Synthesis and reactivity of bis-pentamethylcyclopentadienyl diiododialane $(Cp^*AlI)_2$: an aluminium(II) precursor to $(Cp^*Al)_4$†

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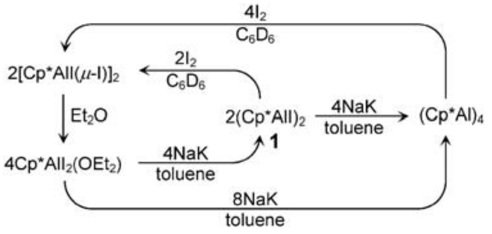
Use of an alternative aluminium(III) starting material has led to the isolation of a new aluminium(II) diiododialane, which functions as an intermediate in the synthesis of $(Cp^*Al)_4$, reacts oxidatively with methyllithium, and undergoes oxidative cleavage of the Al–Al bond with an aryl azide.

Since the discovery of $(Cp^*Al)_4$ (Cp* = pentamethylcyclopentadiene) over 15 years ago by Schnöckel and coworkers,[1] several syntheses of complexes bearing aluminium atoms in the +1 formal oxidation state have been published including tetrameric aluminium clusters, monomeric aluminium–carbene analogues, and a dimeric complex which has been proposed to contain an Al–Al double bond.[2] The reactivity of $[Cp^*Al]_4$ itself is quite remarkable, with examples including the formation of aluminium–transition metal and aluminium–lanthanide bonds,[3] as well as a number of aggregated and base-stabilized iminoalanes.[4]

Interestingly, no aluminium(II) intermediate has been reported during reduction from dimeric $[Cp^*AlI(\mu\text{-}I)]_2$ to $(Cp^*Al)_4$,[5] in spite of considerable literature precedent for aluminium(II) complexes. The first structurally characterized example of an isolable molecule with an Al–Al bond, R_2AlAlR_2 (R = $CH(SiMe_3)_2$),[6] exists in the +2 formal oxidation state, as does $Trip_2MMTrip_2$ (M = Al, Ga; Trip = 2,4,6-i-$Pr_3C_6H_2$).[7] $Cp^*{}_3Al_5I_6$, a related complex formed from Al_2I_6 and $\frac{3}{4}(Cp^*Al)_4$, has an average formal oxidation state for aluminium of 1.8.[8] Dinuclear aluminium compounds in the +2 formal oxidation state supported by Cp* ligands would be useful starting materials for syntheses of aggregated or monomeric aluminium imides, a Group 13 analog of $[Cp^*Zn–ZnCp^*]$,[9] and would provide valuable mechanistic information regarding the formation of $(Cp^*Al)_4$.

Our attempts to isolate an aluminium(II) product from $[Cp^*AlI(\mu\text{-}I)]_2$ by using half the amount of Na/K alloy than is called for in the synthesis of $(Cp^*Al)_4$ resulted in intractable mixtures. Nevertheless, turning to monomeric aluminium(III) starting materials, we discovered that reduction of $Cp^*AlI_2(OEt_2)$[10] with one equivalent of Na/K alloy in toluene afforded the diiododialane product $(Cp^*AlI)_2$ (**1**) as air-sensitive yellow blocks from toluene in a moderate yield (Scheme 1). The X-ray crystal structure (Fig. 1)‡ reveals a shorter Al–Al bond distance (2.5321(10) Å) than was previously observed in the related complex $(Ar'AlI)_2$ (2.609(2) Å) (Ar′ = C_6H_3-2,6-$Dipp_2$; Dipp = C_6H_3-2,6-Pr^i).[2d] The Al–Al bond distance is generally shorter than that of most neutral aluminium(II) complexes without bridging ligands, and is within error of the shortest Al–Al distances observed in $(Al_2I_2{\cdot}OEt_2)_2$ (2.52(2) Å) and $(Al_2Br_2{\cdot}MeOPh)_2$ (2.527(6) Å).[11] The torsion angle between the two iodides is 91.14(3)°, which is unlike the *trans*-orientation observed previously in $(Ar'AlI)_2$, but is presumably due to the large difference in the steric influences of Cp* and terphenyl ligands.[2d] The Cp* ring and methyl carbon atoms in **1** are essentially coplanar, with a maximum out-of-plane deviation in the ring at C(5) of 0.014 Å, and a maximum 4.78° bend away from aluminium observed at C(9). The aluminium–ring carbon distances fall in a narrow range from 2.173(2) to 2.344(3) Å, consistent with η^5-coordination of both Cp* ligands.



Scheme 1

Diiododialane **1** can be reduced further using two equivalents of Na/K alloy in toluene to produce $(Cp^*Al)_4$ in mode-

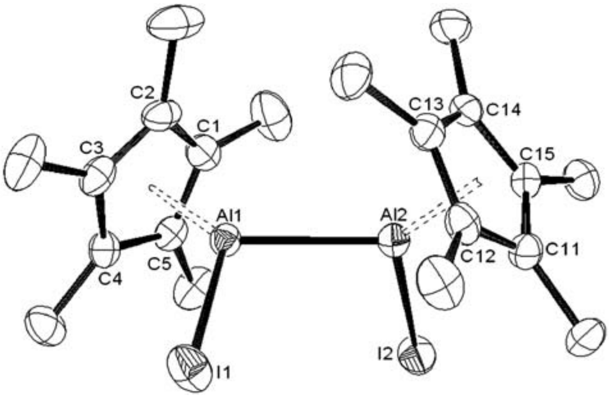


Fig. 1 Molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

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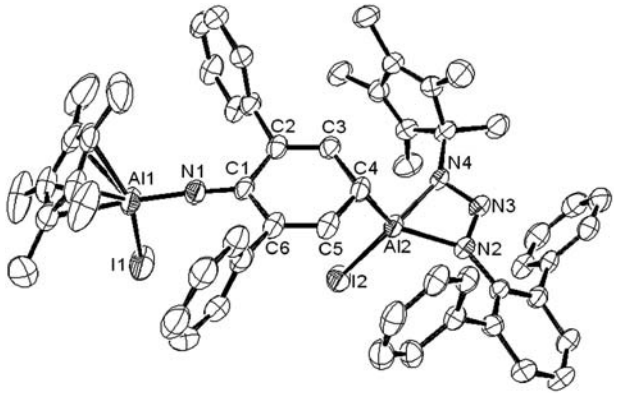


Fig. 2 Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, a pentane molecule, and the aryl methyl groups are removed for clarity.¶

rate yield. Oxidation of **1** with iodine in C_6D_6 resulted in $[Cp^*AlI(\mu\text{-}I)]_2$, as identified by ^1H and ^{27}Al NMR spectroscopy. No signals attributable to **1** were observed during oxidation of $[Cp^*Al]_4$ with two equivalents of iodine; rather, ^1H and ^{27}Al NMR spectroscopy revealed only a mixture of $(Cp^*Al)_4$ and $[Cp^*AlI(\mu\text{-}I)]_2$. These results are summarized in Scheme 1.

In addition to probing the reduction and oxidation chemistry of **1**, we also explored ligand substitution on the aluminium atoms and reactions at the Al–Al bond. Stirring a solution of **1** and two equivalents of diethyl ether-free MeLi in toluene led to the formation of the dinuclear aluminium complex $[Cp^*AlMe(\mu\text{-}I)]_2$ (**2**), which was isolated as colorless plates from pentane in 32% yield. A black precipitate formed during the course of the reaction, however the exact nature of the byproducts could not be determined. Formation of $(Cp^*Al)_4$ was not observed by ^1H or ^{27}Al NMR. The molecular structure of **2** can be regarded as the iodide analogue of $[Cp^*AlMe(\mu\text{-}Cl)]_2$,[12] with each aluminium in a pseudo-tetrahedral environment provided by two bridging iodides, one terminal methyl group, and a Cp* ligand (see ESI†). In spite of the different bridging halogen, the bond lengths and angles in **2** are nearly identical to those observed in $[Cp^*AlMe(\mu\text{-}Cl)]_2$, which also exhibits an η^3 Cp*–Al coordination mode.§

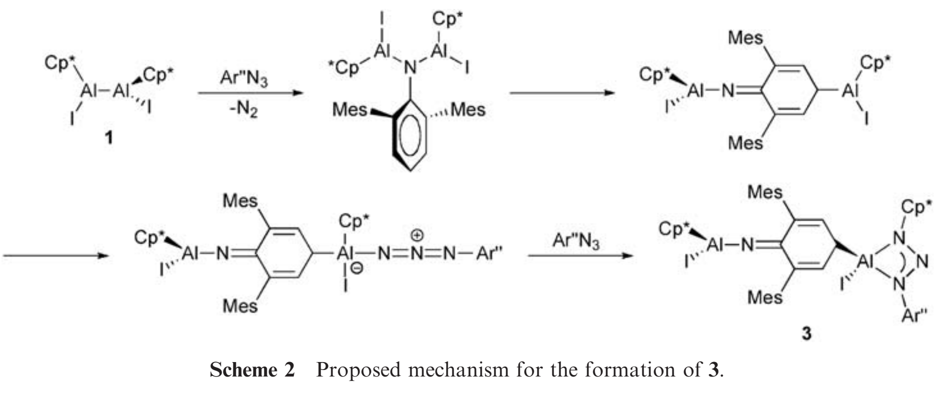
Imides of the Group 13 metals have been formed by oxidation of an M^I–M^I bond with alkyl and aryl azides,[4,13] however no examples of M^{II}–M^{II} bond oxidation with azides have been reported. Treatment of **1** with $2Ar''N_3$ ($Ar'' = C_6H_3\text{-}2,6\text{-}Mes_2$, $Mes = C_6H_2\text{-}2,4,6\text{-}(CH_3)_3$) led to the formation of the unusual complex **3** in 58% yield, which bears both three-coordinate and four-coordinate aluminium atoms (Fig. 2). The mechanism (Scheme 2) leading to **3** may involve oxidation of the Al–Al bond in **1** by $Ar''N_3$ to form a dimeric imino alane $(Cp^*(I)Al)_2NAr''$ intermediate, as has been similarly observed by Roesky and coworkers in reactions of $(Cp^*Al)_4$ and R_3SiN_3 ($R = Pr^i$, Ph, Bu^t).[14] Following migration of one aluminium fragment to the *para*-position on the central aryl ring, the electron deficient *para*-aluminium atom is trapped by another molecule of $Ar''N_3$. Finally, Cp* migrates to the adjacent nitrogen of the azide and the triazene ring forms.[15]

The Al(1)–Cp* ring carbon bond distances and angles are consistent with an η^5-coordination mode. The Al(1)–N(1) bond length (1.734(3) Å) in **3** is among the shortest known,[16] and the Al(1)–N(1)–C(1) angle (172.6(3)°) is nearly linear. These data are suggestive of significant lone-pair π-donation from N(1) onto Al(1), and explains why Al(1) does not bind the additional equivalent of $Ar''N_3$ as does the more electron-deficient Al(2).

The distances N(1)–C(1) (1.271(5) Å), C(2)–C(3) (1.354(5) Å), and C(5)–C(6) (1.353(5) Å) are typical of non-aromatic double bonds, while the remaining ring carbon–carbon distances (range = 1.457(6) to 1.491(6) Å) are typical alkane distances.[17] The environment at C(4) deviates only slightly from an idealized tetrahedral geometry with angles ranging from 103.9(3)° to 113.2(3)°. The four-membered AlN_3 ring is almost planar, with bond lengths Al(2)–N(2) (1.928(3) Å), Al(2)–N(4) (1.942(3) Å), N(2)–N(3) (1.327(4) Å), and N(3)–N(4) (1.297(4) Å), which suggest a delocalized κ^2 amidinate-like azide coordination mode. These bond distances and angles are consistent with the assignment of single and double bonds depicted in Scheme 2.

$Cp^*GaI_2(OEt_2)$ was prepared as a potential precursor to a gallium analog of **1**, and its reduction with one equivalent of Na/K alloy in toluene gave yellow crystals following filtration and crystallization from toluene. The product was identified by ^1H NMR spectroscopy and X-ray crystallography as the mixed gallium(I/III) complex $Cp^*GaGa(I_2)Cp^*$, previously reported by Jutzi and coworkers.[18]

To summarize, a new, reactive Al(II) diiododialane complex **1** has been prepared. In addition to functioning as a viable intermediate in the synthesis of $(Cp^*Al)_4$, complex **1** undergoes substitution chemistry and reacts with azides to form an



Scheme 2 Proposed mechanism for the formation of **3**.

unusual imino alane product. We are presently focusing on elucidation of the mechanisms leading to the formation of **2** and **3**, and a study the reactivity of **1** towards alkyl and aryl azides, long chain alkyl transfer reagents, and halide abstraction reagents.

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Notes and references

‡ Crystal data for **1**: $C_{20}H_{30}Al_2I_2$, M_r = 578.22, T = 113(2), monoclinic, space group $P2_1/n$, a = 8.7521(12), b = 14.660(2), c = 18.022(2) Å, β = 93.253(2)°, V = 2308.7(5) Å^3 , μ = 2.801 cm^{-1}, Z = 4, 10 124 reflections measured, 3886 unique (R_{int} = 0.0202), final R indices [$I > 2\sigma(I)$] $R(1)$ = 0.0202, w$R2$ = 0.0528. CCDC 684 336. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b806804f

§ Crystal data for **2**: $C_{22}H_{36}Al_2I_2$, M_r = 608.27, T = 157(2), monoclinic, space group $P2_1/n$, a = 8.516(3), b = 9.716(4), c = 15.352(6) Å, β = 92.465(5)°, V = 1269.1(9) Å^3, μ = 2.552 cm^{-1}, Z = 2, 5355 reflections measured, 2127 unique (R_{int} = 0.0324), final R indices [$I > 2\sigma(I)$] $R(1)$ = 0.0187, $wR2$ = 0.0500. CCDC 684 338. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b806804f

¶ Crystal data for **3**·(n-pentane)$_{0.5}$: $C_{70.5}H_{86}Al_2I_2N_4$, M_r = 1297.19, T = 150(2), triclinic, space group P-1, a = 10.6194(10), b = 15.9477(15), c = 21.317(2) Å, α = 105.315(2), β = 94.491(2)°, γ = 102.408(1)°, V = 3365.5(5) Å^3, μ = 1.246 cm^{-1}, Z = 2, 41 370 reflections measured, 15 352 unique (R_{int} = 0.0727), final R indices [$I > 2\sigma(I)$] $R(1)$ = 0.0563, $wR2$ = 0.1330. CCDC 684337. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b806804f

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