Reversible Reductive Elimination in Aluminum(II) Dihydrides

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Abstract: Oxidative addition and reductive elimination are defining reactions of transition-metal organometallic chemistry. In main-group chemistry, oxidative addition is now well-established but reductive elimination reactions are not yet general in the same way. Herein, we report dihydrodialanes supported by amidophosphine ligands. The ligand serves as a stereochemical reporter for reversible reductive elimination/oxidative addition chemistry involving AlI and AlII intermediates.

Oxidative addition to aluminum(I) compounds is now well-established, but examples of reductive elimination from AlII to AlI—and strategies to engineer it—are much scarcer. AlI compounds can be broadly divided into neutral and anionic classes. Of the neutral compounds, oxidative addition of E-H and E-X bonds has been reported for (Cp*Al)4 ([1], Figure 1), bulkier derivatives,[2] and for NacNacAl(I) ([2], Figure 1).[3] More recently, several anionic AlI compounds have been reported. Starting with the dimeric precursor to IV,[4] several AlI compounds supported by diamido ligands have been prepared.[5] Diverging from diimides, mixed amido/alkyl[6] and dialkyl[7] AlI anions are now also known. Unsurprisingly, the anionic systems are even more reactive than the neutral compounds and also exhibit oxidative addition chemistry.

Reductive elimination chemistry at aluminum is much less developed. This is unsurprising considering the lower stability of the AlI oxidation state compared to AlII. Nevertheless, there are notable examples of reductive elimination from AlII. Cp*2AlH reversibly reductively eliminates Cp*H to form Cp*AlI.[1b,8] Dipp NacNacAlH2 undergoes reversible oxidative addition to DippNacNacAlI ([2], Figure 1), though the product III has not been isolated (DippNacNac = (DippNCMe)2CH).[9] Most remarkably, the monomeric AlI anion IV reversibly inserts into the C–C bond of benzene (by oxidative addition).[10]

A notable characteristic of main-group systems is that base-coordination can induce reductive elimination. For example, treating Si2Cl6 with Lewis bases induces reductive elimination, to form SiCl4 and base-coordinated SiCl4.[11] Similar reactivity was recently reported for the dialane V, which disproportionates to AlI and AlII fragments upon treatment with Lewis bases.[12]

We have reported AlII dihydrides 1a and 1b supported by mixed-donor N/P ligands that exhibit flexible coordination behavior.[13] Notably, the same ligand class was used by Kato to mediate reversible oxidative addition to SiII compounds.[14] We thus wondered whether the amidophosphine ligands of 1a and 1b might prime AlII systems for reductive elimination.

The study of dialanes—AlII compounds—predates most work on AlI. Dialanes are prone to disproportionation to Al0 and AlIII, but this can be avoided using bulky substituents.[15] Despite the useful and extensive reactivity of aluminum-(III) hydrides,[16] there are scant examples of AlII hydrides.

Figure 1. Selected neutral and anionic aluminum(I) and aluminum(II) compounds exhibiting (reversible) reductive elimination/oxidative addition behaviour. Dipp = 2,6-diisopropylphenyl. (2,2,2)-cryptand = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.
Jones has reported the NHC-coordinated parent dialane Al₂H₄ as well as amidinato- and guanadino-coordinated dihydrodialanes. The reactivity of these compounds has not been explored.

Here, we report the reversible reductive elimination reactivity of dihydrodialanes supported by amidoophosphine ligands. The complex stereochemistry of the N/P ligand enables the detection of “hidden” reductive elimination processes by revealing the interconversion of multiple diastereomers by reversible reductive elimination.

We initially prepared the dihydrodialanes 3a and 3b by reduction of Al₃ dihydrides 1a and 1b (Scheme 1). Jones et al. used MgI reducing agents to access hydride-substituted dialanes. Accordingly, treatment of 1a or 1b with [MesNacNacMg]₂ forms the Al₃ dihydrido dialanes 3a and 3b, alongside the expected MgI hydride. The formation of 3a and 3b was slow (2–4 days at 70°C) and limited quantities of starting material were converted (1a: 22%, 1b: 12%). In practice, the dialanes 3a and 3b are accessed in better yields from reduction of the OTf substituted Al₃ hydrides 2a and 2b, which leads to good conversion to 3a and 3b (3a 43%, 3b 78%) and acceptable isolated yields (3a 20%, 3b 43%).

Reducing instead Al₃ dihydrides with decreased steric bulk at the nitrogen center—4a and 4b—further improves the reaction. The reduction to the dialanes 5a and 5b proceeds smoothly with quantitative conversion and in good yields (5a 81%; 5b 37%).

The Al₃ dihydrodialanes 3 and 5 are structurally very similar. X-ray crystallography reveals the expected four-coordinate tetrahedral geometry at the aluminum centers, which are κ'-coordinated by the amidoophosphine ligands. Although the parent dialane Al₂H₄ is predicted to favor hydride-bridged structures, base coordination induces H₂Al₂AlH₂ connectivity and terminal hydrides. Thus, crystallography reveals terminal hydride substituents; this is consistent with the observed infrared terminal Al-H stretches which, as would be expected, are at lower wavenumber than the dihydride precursors (e.g. 5: 1688–1725 cm⁻¹; 4: 1795–1802 cm⁻¹).

In all of the structures, stereocenters at aluminum and in the ligand lead to crystallographic disorder in the norbornene backbone due to co-crystallization of multiple diastereomers (see later). We also note that in solving the structure of 5a (Figure 2) we identified a cocystalized minor component with a substantially shorter Al-Al distance than 5a.

![Figure 2: X-ray crystal structure of 5a (ligand hydrogen atoms omitted). Thermal ellipsoids at 50% probability. Only the major component of the disordered ligand is shown (5a-B).](image)

Unsurprisingly, increasing the steric bulk at the nitrogen or phosphorus centers increases N-Al and P-Al distances (Table 1). The Al−Al bond distances follow the same general trend, though the Al−Al bond distance in the N-mesityl dialane 5b is longer than in its Dipp counterpart 3b (2.886(2) vs. 2.8386(18) Å).

The Al−Al bond distances in 3 and 5 are remarkably long. The shortest distance is found in 5a, which at 2.6585(16) Å is close to reported amidinato aluminum(II) hydride dimers (2.57–2.67 Å). The Al−Al distances in 3b and 5b are much longer than any previously reported for 3- or 4-coordinate dialanes, including that of the dialane(4) [(Bu₂Si)₂Al]. (2.751 Å). Since dialane(6) compounds on average have longer Al−Al distances than dialane(4) (Figure S1), the long Al−Al distances in 3 and 5 are consistent with the large steric bulk of the ligands.

To understand why the Dipp-substituted 3b has a shorter Al−Al bond than its Mes analogue 5b, we used an energy decomposition analysis. Multiple density functional theory

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**Table 1**: Selected bond distances [Å] and angles [°] from the X-ray structures of 3a, 3b, 5a, and 5b.

|          | Al−Al | N−Al | P−Al | N−Al−P |
|----------|-------|------|------|--------|
| 3a       | 2.7323(19) | 1.927(2) | 2.4977(11) | 85.12(7) |
| 3b       | 2.8386(18) | 1.939(2) | 2.4982(10) | 85.06(7) |
| 5a       | 2.6586(16) | 1.918(2) | 2.4677(9)  | 85.36(6) |
| 5b       | 2.886(2)  | 1.911(3) | 2.4671(11) | 86.51(8) |
methods, both with and without dispersion correction, underestimate the Al–Al bond in 5b by ≈0.3 Å (e.g., M062X-GD3/def2SVPP vs. X-Ray: 2.581 vs. 2.886(2) Å, Table S6). We ascribe the difference between predicted (gas phase) and experimental Al–Al distances to intermolecular dispersion interactions in the crystal structures. Indeed, a relaxed potential energy scan of the Al–Al distance in 5b (M062X-GD3/def2SVP) reveals a minimal cost of 15 kJ mol⁻¹ to increase the distance from the DFT-optimized value to the experimentally observed one. Consistent with this, SAPT(2)/6–311G* computations on models of 3b and 5b extracted from M062X/Def2SVPP optimized geometries (Figure S3) revealed stabilizing intramolecular interactions of near identical magnitude. Although 3b obtains greater stabilization from dispersion, this is offset by larger exchange interactions (Figure S3) leading to near identical stabilization overall (3b, 5b: −34.4, −32.7 kJ mol⁻¹). Thus, we believe the differing solid-state Al–Al bond distances in 3b/5b arise from intermolecular dispersion in the crystalline material.

³¹P{¹H} NMR spectroscopy of isolated 3 and 5 reveals they exist as mixtures of stereoisomers. Taking the NMes/P tBu₂ coordinated dialane 5a as an illustrative example, [21] crystalline samples dissolved in C₆D₆ give rise to a spectrum (Figure 3a.iii) containing three resonances; two singlets at δ 17.8 and 16.7 and a pair of mutually coupled doublets at δ 17.5 and 16.9 (JPP = 17.8 Hz). These resonances are ca. 10 ppm downfield from Al³⁺ dihydride starting material 4a. In the ¹H NMR spectrum, a broad resonance is observed for the Al–H groups at δ 4.6. Although the ¹H spectrum is complex, certain distinctive resonances (e.g., mesityl-CH₃ groups and norbornene CH₂ groups) again reveal the presence of three stereoisomers (see SI).

The spectroscopic situation is even more tortuous [22] when the reduction at room temperature of 4a by [MesNacNacMg]₂ is monitored by ³¹P{¹H} NMR spectroscopy. In addition to the three stereoisomers in the crystalline samples of dialane 5a, three other stereoisomers are also present, resulting in the observation of a total of 8 resonances (Figure 3a.i). To understand these spectra, it is necessary for us to consider the possible stereoisomers of 5a.

The dialanes 3 and 5 have 16 possible stereoisomers (although they contain 6 stereocenters, those on the norbornenyl backbone can be treated as a single center for our
purposes), which on inspection reduce to the six diastereomers A–F (Figure 3a) (see SI). In diastereomers A–C the phosphine ligands are located anti across the Al–Al bond, the variation between A–C arising from the relative orientation of the norbornene CH2 bridges (e.g. “cis” or “trans”). A–C are the diastereomers present in crystallographically characterized 3 and 5, and those observed spectroscopically in solutions of isolated 5a. Diastereomers A and B are meso compounds, due to the inversion center between the two Al atoms, rendering the phosphorus centers equivalent. We assign the singlets observed in the 31P[1H] NMR spectrum at δ 17.8 and 16.7 to these isomers. Diastereomer C has inequivalent phosphorus centers which we therefore assign to the doublets at δ 17.5 and 16.9.

Diastereomers D–F have the phosphorus ligands located syn about the Al–Al bond. These diastereomers are observed in solution alongside A–C when the room-temperature reduction of the dihydride precursors is monitored by NMR spectroscopy, and the three isomers should result in four 31P NMR signals. The first two isomers D and E have equivalent phosphorus centers; F has two inequivalent phosphorus centers which could be expected to couple. The four expected resonances are found as singlets at δ 18.1, 17.7, 17.6 and 16.9; no doublets are observed for F, which we attribute to a decrease in the magnitude of 3J_{ph} as the P-Al-Al-P torsion angle is reduced from ≈ 180° in C to ≈ 90° in F.

Consistent with the observation of all six diastereomers of 5a in solution, and the experimentally observed order of stability, DFT calculations (M062X/Def2SVPP) reveal that diastereomers A–F fall within 23 kJ mol⁻¹ of each other (Figure 3a). Notably, the isomer with the lowest calculated energy, 5a-C, is also found as the major species in solutions of crystalline 5a (≈ 60% 5a-C, remainder 5a-A and 5a-B). Isomers D–F with syn phosphorus centers are higher in energy than A–C.

We carried out an energy decomposition analysis to deconvolute ligand/ligand interactions and reveal the origins of the preference for isomers A–C. SAPT(2)/6–311G* computations were used to decompose the interactions between ligands in models of the 5a-C/5a-F structures (geometries extracted from M062X/Def2SVPP optimized structures, see SI). Substantial stabilizing non-covalent interactions were found to occur between the ligand N and P substituents (Figure S4). Whilst attractive dispersion interactions were found to occur between the ligand N and P substituents (Figure S4). Substantial stabilizing non-covalent interactions contribute to a decrease in the magnitude of 3J_{ph} (as could be expected by a k2-(amidophosphine)AlH2 compound related to 1a and 4a by AlII intermediate 6 (NDipp) or 7 (NMe2) reforms the dihydridalanes 3 and 5, thus regenerating two Al-based stereocenters. Over time these processes bring mixtures of A–F to thermodynamic equilibrium.

Besides reversible reductive elimination, other mechanisms for inversion of stereochemistry at aluminum are conceivable. We can discount a mechanism involving inversion of stereochemistry at aluminum by reversible phosphine dissociation from one Al center on the basis that this pathway is unfavorable. We have already reported that the energetic cost for phosphine dissociation for a k2-(amidophosphine)AlH2 compound related to 1a and 4a by AlII radical does not generate the AlIII dihydrides 1 or 4 (as could be expected by H-atom abstraction from nBu3SnH by an AlII radical).

Nikonov et al. reported the reductive elimination of Al–H bonds from AlIII. In this case, the equilibrium constant for reductive elimination is large enough to detect the AlIII and AlII compounds 1 and 3 alongside the AlIII dihydride. In contrast, from 3 or 5 we did not observe AlII or AlIII species in equilibrium, indicating the equilibrium constant for their formation from 3 or 5 is low. Nevertheless, there is further experimental evidence for reversible Al–H reductive elimination from dihydridalanes 3 and 5.

When a mixture of the nBu3SnH does not generate the AlII dihydrides 1 or 4 as could be expected by H-atom abstraction from nBu3SnH by an AlII radical)
The formation of the Al\textsuperscript{III} dihydride by-products is explained by reductive elimination of Al–H bonds from the dialane product 3 under reaction conditions.

Very few reactions of dihydrodialanes or dialane(6) compounds have been reported. We thus investigated some rudimentary reactivity of the dihydrodialane 5a. Reported dialane(4) compounds are oxidized by iodine\textsuperscript{[15]}\textsuperscript{[8]} In contrast, when 5a is treated with iodine the Al–H bonds are selectively iodinated in preference to the Al–Al bond, and diiododialane 9 is formed instead (Scheme 3). Crystallization of 9 from toluene solution allowed its solid-state structure to be determined, revealing that replacement of the Al–H substituents with iodides has minimal impact on the Al–Al bond distance or other structural features compared to 5a (Al–Al 5a: 2.6586(16) Å; 9: 2.664(3) Å).

In summary, we have prepared a series of N,P-coordinated dihydrodialanes. Increasing the steric bulk of the N or P substituents lengthens the Al–Al bond distance. The stereo centres of Al\textsuperscript{III} compounds 3 and 5 reveal the interconversion of diastereomers by reversible reductive elimination. This suggests that stereoactive ligands could be useful tools for probing “hidden” reversible reductive elimination processes elsewhere in main-group chemistry, similar to the use of chiral silanes as mechanistic probes in B(C\textsubscript{6}F\textsubscript{3})\textsubscript{4} chemistry\textsuperscript{[23]} We are now investigating whether greater control of reductive elimination is possible by varying the nature of the donor ligand (phosphine in 3 and 5).

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** aluminum · low oxidation state · oxidative addition · reduction · reductive elimination

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The minor component has an Al–Al distance of 2.64(2), 0.09 Å shorter than 5a. We believe it could arise from a co-crystallised Al dimer. For further details, see SI.

The behavior of 3a, 3b and 5b is consistent with of 5a.

And torturous.