Comproportionation of a dialuminyne with alane or dialane dihalides as a clean route to dialuminenes

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Comproportionation of a dialuminyne with alane or dialane dihalides as a clean route to dialuminenes

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**Dialuminenes RAlAlR (R = m-terphenyl or bulky aryl) react with the aromatic solvents (e.g. benzene or toluene) in which they dissolve. We synthesized -SiMe$_3$ substituted derivatives of known terphenyl ligands to increase their solubility in alkanes which have lower reactivity than arenes. The new dialuminene was synthesized via the comproportionation reaction of Na$_2$(AlAr^{iPr4}-4-SiMe$_3$)$_2$ (3) (Ar^{iPr4}-4-SiMe$_3$ = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$-4-SiMe$_3$C$_6$H$_2$) with either the diiodide Al(Et$_2$O)I$_2$Ar^{iPr4}-4-SiMe$_3$ (1) or the 1,2-diiododialane 4-SiMe$_3$Ar^{iPr4}(I)Al-Al(I)Ar^{iPr4}-4-SiMe$_3$ (2). This cleanly generates the dialuminene 4-SiMe$_3$Ar^{iPr4}AlAlAr^{iPr4}-4-SiMe$_3$ which was trapped as its cycloaddition product (4) with benzene. Even in non-aromatic, essentially inert, solvents red 4 decomposes to colorless solutions. This indicates that the instability of the free dialuminene is an inherent property rather than arising from of the method of synthesis, solvent employed, or the presence of impurities.**

The recognition in the 1970s and 80s that the heavier p-block elements can form multiple bonds to each other[1–3] led to the synthesis of series of alkene and alkyne analogues derived from the heavier members of the group 13, 14, and 15 elements.[4] The compounds with multiple bonds between aluminium atoms are of special interest due to their very high reactivity[5–9] and their calculated diradical character.[10] However this apparent diradical character makes them difficult to isolate as neutral species. Thus, many structurally characterized Al-Al multiply bonded molecules (Scheme 1) are anionic[11–13] and derived from the reduction of a bonding π-type LUMO in a neutral species. Alternatively, complexation of the aluminium atoms by Lewis bases confers stability on the multiple bonded
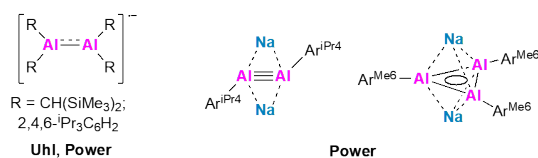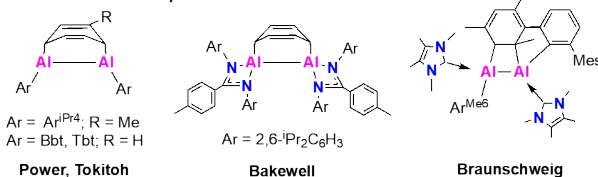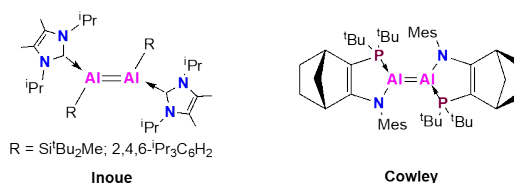

Scheme 1. Representative Al-Al multiple bonded species. Ar^{iPr4} = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$, Ar^{Me6} = 2,6-Mes$_2$C$_6$H$_3$, Bbt = 2,6-{CH(SiMe$_3$)$_2$}$_2$C$_6$H$_3$, Tbt = 2,6-{CH(SiMe$_3$)$_2$}$_2$-4-^{t}BuC$_6$H$_3$.

compounds.[14–16] Another important compound class related to the multiple bonded species are the cycloaddition derivatives of Al=Al bonded moieties and solvent arenes.[17–21] This is a reversible process in some cases.[18–20]

The first isolated Al-Al π-bonded compounds resulted from one electron reduction of the tetraorganodialanes R$_2$Al-AlR$_2$ (R = CH(SiMe$_3$)$_2$, C$_6$H$_3$-2,4,6-^{i}Pr$_3$).[12,22] Their EPR spectra showed the unpaired electron to be located predominantly in the π-type SOMO between the two Al atoms thereby generating multiple bond character and shortened Al-Al bonds.[11,12]

While the sterically demanding terphenyl ligand Ar^{iPr4} (Ar^{iPr4} = 2,6-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) allowed the isolation of the neutral dimetallenes Ar^{iPr4}EEAr^{iPr4} (E = Ga–Tl)[23–25] which dissociate to :EAr^{iPr4} monomers in solution, the Al congener Ar^{iPr4}AlAlAr^{iPr4}

could not be isolated from hexanes or ether, due to its poor solubility.[17] Rather, it could only be trapped and characterized as its cycloaddition products with toluene or $Me_3SiCCSiMe_3$ following the reduction of the halide derivative AlI_2Ar^{iPr4} in Et_2O.[17,26] However, the dianionic dialuminyne $Na_2(AlAr^{iPr4})_2$ and the trimeric $Na_2(AlAr^{Me6})_3$ (Ar^{Me6} = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) were isolable by reduction of AlI_2Ar^{iPr4} and AlI_2Ar^{Me6} with excess Na metal.[13] The anions contained in these salts are analogues of the corresponding Ga species $Na_2(GaAr^{iPr6})_2$[27] (Ar^{iPr6} = 2,6-(2,4,6-$^iPr_3C_6H_2)_2C_6H_3$) and $Na_2(GaAr^{Me6})_3$[28] isolated earlier by Robinson and coworkers. By increasing the steric demand of the terphenyl ligand on the group 13 elements, the crystalline metallanediyls :EAr^{iPr6} (E = In, Tl)[29,30], :$GaAr^{iPr8}$ (Ar^{iPr8}= 2,6-(2,4,6-$^iPr_3C_6H_2)_2$-3,5-$^iPr_2C_6H$) and :Ga(2,6-(2,6-$^iPr_2C_6H_3)_2$-3,5-$^iPr_2C_6H$)[31] were isolated. Following these results, we recently reported the synthesis of a stable one-coordinate aluminium species :$AlAr^{iPr8}$.[32] A favorable dimerization energy of :$AlAr^{iPr8}$ to yield $Ar^{iPr8}AlAlAr^{iPr8}$ (ΔG = -20 kJ mol^{-1}) was calculated although this dimer was not isolated and only the monomer :$AlAr^{iPr8}$ was obtained from solution. Nonetheless, calculations suggested $Ar^{iPr8}AlAlAr^{iPr8}$ as the reactive species with H_2 (cf. monomeric :$GaAr^{iPr8}$ does not react with H_2 although the dimer $Ar^{iPr4}GaGaAr^{iPr4}$ is highly reactive).[33]

Tokitoh and coworkers isolated dialuminene-benzene cycloaddition products by reduction of the 1,2-dibromodialanes Bbt(Br)Al-Al(Br)Bbt (Bbt = 2,6-{CH(SiMe_3)_2}_2C_6H_3) and Tbt(Br)Al-Al(Br)Tbt (Tbt = 2,6-{CH(SiMe_3)_2}_2-4-$^tBuC_6H_2$) with KC_8 in benzene.[18,34] They further showed that these complexes act as synthetic equivalents to dialuminenes by the reversible dissociation of the benzene to yield ArAlAlAr in solution. The complexed benzene could also be irreversibly exchanged with naphthalene, anthracene, or $Me_3SiCCSiMe_3$ while the reaction with H_2 to give {AlH(μ-H)Ar}_2 (Ar = Bbt, Tbt) was also observed under ambient conditions.[19]

As mentioned above, stable compounds containing Al=Al double bonds were only recently isolated through coordination of Lewis bases to the reactive Al centers and are so far limited to a few examples. Thus Inoue and coworkers reported the carbene complexed dialuminenes (NHC)RAl=AlR(NHC) (R = Si$^tBu_2$Me, 2,4,6-$^iPr_3C_6H_2$; NHC = 1,3-diisopropyl-4,5-dimethyl-imidazolin-2-ylidene)[14,15] and Cowley and coworkers reported the synthesis of an amidophosphine supported dialuminene which reversibly dissociates to monomers in solution.[16] However the coordination of Lewis bases to the aluminium atoms does not guarantee stability of the Al=Al bonded moiety. The amidinate supported dialuminene (Am^{Dipp})Al=Al(Am^{Dipp}) (Am^{Dipp} = C{N(2,6-$^iPr_2C_6H_3$)}_2(4-MeC_6H_4)) of Bakewell and coworkers, generated by hydrogen abstraction from AlH_2Am^{Dipp} by Al(BDI^{Dipp}) (BDI^{Dipp} = C{C(Me)N(2,6-$^iPr_2C_6H_3$)}_2) at 80°C, went on to react with the benzene solvent to give the respective cycloaddition product.[21] Reduction of the carbene supported terphenyl aluminium diiodide Al(NHC')I_2Ar^{Me6} (NHC' = 1,3,4,5-tetramethylimidazol-2-ylidene) apparently gave Ar^{Me6}(NHC')AlAl(NHC')Ar^{Me6} which added across a C=C bond of a flanking aryl ring, and the monomer Al(NHC')Ar^{Me6} which ring opened the benzene or toluene solvent to give dihydropentalene type structures.[20]

Despite these advances, compounds of the type RAlAlR free of complexing ligands remain unisolated. Recent reports on the synthesis of the one-coordinate Al species[32,35,36] have illustrated the importance of reducing agent selection to access low oxidation state Al compounds—the products are obtained only when Na metal dispersed on NaCl powder is used. As the chemistry of dialuminenes remains underdeveloped, we revisited their synthesis with the objective of developing isolable ArAlAlAr species that are soluble in solvents with which they do not react. The direct stoichiometric reduction of the aluminium iodide precursors with alkali metals did not yield the targeted dialuminene, instead decomposition occured with elimination of the terphenyl arene. This led us to investigate alternative methods of their preparation free of alkali metal reductants. We found that the comproportionation reaction between a dialuminyne salt and aluminium iodides proceeded rapidly in benzene to cleanly afford a dialuminene-benzene complex. However, the comproportionation reaction in nonreactive ether or alkane solvents led to decomposition of the mixture, indicating an inherent instability of the dialuminene. Despite this, the reaction offers a new synthetic route to reactive Al-Al multiple bonded species.

Using the -$SiMe_3$ modified ligand Ar^{iPr4}-4-$SiMe_3$ (Ar^{iPr4}-4-$SiMe_3$ = 2,6-(2,6-$^iPr_2C_6H_3)_2$-4-$SiMe_3C_6H_2$), we anticipated that the extra aliphatic groups would increase the solubility of ArAlAlAr sufficiently to permit its handling in non-aromatic solvents with which it does not react (e.g. hexane, ether). The Hammett constant σ_{para} = -0.07 for -$SiMe_3$[37] also suggested it would have minimal electronic effects on the Al=Al moiety in comparison to the Ar^{iPr4} derivative (σ_{para} for H = 0). Addition of $LiAr^{iPr4}$-4-$SiMe_3$ to AlH_3NMe_3 in Et_2O afforded the aluminate salt $Li(Et_2O)AlH_3Ar^{iPr4}$-4-$SiMe_3$ as a white solid. Subsequent treatment with CH_3I (5 eq) gave the iodide $Al(Et_2O)I_2Ar^{iPr4}$-4-$SiMe_3$ (**1**). The Al-I distances in **1** (Figure 1) are 2.5288(7) Å and 2.5578(7) Å, an Al-C bond length of 1.9936(19) Å and Al-O bond being 1.8703(15) Å. Treating **1** with KC_8 (1.3 eq) gave the yellow 1,2-diiododialane 4-$SiMe_3Ar^{iPr4}$(I)Al-Al(I)Ar^{iPr4}-4-$SiMe_3$ (**2**) (Scheme 2). The Al-Al distance of 2.604(2) Å in **2** is nearly identical to that of Ar^{iPr4}(I)Al-Al(I)Ar^{iPr4} (2.609(2)Å). The I atoms are disordered over two sites with Al-I distances of 2.5083(11) and 2.5354(13) Å but in each case the coordination around the Al atom is trigonal planar. The UV-Visible spectrum of **2** showed a single absorbance at 386 nm.
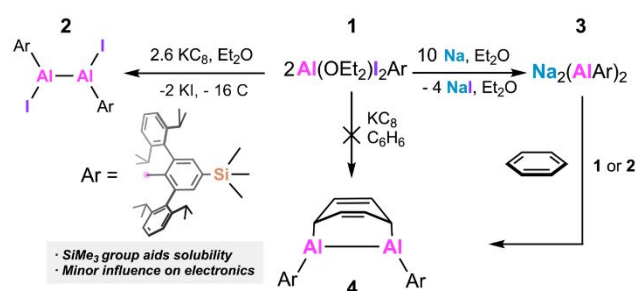
Scheme 2. Synthetic routes to compounds **2**, **3** and **4**.
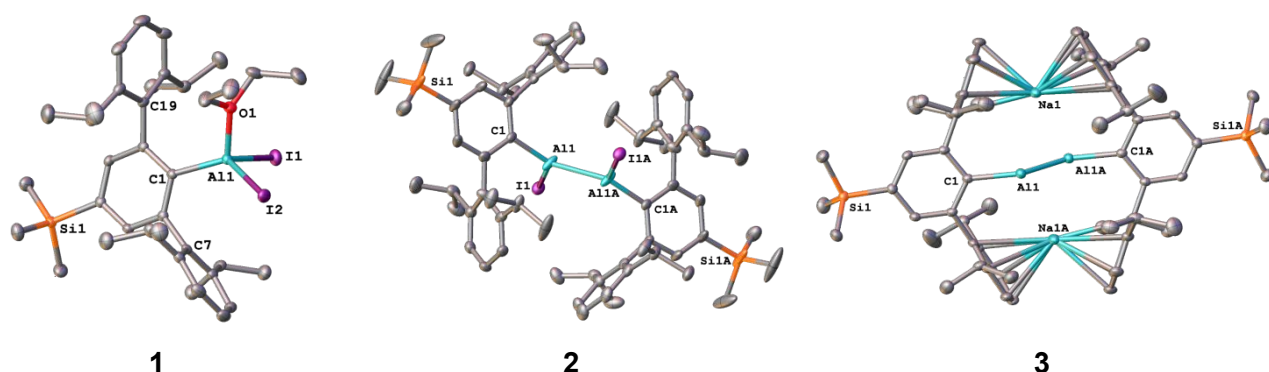
1   **2**   **3**

Figure 1. Thermal ellipsoid plots (30%) of **1** (left), **2** (middle), and **3** (right). Disordered atoms, solvent molecules, and hydrogen atoms are not shown. Selected bond distances (Å) and angles (°): [**1**]: Al(1)-I(1): 2.5287(7), Al(1)-I(2): 2.5578(8), Al(1)-C(1): 1.993(2), Al(1)-O(1): 1.8704(16), C(1)-Al(1)-I(1): 124.12(6), C(1)-Al(1)-I(2): 108.44(6), I(1)-Al(1)-I(2): 106.87(2), I(1)-Al(1)-O(1): 104.87(5) I(2)-Al(1)-O(1): 96.68(5). [**2**]: Al(1)-Al(1A): 2.604(3), Al(1)-I(1): 2.5087(17), Al(1)-C(1): 1.955(4), C(1)-Al(1)-Al(1A): 130.09(12), C(1)-Al(1)-I(1): 113.73(11), I(1)-Al(1)-Al(1A): 115.95(10), C(1)-Al(1)-Al(1A)-C(1A): 180. [**3**]: Al(1)-Al(1A): 2.4255(9), Al(1)-C(1): 2.0410(15), Al(1)-Na(1): 3.1403(8), Al(1)-Na(1A): 3.1138(9), Na-C(avg):2.968, C(1)-Al(1)-Al(1A)-C(1A): 180.

The reduction of **1** with excess Na in the form of either Na mirror or 5% w/w Na/NaCl in Et$_2$O gave a dark green-brown solution. Removal of the volatile components and extraction of the residue with hexanes and then toluene gave two fractions: the hexanes extract, despite having a dark red color, contained 4-SiMe$_3$-Ar^{iPr4}H as the only identifiable product (isolated yield 62% based on **1**), indicating a significant amount of decomposition under reducing conditions. From the dark green toluene extract the anionic dialuminyne complex Na$_2$(4-SiMe$_3$-Ar^{iPr4}AlAlAr^{iPr4}-4-SiMe$_3$) **3** was isolated as dark green crystals in ca. 30% yield. The structure of **3** shows two crystallographically independent molecules with Al-Al distances of ca. 2.43 Å which is near to the 2.428(1) Å in Na$_2$(Ar^{iPr4}AlAlAr^{iPr4}).[13] The Na-Al distances are in the range 3.1016(8) to 3.1403(8) Å, and the average Na-C distance is 2.968 Å. The UV-Visible spectrum of **3** displays absorbances at 344 nm, 470 nm, and at 612 nm with a shoulder at 660 nm (cf. 354, 456, and 600 nm in Na$_2$(Ar^{iPr4}AlAlAr^{iPr4}). Overall, the new compounds showed little deviation from their Ar^{iPr4} substituted counterparts while having the desired increased solubility properties. However, attempts to reduce **1** or **2** with alkali metals to the dialuminene 4-SiMe$_3$-Ar^{iPr4}AlAlAr^{iPr4}-4-SiMe$_3$ under a variety of conditions were unsuccessful.

As a result of the difficulty with direct reduction to the dialuminene (see above), we tested the comproportionation reaction of the dialuminyne **3** with the aluminium iodides **1** or **2**. Treating **3** with excess **1** in C$_6$D$_6$ resulted in the formation of **2** with a trace amount of a new product that was later determined to be the dialuminene-benzene cycloaddition species **4**. Mixtures of **1** or **2** with a slight excess of **3** in C$_6$D$_6$ gave dark brown solutions that indicated consumption of the iodide materials along with formation of **4** in the ^{1}H NMR spectra. On a preparative scale an equimolar mixture of **1** and **3** was dissolved in benzene, resulting in rapid formation of a red solution. Filtration and concentration of the solution to ca. 1 mL followed by storage at ca. 8°C afforded red crystals of the dialuminene-benzene cycloaddition complex **4** (Figure 2). ^{1}H NMR monitoring of the reaction indicated the formation of no other Ar^{iPr4}-4-SiMe$_3$ substituted species except **4**.

The Al-Al bond length in **4** is 2.5585(6) Å with Al-C$_{ipso}$ distances of 1.9681(14) and 1.9743(13) Å while the Al-C distances to the bridging cyclohexadiene moiety are 2.0000(15) and 1.9976(14) Å. The Al atoms are almost planar coordinated (Σ°Al = 358.57(9)°, 359.57(9)°) and the C(67)-Al(1)-Al(2)-C(70) torsion angle is 34.18(9)°. UV-Visible spectroscopy in hexanes showed an absorbance at 323 nm with a weaker shoulder spanning the range ca. 430 to 530 nm. A broad absorbance in the same region was found earlier for the BbtAlAlBbt benzene complex mentioned above.[18]

The isolation of **4** is consistent with the growing number of cycloaddition products that have been isolated from the reaction of arenes and Al=Al bonded species.[17,18,20,21] Its formation indicates that the dialuminene ArAlAlAr is obtained cleanly from the reaction between **3** and **1** or **2**. The direct reduction of **1** in benzene with ≥2 eq. of alkali metal reducing agents did not afford the dialuminene but instead gave red solutions for which ^{1}H NMR spectroscopy showed the
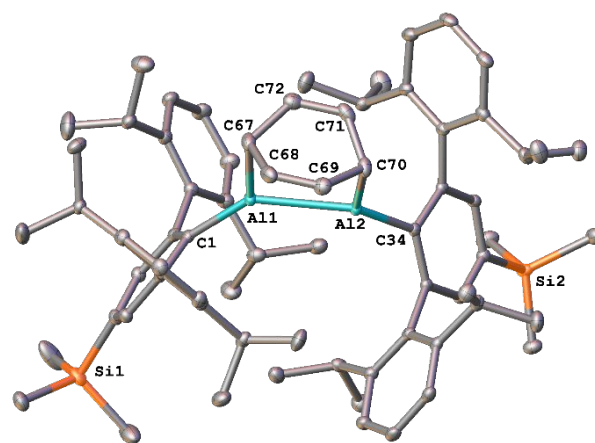
Figure 2. Thermal ellipsoid plot (30%) of **4**. Selected bond lengths (Å) and angles (°): Al(1)-Al(2): 2.5585(6), Al(1)-C(1): 1.9681(14), Al(2)-C(34): 1.9743(13), Al(1)-C(67): 2.0000(15), Al(2)-C(70): 1.9976(14), C(67)-C(68): 1.500(3), C(68)-C(69): 1.337(2), C(69)-C(70): 1.502(2), C(70)-C(71): 1.498(2), C(71)-C(72): 1.338(2), C(72)-C(67): 1.500(2), C(1)-Al(1)-Al(2): 136.83(4), C(1)-Al(1)-C(67): 128.87(6), C(67)-Al(1)-Al(2): 93.87(4), C(34)-Al(2)-Al(1): 136.76(4), C(34)-Al(2)-C(70): 127.02(6), C(70)-Al(2)-Al(1): 94.79(4).

generation of the free arene 4-SiMe$_3$-Ar^{iPr4}H as the major product with no signals assignable to **4**.

Complex **4** was observed to be soluble in benzene and cyclohexane as well as being sparingly soluble in hexanes or ether. While **4** showed no signs of decomposition in benzene after several days, solutions of **4** in hexane or cyclohexane gradually lost their color overnight. This is probably due to reversible dissociation of **4** and a shift of the equilibrium toward benzene and the free dialuminene, which subsequently decomposes or rearranges. Attempts to comproportionate **1** or **2** with **3** in Et$_2$O or hexanes afforded a dark purple solution that also rapidly faded to colorless. We conclude that the instability of the dialuminene 4-SiMe$_3$-Ar^{iPr4}AlAlAr^{iPr4}-4-SiMe$_3$ is an inherent property of the compound rather than an artifact of the synthetic route employed or impurities in the system.

In summary, we have shown that the dialuminene 4-SiMe$_3$-Ar^{iPr4}AlAlAr^{iPr4}-4-SiMe$_3$ is cleanly generated stoichiometrically in solution via the reaction of **1** or **2** with **3**. Its decomposition in hexanes or ether indicates that it is inherently unstable, probably as a result of its singlet diradical character.[10,38] However, it can be trapped as **4** by its reaction with benzene. Further investigations into the use of **3** as a reducing agent to generate Al-Al multiply bonded species are underway.

Conflicts of interest

There are no conflicts to declare.

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