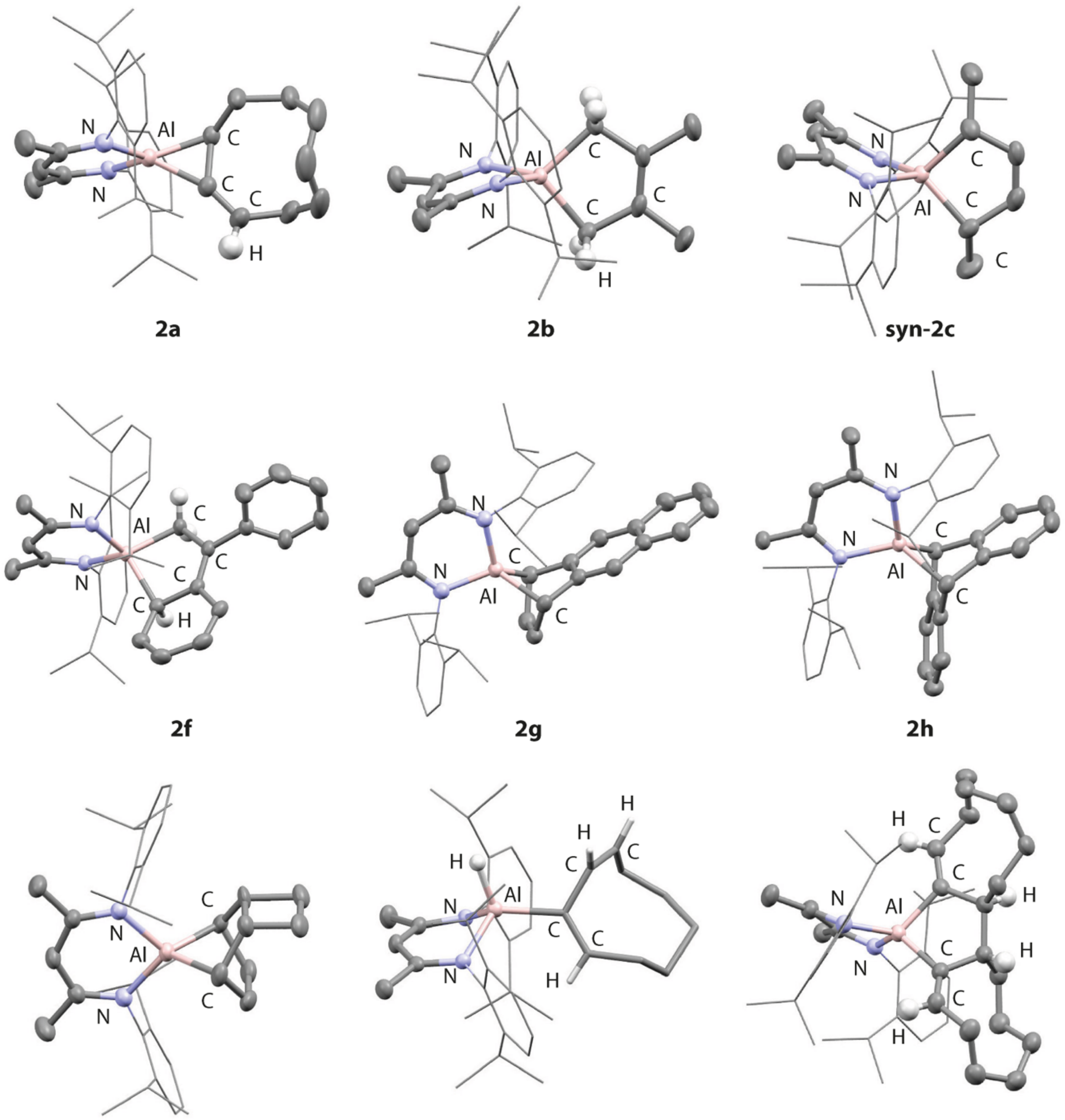
In the case of **2e-2h**, **1** is a high enough energy species to effect the dearomatisation of a benzene ring. For example, the formation of **2e-f** occurs with dearomatisation due to the reactive 1,3-diene fragment forming part of a phenyl substituent. **2f** demonstrates a series of resonances in 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 aluminium atom. A related reaction of **1** with benzophenone was recently reported by Nikonov and co-workers.[42] The reaction of **1** with anthracene yields a kinetic 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 centres could be observed in benzene-d$_6$ for **2g** and **2h** at δ = 3.81 (dd, $^3J_{H\text{-}H}$ = 4.7 Hz, 3.5 Hz) and 4.07 ppm respectively.

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 aluminium. 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.[43] The structure of **2c** as determined by single crystal X-ray diffraction is very similar and this molecule crystallises 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-centre and localised 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 that in **2b**. Both trends are indicators of stretched Al–C bonds in the dearomatised compounds. The structure of **2g** was determined by single crystal X-ray diffraction experiment on a sample purified by fractional crystallisation of kinetic 1 : 0.4 mixture of **2g**:**2h**. Although **2g** crystallised preferentially, the data were modelled as 96 : 4 mixture of **2g**:**2h**.

	1[14]	**2a**[a]	**2b**	**2c**	**2f**
Al–N	1.957(2)	1.889(2)	1.9051(14)	1.9089(15)	1.9029(17)
		1.887(2)	1.9236(15)	1.9344(15)	1.9120(17)
N–Al–N	89.86(8)	97.1(1)	96.09(6)	95.94(6)	96.96(7)
Al–C(sp^3)		1.952(3)	1.9634(19)	1.985(2)	1.981(2)
			1.9737(17)	1.990(2)	2.013(2)
Al–C(sp^2)		1.913(3)	–		–
C–Al–C		47.7(1)	94.10(8)	92.28(9)	89.03(9)
C=C		1.309(5)	1.336(3)	1.318(3)	1.357(3)

	2g[c]	**2h**	**3**[d]	**4a**	**4b**
Al–N	1.9053(18)	1.9108(12)	1.9260(17)	1.9111(18)	1.9381(16)
	1.9089(18)	1.9134(12)	1.9252(16)	1.9081(17)	1.9212(17)
N–Al–N	96.28(8)	97.02(5)	96.15(7)	95.16(8)	95.93(7)
Al–C(sp^3)	2.047(2)	2.0495(15)	1.994(6)	–	–
	2.056(2)	2.0499(15)	2.018(5)		
Al–C(sp^2)	–	–	**–**	1.964(2)	1.980(2)
					1.983(2)
C–Al–C	78.35(9)	78.15(6)	82.8(2)	–	91.37(8)
C=C	1.342(3)	–	**n.r.**	1.326(3)	1.331(3)
				1.323(5)	1.331(3)

Table 1. Selected bond lengths (Å) and angles (º) from single crystal X-ray diffraction data for **2a**-c, **2f-h**, **3**, and **4a-b**. [a] molecule A, 1 of 6 in the asymmetric unit. [b] cocrystallised 9:1 mixture of **syn-2C** : **anti-2c**. [c] cocrystallised 96:4 mixture of **2g:2h** with positional disorder of the anthracene unit. [d] disordered across two sites.



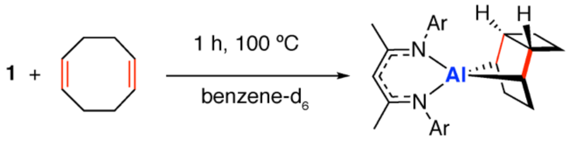
2a **2b** **syn-2c**

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**.

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 hours results in a characteristic colour change from red orange to bright yellow. **3** was recrystallised by vapour diffusion of pentane into a concentrated toluene solution to afford **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.[18] 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.[44] 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,[45-47] cheletropic reactions with homoconjugated dienes are extremely rare.



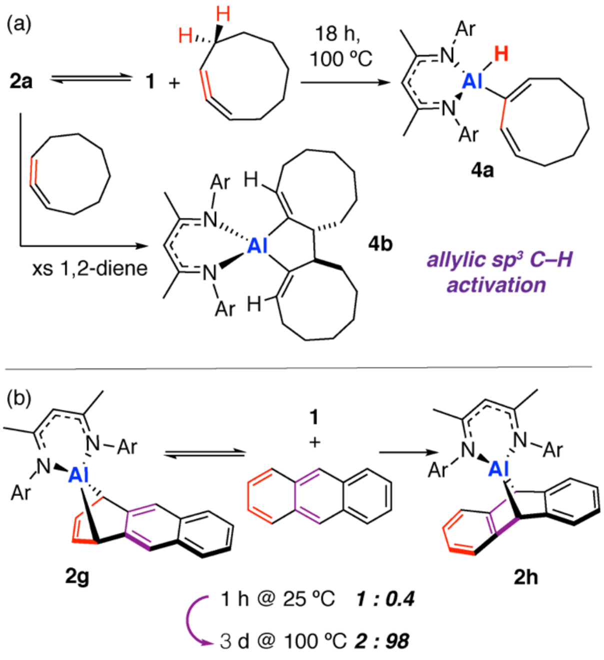
3

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.[15] The equilibria between **1** + alkene ← → aluminocyclopropane has been probed through variable temperature NMR spectroscopy and cross-over 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 aluminium.

A series of reactions were conducted to investigate reversibility in the reaction of **1** with dienes. Heating samples of **2a** for 18h at 100 °C in benzene-d_6 resulted in the formation of **4a**, the product of allylic sp^3 C–H activation. 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 metallated 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 metallated dienes related to **4a** have proven remarkably adept in synthesis,[48,49] in part due to their ease of access from the hydroalumination of 1,3-diynes, there are limited examples of crystallographically characterised aluminium 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 1h at 100 °C. **4b** is derived from the insertion of 1,2-cyclononadiene into the Al–C(sp^3) bond of **2a**. **4b** contains a 2,5-dimetallated 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 supporting information, 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 dimerisation was observed to occur in parallel to the formation of **4b**, a control reaction between the dimerised hydrocarbon fragment and **1** did not result in the formation of **4b** (see supporting information, 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.

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. 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. **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 non-reversible. This hypothesis was confirmed by a cross-over 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 aluminium(III) dihydride **1-H$_2$**. **2h** remained unreacted. A further cross-over reaction with **2g** : **2h** and C_6F_6 led to the reformation of anthracene and a known C-F alumination compound (compound **S1**, see supporting information for details. Similarly, heating samples of **2f** in the presence of an excess (10 equiv.) of C_6F_6 at 100 °C showed complete conversion of **2f** to the same C-F aluminated product (supporting information). These experiments demonstrate the reversibility of the reaction between **1** and 1,1-diphenylethylene and anthracene.



Scheme 3. Reversibility in the reactions of **1** with 1,2-cyclononadiene 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 modelled 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 characterised 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 isomerisation of the diene from the *s*-trans to *s*-cis isomer prior to the cycloaddition (ΔG°_{298K} = +2.7 kcal mol^{-1}). Subsequent formation of **Int-1b**, an encounter complex of **1** and the diene is endergonic (ΔG°_{298K} = +7.4 kcal mol^{-1}) and leads directly to **TS-1b** ($\Delta G^{\ddagger}_{298K}$ = +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 (ΔG°_{298K} = –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.

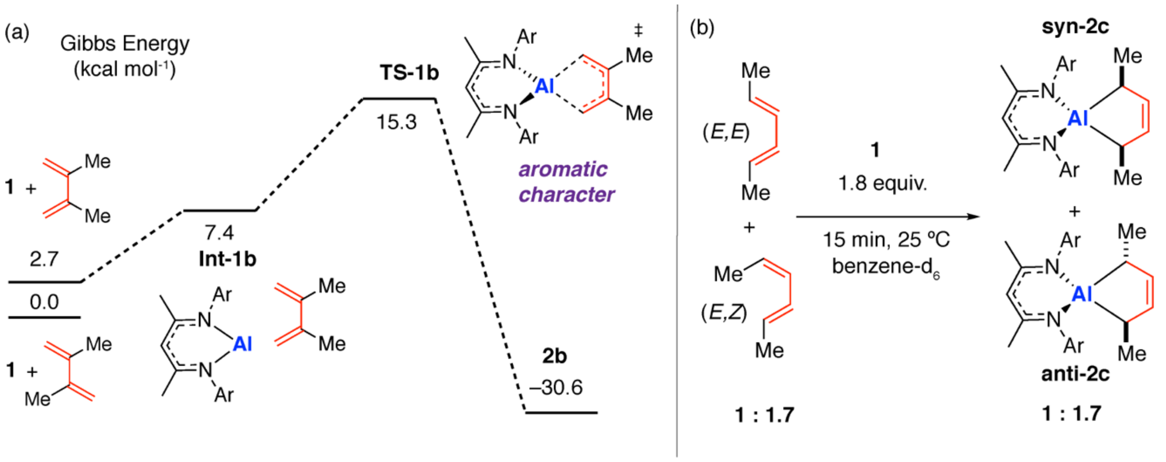


Figure 3. (a) Calculated mechanism for the concerted pericyclic reaction of **1** with 2,3-dimethylbutadiene to form **2b**. (b) Stereochemical probe experiments with a mixture of (*E*,*E*) and (*E*,*Z*)-2,4-hexadiene.

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** ($\Delta G^{\ddagger}_{298K}$ = +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.[50] 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 non-aromatic (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 analysed 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** lead to a 1 : 1.7 mixture of *anti* : *syn* **2c**. The experiment strongly suggests that reaction is stereospecific with the (*E,E*) isomer leading exclusively to *syn*-**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 ºC 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.[51,52] In the current case, both concerted and stepwise pathways could be identified by DFT calculations. The stepwise pathway has the lowest energy barriers and is a more likely proposition than the concerted mechanism. Hence, reaction of **1** with a single alkene unit of 1,5-COD results in formation of aluminocyclopropane **Int-2** (ΔG°_{298K} = +8.3 kcal mol^{-1}). Approach of the second alkene unit to aluminium results in the formation of **Int-3** (ΔG°_{298K} = +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** ($\Delta G^{\ddagger}_{298K}$ = +21.2 kcal mol^{-1}) forming **3** (ΔG°_{298K} = –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.**

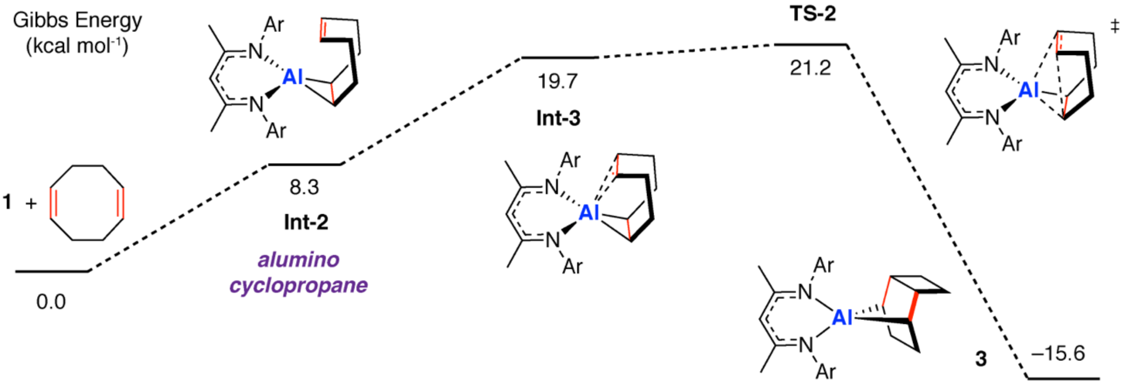


Figure 4. Calculated mechanism for stepwise reaction of **1** with 1,5-cyclooctadiene to form **3**.

Conclusions

In summary, we report the reactions of a monomeric aluminium(I) complex with a series of 1,2-, 1,3- and 1,5-dienes. In the case of the non-conjugated dienes 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 aluminium(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 realisation 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.

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