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# One-pot, room-temperature conversion of dinitrogen to ammonium chloride at a main-group element

Marc-André Légaré<sup>1,2,3</sup>, Guillaume Bélanger-Chabot<sup>1,2,4</sup>, Maximilian Rang<sup>1,2</sup>, Rian D. Dewhurst<sup>1,2</sup>, Ivo Krummenacher<sup>1,2</sup>, Rüdiger Bertermann<sup>1,2</sup> and Holger Braunschweig<sup>1,2</sup>

The industrial reduction of dinitrogen ( $N_2$ ) to ammonia is an energy-intensive process that consumes a considerable proportion of the global energy supply. As a consequence, species that can bind  $N_2$  and cleave its strong N-N bond under mild conditions have been sought for decades. Until recently, the only species known to support  $N_2$  fixation and functionalization were based on a handful of metals of the s and d blocks of the periodic table. Here we present one-pot binding, cleavage and reduction of  $N_2$  to ammonium by a main-group species. The reaction—a complex multiple reduction-protonation sequence—proceeds at room temperature in a single synthetic step through the use of solid-phase reductant and acid reagents. A simple acid quench of the mixture then provides ammonium, the protonated form of ammonia present in fertilizer. The elementary reaction steps in the process are elucidated, including the crucial N-N bond cleavage process, and all of the intermediates of the reaction are isolated.

ue to its presence in amino acids, the element nitrogen is essential for life on Earth. However, its extremely stable elemental form (dinitrogen, N2) makes it difficult to utilize nitrogen either biologically or synthetically. The century-old Haber-Bosch process<sup>1</sup>, which converts N<sub>2</sub> and H<sub>2</sub> into ammonia over an iron catalyst at high temperatures (400-600 °C) and pressures (20-40 MPa), is still the major source of ammonium fertilizer and other synthetic nitrogen compounds worldwide. Consequently, over 1% of the world's generated energy is dedicated to the synthesis of ammonia. The importance of this energy-intensive process, and the 1965 discovery of transition metal complexes containing bound N2 units2, has motivated over half a century of research into transition-metal-catalysed fixation of N2 and its conversion into ammonia and other useful nitrogen compounds<sup>3-10</sup>. Although this research has yet to uncover a practical method for N<sub>2</sub> reduction under mild conditions, progress towards nitrogen fixation and conversion by molecular complexes remains the exclusive preserve of transition metals because other elements of the periodic table generally lack the advantageous oxidation-state and orbital diversity of transition metals.

Outside the *d*- and *f*-block metals, until very recently only the alkali metal lithium was known to react with  $N_2$  at room temperature to give an isolable product<sup>11</sup> and, in both biological and synthetic settings, transition metals were the only elements with a demonstrated ability to enable the fixation and functionalization of  $N_2$ . In 2018 we reported the reaction of a *p*-block molecule with  $N_2$  under transition-metal-free conditions by taking advantage of the emerging concept of main-group metallomimetics: *p*-block compounds able to react like transition metal complexes<sup>12-14</sup>. In this way, transient dicoordinate borylenes<sup>15-17</sup> of the form  $[L \rightarrow B-R]$  (where L is a neutral Lewis donor unit, for example, a carbene, and R is an anionic substituent, for example, aryl) were shown to be capable

of binding, partially reducing and even coupling N<sub>2</sub> (refs. <sup>18–20</sup>). Following our work, a number of porous carbon-based nanomaterials were reported to effect the electrocatalytic reduction of N<sub>2</sub> to various nitrogen-containing products, including ammonia<sup>21,22</sup>. Our transition-metal-free boron fixation processes and subsequent chemistry led to a number of species containing central N<sub>2</sub> (and N<sub>4</sub>) units bound to boron-containing fragments; however, the complete cleavage of the strong N–N bond of N<sub>2</sub>, a critical step in the potential synthesis of ammonia (and amines) from N<sub>2</sub>, remains elusive in a main-group complex.

Although a number of different N<sub>2</sub> binding modes with transition metals exist, recent advances in the catalytic synthesis of ammonia from N<sub>2</sub> using molecular transition metal species have focused on complexes featuring N<sub>2</sub> as a terminally bound ligand<sup>23</sup>. In such complexes, a reduction-protonation cascade involving six electrons and six protons can lead to the total reduction of N<sub>2</sub> to two equivalents of ammonia, according to a mechanism known as the Chatt cycle, which is relevant to biological nitrogenase chemistry<sup>24</sup>. Some side-on bridging N<sub>2</sub> transition metal complexes have also been hydrogenated in a stepwise manner, albeit through a completely different mechanism<sup>25</sup>. In contrast, the reactivity of end-on bridging N<sub>2</sub> complexes is dominated by N<sub>2</sub> release and photolytic or thermal cleavage of the bridging N<sub>2</sub> ligand, producing two transition metal nitride complexes, the latter being of relevance to ammonia synthesis<sup>23,26-28</sup>. Indeed, the rate-limiting step of the Haber-Bosch process is the cleavage of the N-N triple bond on the catalyst to form surface nitrides<sup>29</sup>. However, in transition metal complexes, the direct cleavage of a bridging N2 ligand-a six-electron reduction process-typically requires strongly reducing metal centres or unusual multimetallic mechanisms<sup>30</sup>. We hypothesized that, under the right circumstances, binding N<sub>2</sub> in an end-on bridging fashion could allow the ammonia synthesis process to be separated into

<sup>1</sup>Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Würzburg, Germany. <sup>2</sup>Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Würzburg, Germany. <sup>3</sup>Present address: Department of Chemistry, McGill University, Montréal, Québec, Canada. <sup>4</sup>Present address: Département de Chimie, Université Laval, Québec, Québec, Canada. <sup>Ke</sup>e-mail: h.braunschweig@uni-wuerzburg.de

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**Fig. 1** | **A** one-pot, borylene-mediated synthesis of ammonium chloride from  $N_2$ , and elucidation of the individual reduction-protonation steps involved. The solid-state structures of **5-8** are presented with 50% probability displacement ellipsoids. Peripheral hydrogen atoms and carbon ellipsoids have been removed for clarity. All depicted hydrogen atoms, except the carbon-bound hydrogen atom in **8**, were crystallographically located. Atom codes: grey, carbon; white, hydrogen; green, boron; purple, potassium; blue, nitrogen. N<sub>2</sub> was applied at pressures of -5 atm. KC<sub>8</sub> and B(OH)<sub>3</sub> were applied as 10-15 molar equivalents relative to boron. All reactions involving N<sub>2</sub> were kept below -50 °C until application of gaseous N<sub>2</sub>, after which they were warmed to room temperature. All other reactions were conducted at room temperature. Selected bond distances (Å) for **5**: B-N 1.399(2) (average), B-C<sup>CAAC</sup> 1.561(3) (average); for **6**: B-N 1.415(1), B-C<sup>CAAC</sup> 1.535(2); for **7**: B-N 1.505(2) (average), B-C<sup>CAAC</sup> 1.465(2) (average); for **8**: B-N 1.376(2), B-C<sup>CAAC</sup> 1.616(3). Purple dots denote unpaired electrons.

three sequential two-electron/two-proton steps, which may allow it to proceed with lower energy barriers than a sequence involving a six-electron reduction followed by addition of six protons as described above<sup>23,31</sup>. A similar approach was recently employed by Liddle and co-workers<sup>32</sup> in the reduction of N<sub>2</sub> to ammonia on titanium through an initial four-electron reduction step. However, to our knowledge a cascade mechanism of two-electron/two-proton steps for complete N<sub>2</sub> reduction from an end-on bridging complex has never been fully characterized.

In this context, we envisaged that using *p*-block elements for nitrogen fixation could allow the discovery of new  $N_2$  reduction chemistry distinct from that of transition metals. In contrast to transition metals, compounds of the light *p*-block elements do not undergo reduction events in a partially filled *d*-electron subshell. As such, the binding of  $N_2$  by an element with limited redox flexibility, such as boron, could lead to an N-centred redox chemistry distinct from those common in classical transition metal  $N_2$  adducts, in which reduction predominantly occurs at the transition metal centre or auxiliary ligands<sup>33</sup>. Our recent discovery of direct binding of dinitrogen to boron in the complex [{(CAAC)(Dur)  $B_{2}(N_{2})$ ] (2, where CAAC is 1-(2,6-diisopropylphenyl)-3,3,5,5-tetr amethylpyrrolidin-2-ylidene<sup>34</sup> and Dur is 2,3,5,6-tetramethylphenyl; Fig. 1)<sup>18-20</sup> provided a platform to test the possibility of repeated reduction-protonation steps from an end-on bridging N2 complex and ultimately the cleavage of the N-N triple bond. Indeed, the first two-electron/two-proton reduction-protonation cycle was demonstrated to be facile in our previous report of the syntheses of the dipotassium compound  $K_2[\{(CAAC)(Dur)B\}_2(N_2)]$  (3) and its doubly protonated diradical congener [{(CAAC)(Dur)B}<sub>2</sub>(N<sub>2</sub>H<sub>2</sub>)] (4, Fig. 1). We hypothesized that repeated reduction-protonation cycles starting from 4 may lead to complete N-N cleavage and ultimately a *p*-block-element-based process for the synthesis of ammonia, which would also constitute a stepwise dinitrogen-to-ammonia mechanism from a bridging N<sub>2</sub> complex.



**Fig. 2 | Schematic of the overall mechanism of the borylene-mediated ammonium synthesis.** Initial reduction of the radical [(CAAC)BBrDur] provides hypothetical borylene species **A**, from which sequential two-electron and two-proton steps and a final acid quench step provide ammonium. All seven reduction-protonation processes can be performed in a single step and reaction vessel using the solid-state reductant KC<sub>8</sub> and solid-state protonating agent B(OH)<sub>3</sub>; a subsequent acid quench can also be performed in the same vessel without an isolation step. The overall process therefore constitutes a one-pot reaction. Compounds in blue boxes have been reported previously<sup>18</sup>. Text in orange circles denotes the formal reduction-protonation extent of the N<sub>2</sub> unit.

#### **Results and discussion**

Outcomes of reduction of the hydrazino diradical species. Upon exposure of hydrazino diradical 4 (Fig. 1) to an excess of the reductant potassium graphite (KC8) in benzene, the deep blue reaction mixture instantaneously turned black, and the <sup>11</sup>B NMR spectrum of this mixture showed no signal. Filtration of the mixture and recrystallization of the resulting black solution in hexanes afforded a dark crystalline solid (78% yield), which was found to be paramagnetic, as evidenced by the strong signal observed in its electron paramagnetic resonance (EPR) spectrum (Supplementary Fig. 12). Single-crystal X-ray diffraction (SCXRD) confirmed this species to be the radical amide K[(CAAC)(Dur)B(NH)] (5, Fig. 1), arising from the direct reductive cleavage of the N-N bond of 4. Potassium amide radical 5 exists in the solid state as a dimer, held together by the two potassium atoms, each of which binds to both amide nitrogen atoms and two further arene rings. The core N-B-C-N unit of 5, the  $\pi$  system of which is expected to host five electrons,

is effectively planar (torsion angles of  $13.5(3)^{\circ}$  and  $17.6(3)^{\circ}$ ). These geometric features, as well as the average B–N and B–C<sup>CAAC</sup> bond distances (1.399(2) and 1.561(3) Å, respectively) and the EPR signature of **5**, are consistent with a delocalized (captodatively stabilized) C-centred CAAC–B radical<sup>35</sup>.

The outcome of the reduction of **4** with KC<sub>8</sub> is highly dependent on the moisture accompanying samples of the former, which itself is prepared using water. Samples of **4** dried extensively by the use of azeotropic distillation and 4 Å molecular sieves produce **5** as described above; however, reduction of incompletely dried samples produces colourless solutions, indicative of a different product. Removal of solvent and recrystallization of the latter resulted in isolation of a colourless diamagnetic solid with an <sup>11</sup>B NMR spectroscopic resonance at  $\delta$ =46 ppm and a crystallographically-derived structure corresponding to the aminoborane [B(CAACH)(Dur) (NH<sub>2</sub>)] (**8**, 84% yield; Fig. 1), the product of a formal addition of one N–H bond of ammonia across the C=B double bond of the

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hypothetical borylene [(CAAC)B(Dur)] (**A**, Fig. 2). Although the two enantiomers of the chiral compound **8** are superimposed in its solid-state structure and cause disorder, **8** is clearly identifiable as a conventional aminoborane, with a short bond between the boron atom and the  $\pi$ -donating nitrogen atom (1.376(2) Å). Interestingly, with regards to the stoichiometry of N<sub>2</sub>, the formation of **8** corresponds to a further two-electron/four-proton transfer to **5**, effectively completing the full six-electron/six-proton reduction of N<sub>2</sub> to NH<sub>3</sub>, with the latter still being bound to the boron-containing species (Fig. 2). This identification of **8** as a proammonia complex was subsequently underlined by its hydrolysis with concentrated hydrochloric acid (a non-redox process), leading to the detection of ammonium by <sup>14</sup>N{<sup>1</sup>H} NMR spectroscopy and to the decomposition of the boron-containing moieties to a mixture in which we were only able to identify DurB(OH)<sub>2</sub> and [CAAC-H]+Cl<sup>-</sup> by SCXRD.

One-pot synthesis of ammonium from dinitrogen. Encouraged by the cascade nature of the reduction-protonation steps implied by the synthesis of 8 from 4 in the presence of both reductant (KC<sub>8</sub>) and protonating agent (water), probably through 5 as an intermediate, we envisaged the possibility of preparing the proammonia borane 8 directly from boryl radical 1, the precursor required for the initial N<sub>2</sub> fixation, and N<sub>2</sub>. A challenge that we identified early on, however, was the unwanted potential reactions of the putative borylene intermediate [(CAAC)B(Dur)] (A, Fig. 2) and/or the reductant (KC<sub>8</sub>) with the proton source (water). For this reason, we chose the weakly protic reagent boric acid  $(B(OH)_3)$  as the proton source, reasoning that its poor solubility in organic solvents would limit its reactivity with intermediate A or KC8. Preliminary tests hinted at the plausibility of this strategy: stirring a toluene solution of 2 with excess KC<sub>8</sub> and B(OH)<sub>3</sub> for 16h led to isolation of 8 in 67% yield, while reduction of 1 in the presence of  $B(OH)_3$ provided the C-H activation product<sup>18</sup> observed when the reaction is performed in the absence of B(OH)<sub>3</sub>, suggesting that A is inert towards B(OH)<sub>2</sub>. Thereby, room-temperature reduction of 1 with KC<sub>8</sub> (10 equiv.) in the presence of N<sub>2</sub> (or  ${}^{15}N_2$ ) gas (5 or 3 atm, respectively) and B(OH)<sub>3</sub> (15 equiv.) provided ammonia adduct 8 (or 8-15N) after 4h of reaction (near-full conversion by NMR spectroscopy; 65% or 30% isolated yield of 8 and 8-15N, respectively). Repeating the N<sub>2</sub> reaction with a direct acid-quench step (aqueous HCl, 11 M) provided a 27% yield of ammonium chloride, the conjugate acid of ammonia. This relatively low yield is probably due to an inability to completely extract the product from the complex reaction mixture. This reaction constitutes a simple one-pot, two-step protocol for the transition-metal-free reduction of N<sub>2</sub> to ammonium. Production of [<sup>15</sup>NH<sub>4</sub>]Cl was also confirmed by <sup>15</sup>N{<sup>1</sup>H} insensitive-nuclei-enhanced polarization transfer NMR spectroscopy upon acidolysis of the labelled ammonia adduct 8-15N.

Isolation of remaining intermediates in the dinitrogen-to**ammonium process.** A further advantage of the use of  $B(OH)_3$  is that, in contrast to water, it provides excellent control over protonation reactions and, because of its poor solubility, can be easily and completely removed from the products. This, in turn, allowed us to perform each individual reduction and protonation step of the dinitrogen-to-ammonium process and isolate all of the remaining intermediates, confirming the reductive cascade nature of the reaction. We found that exposing a near-black benzene solution of 5 to excess  $B(OH)_3$  led to a complete colour change of the mixture to bright orange within 20 min. Filtration of the reaction mixture and slow evaporation of the solvent resulted in isolation of boryl radical [(CAAC)(Dur)B(NH<sub>2</sub>)] (6) as bright orange crystals (90% yield), the structure of which was confirmed by SCXRD (Fig. 1). The structure of 6 is similar to that of the related amide radical 5, but more closely resembles one half of the structure of diradical 4, both species having chemically identical [B(CAAC)(Dur)(NH)] units (B-N bond lengths, 1.415(1) Å (6), 1.435 Å (4); B-CCAAC bond lengths, 1.535(2) Å (6), 1.512(3) Å (4))<sup>18</sup>. The EPR spectrum of 6 (Supplementary Fig. 16) is virtually indistinguishable from that of amide radical 5 (Supplementary Fig. 12), which is understandable given that the majority of the spin density of these two radicals likely resides on the CAAC carbene C atom and a similarly delocalized N-B-C-N core (see above; average B-N and B-CCAAC bond lengths, 1.399(2) and 1.561(3) Å, respectively). Compound 6 corresponds to the product of two reduction-protonation sequences from the borylene-dinitrogen adduct 2, and thereby occupies the same conceptual space as hydrazine (N<sub>2</sub>H<sub>4</sub>) on the nitrogen-to-ammonia reduction pathway. Intrigued by this similarity, we irradiated a benzene solution of [(CAAC)(Dur)B(CO)]<sup>36</sup>—a process assumed to generate the putative borylene A by photodecarbonylation-in the presence of hydrazine, providing 6 in 27% yield after purification (Fig. 1, bottom). This reaction highlights the relationship of 6 with hydrazine on the dinitrogen-to-ammonia reduction pathway and reveals an intriguing and unprecedented generation of boron-containing radicals by homolytic N-N bond cleavage.

Exposure of a bright orange, <sup>11</sup>B-NMR-silent solution of 6 to excess KC<sub>8</sub> was accompanied by a colour change to deep purple, the mixture exhibiting a new, broad <sup>11</sup>B NMR spectroscopic signal ( $\delta$ =6ppm). Filtration of the mixture and thorough extraction led to essentially quantitative isolation of dark red crystals, the molecular structure of which was confirmed by SCXRD to be that of the CAAC-stabilized boryl anion K[(CAAC)(Dur)B(NH<sub>2</sub>)] (7, 92% yield; Fig. 1). The solid-state structure of boryl anion dimer 7 shows the presence of very short B–C bonds (1.464(2), 1.465(2) Å)and relatively long C-N (1.471(2), 1.470(2)Å) and B-N bonds (1.506(2), 1.503(2) Å), in line with those of related CAAC-stabilized boryl anions<sup>37,38</sup> and consistent with their alternative description as zwitterionic alkylideneborates with B=C double bonds. Although isolable, 7 is highly reactive, undergoing facile protonation to proammonia compound 8 with extended handling and/or storage. Selective protonation of 7 can be achieved using B(OH)<sub>3</sub>, affording 8 as the sole product according to NMR spectroscopy, and thus closing the reaction sequence from 1 to 8 and ultimately [NH<sub>4</sub>]Cl.

#### Conclusions

This work, as summarized in Fig. 2, comprises the one-pot, two-step chemical conversion of N2 to ammonium without transition metals, and the isolation of the intermediate products of every two-electron/two-proton step in the process. Notably, this dinitrogen-to-ammonium process proceeds by a stepwise reduction-protonation mechanism via an end-on bridging N<sub>2</sub> species. It should be noted that the B(OH)<sub>3</sub> used as protonating agent in this work is very mild compared with those used in transition-metal-based catalytic processes for N<sub>2</sub> conversion, which are often relatively strong organic acids (for example, 2,6-lutidinium salts), triflic acid or tetra(fluoroaryl)borate superacids<sup>5,8,28</sup>, indicating the existence of highly nucleophilic nitrogen atoms throughout our process. The success of these reactions can thus be attributed to the unwillingness of the electron-rich boron atoms in our system to accept further electrons (in contrast with many transition metal complexes), forcing the reduction steps to occur predominantly on the N<sub>2</sub> moiety and thereby facilitating N-N cleavage and protonation. Thus, in this regard, the limited metallomimicry of the borylene system is a distinct advantage, promoting a facile cascade mechanism with reduction events largely centred on nitrogen. The one-pot chemical conversion of N2, while not a catalytic process, is a convincing demonstration of the ability of main-group elements in low oxidation states not only to activate very inert small molecules but also to mediate their conversion through cascades of redox and protonation processes.

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#### **Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/ s41557-020-0520-6.

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#### Methods

**General synthetic considerations.** All syntheses were carried out under an atmosphere of argon or nitrogen in argon-filled gloveboxes or using standard Schlenk techniques. Compounds **1–4**, as well as [(CAAC)B(CO)Dur], were prepared according to literature procedures<sup>18,35</sup>. Solvents were dried by distillation over appropriate drying agents<sup>39</sup> and stored over molecular sieves.  $C_6D_6$  was dried, degassed and stored over molecular sieves. Anhydrous hydrazine was obtained by distilling concentrated aqueous hydrazine over sodium hydroxide under an inert atmosphere. Hydrazine was introduced to reaction mixtures by condensation under vacuum and the amounts used were estimated by pressure measurements in a vacuum line with calibrated volumes.

Synthesis of new compounds. Synthesis of amide radical 5. A blue solution of 4  $(20 \text{ mg}, 22 \mu \text{mol})$  in C<sub>6</sub>D<sub>6</sub> (~1.5 ml) was stirred overnight over molecular sieves (4Å) to remove trace moisture arising from the previous hydrolysis step. Once sufficiently dry, the solution was added to solid  $\tilde{K}C_8$  (30 mg, 222  $\mu mol)$  with stirring. The mixture immediately turned very dark green (almost black). After ~5 min, the solution was filtered and analysed by 11B NMR spectroscopy, which did not show any signal. The residue was extracted with more benzene  $(3 \times 1 \text{ ml})$ and the combined organic fractions were subsequently evaporated to dryness and the residue was recrystallized from a cooled hexanes solution. The product was obtained as black crystals suitable for X-ray diffraction analysis (17 mg, 78%). EPR (continuous wave, X band, toluene, room temperature): g (the magnetic field at which an EPR line is observed) = 2.0030,  $a^{(11B)} = 5.6$  MHz,  $a^{(14N)} = 18.0$ and 15.5 MHz (a = hyperfine splitting constant). The spectrum shows additional partially resolved hyperfine couplings (a = 0.5 G), probably due to the NH hydrogen, which could not, however, be successfully included in the simulation. High-resolution mass spectrometry (HRMS) (toluene, liquid injection field desorption ionization (LIFDI)): [M-K+H]+ 445.3747 (calculated 445.3749). Infrared spectroscopy of 5 revealed only very weak bands in the N-H stretch region. This situation is attributed to the dimeric nature of 5. See Supplementary Figs. 10-13 for spectra of 5.

Synthesis of aminoborane 8. The first method was one-pot reduction-protonation of 2 using a KC<sub>8</sub>/B(OH)<sub>3</sub> mixture. Toluene (1.5 ml) was rapidly added to a solid mixture of 2 (20 mg, 23 µmol), B(OH)<sub>3</sub> (14 mg, 226 µmol) and KC<sub>8</sub> (31 mg, 226 µmol). The suspension was stirred overnight, filtered and the residue was extracted once with toluene (0.5 ml). All volatiles were evaporated from the filtrate in vacuo to afford 8 as a colourless solid, which was further purified by recrystallization from a saturated pentane solution at -30 °C (13.0 mg, 67% yield). <sup>1</sup>H NMR (500 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 7.2 (m, 2H, 2,6-diisopropylphenyl (Dip)(*m*-Ar) overlapping with Dip(p-Ar)), 7.14 (m, 1H, Dip(m-Ar)), 6.87 (s, 1H, Dur(Ar)) 4.29 (septet, <sup>3</sup>*J*=6.8 Hz, 1H, Dip(CHMe<sub>2</sub>)), 4.08 (s, 1H, CAAC-H), 3.60 (septet, <sup>3</sup>J=6.7 Hz, 1H, Dip(CHMe<sub>2</sub>)), 3.52 (d, <sup>2</sup>J=1.6 Hz, 1H, NH<sub>2</sub>), 3.09 (d, <sup>2</sup>J=1.6 Hz, 1H, NH2), 2.25 (s, 3H, Dur(Me)), 2.21 (s, 3H, Dur(Me)), 2.13 (s, 6H, Dur(Me)), 1.84 (d,  ${}^{2}J$  = 12.4 Hz, 1H, CAAC(CH<sub>2</sub>)), 1.71 (d,  ${}^{2}J$  = 12.4 Hz, 1H, CAAC(CH<sub>2</sub>)), 1.44 (d, <sup>3</sup>*J*=6.7 Hz, 3H, Dip(CHMe<sub>2</sub>)), 1.38 (d, <sup>3</sup>*J*=6.8 Hz, 3H, Dip(CHMe<sub>2</sub>)), 1.37 (s, 3H, CAAC(BCMe<sub>2</sub>), 1.34 (d, <sup>3</sup>J=6.8 Hz, 3H, Dip(CHMe<sub>2</sub>)), 1.32 (d, <sup>3</sup>J=6.7 Hz, 3H, Dip(CHMe<sub>2</sub>)), 1.26 (s, 3H, CAAC(NCMe<sub>2</sub>), 1.10 (s, 3H, CAAC(NCMe<sub>2</sub>), 0.92 (s, 3H, CAAC(BCMe<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 153.1 (Dip(o-Ar)), 152.2 (Dip(o-Ar)), 144.4 (broad, Dur(B-C)), 141.8 (Dip(Ar-N)), 134.7 (Dur(C-Me)), 134.2 (Dur(C-Me)), 133.7 (Dur(C-Me)), 132.7 (Dur(C-Me)), 130.9 (Dur(C-H)), 127.2 (Dip(p-Ar)), 125.1 (Dip(m-Ar)), 124.9 (Dip(m-Ar)), 68.4 (broad, CAAC(BC-H)), 61.8 (CAAC(NCMe<sub>2</sub>)), 60.1 (CAAC(CH<sub>2</sub>), 40.7 (CAAC(BCMe2)), 30.8 (CAAC(NCMe2)), 29.7 (Dip(CHMe2)), 28.9 (CAAC(BCMe2), 28.3 (CAAC(NCMe2), 28.2 (CAAC(BCMe2), 27.7 (Dip(CHMe2)), 26.2 (Dip(CHMe<sub>2</sub>)), 26.1 (Dip(CHMe<sub>2</sub>)), 24.9 (Dip(CHMe<sub>2</sub>)), 24.7 (Dip(CHMe<sub>2</sub>)), 21.5 (Dur(Me)), 20.6 (Dur(Me)), 20.1 (Dur(Me)), 20.0 (Dur(Me)) ppm. 11B NMR (160 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): 46 ppm. HRMS (toluene, LIFDI): [M<sup>+</sup>] 446.3821 (calculated 446.3838). Infrared (attenuated total reflection (ATR), solid, N-H stretch, cm<sup>-1</sup>): 3474, 3379. See Supplementary Figs. 1-3, 6 and 8 for spectra of 8.

The second method involved reduction of **4** to **8**. A blue solution of **4** (40 mg, 45 µmol) in C<sub>6</sub>D<sub>6</sub> (~1 ml), containing moisture from its synthesis by hydrolysis, was added to solid KC<sub>8</sub> (60 mg, 444 µmol) with stirring, and the solution rapidly became colourless. After ~30 min, the mixture was filtered to give a colourless solution that was analysed by <sup>11</sup>B NMR spectroscopy, showing a new signal at  $\delta$ =46 ppm. The residue was extracted with more benzene (3×1 ml) and the combined organic fractions were subsequently evaporated to dryness under vacuum and the residue was recrystallized from a cooled hexanes solution to give **8** as colourless crystals (34 mg, 84%).

The third method was reduction–protonation of N<sub>2</sub> using **1** and a KC<sub>8</sub>/B(OH)<sub>3</sub> mixture. A solid mixture of **1** (150 mg, 295 µmol), B(OH)<sub>3</sub> (273 mg, 4.42 mmol) and KC<sub>8</sub> (598 mg, 4.42 mmol) in a pressure flask was cooled to -78 °C. Toluene (~25 ml) was then added very slowly to the mixture via a cannula, after which the flask was immediately pressurized with N<sub>2</sub> (~5 atm) under vigorous stirring. The suspension was allowed to warm slowly to room temperature, stirred for 4 h and subsequently filtered. The residue was extracted once with toluene (15 ml) and the organic fraction was dried to afford **8** as a colourless solid, which was further purified by recrystallization from a saturated pentane solution at -30 °C (80.0 mg, 65% yield).

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The fourth method was reduction-protonation of 15N2 using 1 and a KC8/B(OH)3 mixture to yield 8-15N. [(CAAC)BBr(Dur)] (1, 75.0 mg, 147 µmol), B(OH)<sub>3</sub> (136 mg, 2.20 mmol) and KC $_8$  (299 mg, 2.20 mmol) were placed in a glass reactor equipped with a Teflon valve. Toluene was degassed under vacuum and condensed over the solid mixture at -196°C. The solvent was warmed to approximately -80 °C, at which point the reactor was flushed with  ${}^{15}N_2$ . Further  ${}^{15}N_2$  (in a calibrated volume) was then condensed into the reactor at -196 °C and the reactor was sealed, ultimately providing a pressure of ~3.3 atm at the end of the reaction at room temperature. The mixture was allowed to warm to room temperature. stirred for 4 h and subsequently filtered. The solid residue was extracted with four portions (~3 ml each) of benzene. The combined liquid fractions were evaporated to dryness to give a residue in which  $8^{-15}$ N was identified as the main product. This solid was rinsed with pentane to yield pure 8-15N as colourless crystals (20 mg, 30%). The pentane fraction was evaporated to dryness to yield a further white solid in which 8-15N is also the main component (39 mg), indicating a high conversion to 8-15N. The NMR spectra of 8-15N are identical to those of 8 apart from the following data. <sup>1</sup>H NMR (500 MHz, 298 K,  $C_6D_6$ ):  $\delta$  3.51 (dd, <sup>1</sup> $J_{1H-15N}$  = 80 Hz,  ${}^{2}J_{1H-1H} = 1.6 \text{ Hz}, 1H, NH_{2}$ , 3.09 (dd,  ${}^{1}J_{1H-15N} = 80 \text{ Hz}, {}^{2}J_{1H-1H} = 1.6 \text{ Hz}, 1H, NH_{2}$ ) ppm.  $J_{\text{III-III}}^{\text{III-III}} = 1.01\text{ m}, \dots, 1.12, 9.003 \text{ (also of the second secon$ 40.7 (d,  ${}^{3}J_{13C-15N} = 0.8$  Hz, CAAC(BCMe<sub>2</sub>)) ppm.  ${}^{15}N$  NMR (51 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ-321.0 (CAAC(NDip))-282.1 (NH<sub>2</sub>) ppm. Infrared (ATR, solid, <sup>15</sup>N-H, cm<sup>-1</sup>): 3465, 3374. HRMS (toluene, LIFDI): [M<sup>+</sup>] 447.3790 (calculated 447.3797). See Supplementary Figs. 4, 5, 7 and 9 for spectra of 8-15N.

General method for the qualitative hydrolysis of 8 and 8-<sup>15</sup>N to form <sup>14/15</sup>NH<sub>4</sub>Cl. A drop of concentrated aqueous HCl (~37%) was added to NMR samples of 8 and 8-<sup>15</sup>N in C<sub>6</sub>D<sub>6</sub>. The tubes were vigorously shaken and demineralized water with ~10% D<sub>2</sub>O (~0.2 ml) was added. The organic layer was separated and removed and NH<sub>4</sub>Cl was identified by <sup>14</sup>N{<sup>1</sup>H} (from 8) or <sup>15</sup>N{<sup>1</sup>H} (from 8-<sup>15</sup>N) insensitive-nuclei-enhanced polarization transfer NMR spectroscopy, which showed a single resonance in both cases at  $\delta = -359$  and -360 ppm, respectively. The <sup>14/15</sup>N NMR shifts and the <sup>15</sup>N-H *J*-coupling constant of 73 Hz are identical to the literature data of NH<sub>4</sub>Cl.

One-pot synthesis of NH<sub>4</sub>Cl from N<sub>2</sub>, 1 and a KC<sub>8</sub>/B(OH)<sub>3</sub> mixture. A solid mixture of 1 (104 mg, 196 µmol), B(OH)<sub>3</sub> (200 mg, 3.23 mmol) and KC<sub>8</sub> (420 mg, 3.11 mmol) was cooled to -78 °C in a closed pressure flask. Toluene was then added very slowly to the mixture via a cannula, after which the flask was immediately pressurized with N<sub>2</sub> (~5 atm) with vigorous stirring. The suspension was allowed to warm slowly to room temperature and then stirred for 4 h, after which concentrated aqueous HCl (11 M, 2 ml) was added drop-wise at 0 °C. The resulting biphasic mixture was stirred overnight at room temperature, then extracted with a phosphate buffer solution (0.5 M, pH 7) until 11 of aqueous phase was obtained in a volumetric flask. The ammonium chloride concentration of this solution was quantified using the indophenol method (yield 53 µmol, 27%)<sup>40</sup>.

Synthesis of aminoboryl radical 6. The first method was protonation of 5. A black solution of 5 (12 mg, 12 µmol) was added to solid B(OH)<sub>3</sub> in a vial (15 mg, 250 µmol, 10 equiv. relative to B) and stirred at room temperature for 20 min. During this time, the solution turned bright orange, with no hint of the dark green colour of 5 being apparent. The reaction mixture was filtered through a glass filter in a Pasteur pipette in a glovebox and the colourless residue was extracted with additional C<sub>6</sub>D<sub>6</sub>. NMR analysis of the filtrate did not reveal the formation of a new diamagnetic substance. The filtrate was slowly evaporated to dryness, leading to the isolation of 6 as orange crystals (10 mg, 90%). Radical 6 was characterized by SCXRD and EPR spectroscopy. Their structural similarities result in the EPR spectrum of 6 being indistinguishable from that of radical 5; however, analysis of the N-H stretching bands of 5 and 6 in their infrared spectra enables them to be distinguished and can be used to confirm the protonation of 5 to 6. EPR (continuous wave, X band, toluene, room temperature): g = 2.0030,  $a^{(11B)} = 5.8$  MHz,  $a^{(14N)} = 18.0$  and 15.6 MHz. The spectrum shows additional partially resolved hyperfine couplings (a = 0.5 G), probably due to the NH<sub>2</sub> hydrogen nuclei, although these could not, however, be successfully included in the simulation. Infrared (ATR, solid, N-H, cm<sup>-1</sup>): 3498, 3402. HRMS (toluene, LIFDI): [M]+ 445.3747 (calculated 445.3749). See Supplementary Figs. 14-17 for spectra of 6.

The second method was photolytic reaction of hydrazine with borylene carbonyl [DurB(CO)(CAAC)]. A solution of [DurB(CO)(CAAC)] (41 mg, 90  $\mu$ mol) in C<sub>6</sub>D<sub>6</sub> was placed in a J.-Young-style NMR tube. Anhydrous hydrazine (~50  $\mu$ mol) was condensed into the mixture at ~196 °C. After warming to room temperature, the thawed biphasic mixture was placed under a mercury vapor lamp (current 19 A, voltage 26 V) for 18 h, resulting in a colour change from orange to red-orange. EPR and NMR spectroscopic analyses suggested that a single paramagnetic species comprised the bulk of the mixture. The volatile components were removed under vacuum and the red-orange solid was washed several times with hexane and dissolved in toluene/hexane. A crop of red crystals was obtained upon standing at ~30 °C for a few days, and these were washed twice with pentane (11 mg, 27%). Yields can be increased by processing the hexane washings and the recrystallization supernatants. Compound **6** obtained in this way is spectroscopically identical to samples obtained by protonation of **5** (see the first method).

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Synthesis of aminoboryl anion dimer 7 by reduction of 6. An orange solution of radical 6 (10 mg, 22  $\mu$ mol) in C<sub>6</sub>D<sub>6</sub> (~1 mL) was added to solid KC<sub>8</sub> (30 mg, 221 µmol) in a vial and stirred at room temperature. The solution began to turn deep purple immediately upon addition. After stirring for 15 min, the mixture was filtered through a glass filter in a Pasteur pipette and the residue was extracted with additional C6D6. NMR spectroscopic analysis of the filtrate revealed the formation of 7 as a single new diamagnetic substance. The filtrate was slowly evaporated to dryness and rapidly rinsed with a small amount of hexane, leading to the isolation of 7 as black crystals (10 mg, 92%). Compound 7 is highly sensitive to protonation by trace moisture and should be handled with care. 7 can be quantitatively protonated to 8 by stirring it over B(OH)<sub>3</sub> in benzene for 30 min at room temperature. <sup>1</sup>H NMR (500 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 7.16 (s, C<sub>6</sub>H<sub>6</sub> solvate), 6.86 (d, <sup>3</sup>*J*=7.4 Hz, 4H, Dip(*m*-Ar)), 6.72 (t, <sup>3</sup>*J*=7.4 Hz, 2H, Dip(*p*-Ar)), 6.55 (s, 2H, Dur(p-CH), 4.20 (septet, <sup>3</sup>J=6.8 Hz, 4H, Dip(CHMe<sub>2</sub>)), 2.51 (s, 12H, Dur(Me)), 2.05 (s, 12H, Dur(Me)), 1.99 (s, 4H, CAAC(CH<sub>2</sub>)), 1.44 (s, 12H, CAAC(CMe<sub>2</sub>), 1.42 (s, 12H, CAAC(CMe<sub>2</sub>), 1.28 (d, <sup>3</sup>J=6.8 Hz, 12H, Dip(CHMe<sub>2</sub>)), 1.02 (d, <sup>3</sup>J=6.8 Hz, 12H, Dip(CHMe<sub>2</sub>)), 0.52 (broad s, 1H, NH<sub>2</sub>), 0.49 (broad s, 1H, NH<sub>2</sub>) ppm. <sup>1</sup>H diffusion-ordered spectroscopy (DOSY) NMR experiments suggest that the compound remains a dimer in benzene solution, which is consistent with the observation of two different yet close <sup>15</sup>N NMR signals for the NH<sub>2</sub> groups, suggesting an unsymmetrical dimer. Although 15N-1H heteronuclear single-quantum coherence spectroscopy and <sup>15</sup>N-<sup>1</sup>H heteronuclear multiple-bond correlation spectroscopy experiments allow us to locate unambiguously two N-H (not NH<sub>2</sub>) protons (one on each inequivalent N) in the dimer, the remaining two proton signals could not be located. This could tentatively be attributed to fluctional H migration processes—possibly to the B and/or CCAAC atoms—that selectively affect only two N-H protons because of geometrical constraints in the dimer. <sup>11</sup>B NMR (160 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 25 ppm. <sup>13</sup>C NMR (126 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 157.5 (located by heteronuclear multiple-bond correlation spectroscopy, Dur(B-C)), 151.9 (Dip(o-Ar)), 150.0 (Dip(N-Ar)), 137.0 (Dur(m-Ar)), 133.0 (Dur(o-Ar)), 128.5 (C6H6 solvate), 128.1 (Dur(CH)), 124.6 (Dip(m-Ar)), 123.0 (Dip(p-CH)), 61.5 (CAAC(CH2)), 61.2 (CAAC(CMe2)), 42.5 (CAAC(CMe2)), 33.7 (CAAC(CMe2)), 28.8 (CAAC(CMe2)), 26.7 (Dip(CHMe2)), 25.9 (Dip(CHMe2)), 24.7 (Dip(CHMe2)), 22.0 (Dur(Me)), 20.4 (Dur(Me)) ppm. <sup>15</sup>N NMR (shifts inferred from <sup>15</sup>N-<sup>1</sup>H heteronuclear single-quantum coherence spectroscopy and <sup>15</sup>N-<sup>1</sup>H heteronuclear multiple-bond correlation spectroscopy experiments, 51 MHz, 298 K,  $C_6D_6$ ):  $\delta$ -344.3 (B-NH), -343.3 (B-NH), -296.6 (CAAC) ppm. HRMS (toluene, LIFDI): [M-K+H]+ 446.3822 (calculated 446.3827). Infrared spectroscopy of 7 revealed only very weak bands in the N-H stretch region. This situation is attributed to the dimeric nature of 7. See Supplementary Figs. 18-26 for spectra of 7.

**NMR spectroscopy**. General NMR spectroscopic details. Solution NMR spectra were acquired on a Bruker Avance I 400 NMR spectrometer (<sup>1</sup>H: 400.57 MHz) or a Bruker Avance I 500 spectrometer (<sup>1</sup>H: 500.13 MHz). Chemical shifts ( $\delta$ ) are given in ppm and internally referenced to the carbon nuclei (<sup>13</sup>C{<sup>1</sup>H}) or residual protons (<sup>1</sup>H) of the solvent. <sup>11</sup>B{<sup>1</sup>H} NMR spectra were referenced to [BF<sub>3</sub>·OEt<sub>2</sub>] as an external standard. <sup>14</sup>N and <sup>15</sup>N spectra were referenced to nitromethane + 10% CDCl<sub>3</sub> as an external standard.

DOSY NMR spectroscopy experiments. 1H DOSY measurements of 7 and 8 in C<sub>6</sub>D<sub>6</sub> were performed at 298.15 K in 5 mm NMR tubes on a Bruker Avance Neo 400 spectrometer equipped with a 5 mm BBFO iProbe (BBFO stands for broad band fluorine observation) with a z-axis gradient coil capable of producing pulsed magnetic field gradients of 51 G cm<sup>-1</sup>. Temperature calibration was performed with a standard sample of 4% CH<sub>3</sub>OH in CD<sub>3</sub>OD. The gradient coil was calibrated to  $4.995745\,G\,mm^{-1}$  at 298.15 K using a 'doped water' NMR sample (0.1 mg GdCl\_3/mL  $D_2O + 1\% H_2O + 0.1\%$  <sup>13</sup>CH<sub>3</sub>OH, 40 mm fill height). Data were acquired and processed using Bruker Topspin 4.0.7 software. The DOSY data were recorded with a stimulated echo BPP-LED sequence (longitudinal eddy current delay (LED) sequence with bipolar gradient pulse pairs (BPP) for diffusion and additional spoil gradients). The diffusion time  $\Delta$  (50 ms) was kept constant in each DOSY experiment while the 'smoothed square' diffusion gradients were incremented from 2% to 95% of maximum gradient strength in 24 linear steps. One-component fittings of the gradient strength dependence of the signal areas were performed by a Levenberg-Marquardt algorithm incorporated in the Topspin 4.0.7 software.

**Further spectroscopic and spectrometric details.** EPR measurements at the X band (9.38 GHz) were carried out using a Bruker ELEXSYS E580 CW EPR spectrometer equipped with an Oxford Instruments helium cryostat (ESR900) and a MercuryiTC temperature controller. Spectral simulations were performed using MATLAB 8.6.0.267246 (R2015b) and the EasySpin 5.1.9 toolbox<sup>41</sup>. The EPR spectrometer was calibrated by using 2,2-diphenyl-1-picrylhydrazyl (dpph) with a g value of 2.0037 as a standard. Solid-state infrared spectra were acquired on a Bruker Alpha spectrometer using a setup with a Bruker diamond crystal single-reflection ATR system. HRMS data were obtained from a Thermo Scientific Exactive Plus spectrometer in LIFDI mode.

**SCXRD.** *General considerations.* The crystal data of **8** were collected on a Bruker X8-APEX II diffractometer with a charge-coupled device area detector

and multilayer mirror monochromated Mo K $\alpha$  radiation. The crystal data of 5–7 were collected on a Rigaku Synergy Dualflex Hypix diffractometer with a complementary metal–oxide–semiconductor area detector and multilayer mirror-monochromated Cu K $\alpha$  radiation. The structures were solved using the intrinsic phasing method<sup>42</sup> refined with the SHELXL program<sup>43</sup> and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. Unless otherwise noted, all hydrogen atoms were assigned to idealized geometric positions. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1971191-1971194. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, www.ccdc.cam.ac.uk/data\_request/cif.

*Crystallographic details for 5.* The coordinates of H1 (residues 1 and 2) were refined but the distances between atoms N1 and H1 (residues 1 and 2) were kept at the value of 0.91 Å using the DFIX restraint. Crystal data:  $C_{60}H_{90}B_2K_2N_4$ ,  $\lambda = 1.54184$  Å,  $M_r = 967.17$ , bronze-coloured blade, 0.193 × 0.050 × 0.039 mm<sup>3</sup>, triclinic space group  $P\overline{1}$ , a = 10.7085(2) Å, b = 16.6116(3) Å, c = 18.0545(4) Å,  $\alpha = 69.131(2)^\circ$ ,  $\beta = 89.791(2)^\circ$ ,  $\gamma = 74.733(2)^\circ$ , V = 2,880.52(11) Å<sup>3</sup>, Z = 2,  $\rho_{citcd} = 1.115$  g cm<sup>-3</sup>,  $\mu = 1.736$  mm<sup>-1</sup>, F(000) = 1052, T = 100(2) K,  $R_1 = 0.0479$ ,  $wR^2 = 0.1249$ , 10,919 independent reflections [ $2\theta \le 140.15^\circ$ ] and 645 parameters (two restraints), maximum/minimum residual electron density 0.85 e Å<sup>-3</sup> at 0.5729 0.7247 0.3598 [0.85 Å from K1\_2]/−0.62 e Å<sup>-3</sup> at 0.5148 0.6492 0.3817 [0.69 Å from K1\_2]. See Supplementary Fig. 27 for the solid-state structure of **5**.

*Crystallographic details for* 6. Crystal data:  $C_{30}H_{46}BN_{2^{\circ}}\lambda = 1.54184$  Å,  $M_t = 445.50$ , orange blade,  $0.248 \times 0.200 \times 0.140$  mm<sup>3</sup>, triclinic space group  $P\overline{1}$ , a = 9.49530(10) Å, b = 11.55080(10) Å, c = 12.9846(2) Å,  $\alpha = 89.4810(10)^{\circ}$ ,  $\beta = 76.2920(10)^{\circ}$ ,  $\gamma = 76.5540(10)^{\circ}$ , V = 1344.04(3) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.101$  g cm<sup>-3</sup>,  $\mu = 0.464$  mm<sup>-1</sup>, F(000) = 490, T = 100(2) K,  $R_1 = 0.0390$ ,  $wR^2 = 0.1060$ , 5,102independent reflections  $[2\theta \le 140.14^{\circ}]$  and 318 parameters (two restraints), maximum/minimum residual electron density 0.24 e Å<sup>-3</sup> at 0.2834 0.3467 0.8298 [0.75 Å from C2]/-0.21 e Å<sup>-3</sup> at 0.1947 0.3145 0.9227 [0.65 Å from C2]. See Supplementary Fig. 28 for the solid-state structure of **6**.

Crystallographic details for 7. The coordinates of H1 and H2 (residues 0 and 1) were refined but the distances between atoms N1/H1 and N1/H2 (residues 0 and 1) were kept at the value of 0.91 Å using the DFIX restraint. The molecule co-crystallizes with a half benzene molecule that is disordered about an inversion centre and was refined using an idealized geometry with the Afix 6 keyword. The displacement parameters of atoms C1-C6 (benzene) were restrained to the same value with similarity restraint SIMU. Uii displacement parameters of C1-C6 (benzene) were restrained with the ISOR keyword to approximate isotropic behaviour. Rigid bond restraints were applied to residue 2 (benzene) with the keyword RIGU. Crystal data:  $C_{63}H_{95}B_2K_2N_4$ ,  $\lambda = 1.54184$  Å,  $M_r = 1008.24$ , orange blade,  $0.194 \times 0.119 \times 0.049 \text{ mm}^3$ , triclinic space group  $P\overline{1}$ , a = 12.8434(2) Å, b = 13.1929(3) Å, c = 18.2794(3) Å,  $\alpha = 81.594(2)^{\circ}$ ,  $\beta = 89.1760(10)^{\circ}$ ,  $\gamma = 80.114(2)^{\circ}$ ,  $V = 3,018.34(10) \text{ Å}^3$ , Z = 2,  $\rho_{\text{calcd}} = 1.109 \text{ g cm}^{-3}$ ,  $\mu = 1.674 \text{ mm}^{-1}$ , F(000) = 1098, T = 100(2) K,  $R_1 = 0.0469$ ,  $wR^2 = 0.1273$ , 11,468 independent reflections  $[2\theta \le 140.144^{\circ}]$  and 695 parameters (112 restraints), maximum/minimum residual electron density 0.57 e Å-3 at -0.0076 0.0682 0.0524 [0.64 Å from C4 2]/-0.42 e Å-3 at 0.7587 0.3262 0.3332 [0.68 Å from K1]. See Supplementary Fig. 29 for the solid-state structure of 7.

Crystallographic details for 8. The coordinates of H1 and H2 of residue 0 were refined but the distances between atoms N1/H1 and N1/H2 were kept at the value of 0.91 Å using the DFIX restraint. One of the isopropyl moieties of the 2,6-diisopropylphenyl group could be modelled as a two-part disorder with a refined ratio of 0.73:0.27, in which the isopropyl is found in two orientations related by a rotation about the aryl-C axis. The protonated CAAC moiety is found as two conformers, which was modelled as a two-part disorder with a refined ratio of 0.74:0.26. The two disorders were refined independently (two free variables) but may be related because H-H distances between the CAAC methyl groups and the isopropyl groups are too short when the isopropyl disorder is not modelled. The displacement parameters of atoms C8 and C8a of residue 0 were constrained to the same value with the EADP keyword. The displacement parameters of atoms C1, C1a, C3, C3a, C4, C4a, C7, C7a, C8, C8a, C2, C2a, C5, C5a, C6 and C6a of residue 0 and C8-C12a of residue 2 (2,6-diisopropylphenyl) were restrained to the same value with similarity restraint SIMU. The distances between atoms C4/C7, C4a/C7a, C4/C8, C4a/C8a, C2/C5, C2/C6, C2a/C6a, C2a/C5a of residue 0 were restrained during refinement to the same value with the SADI restraint. The Uii displacement parameters of atoms C4, C4a, C2 and C2a of residue 0 were restrained with the ISOR keyword to approximate isotropic behaviour. The 1-2 and 1-3 distances in atoms C8a-C12a of residue 2 were restrained to the same values with the SAME command. Crystal data:  $\rm C_{30}H_{47}BN_2, \lambda\,{=}\,0.71073$  Å,  $M_r$  = 446.50, colourless prisms, 0.537 × 0.377 × 0.172 mm<sup>3</sup>, triclinic space group  $P\bar{1}, a=9.372(4)$  Å, b=11.500(4) Å, c=13.271(9) Å,  $\alpha=88.76(2)^{\circ}, \beta=76.074(17)^{\circ}, \beta=10.074(17)^{\circ}$  $\gamma = 77.292(11)^\circ$ , V = 1353.6(12) Å<sup>3</sup>, Z = 2,  $\rho_{calcd} = 1.096$  g cm<sup>-3</sup>,  $\mu = 0.062$  mm<sup>-1</sup> F(000) = 492, T = 100(2) K,  $R_1 = 0.0692$ ,  $wR^2 = 0.1293$ , 5,549 independent reflections

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 $[2\theta \le 52.744^\circ]$  and 419 parameters (357 restraints), maximum/minimum residual electron density 0.34 e Å<sup>-3</sup> at 0.2788 0.5392 0.7730 [0.79 Å from C3\_1]/-0.31 e Å<sup>-3</sup> at 0.0455 0.3944 0.9155 [0.11 Å from C7A]. See Supplementary Fig. 29 for the solid-state structure of **8**.

#### Data availability

Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 1971191 (8), 1971192 (7), 1971193 (5) and 1971194 (6). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/. Further data supporting the findings of this study are available from the corresponding author upon reasonable request.

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#### Author contributions

Experiments were designed by M.-A.L., G.B.-C., R.D.D. and H.B. and performed by M.-A.L., M.R. and G.B.-C. Data analysis was performed by M.-A.L., G.B.-C. and the article was written by M.-A.L. and R.D.D. X-ray crystallography was performed by G.B.-C. The EPR investigation was performed by I.K. and the NMR experiments were performed by R.B. The project was overseen by H.B. All authors read and commented on the manuscript.

#### **Competing interests**

The authors declare no competing interests.

#### **Additional information**

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Correspondence and requests for materials should be addressed to H.B.

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