EurJIC
European Journal of Inorganic Chemistry

Communications
doi.org/10.1002/ejic.202000919

Chemistry Europe
European Chemical Societies Publishing

Structurally Defined Ring-Opening and Insertion of Pinacolborane into Aluminium-Nitrogen Bonds of Sterically Demanding Dialkylaluminium Amides

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Dedicated to Professor Alan Welch on the occasion of his retirement from Heriot-Watt University

Dialkylaluminium amides iBu$_2$Al(TMP) and iBu$_2$Al(HMDS) can perform catalytic hydroboration of ketones with pinacolborane to form the expected boronic esters. However, repeating the same reactions stoichiometrically without a ketone leads unexpectedly to ring-opening of pinacolborane and insertion of its open chain into the Al–N(amido) bond. To date there has been limited knowledge on decomposition pathways of HBpin despite its prominent role in hydroboration chemistry. X-ray crystallography shows these mixed Al–B products [iBu$_2$Al{OC(Me)$_2$C(Me)$_2$O}B(H)(NR$_2$)]$_2$ (NR$_2$ = TMP or HMDS) form dimers with an (AlO)$_2$ core and terminal B–N bonds. Since the bond retention (B–H) and bond breaking (B–O) in these transformations seemed surprising, DFT calculations run using M11/6-31G(d,p) gave an energy profile consistent with a σ-bond metathesis mechanism where London dispersion interactions between iBu and (amide) Me groups play an important stabilising role in the final outcome.

Since Knochel introduced pinacolborane, HBpin, to synthetic laboratories in 1992,[1] its use in synthesis and catalysis has escalated as predicted in his seminal paper.[2] A successful example of organic transformations catalysed by aluminium compounds involving HBPin is the hydroboration of carbonyl substrates.[3] Studied in depth, the reaction mechanism is typically proposed to proceed via a two-step pathway: first an aluminium hydride catalyst hydroaluminates the substrate (e.g., a ketone), while second a σ-bond metathesis occurs with HBpin yielding the boronic ester product and regenerating the Al hydride catalyst. Several intermediates potentially involved in this second step have been isolated,[4] including from our own work benzaldehyde derivative (HMDS)$_2$Al(μ-OCH$_2$Ph)$_2$Li(THF)$_2$,[5] and benzophenone derivative [(TMP){Ph$_2$(H)CO}Al{μ-OC(H)Ph$_2$}]$_2$[6] (TMP = 2,2,6,6-tetramethylpiperidide; HMDS = 1,1,1,3,3,3-hexamethyldisilazide). That notwithstanding, a study by Aldridge[7] on reducing CO_2 using a range of NacNac-chelated Al hydride complexes has indicated that the required Al–O/B–H σ-bond metathesis is not always viable, thus thwarting the turnover step in the catalytic cycle. Instead, following hydroalumination of the C=O group an Al boryloxy complex forms, which in turn extrudes formaldehyde, with a significant difference in reaction rates between HBcat and 9-BBN implying that the Al boryloxy complex is generated by a C–O/B–H σ-bond metathesis.

Adding more complexity to the role/s of HBPin in catalysis, Thomas provided convincing NMR and kinetic evidence establishing that hydroboration reactions of alkynes and alkenes were catalysed by in situ generation of BH_3 and borohydride species from HBPin decomposition mediated by nucleophiles such as nBuLi and nBu$_2$Mg, previously thought to be the active catalysts.[8] The mechanisms of these nucleophile-promoted HBPin decompositions and co-products formed still remain to be determined. Similarly and pre-dating this study, Harder reported that calcium hydride, [^{DIPP}NacNacCa(H)(THF)]$_2$, acted as a "Trojan horse" in facilitating decomposition of HBcat to B$_2$(cat)$_3$, BH_3 and other boron products, during hydroboration of diphenylethene with HBCat, concluding that the true catalyst was also BH_3.[9] Clearly, more information is needed on decomposition pathways involving HBPin especially in processes relevant to catalysis since the decomposition pathway of the catalyst used will determine its maximum lifetime, and thus the required catalyst loading. Towards this goal, here we report the surprising outcomes of a combined experimental and theoretical study probing the reactivity of HBpin towards the neutral dialkylaluminium amides iBu$_2$Al(TMP) **1** and iBu$_2$Al(HMDS) **2**.

Previously, hydride-free iBu$_2$Al(TMP) **1**, was reported to catalyse hydroboration of ketones with HBpin at room temperature via a β-hydride transfer mechanism.[6] Testing the reproducibility of this initiation pathway to other alkylaluminium amides, **2** was prepared by salt metathesis between iBu$_2$AlCl and Li(HMDS), isolating the desired compound as an oil in high yield. A control reaction performed in a J. Young's NMR tube between iBu$_2$Al(HMDS) and benzophenone in C$_6$D$_6$

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202000919

solution monitored by ^{1}H NMR spectroscopy revealed signals consistent with isobutene [^{1}H NMR: δ 1.58 (t, J = 1.20 Hz, 6H); 4.72 (sept. J = 1.20 Hz), 2H], the co-product of β-hydride transfer. This implies that **2** acts as a masked hydride in the same way as TMP analogue **1.**

To try and uncover potential decomposition pathways in hydroboration reactions utilising **1** as the catalyst, we performed a stoichiometric reaction between *i*Bu$_2$Al(TMP) and HBpin in C_6D_6 in a J. Young's NMR tube. We expected a mixture of products such as *i*BuBpin and (TMP)Bpin. Instead, crystals of **3** were obtained (56 % crystalline yield, Scheme 1).

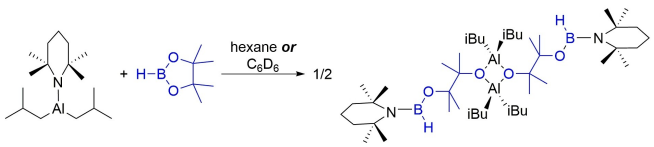
Reaction scale up and X-ray diffraction studies of **3** revealed its novel molecular structure of formula [*i*Bu$_2$Al{OC(Me)$_2$C(Me)$_2$O}B(H)(TMP)]$_2$ (Figure 1).

Deposition Numbers 2019982 (**3**) and 2019983 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Surprisingly, **3** retains the typically more reactive B–H bond (416 kJ/mol dissociation energy), yet cleaves the doubly stronger B–O bond (890 kJ/mol dissociation energy).[10] This is significant as for hydroboration catalysis to proceed cleavage of the B–H bond is necessary. The formula of **3** indicates that the 5-atom BOCCO ring of HBPin has opened during the reaction and inserted into the Al–N bond of the amide. Concomitantly the amide has transferred from Al to B. From a general perspective considering the relative strengths of such bonds,[10] these bond transformations pose some interesting questions as to the driving force behind the formation of **3**.

To probe this surprising reactivity DFT calculations were performed at the M11/6-31G(d,p)[11] level of theory using Gaussian 16. For brevity full details are given in the SI. Compound **3** is proposed to form through a σ-bond metathesis mechanism involving initial complexation of HBPin and **1** to form a Reaction complex (**RC**) (△H = −14.2 kcal/mol, Figure 2).

RC represents a local minimum on the potential energy surface. From this point the non-covalently bound **RC** forms the 4-bond cyclic intermediate complex (**Int1**) in a barrierless reaction. **Int1** is surprisingly stable (△H = −13.0 kcal/mol, relative to **RC**, Figure 2) primarily due to the flexible coordination of B and Al, which can distort from a trigonal to a tetrahedral geometry to support the extra bond formation (see SI for 3D structures of all optimised species). The stability of **Int1** is also seen in the barrier to forming the product of the reaction. The transition state (**TS1**) involves breaking concertedly the Al–N and B–O bonds involved in the reactive core. While the activation energy for this step is achievable under the room temperature and STP reaction conditions (△H* = 17.0 kcal/mol, Figure 2) the relative stability of the product (Prod) drives this reaction. Additional steric bulk provided by the substitution on the TMP rings and *i*Bu groups on Al would prima facie destabilise the system. However, in forming **Prod** the additional London dispersion interactions[12] between alkyl groups (Figure S21, H···H dispersion interactions of lengths 2.13, 2.26, 2.29 Å) helps stabilise the resulting intermediate from the bond formation. This hypothesis was corroborated by modelling the reaction with modified substrates using only (Me)$_2$Al(piperidide) as the reactant (see SI).



Scheme 1. Synthesis of the dimeric Bpin ring-opening product **3**.

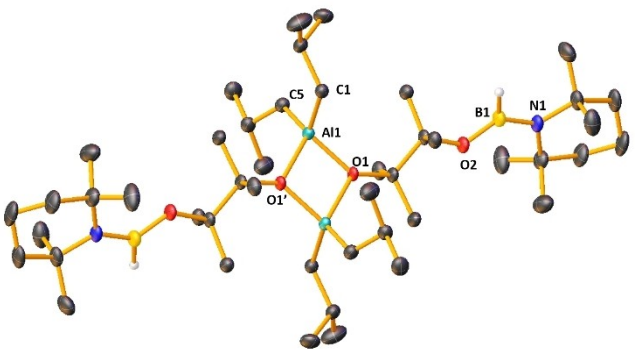


Figure 1. Molecular structure of **3**. Hydrogen atoms, except B–H hydride have been omitted for clarity. Thermal ellipsoids are drawn at 40 % probability. Symmetry operations used to generate equivalent atoms −x; −y; 1−z. Selected bond lengths (Å) and angles (°): Al1–O1, 1.877(1); Al–O1', 1.862(1); Al1–C5, 1.979(2); Al1–C1, 1.987(2); B1–O2, 1.364(3); B1–N1, 1.422(3); B1–H1, 1.07(2); C5–Al1–O1, 118.51(8); C1–Al1–O1, 110.59(8); C5–Al1–O1', 115.71(8); C1–Al1–O1', 110.40(8); C1–Al1–C5, 115.35(9); O1–Al1–O1', 81.73(6); H1–B1–N1, 124(1); H1–B1–O2, 116(1); O2–B1–N1, 120.3(2). This structure and that of **4** have been deposited in the CSD under codes 2019982 and 2019983.

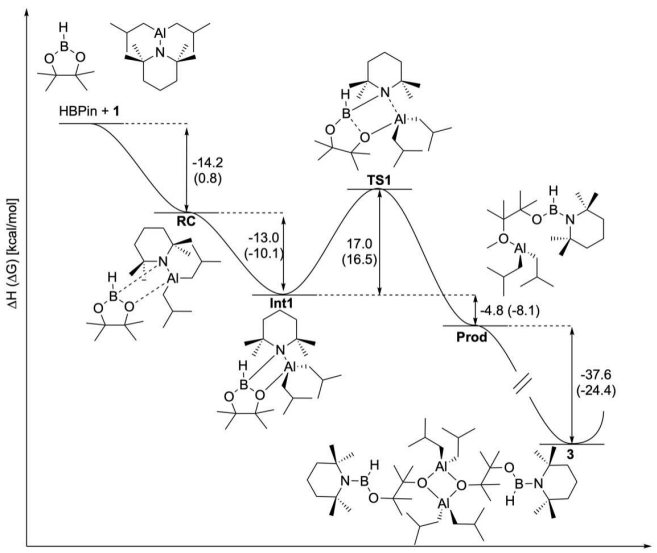


Figure 2. Relative enthalpy surface (in kcal/mol) for the reaction between HBPin and **1**. Values in parentheses indicate the change in Gibb's Free energy (△G in kcal/mol) associated with each step.

In this discussion we have focussed primarily on the relative enthalpies of the reaction mechanism. Naturally, the reaction rates and equilibria will depend on the corresponding Gibbs free enthalpies (△G), which have been computed by applying the harmonic oscillator/rigid rotor approximation and are provided in Figure 2 (values in parentheses). However, the △G values should be viewed with some caution as the harmonic oscillator/rigid rotor approximation is known to be problematic in the case of weakly bound complexes, such as **RC**, due to the large number of low-energy vibrational modes, which in turn have a large contribution to the entropy. Nonetheless, it is interesting to note the qualitative effect of the entropy on the enthalpy profile. The inclusion of entropy disfavours the formation of **RC**, with a decrease in the number of degrees of freedom in the system, although the complex formation is only mildly endergonic on the free enthalpy surface (△G = 0.8 kcal/mol, Figure 2). The subsequent formation of **Int1**, **TS**, and **Prod**, are relatively unaffected by the inclusion of entropy. Finally, the formation of **3**, while less favourable when entropy is considered, remains a strongly exergonic process (△G = −24.4 kcal/mol, Figure 2).

Crystalline **3** exists as a centrosymmetric dimer featuring a planar kite-shaped Al–O–Al–O core. The Al centre exists in a distorted tetrahedral geometry comprising two O and two C atoms with bond angles spanning 110.96(7)–117.22(7)°, whilst the B centre is distorted trigonal planar with bond angles in the range 117(2)–122.7(2)°. TMP and Al components sit at opposite ends of the ring-opened B-pinacol unit. The ^{1}H NMR spectrum of **3** displays the hydride resonance as a broad singlet at 4.75 ppm in C_6D_6 solution, which sharpens upon applying ^{11}B decoupling. In comparison, the HBpin hydride resonance is a broad quartet at 4.17 ppm with a J coupling constant of 171.56 Hz, in C_6D_6. The ^{11}B NMR spectrum of **3** displays a broad singlet resonance at 30.0 ppm, while for HBpin this signal occurs as a doublet at 28.1 ppm (J = 174 Hz). The lack of observed splitting in the ^{1}H and ^{11}B NMR spectra of **3** could be a result of signal broadening due to a quadrupolar nucleus (^{11}B) in an asymmetrical environment. A ^{1}H DOSY NMR experiment[13] on **3** in C_6D_6 solution gave an estimated molecular weight of 830 g/mol, consistent with retention of the dimer in solution (818.73 g/mol; −1% error). The ^{13}C{^{1}H} NMR spectrum displayed all the expected signals, though no signal was observed in the ^{27}Al spectrum.

A similar outcome is seen reacting together *i*Bu_2Al(HMDS) **2** and HBpin in hexane. Crystalline [*i*Bu_2Al{OC(Me)$_2$C(Me)$_2$O}B(H)(HMDS)]$_2$, **4**, is formed in a low 24% isolated yield. Its molecular structure both in the crystal and in C_6D_6 are analogous to those of **3** (see SI and Figure S13).

Next, **2**, **3**, and **4** were applied as pre-catalysts for hydroboration of benzophenone with HBpin to check their catalytic viability (Table 1). The reduction of benzophenone with 5 mol% of **2** as a pre-catalyst is slower than with **1**, requiring 3 hours to reach 97% conversion, compared to only 0.5 hours to reach 94% conversion with **1** as reported previously.[6] This suggests that β-hydride transfer in forming the active Al hydride pre-catalyst is significantly faster with **1** than with **2**. Employing 5 mol% of TMP-borane **3** as a pre-catalyst managed only a 35% yield of Ph_2CHOBpin, after 17 hours, in contrast to the near quantitative conversion obtained within 0.5 hours using **1**. As expected from its similarity to **3**, HMDS-borane **4** also performs poorly as a pre-catalyst, with only 24% conversion after 21 hours at room temperature using 5 mol%. This implies that both **3** and **4** could exist as off-cycle products from hydroboration with **1** and **2** as pre-catalysts, respectively. Therefore, **3** and **4** can be considered deactivation products from these monometallic aluminium pre-catalysts. Though both possess a B–H bond, they are occupied within bulky neutral environments, that greatly diminishes their reducing capability compared to those of charged ate analogues such as the trialkoxyborohydride formed via addition of nucleophilic NaO*t*-Bu to HBpin.[14] However, note that when **1** is used as a pre-catalyst in hydroborations no signals corresponding to **3** are seen in ^{11}B NMR spectra. This indicates that in the presence of benzophenone the rate of hydroboration is greater than the rate of B–O cleavage and formation of **3**.

Table 1. Hydroboration of benzophenone with HBpin catalysed by selected aluminium catalysts.

Catalyst (5 mol% [Al])[a]	Yield [%]	Time [h]
iBu_2Al(TMP), **1**	94	0.5
iBu_2Al(HMDS), **2**	97	3
[*i*Bu_2Al{OC(Me)$_2$C(Me)$_2$O}B(H)(TMP)]$_2$, **3**	35	17
[*i*Bu_2Al{OC(Me)$_2$C(Me)$_2$O}B(H)(HMDS)]$_2$, **4**	24	21

[a] Conditions: 5 mol% [Al] catalyst loading, C_6D_6 solvent, room temperature. All yields estimated against ^{1}H NMR internal standard hexamethylcyclotrisiloxane.

It is notable that such well-defined examples of elucidated decomposition products of HBpin of relevance to catalysis are very rare. B_2pin_3 is a known, crystallographically-characterised decomposition product of HBpin.[15] The structure of B_2pin_3 has a central O(Me$_2$)C–C(Me$_2$)O unit from ring-opening of a HBpin molecule, but otherwise bears little resemblance to **3** or **4**. Hill reported observing trace amounts of B_2pin_3 in hydroboration of imines, catalysed by ^{DIPP}NacNacMg(*n*Bu), under forcing conditions.[16] Other documented examples in main group systems are known,[17–21] but for most examples of cleavage of one or both B–O bonds in HBpin or HBcat one has to turn to transition metal, lanthanide, or actinide complexes.[22–30] Ligand redistribution reactions between alanes AlX_3 and boranes BY_3 to $AlX_{3-n}Y_n$ and $BY_{3-n}X_n$ are also well documented.[31,32] This redistribution reactivity has been harnessed to generate the active catalyst Et_2AlH from a Et_3Al pre-catalyst and HBpin in the hydroboration of acetylenes.[4c] Similarly, *i*Bu_2AlH and HBpin also undergo ligand scrambling generating *i*BuBpin and *i*Bu_3B, amongst other products.

In summary, light has been shed on the decomposition of HBpin when used stoichiometrically with alkylaluminium amides. When used catalytically these Al amides can hydroborate ketones with HBpin at room temperature via a putative R_2AlH intermediate. Such well-defined examples of the breakdown of HBpin with main group metal compounds are rare, but they are important given the recent escalation of activity in main group homogeneous catalysis. The products of these

reactions were unexpected since they formed via opening of the HBpin ring and its concomitant insertion into the Al–N (amide) bond. Adding intrigue, DFT calculations suggested that attractive dispersion forces involving alkyl groups on the Al compound are a key feature within the reaction coordinate. It is rare for London dispersion forces to be mentioned in the context of TMP-aluminate chemistry[33] or TMP's general role in synergistic bimetallic reactions,[34] but as recently highlighted in a seminal review by Liptrot and Power,[35] such weak forces can significantly impact inorganic and organometallic structures involving bulky ligands. Future interrogation or re-interrogation of TMP and related bimetallic compounds may find that London dispersion forces are more significant than initially evidenced.

Acknowledgements

We thank Prof. Eva Hevia and Dr David Nelson for insightful comments, and to the EPSRC (DTP award EP/M508159 to V. A. P.) for funding. Computational results were done via the EPSRC funded ARCHIE-WeSt High Performance Computer (www.archie-west.ac.uk) (EPSRC grant no. EP/K000586/1). The data set underlying this research can be located at https://doi.org/10.15129/897a827d-a07c-4fc8-925d–2e1cc0b1baba.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Aluminium · Density functional calculations · Homogeneous catalysis · Hydroboration · Main group chemistry

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Manuscript received: October 1, 2020
Revised manuscript received: October 26, 2020
Accepted manuscript online: October 30, 2020