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Aluminium Compounds

Very Important Paper

Reversible Dissociation of a Dialumene**

Rosalyn L. Falconer, Keelan M. Byrne, Gary S. Nichol, Tobias Krämer,* and Michael J. Cowley*

Abstract: Dialumenes are neutral Al 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 species. Reactivity studies reveal two modes of reaction: as dialumene or as aluminyl monomers.

Introduction

Like other low oxidation-state main group systems, Al compounds are revealing potential in bond-activation and catalysis.[1] Dialumenes are neutral Al compounds with Al=Al multiple bonds. They sit alongside the prototypical neutral Al compounds (Cp*Al), 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=AlR). 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 RAl=AlR 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=AlR or RAI 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 1c).[11] We thus targeted isolable Al compounds of the same amidophosphine ligand.

Figure 1. a) Base-coordinated dialumenes (R(Si=Me)Bu₂Si; Tip=2,4,6-trisopropylphenyl). b) “masked” dialumenes (Ar*=2,6-(2,6-dimethylphenyl)phenyl; Bbp=2,6-(bis(trimethylsilyl)methyl)methylphenyl). c) Reversible reductive elimination in VI (Mes=2,4,6-trimethylphenyl).

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

Results and Discussion

We prepared dialumene I 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, $^3$P{1H} 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 I was isolated as a dark purple solid in 31% yield from toluene at −30°C. UV/vis spectroscopy revealed $\lambda_{\text{max}}$ 567.0 nm, which we assign to a π to π* transition (Figure S3, Table S10). At 293 K, I decomposes over 1–2 days in THF, toluene or hexane solutions.

The solid-state structure of dialumene I, 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 I (88/12%) with distinct geometries around the Al core. The amidophosphine ligands enforce narrow N1−Al1−P1 angles (83–84°). The Al=Al distance in I is shorter by 0.1–0.2 Å than in the related Al(II) dihydrodialane VI or in Uhl’s dialane(4)((SiMe3)$_3$HC)$_2$Al−(CH(SiMe$_3$)$_3$)$_2$ (I 2.5190(14)/2.471(13) Å; VI 2.6586(16) Å; Uhl’s dialane 2.660(1) Å). Compared to I and II, the Al=Al core of I is much less planar (I θ = 48.8°/51.2°; I: 0°; II: 17.3°/23.7°). We note that the pyramidalised Al centres in I are stereoergic: 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 I is distinct from previous base-coordinated dialumenes I and II. Natural Bond Orbital (NBO) analysis of I shows natural localised molecular orbitals (NLMOs) representing Al=Al π-bonds or lone pairs. Classical valence attractors, M1-M3, are found near the Al 2 unit. M3 is centred on the Al bond; its basin population is 1.11e. M1 and M2 are each above or below an Al centre, “slipped” from the plane of Al=Al bond; their basin population is 0.91e. 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 “dumbbell” shaped electron basins, and their populations sum to approximately 4e−.

Topological analysis of the ELF of I (Figure 3b) reveals a quite different picture. The characteristic pattern of attractors and basins for a slipped π-bond is observed. Three valence attractors, M1−M3, are found near the Al$_2$ unit. M3 is centred on the Al=Al bond; its basin population is 1.11e. M1 and M2 are each above or below an Al centre, “slipped” from their positions in a classical double bond. The basins of M1/M2 are each populated by $\sim$1.30e ; the summed basin populations (3.76e−) correspond with the 4e− available for bonding from the two Al$_2$ centres of I.

Figure 2. X-ray crystal structure of dialumene I (H atoms omitted for clarity). Thermal ellipsoids at 50% probability. Major component of disordered Al/ligand displayed [IA]. Selected bond distances [Å] and angles [°]: Al(II)−Al(II) 2.5190(14); N1−Al(II) 1.909(2); P1−Al(II) 2.4816(9); N1−Al(II)−P1 84.86(7); θ = 48.8; τ = 0.71.
electropositive Al centres and associated QTAIM parameters ($\sigma_{\text{bcp}} = 0.310 \text{ eÅ}^{-3}$, $\nabla^2 \sigma_{\text{bcp}} = +1.180 \text{ eÅ}^{-5}$, $H_{\text{bcp}} = −0.107 E_{\text{b}} \text{ Å}^{-3}$, $G_{\text{bcp}}/\sigma_{\text{bcp}} < 1$). Meanwhile the Al−N bonds exhibit stronger ionic character ($\sigma_{\text{bcp}} = 0.499 \text{ eÅ}^{-3}$, $\nabla^2 \sigma_{\text{bcp}} = +8.410 \text{ eÅ}^{-5}$, $H_{\text{bcp}} = −0.094 E_{\text{b}} \text{ Å}^{-3}$, $G_{\text{bcp}}/\sigma_{\text{bcp}} < 1$). The Al−Al bond features weak shared-shell covalent character, as judged by the charge concentration and topological parameters at its bcp ($\sigma_{\text{bcp}} = 0.349 \text{ eÅ}^{-3}$, $\nabla^2 \sigma_{\text{bcp}} = −1.390 \text{ eÅ}^{-5}$, $H_{\text{bcp}} = −0.135 E_{\text{b}} \text{ Å}^{-3}$, $G_{\text{bcp}}/\sigma_{\text{bcp}} < 1$). In accordance with the ELF results, the values of both $\sigma_{\text{bcp}}$ 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 ($\rho_{\text{bcp}} = 0.195$).

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 $\text{TS}_{\text{2A}}$ (see later) which unequivocally has a planar Al−Al double bond ($\delta(\text{Al},\text{Al}) = 1.21$). In trans-bent dialumene I, $\delta(\text{Al},\text{Al})$ 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 I. Al−Al bond distance, and computational bond order and delocalisation-index criteria all support the conclusion that the Al−Al bond in I is intermediate between single and double bonds, with bond order ≈ 1.3.

Why is dialumene I so different from I and II? We used DFT calculations on a set of minimal base-coordinated dialumenes with NHC or PMe₃ donors and hydride, phenyl, silyl or amino substituents (Table 1) to answer this question.[15]

The structures of the model dialumenes depend strongly on the substituent and Lewis base (NHC or PMe₃). Electropositive substituents (SiMe₃) provoke shorter Al−Al bonds, wider R−Al−L angles, and more planar structures. More electronegative (Si < H < Ph < 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 PMe₃ 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 $\text{R}(\text{L})\text{Al}=\text{Al}(\text{L})\text{R}$. In disilenes, trans-bend angles and Si−Si bond distances are correlated with the singlet-triplet energy gap ($\Delta E_{\text{ST}}$) of the notional or real silylene monomers, $\text{SiR}_2$.[17] We find that the same relationship applies to dialumenes: Al−Al bond dissociation energy increases as $\Delta E_{\text{ST}}$ for the monomeric $\text{R}(\text{L})\text{Al}$; fragments decreases (Figure S11). The result is that dialumene bond dissociation energy/geometry can be predicted based on properties of the $\text{R}(\text{L})\text{Al}$ (aluminyl) monomer.

We attribute the stronger and more planar Al=Al bonds of NHC- vs. PMe₃-coordinated dialumenes to the strong...
donor ability of the NHC, which raises the R(L)Al HOMO, narrowing $\Delta E_{\text{TS}}$. In contrast, the low dissociation energy for Me$_2$N(PMe$_3$)Al = Al(PMe$_3$)NMe$_2$, (2.1 kcal mol$^{-1}$) is explained by the large $\Delta E_{\text{TS}}$ for the Me$_2$N(PMe$_3$)Al fragment (32.4 kcal mol$^{-1}$).

Returning to dialumene 1, we can ascribe its extreme trans-bending to the electronegative/r-donating NR$_2$ substituent and narrow 85° N1-Al1-P1 angle enforced by the ligand, which both increase $\Delta E_{\text{TS}}$ 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 1A and 1C (Table S7). To explore the possible dissociation of 1, we turned to its solution-phase behaviour.

Dialumene 1 is predominantly dimeric in solution. Its $^{31}$P{[H] NMR spectrum at 300 K has one broad signal at $\delta$ 21.3 ($\Delta$ $\nu_{\text{g}}$ = 134 Hz) (Figure 4a). $^1$H 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-I, A-C (Figures 4a, S1), each of which must have distinct $^{31}$P signals. A and B are meso compounds with equivalent phosphorus centres—each will give rise to a singlet. IC has inequivalent phosphorus centres, so two $^{31}$P resonances (potentially doublets with $J_{\text{PP}}$). The pattern of DFT-predicted $^{31}$P signals confirms our stereochemical analysis (Figure 4c, S15).

At 300 K, the broad $^{31}$P{[H] resonance at $\delta$ 21.3 indicates diastereomers 1A-C are exchange. Cooling to 243 K, resolves this broad signal into two singlets (8 20.4 and 20.0). At 203 K, the higher field signal (8 19.5) broadens and approaches coalescence ($\Delta$ $\nu_{\text{g}}$ = 148 Hz).

The dynamic $^{31}$P{[H] NMR behaviour of 1 arises from a combination of intra- and intermolecular exchange processes that change diastereomers 1A-C. In the low temperature regime ($\leq$ 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$_{1A-1B}$ (11.3 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 $\Delta G_{\text{dissoc}}$ = + 7.1 kcal mol$^{-1}$). 2D H 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 $\Delta G$ for [1A + 1B] $\rightarrow$ 1C as 0.8 $\pm$ 0.2 kJ mol$^{-1}$ (0.19 $\pm$ 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 1 and II, 1 can react with alkenes and alkynes to form 4-membered aluminiumacycles. Treatment of 1 with ethene (1 atm) at room temperature results in rapid (5–20 mins) conversion to dialuminacylobutane 4 by formal [2+2] cycloaddition of the Al–Al and C–C bonds. Similarly, diphenylacetylene reacts with 1 to form dialuminacylobutene 5 (Scheme 2). $^{31}$P{[H] 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: $\delta$ 11.6 (d, $J_{\text{PP}}$ = 12 Hz), 11.5 (s), 11.5 (s), 11.4 (d, $J_{\text{PP}}$ = 12 Hz); 5: $\delta$ 11.0 (br s), 10.7 (s), 10.4 (s), 10.3 (br s); see S1).

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

|                  | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       | 1       |
|------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|                  | Al=Al   | L-Al=Al | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 | L=Al-P1 |
|                  | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     | [A]     |
| $\theta$         | 8.2     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     | 8.4     |
| $\Delta G_{\text{TS}}$ (dissoc) [kcal mol$^{-1}$][b] | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     | 23.1     |
| $\Delta E_{\text{TS}}$ (monomer) [kcal mol$^{-1}$] | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     | 19.2     |

[a] $L$ = NH$_2$, Imidazol-2-ylidine (C$_2$H$_4$N$_2$).[b] $\theta$ = trans-bend angle, see Figure 2. Unless otherwise noted, $t$ = 0°. Where two values are listed, complexes are unsymmetrically trans-bent. [c] corrected for basis set superposition error (Table S7). [d] $r$ = 17.8°. [e] $r$ = 20.5°. [f] $r$ = 7.9°. [g] $r$ = 19.8°.

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Figure 4. 

a) VT $^{31}P\{^1H\}$ NMR spectroscopy of 1 (161 MHz, [D$_8$]toluene) recorded at 203–300 K. 
b) Inversion at aluminium exchanges 1A and 1B. 
   - 1A (Al-R,S) $\delta_p$(DFT) = 15.1
   - 1B (Al-S,R) $\delta_p$(DFT) = 18.7

c) Dissociation and recombination exchanges diastereomers 1A/B and 1C
   - 1C (Al-R,S) $\delta_p$(DFT) = 18.1
   - 1C (Al-S,R) $\delta_p$(DFT) = 19.3

 d) Reaction profile for “trans-flip” isomerisation in 1

Figure 4. a) $^{31}P\{^1H\}$ NMR spectra of 1 (161 MHz, [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$_6$H$_6$ solvent).
X-ray crystallography reveals the geometry of the C$_2$Al$_2$ 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–C 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 Me$_3$SiC=CSiMe$_3$, the observed product is derived not from 1 but rather from its monomer, 3. On addition of Me$_3$SiC=CSiMe$_3$, purple solutions of 1 become yellow within three hours. $^{31}$P{$^1$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 Me$_3$SiC=CSiMe$_3$ is aluminacyclopropene 6 (Figure 5). 6 has the narrow Cl–Al–C2 angle expected for aluminacyclopropanes (42.05(9)°) and its Cl–C2 distance is typical for a double bond (1.367(2) Å). Cycloaddition reactions with alkenes 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 Me$_3$SiC=CSiMe$_3$, though with other alkenes 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 $\Delta E_{S,T}$ on the transient aluminyl monomers. This large $\Delta E_{S,T}$ 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.

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**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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Reversible Dissociation of a Dialumene

A highly trans-bent dialumene has marginal Al=Al double-bond character and, in solution, can dissociate into monomeric aluminy fragments. Reactivity studies reveal that both the dialuminene and aluminy monomer can be trapped by varying the reaction partner. DFT calculations elaborate the origins of the extreme trans-bending, weak Al=Al bond, and define substituent effects in dialumenes.