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How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 24702–24708

International Edition: doi.org/10.1002/anie.202111385

German Edition: doi.org/10.1002/ange.202111385

Reversible Dissociation of a Dialumene**

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Abstract: Dialumenes are neutral Al^I compounds with Al=Al multiple bonds. We report the isolation of an amidophosphine-supported dialumene. Our X-ray crystallographic, spectroscopic, and computational DFT analyses reveal a long and extreme trans-bent Al=Al bond with a low dissociation energy and bond order. In solution, the dialumene can dissociate into monomeric Al^I species. Reactivity studies reveal two modes of reaction: as dialumene or as aluminyl monomers.

Introduction

Like other low oxidation-state main group systems, Al^I compounds are revealing potential in bond-activation and catalysis.^[1] Dialumenes are neutral Al^I compounds with Al=Al multiple bonds. They sit alongside the prototypical neutral Al^I compounds (Cp*Al)₄ and NaCNacAl(I), and the rapidly developing class of anionic aluminyl compounds.^[2]

Dialumenes can be divided into two classes: base-coordinated dialumenes (R(L)Al=Al(L)R), which are iso-electronic with alkenes, and “transient” dialumenes (RAI=AIR). Two base-coordinated dialumenes have been reported. The first, silyl substituted **I**, was reported by Inoue in 2017.^[3a] An aryl analogue, **II**, followed (Figure 1).^[3b] Though base-free dialumenes (**III**) are yet to be isolated, “masked” examples that behave as RAI=AIR are known. Power reported the toluene adduct **IV**,^[4] and Tokitoh the related benzene adduct **V**.^[5]

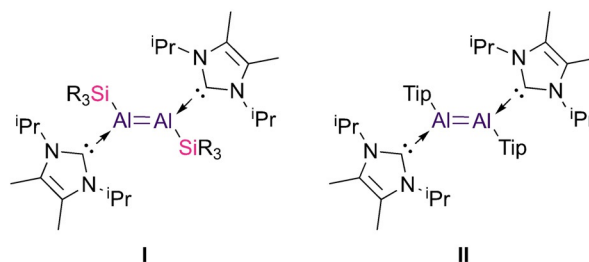
Dialumenes readily activate dihydrogen and other small molecules.^[5,6] Inoue’s **I** and **II** catalytically reduce CO₂ with HBPIn.^[3b,7] This capability comes from closely-spaced frontier molecular orbitals, which beget high reactivity. Even considering the only isolated examples, **I** and **II**, it is clear that understanding the interplay between substituents, bonding,

and reactivity in dialumenes is critical to their further development.

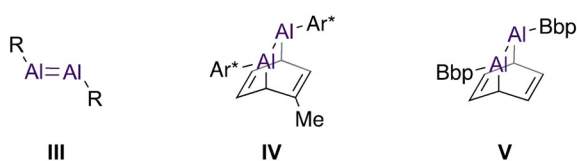
Base-coordinated and base-free dialumenes are clearly related, but insights from experiment and theory reveal very different pictures of bonding. Dialumenes **I** and **II** feature planar or moderately trans-bent Al=Al bonds with double bond character, do not dissociate, and react as dialumenes. In contrast, donor-free dialumenes **III** feature low Al=Al bond orders and substantially trans-bent geometry.^[8] These dialumenes can dissociate readily in solution; **V** appears to react as either RAI=AIR or RAl: species.^[9] Recently, Power showed that a larger terphenyl substituent allows access to an RAl: monomer rather than **IV**.^[10]

A transient N,P-coordinated aluminyl monomer was implicated in our recent studies of reductive elimination in the Al(II) dihydrodialane **VI** (Figure 1 c).^[11] We thus targeted isolable Al^I compounds of the same amidophosphine ligand.

a) Base-coordinated dialumenes



b) Transient and ‘masked’ dialumenes



c) Reversible reductive elimination in an Al(II) dihydride

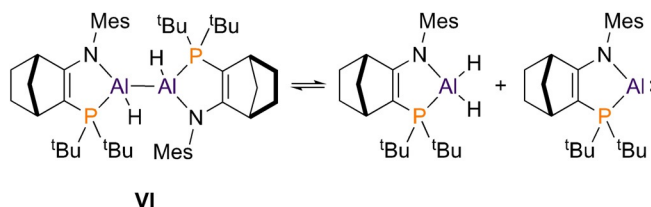


Figure 1. a) Base-coordinated dialumenes (R₃Si = Me^tBu₂Si; Tip = 2,4,6-triisopropylphenyl). b) “masked” dialumenes (Ar* = 2,6-(2,6-diisopropylphenyl)phenyl; Bbp = 2,6-(bis(trimethylsilyl)methyl)phenyl). c) Reversible reductive elimination in **VI** (Mes = 2,4,6-trimethylphenyl).

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[**] A previous version of this manuscript has been deposited on a preprint server (<https://doi.org/10.33774/chemrxiv-2021-6443s>).

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: <https://doi.org/10.1002/anie.202111385>.

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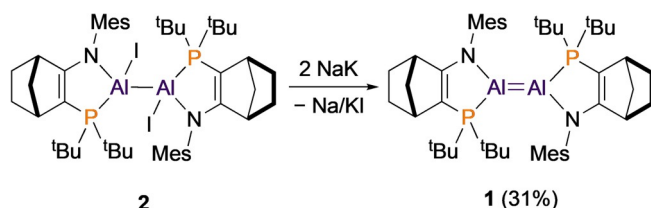
We report here the base-coordinated dialumene **1**. Our studies demonstrate that **1** has an unusually weak Al=Al bond with low bond-order and an extreme trans-bent geometry. We reveal how the amidophosphine ligand of **1** is the origin of these effects. In solution, **1** dissociates and can react as either dialumene or monomeric aluminyl.

Results and Discussion

We prepared dialumene **1** by reduction from the Al(II) precursor diiododialane **2** (Scheme 1). Treatment of **2** with 2 equiv Na/K alloy in THF led to a colour change from yellow to dark purple. After 5 hours, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy revealed consumption of **2** and a new broad resonance at δ 21.3, as well as minor amounts of dihydrodialane **VI**. Crystalline dialumene **1** was isolated as a dark purple solid in 31% yield from toluene at -30°C . UV/vis spectroscopy revealed λ_{max} 567.0 nm, which we assign to a π to π^* transition (Figure S3, Table S10). At 293 K, **1** decomposes over 1–2 days in THF, toluene or hexane solutions.

The solid-state structure of dialumene **1**, determined by X-ray crystallography, reveals a highly trans-bent Al=Al bond in *E* configuration (Figure 2). Two-site disorder of the Al positions reveals major and minor isomers of **1** (88/12%) with distinct geometries around the Al₂ core. The amidophosphine ligands enforce narrow N1–Al1–P1 angles (83–84°). The Al=Al distance in **1** is shorter by 0.1–0.2 Å than in the related Al(II) dihydrodialane **VI** or in Uhl's dialane(4) ((SiMe₃)₂HC)₂Al–Al(CH(SiMe₃)₂)₂ (**I** 2.5190(14)/2.471(13) Å; **VI** 2.6586(16) Å; Uhl's dialane 2.660(1) Å).^[12] Nevertheless, the Al=Al distance in **1** is notably longer (~0.1 Å) than in Inoue's dialumenes [**I** 2.3943(16); **II** 2.4039(8)]. Compared to **I** and **II**, the Al=Al core of **1** is much less planar (**1** $\theta = 48.8^\circ/51.2^\circ$; **I**: 0° ; **II**: $17.3^\circ/23.7^\circ$). We note that the pyramidalised Al centres in **1** are stereogenic; the major and minor isomers in the solid-state structure have opposite stereochemistry at the Al centres.

DFT calculations reveal that the bonding situation in **1** is distinct from previous base-coordinated dialumenes **I** and **II**. Natural Bond Orbital (NBO) analysis of **1** shows natural localised molecular orbitals (NLMOs) representing Al–Al σ - and π -bonds (Figure 3a). Although it retains some apparent π -bond character, the corresponding NLMO of **1** is heavily localised on the aluminium centres; the relevant NLMOs of **I** or **II** more closely resemble classical π -orbitals (Figure S19/20). The localisation of the π -orbital in dialumene **1** results from admixture of the Al–Al σ^* . The extent of this admixture is revealed by the increased s-character of the NLMO of



Scheme 1. Preparation of dialumene **1**.

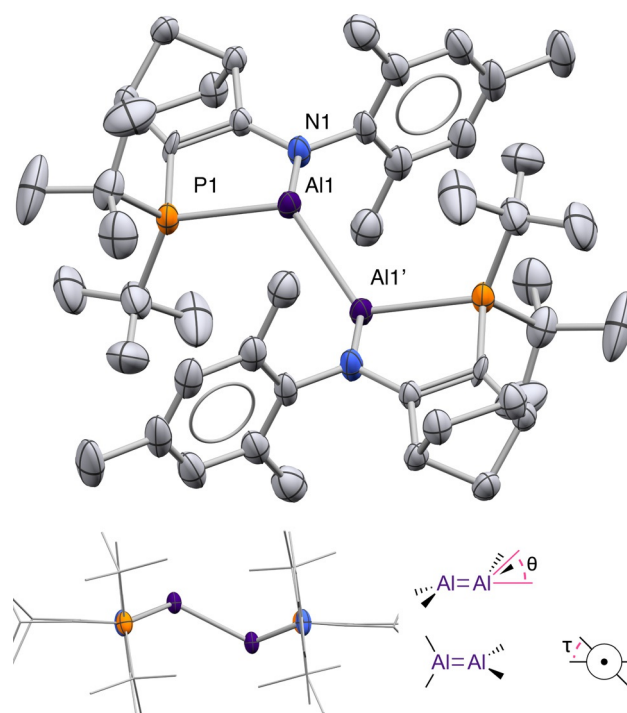


Figure 2. X-ray crystal structure of dialumene **1** (H atoms omitted for clarity). Thermal ellipsoids at 50% probability. Major component of disordered Al/ligand displayed (**1A**). Selected bond distances [Å] and angles [°]: Al1–Al1' 2.5190(14); N1–Al1 1.909(2); P1–Al1 2.4816(9); N1–Al1–P1 84.86(7); $\theta = 48.8$; $\tau = 0.21$.

1 (Al1/Al2 $\text{sp}^{1.25}/\text{sp}^{1.09}$) compared to that in, for example, **II** (Al1/Al2 $\text{sp}^{48.34}/\text{sp}^{23.32}$), where the π -bond is constructed from essentially pure p-orbitals. Consistent with this picture, the Wiberg bond index for the Al=Al bond of **1** is 1.31, which is increased from that of dihydrodialane **VI** (0.91) but lower than in **I** or **II** (1.67, 1.54).

Grützacher and Fässler have proposed simple topographical criteria for distinguishing classical and non-classical multiple bonds.^[13] Their criteria use the Electron Localisation Function (ELF), which identifies regions of localised valence electron density. The ELF of classically π -bonded systems reveals “attractors”—local maxima *M* in the ELF that correspond to electron pairs—above and below the plane of E=E bonds. Each attractor *M* is surrounded by a “basin” of electron density. The topology and electron population of such basins is interpretable in familiar terms as covalent bonds or lone pairs. Classical π -bonded systems have “dumb-bell” shaped electron basins, and their populations sum to approximately $4e^-$.

Topological analysis of the ELF of **1** (Figure 3b) reveals a quite different picture. The characteristic pattern of attractors and basins for a slipped π -bond is observed. Three valence attractors, *M*₁–*M*₃, are found near the Al₂ unit. *M*₃ is centred on the Al–Al bond; its basin population is $1.11e^-$. *M*₁ and *M*₂ are each above or below an Al centre, “slipped” from their positions in a classical double bond. The basins of *M*₁/*M*₂ are each populated by $\sim 1.30e^-$; the summed basin populations ($3.76e^-$) correspond with the $4e^-$ available for bonding from the two Al^I centres of **1**.

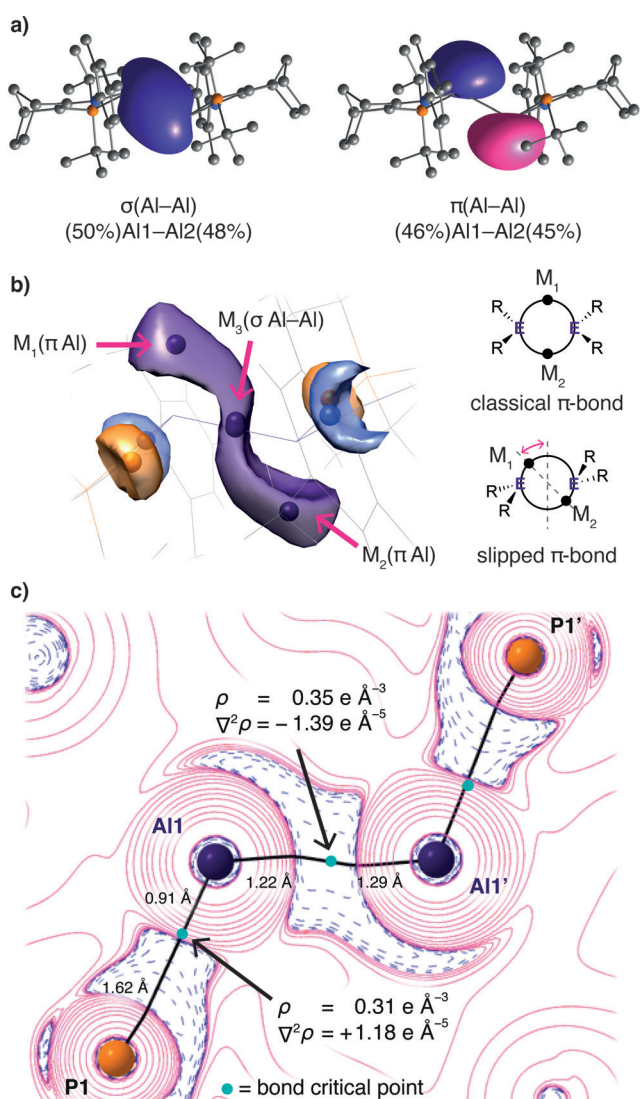


Figure 3. Electronic structure analysis of **1**. a) NLMOs (isovalue = 0.036) of the Al=Al bond. b) ELF localisation domains (isovalue = 0.795) of the Al=Al core. M_n indicates attractors. c) Laplacian of the electron density in the P-Al=Al-P plane. Areas of charge concentration and depletion (blue/pink), bond paths (black) and bond critical points shown.

The positions of attractors M_1 - M_3 in **1** correspond with those in the base-free dialumene Al_2H_2 .^[8a,14] The sigmoidal form of the ELF isosurface of **1** is a feature of bonding in base-free dialumenes, along with low Al-Al bond order (~ 0.5) and diradical character.^[8a] Based on the basin population around M_3 (1.11 e^-), **1** also has low Al-Al bond order. M_1 and M_2 can be interpreted as non-bonding electron density at Al. In contrast, the ELF of planar dialumene **I** reveals features of classical π -bonds: an attractor on each face of the Al=Al bond (Figure S23).

To better determine the Al-Al bond order in **1**, we undertook Quantum Theory of Atoms in Molecules (QTAIM) analysis (Figure 3c and SI). The molecular graph reveals Al-Al, Al-N and Al-P bond paths. The Al-P interactions are polar dative bonds, as revealed by the position of their bond critical points (bcp) closer to the more

electropositive Al centres and associated QTAIM parameters ($\sigma_{\text{bcp}} = 0.310 \text{ e \AA}^{-3}$, $\nabla^2\sigma_{\text{bcp}} = +1.180 \text{ e \AA}^{-5}$, $H_{\text{bcp}} = -0.107 \text{ E}_h \text{ \AA}^{-3}$), ($G_{\text{bcp}}/\sigma_{\text{bcp}} < 1$).^[15] Meanwhile the Al-N bonds exhibit stronger ionic character ($\sigma_{\text{bcp}} = 0.499 \text{ e \AA}^{-3}$, $\nabla^2\sigma_{\text{bcp}} = +8.410 \text{ e \AA}^{-5}$, $H_{\text{bcp}} = -0.094 \text{ E}_h \text{ \AA}^{-3}$, $G_{\text{bcp}}/\sigma_{\text{bcp}} < 1$). The Al-Al bond features weak shared-shell covalent character, as judged by the charge concentration and topological parameters at its bcp ($\sigma_{\text{bcp}} = 0.349 \text{ e \AA}^{-3}$, $\nabla^2\sigma_{\text{bcp}} = -1.390 \text{ e \AA}^{-5}$, $H_{\text{bcp}} = -0.135 \text{ E}_h \text{ \AA}^{-3}$, $G_{\text{bcp}}/\sigma_{\text{bcp}} < 1$). In accordance with the ELF results, the values of both σ_{bcp} and $\nabla^2\sigma_{\text{bcp}}$ are rather low, indicating a weak Al-Al bond. The bond ellipticity parameter suggests a small degree of double bond character ($\epsilon_{\text{bcp}} = 0.195$).

The delocalisation index $\delta(\text{A},\text{B})$ is a quantitative measure for the number of electron pairs exchanged between two atomic basins. When referenced against a chemically-similar comparator compound with a well-defined bonding situation, the delocalisation index can reflect chemical bond order. Here, we use $\delta(\text{Al},\text{Al})$ of the bond in dihydrodialane **VI** to define an Al-Al bond order of 1. At 0.65, $\delta(\text{Al},\text{Al})$ in **VI** is about half that in the planar transition state **TS_{1C-1C}** (see later) which unequivocally has a planar Al=Al double bond ($\delta(\text{Al},\text{Al}) = 1.21$). In trans-bent dialumene **1**, $\delta(\text{Al},\text{Al})$ at 0.80 is only slightly higher than that of dihydrodialane **VI**, but much lower than that of the Al=Al double-bond.^[14]

The combined results of our crystallographic and electronic structure analyses indicate small but significant Al=Al multiple bond character in **1**. Al-Al bond distance, and computational bond order and delocalisation-index criteria all support the conclusion that the Al=Al bond in **1** is intermediate between single and double bonds, with bond order ~ 1.3 .

Why is dialumene **1** so different from **I** and **II**? We used DFT calculations on a set of minimal base-coordinated dialumenes with NHC or PMe_3 donors and hydride, phenyl, silyl or amino substituents (Table 1) to answer this question.^[16]

The structures of the model dialumenes depend strongly on the substituent and Lewis base (NHC or PMe_3). Electropositive substituents (SiMe_3) provoke shorter Al=Al bonds, wider R-Al-L angles, and more planar structures. More electronegative ($\text{Si} < \text{H} < \text{Ph} < \text{N}$) or π -donating substituents induce more trans-bending and longer Al=Al bonds. NHC-coordinated dialumenes always have shorter and more planar Al=Al bonds than their PMe_3 counterparts (Al=Al = 2.42–2.48 Å vs. 2.45–2.60 Å).

These substituent effects mimic those in disilenes, reflecting the isoelectronic relationship between $\text{R}_2\text{Si}=\text{SiR}_2$ and $\text{R(L)Al}=\text{Al(L)R}$. In disilenes, trans-bend angles and Si=Si bond distances are correlated with the singlet-triplet energy gap ($\Delta E_{\text{S-T}}$) of the notional or real silylene monomers, :SiR_2 .^[17] We find that the same relationship applies to dialumenes: Al=Al bond dissociation energy increases as $\Delta E_{\text{S-T}}$ for the monomeric R(L)Al: fragments decreases (Figure S11). The result is that dialumene bond dissociation energy/geometry can be predicted based on properties of the R(L)Al: (aluminum) monomer.

We attribute the stronger and more planar Al=Al bonds of NHC- vs. PMe_3 -coordinated dialumenes to the strong

Table 1: Selected geometrical and thermodynamic properties of model dialumenes calculated at SMD-B3LYP-D3/6-311G(2d,2p)//M062X-D3/def2SVP level^[a]

Al=Al [Å]	2.42	2.44	2.39	2.48	2.45	2.47	2.46	2.60
L-Al-R [°]	101.7	97.1	112.1/106.9	91.9	95.8	92.7	98.7	99.4
θ [°] ^[b]	29.6/47.2 ^[d]	33.4/53.9 ^[e]	19.1/16.3 ^[f]	43.1	46.6	50.5/50.4	41.6/41.0	63.5/44.6 ^[g]
$\Delta G_{298}(\text{dissoc})$ [kcal mol ⁻¹] ^[c]	22.1	20.6	33.2	11.5	19.3	19.7	25.5	2.1
$\Delta E_{S-T}(\text{monomer})$ [kcal mol ⁻¹]	19.2	20.6	12.3	25.5	23.2	25.4	16.4	32.4

[a] L = NHC, Imidazol-2-ylidene (C₃H₄N₂). [b] θ = trans-bend angle, see Figure 2. Unless otherwise noted, $\tau = 0^\circ$. Where two values are listed, complexes are unsymmetrically trans-bent. [c] corrected for basis set superposition error (Table S7). [d] $\tau = 17.8^\circ$. [e] $\tau = 20.5^\circ$. [f] $\tau = 7.9^\circ$. [g] $\tau = 19.8^\circ$.

donor ability of the NHC, which raises the R(L)Al: HOMO, narrowing ΔE_{S-T} . In contrast, the low dissociation energy for Me₂N(PMe₃)Al=Al(PMe₃)NMe₂, (2.1 kcal mol⁻¹) is explained by the large ΔE_{S-T} for the Me₂N(Me₃P)Al: fragment (32.4 kcal mol⁻¹).

Returning to dialumene **1**, we can ascribe its extreme trans-bending to the electronegative/ π -donating NR₂ substituent and narrow 85° N1-Al1-P1 angle enforced by the ligand, which both increase ΔE_{S-T} in the monomeric aluminyl fragment (Table S9). Calculations on the full dialumene **1** predict a bond dissociation energy of 7.1 kcal mol⁻¹, vs. 25.0 and 19.0 kcal mol⁻¹ for **I** and **II** (Table S7). To explore the possible dissociation of **1**, we turned to its solution-phase behaviour.

Dialumene **1** is predominantly dimeric in solution. Its ³¹P{¹H} NMR spectrum at 300 K has one broad signal at δ 21.3 ($\Delta\nu_{1/2} = 134$ Hz) (Figure 4a). ¹H NMR spectroscopy reveals two ligand environments for **1**, in the ratio 54%:46%, indicating at least two (stereo)isomers. The stereogenic Al centres of **1**, in combination with its ligand backbone, mean that there are three possible diastereomers of *E*-**1**, **A-C** (Figures 4a, S1), each of which must have distinct ³¹P signals.^[18] **1A** and **1B** are *meso* compounds with equivalent phosphorus centres—each will give rise to a singlet. **1C** has inequivalent phosphorus centres, so two ³¹P resonances (potentially doublets with ³J_{PP}). The pattern of DFT-predicted ³¹P signals confirms our stereochemical analysis (Figure 4c, S15).

At 300 K, the broad ³¹P{¹H} resonance at δ 21.3 indicates diastereomers **1A-C** are exchanging. Cooling to 243 K, resolves this broad signal into two singlets (δ 20.4 and δ 20.0). At 203 K, the higher field signal (δ 19.5) broadens and approaches coalescence ($\Delta\nu_{1/2} = 148$ Hz).

The dynamic ³¹P{¹H} NMR behaviour of **1** arises from a combination of intra- and intermolecular exchange processes that exchange diastereomers **1A-C**. In the low temperature regime ($\lesssim 300$ K), only intramolecular fluxional processes are operative. The two singlets observed at 243 K are assigned to **1A/B** and **1C**. A “trans-flip” process, fast on the NMR timescale at this temperature, simultaneously inverts the stereochemistry at both aluminium centres (Figure 4b). This has the effect of interconverting diastereomers **1A** and **1B**, generating a (concentration-weighted) time-averaged signal for them. In **1C**, the trans-flip is instead a degenerate

process that exchanges the two inequivalent phosphorus centres, leading to the observed singlet. At 203 K, we assign the broad signal to **1C**, in which the trans-flip is becoming slow on the NMR timescale.

Using DFT calculations we were able to locate the planar transition states **TS_{1A-1B}** and **TS_{1C-1C}** for the trans-flip process (Figure 4d). The barriers for this process range from 8 to 11 kcal mol⁻¹. **TS_{1C-1C}** is higher in energy than **TS_{1A-1B}** (11.35 vs. 9.37 kcal mol⁻¹).

In the higher temperature regime (~ 300 K), exchange between isomers **1A/B** and **1C** becomes active through an intermolecular route. Dissociation of dialumene **1** generates monomeric aluminyl **3**, which can then recombine to form any of the three diastereomers of **1** (Figure 4c). This process is possible due to the low dissociation energy of **1**, (DFT predicts $\Delta G_{298} = +7.1$ kcal mol⁻¹). 2D ¹H EXSY NMR spectroscopy at 300 K reveals exchange cross peaks between resonances for **1A/1B** (time averaged) and **1C** (Figures S6/7). Our DFT calculations place diastereomers **1A-C** very close in energy, spanning just 2 kcal mol⁻¹. Experimental measurements are consistent with this. We were able to determine the equilibrium constants for the exchange of [**1A + 1B**] with **1C** in the temperature range 188–243 K (Figure S5). We can thus estimate ΔG^0 for [**1A + 1B**] \rightarrow **1C** as 0.8 ± 0.2 kJ mol⁻¹ (0.19 ± 0.04 kcal mol⁻¹).

The presence of aluminyl **3** in solution is revealed by dynamic NMR behaviour, but its concentration must be rather low since we did not observe signals for it. Nor did UV-vis spectroscopy in the temperature range 5–65°C reveal absorptions for **3** (Figure S3). Lacking direct spectroscopic evidence, we sought to trap **3**.

Like **I** and **II**,^[3] **1** can react with alkenes and alkynes to form 4-membered aluminacycles. Treatment of **1** with ethene (1 atm) at room temperature results in rapid (5–20 mins) conversion to dialuminacyclobutane **4** by formal [2+2] cycloaddition of the Al=Al and C=C bonds. Similarly, diphenylacetylene reacts with **1** to form dialuminacyclobutene **5** (Scheme 2). ³¹P{¹H} NMR spectroscopy of **4** and **5** reveals distinct signals for three diastereomers in each case. This is a result of the “locking” of the stereogenic aluminium centres enforced by their cyclic structures (**4**: δ 11.6 (d, ³J_{PP} = 12 Hz), 11.5 (s), 11.5 (s), 11.4 (d, ³J_{PP} = 12 Hz);, **5**: δ 11.0 (br s), 10.7 (s), 10.4 (s), 10.3 (br s).; see SI).

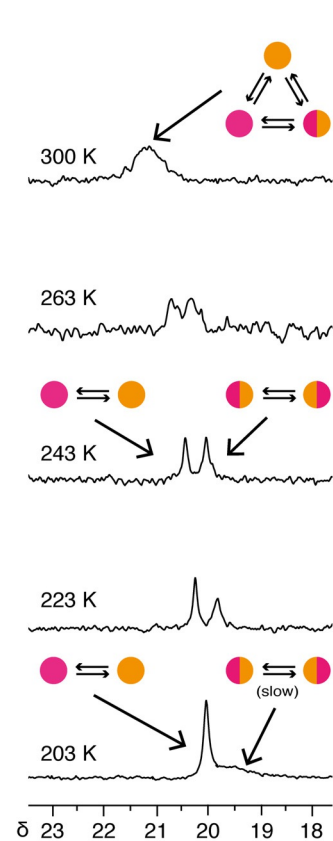
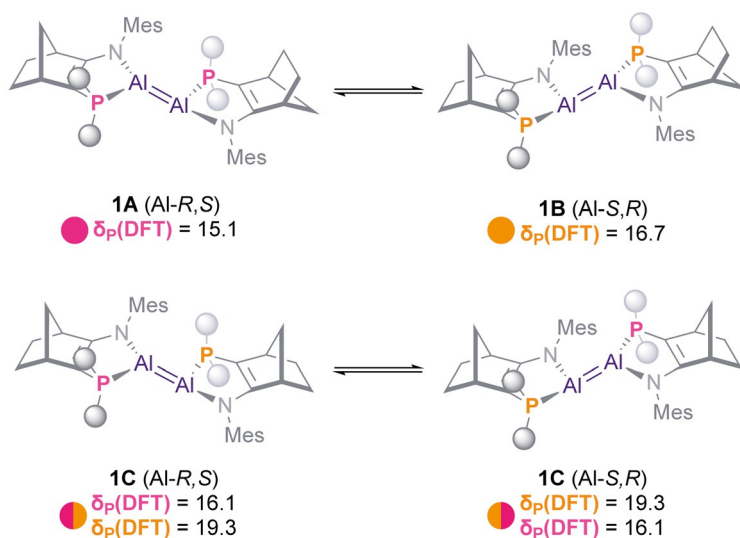
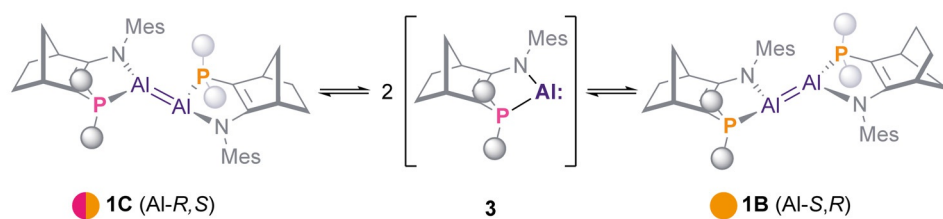
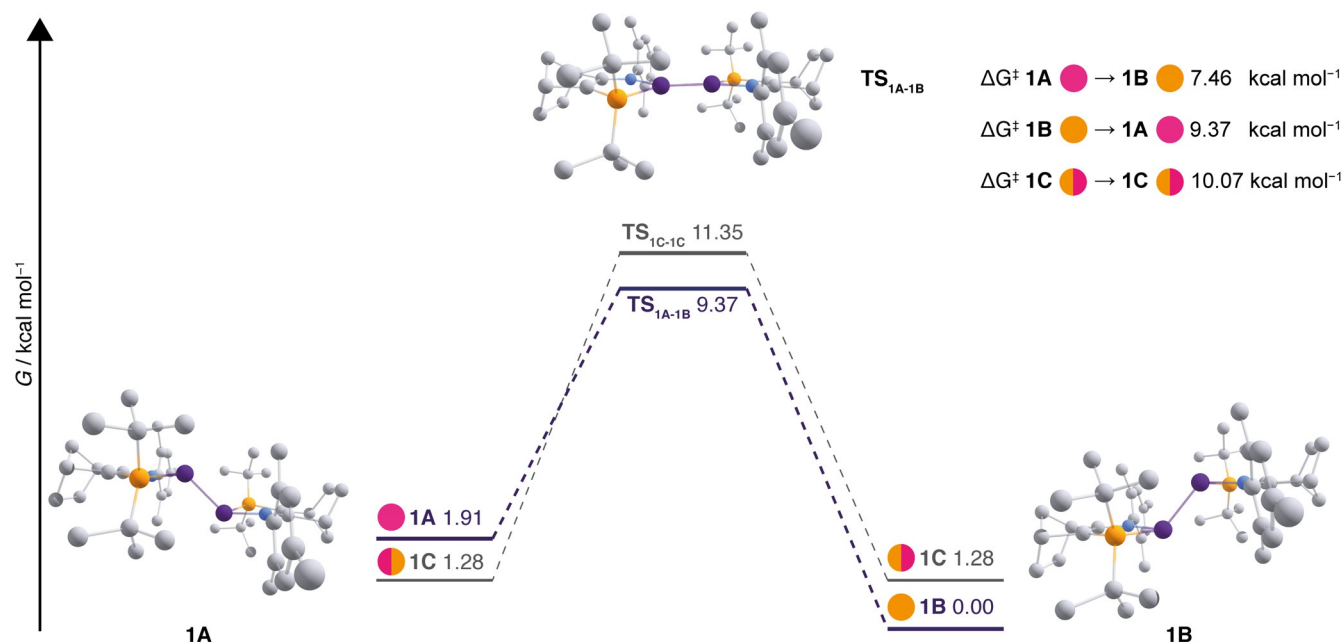
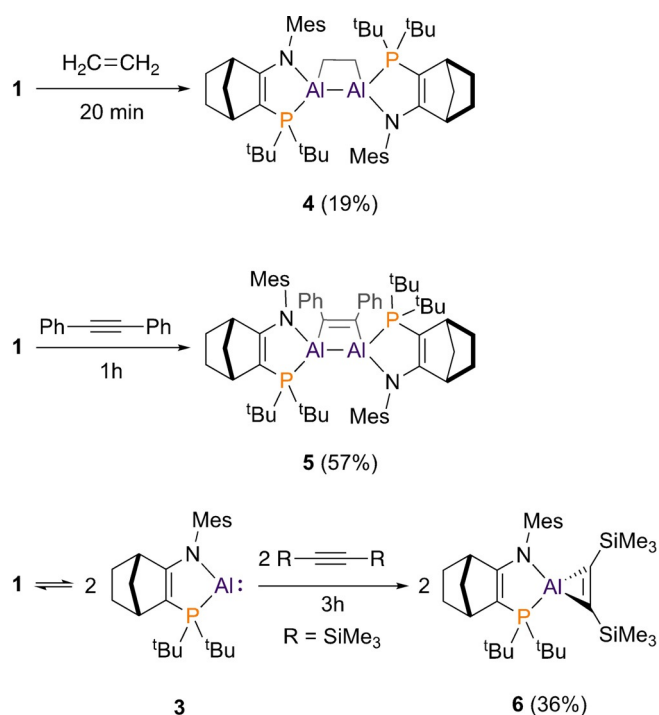
a) VT $^{31}\text{P}\{^1\text{H}\}$ spectroscopy of **1**b) Inversion at Al exchanges diastereomers **1A** and **1B**c) Dissociation and recombination exchanges diastereomers **1A/B** and **1C**d) Reaction profile for 'trans-flip' isomerisation in **1**

Figure 4. a) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **1** (161 MHz, $[\text{D}_8]$ toluene) recorded at 203–300 K. b) Inversion at aluminium exchanges **1A** and **1B**, but is degenerate for **1C**. c) Intermolecular dissociation/recombination of **1** exchanges all diastereomers. d) Reaction energy profile for the “trans-flip” in diastereomers **1A-C** at $T=298.15$ K (geometries optimised at M062X-D3/def2SVP, energies calculated at B3LYP-D3/6-311G(2d,2p) corrected for C_6H_6 solvent).



Scheme 2. Reactivity of dialumene **1** with alkenes/alkynes.

X-ray crystallography reveals the geometry of the C_2Al_2 rings of **4** and **5**. The Al–Al distances in **4** and **5** are not notably longer than in **1**, despite destruction of the Al=Al π bond (**1**, 2.519(1) Å; **4**, 2.558(1) Å; **5**, 2.512(1) Å, see SI). This is rather different to the behaviour of dialumenes **I** or **II** in comparable reactions with alkenes/alkynes. The resulting analogues of **4/5** exhibit substantial Al–Al bond elongation (0.20–0.25 Å) compared to **I/II**. The difference reflects the lower Al=Al bond order in **1** vs. **I/II**.

When dialumene **1** is treated with the bulkier alkyne $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, the observed product is derived not from **1** but rather from its monomer, **3**. On addition of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, purple solutions of **1** become yellow within three hours. $^{31}\text{P}\{^1\text{H}\}$ NMR reveals a broad signal at δ 9.8, characteristic of amidophosphine-coordinated Al(III) compounds.^[19]

X-ray crystallography shows that the product from **1** and $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$ is aluminacyclopropene **6** (Figure 5). **6** has the narrow C1–Al–C2 angle expected for aluminacyclopropenes ($42.05(9)^\circ$) and its C1=C2 distance is typical for a double bond (1.367(2) Å). Cycloaddition reactions with alkynes are a characteristic reaction for neutral aluminyls. A NacNac-coordinated analogue of **6** has been prepared by reduction of Al(III) precursors in the presence of $\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, though with other alkynes direct reaction with NacNacAl(I) is also viable.^[20] Structurally, the AlC_2 core of **5** and its NacNac analogue are closely comparable.

Conclusion

In summary, we have prepared the first isolable dialumene that dissociates in solution. The donor properties of the amidophosphine ligand generate a large $\Delta E_{\text{S-T}}$ on the

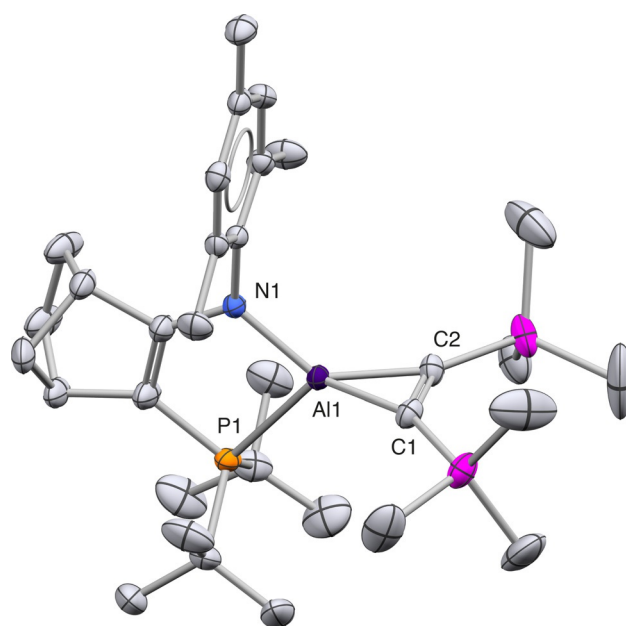


Figure 5. X-ray crystal structure of aluminacyclopropene **6** (H atoms omitted). Thermal ellipsoids at 50% probability. The asymmetric unit comprises two molecules; just one is shown.

transient aluminyl monomers. This large $\Delta E_{\text{S-T}}$ is the origin of the low bond order, high trans-bending, and weak Al=Al bond in **1**. We continue to explore the reactivity of **1** and related systems.

Acknowledgements

This project received funding from the European Research Council (ERC) under the EU Horizon 2020 research and innovation programme (ERC-2016-STG-716315). We acknowledge the Irish Centre for High-End Computing for computational facilities and support. K.M.B. thanks MU for a Graduate Teaching Scholarship.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: aluminium · aluminium(I) compounds · dialumene · low-valent atoms · multiple bonds

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Manuscript received: August 23, 2021

Accepted manuscript online: September 14, 2021

Version of record online: October 7, 2021