# $\mathrm{A}\left[\mathrm{HN}(\mathrm{BH}=\mathrm{NH})_{2}\right]^{2-}$ Dianion, Isoelectronic with a $\beta-$ Diketiminate 

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## Electronic Supporting Information

## Section 1

## In situ ${ }^{11}$ B NMR studies

All catalytic reactions were performed in sealed NMR tubes using undeuterated, dry THF ( 0.5 ml ) using an acetone- $\mathrm{d}_{6}$ capillary as a signal lock. Quantities of metal complex (1 eq.) and ammonia borane ( $\mathrm{AB}, 6 \mathrm{eq}$.) used were as follows:

1 ( $24 \mathrm{mg}, 72 \mu \mathrm{~mol}), \mathrm{AB}(13 \mathrm{mg}, 340 \mu \mathrm{~mol})$
2 (30 mg, $86 \mu \mathrm{~mol}), A B(16 \mathrm{mg}, 520 \mu \mathrm{~mol})$

3 ( $30 \mathrm{mg}, 75 \mu \mathrm{~mol}$ ), $\mathrm{AB}(14 \mathrm{mg}, 450 \mu \mathrm{~mol})$

Control. AB ( $15 \mathrm{mg}, 490 \mu \mathrm{~mol})$


Figure S1. In situ ${ }^{11}$ B NMR spectra of 1, $\mathbf{2}$ and $\mathbf{3}+$ ammonia borane (1:6 mol. eq.) in THF after 0.5 h at $50^{\circ} \mathrm{C}$.


Figure S2. In situ ${ }^{11}$ B NMR spectra of 1, $\mathbf{2}$ and $\mathbf{3}+$ ammonia borane (1:6 mol. eq.) in THF after 16 h at $50^{\circ} \mathrm{C}$.


Figure S3. In situ ${ }^{11}$ B NMR spectrum of [\{DMPnacnac\}AlH ${ }_{2}$ ] (1) + ammonia borane (1:6 mol. eq.) in THF after 16h reflux.


Figure S4. ${ }^{11} \mathrm{~B}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ of [\{DMPnacnac $\left.\} \mathrm{AlH}_{2}\right](1)+{ }^{t} \mathrm{BuNH}_{2} \mathrm{BH}_{3}(1: 1 \mathrm{~mol}$. eq.) after 16 h reflux in toluene.


Figure S5. ${ }^{11} \mathrm{~B}$ NMR spectrum $\left(\mathrm{CDCl}_{3}\right)$ of [\{DMPnacnac $\left.\} \mathrm{AlH}_{2}\right](1)+{ }^{t} \mathrm{BuNH}_{2} \mathrm{BH}_{3}(1: 3 \mathrm{~mol}$. eq.) after 16 h reflux in toluene (a); sublimed from reaction mixture $90^{\circ} \mathrm{C} / 0.5 \mathrm{~mm} \mathrm{Hg}(b)$; sublimed from reaction mixture $120^{\circ} \mathrm{C} / 0.5 \mathrm{~mm} \mathrm{Hg}$ (c).

## Section 2

## Synthesis of New Complexes

## General experimental procedures

All preparations were performed on a double-manifold vacuum line under a nitrogen atmosphere. The products were isolated and stored with the aid of a nitrogen-filled glove box (Saffron type b), equipped with Cu and molecular sieve columns in order to remove $\mathrm{O}_{2}$ and moisture, respectively. All ${ }^{11} \mathrm{~B},{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were recorded using a Bruker DPX 500 MHz NMR spectrometer $\left({ }^{1} \mathrm{H},{ }^{13} \mathrm{C}\right.$ referenced to $\mathrm{SiMe}_{4},{ }^{11} \mathrm{~B}$ referenced to $\mathrm{BF}_{3} \cdot \mathrm{Et}_{2} \mathrm{O}$ ). Elemental ( $\mathrm{C}, \mathrm{H}, \mathrm{N}$ ) analyses were obtained using an Exeter CE-440 Elemental Analyser. Solvents and amine bases were dried by distillation over an appropriate drying agent: THF ( $\mathrm{Na} /$ benzophenone), toluene ( Na ), $\mathrm{CDCl}_{3}\left(\mathrm{P}_{2} \mathrm{O}_{5}\right)$. [\{DMPnacnac\}AlH ${ }_{2}$ ] (1) was prepared as described in the literature. ${ }^{1}$ Ammonia borane and borane tert-butylamine complex were used as supplied (Sigma-Aldrich) and were stored at room temperature.

## [\{DMPnacnac\}AlH $\left(\mathrm{BH}_{4}\right)$ ] 2

A solution of [\{DMPnacnac\}AlH ${ }_{2}$ ] (1) ( $200 \mathrm{mg}, 0.60 \mathrm{mmol}$ ) and borane tert-butylamine complex (104 $\mathrm{mg}, 1.20 \mathrm{mmol}$ ) in 3 ml toluene was heated under reflux for 16 h . The solvent was removed in vacuo and the residue extracted with hot hexane ( 3 ml ). The hexane was evaporated until the product began to crystallise then warmed to redissolve. Slow cooling resulted in formation of crystals of 2 which were collected and washed with hexane (yield $68 \mathrm{mg}, 33 \%$ ).

Found (\%): C 72.39, H 9.16, N 8.84; Calculated for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{AlBN}_{2}$ : C 72.42, H 8.68, N 8.04.
${ }^{11} \mathrm{~B}$ NMR $\left(128.4 \mathrm{MHz}, 25^{\circ} \mathrm{C}, \mathrm{CDCl}_{3}\right), \delta / \mathrm{ppm}=-37.81\left(\mathrm{qn}, \mathrm{J}=84.94 \mathrm{~Hz}, \mathrm{BH}_{4}{ }^{-}\right)$.
${ }^{1} \mathrm{H}$ NMR $\left(400.1 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}, \mathrm{CDCl}_{3}\right), \delta / \mathrm{ppm}=7.12-7.10(\mathrm{~m}, 6 \mathrm{H}, \mathrm{ArH}), 5.20\left(\mathrm{~s}, 1 \mathrm{H},\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$, 2.29 ( $\mathrm{s}, 6 \mathrm{H}, \operatorname{ArMe}$ ), $2.23(\mathrm{~s}, 6 \mathrm{H}, \mathrm{ArMe}), 1.76\left(\mathrm{~s}, 6 \mathrm{H},\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right), 0.17(\mathrm{brq}, \mathrm{J}=60.67$ $\mathrm{Hz}, 4 \mathrm{H}, \mathrm{BH}_{4}{ }^{-}$).
${ }^{13} \mathrm{C}$ NMR ( $100.6 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}, \mathrm{CDCl}_{3}$ ), $\delta / \mathrm{ppm}=170.81(\mathrm{C}=\mathrm{N}), 141.60(\mathrm{Ar}), 134.33(\mathrm{Ar}), 133.76(\mathrm{Ar})$, 129.22 (Ar), 129.14 ( Ar$), 126.87$ ( Ar$), 97.26\left(\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right), 23.38\left(\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$, 18.86 (ArMe), 18.76 (ArMe).


Figure S6. ${ }^{11} \mathrm{~B}$ NMR spectrum of [\{DMPnacnac\}AIH( $\left.\left.\mathrm{BH}_{4}\right)\right](\mathbf{2})$ in $\mathrm{CDCl}_{3}$.




Figure S8. ${ }^{13} \mathrm{C}$ NMR spectrum of [\{DMPnacnac $\left.\} \mathrm{AlH}\left(\mathrm{BH}_{4}\right)\right]$ (2) in $\mathrm{CDCl}_{3}$.
[\{DMPnacnac\}AI\{(NHBH) ${ }_{2}$ NH $\}$ ]
3
A solution of [\{DMPnacnac\}AlH ${ }_{2}$ ] (1) ( $200 \mathrm{mg}, 0.60 \mathrm{mmol}$ ) and ammonia borane ( $37 \mathrm{mg}, 1.20 \mathrm{mmol}$ ) in 3 ml THF was heated under reflux for 16 h . The solvent was removed in vacuo and the residue extracted with hot hexane ( 5 ml ). The hexane was evaporated until the product began to crystallise then warmed to redissolve. Slow cooling resulted in formation of crystals of $\mathbf{3}$ which were collected and washed with hexane (yield $51 \mathrm{mg}, 16 \%$ ).

Crystals suitable for X-ray diffraction were grown by slow cooling of a saturated solution of $\mathbf{3}$ in toluene.

Found (\%): C 60.73, H 7.66, N 15.69; Calculated for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{AlB}_{2} \mathrm{~N}_{5}$ : C 62.88, H 7.54; $\mathrm{N}, 17.46$.
(Note: Organoboron compounds typically give lowered carbon and nitrogen values in elemental microanalysis due to the formation of non-combustible boron carbide and boron nitride by-products. It was noted that $\mathbf{3}$ did not fully combust during analysis) ${ }^{2}$
${ }^{11}$ B NMR ( $128.4 \mathrm{MHz}, 25^{\circ} \mathrm{C}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) $\delta / \mathrm{ppm}=32.57$ (brs, BH ).
${ }^{11}$ B NMR ( $128.4 \mathrm{MHz}, 25^{\circ} \mathrm{C}, \mathrm{CDCl}_{3}$ ), $\delta / \mathrm{ppm}=31.80(\mathrm{br} \mathrm{s}, \mathrm{BH})$.
${ }^{1} \mathrm{H}$ NMR ( $400.1 \mathrm{MHz}, 25^{\circ} \mathrm{C}, \mathrm{C}_{6} \mathrm{D}_{6}$ ), $\delta / \mathrm{ppm}=6.92-6.89(\mathrm{~m}, 6 \mathrm{H}, \mathrm{ArH}), 4.79\left(\mathrm{~s}, 1 \mathrm{H},\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$, 4.69 (br s, 2H, BH), 3.88 (br s, 1H, NH), 2.81 (br s, 2H, NH), 2.14 (s, 12H, ArMe), 1.37 (s, 6H, $\left.\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$.
${ }^{1} \mathrm{H}$ NMR ( $400.1 \mathrm{MHz}, 25^{\circ} \mathrm{C}, \mathrm{CDCl}_{3}$ ), $\delta / \mathrm{ppm}=7.04-7.08(\mathrm{~m}, 6 \mathrm{H}, \mathrm{ArH}), 5.17\left(\mathrm{~s}, 1 \mathrm{H},\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$, 3.99 (br s, 2H, BH), 3.57 (br s, 1H, NH), 2.61 (br s, 2H, NH), 2.23 (s, 12H, ArMe), 1.72 (s, 6H, $\left.\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$.
${ }^{13} \mathrm{C}$ NMR ( $100.6 \mathrm{MHz}, 25{ }^{\circ} \mathrm{C}, \mathrm{CDCl}_{3}$ ), $\delta / \mathrm{ppm}=169.95(\mathrm{C}=\mathrm{N}), 142.46$ ( Ar ), 133.52 ( Ar ), 128.67 ( Ar ), 126.26 ( Ar ), 96.88 ( $\left.\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$, 23.00 ( $\left.\{\mathrm{Me}(\mathrm{ArN}) \mathrm{C}\}_{2} \mathrm{CH}\right)$, 18.92 (ArMe).


Figure S9. ${ }^{11} \mathrm{~B}$ NMR spectrum of [\{DMPnacnac\}AI\{NHBH) $\left.\left.{ }_{2} \mathrm{NH}\right\}\right](3)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S10. ${ }^{11} \mathrm{~B}$ NMR spectrum of [\{DMPnacnac\}Al\{NHBH) $\left.{ }_{2} \mathrm{NH}\right\}$ ] (3) in $\mathrm{CDCl}_{3}$.


Figure S11. ${ }^{1} \mathrm{H}$ NMR spectrum of [\{DMPnacnac\}Al\{NHBH) 2 NH$\left.\}\right](3)$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S12. ${ }^{1} \mathrm{H}$ NMR spectrum of [\{DMPnacnac\}AI\{NHBH) $\left.\left.{ }_{2} \mathrm{NH}\right\}\right]$ (3) in $\mathrm{CDCl}_{3}$.


Figure S13. ${ }^{13} \mathrm{C}$ NMR spectrum of [\{DMPnacnac\}Al\{NHBH) $\left.{ }_{2} \mathrm{NH}\right\}$ ] (3) in $\mathrm{CDCl}_{3}$.

## Section 3

## X-ray Crystallography

Data for all complexes were collected at 180(2) K on a Bruker D8-QUEST diffractometer using an Incoatec I $\mu \mathrm{S}$ Cu microsource ( $\lambda=1.5418 \AA$ ). Crystals were mounted directly from solution using perfuorohydrocarbon oil to prevent atmospheric oxidation, hydrolysis, and solvent loss. Structures were solved using SHELXT [G. M. Sheldrick, Acta Cryst. 2015, A71, 3] and refined using SHELXL-2014 [G. M. Sheldrick, Acta Cryst. 2015, C71, 3].

| CCDC No. | 1554315 | 1554314 |
| :---: | :---: | :---: |
| Compound | $\text { \{DMPnacnac\}Al\{(NHBH) } \left.\left.{ }_{2} \mathrm{NH}\right\}\right]$ $3$ | $\begin{aligned} & \text { \{DMPnacnac\}AIH }\left(\mathrm{BH}_{4}\right) \\ & 2 \end{aligned}$ |
| Chemical formula | $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{AlB}_{2} \mathrm{~N}_{5}$ | $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{AlBN}_{2}$ |
| FW / g.mol ${ }^{-1}$ | 401.10 | 348.26 |
| Crystal system | monoclinic | triclinic |
| Space group | P $21 / \mathrm{n}$ | P-1 |
| $a / \AA$ | 7.7071(2) | 7.5494(2) |
| b/ $\AA$ | 17.9986(4) | 11.8306(3) |
| $c / \AA$ | 16.4691(4) | 13.1813(3) |
| $\alpha /{ }^{\circ}$ | 90 | 65.4048(11) |
| $\beta /{ }^{\circ}$ | 95.2610(10) | 76.0634(12) |
| $\gamma /{ }^{\circ}$ | 90 | 84.0974(13) |
| $V / \AA^{3}$ | 2274.92(10) | 1038.95(5) |
| Z | 4 | 2 |
| $\rho_{\text {calcd }} / \mathrm{g} \cdot \mathrm{cm}^{-3}$ | 1.171 | 1.113 |
| $\mu / \mathrm{mm}^{-1}$ | 0.892 | 0.869 |
| Reflections collected | 31290 | 11820 |
| Independent reflections | 4026 | 3633 |
| $R_{\text {int }}$ | 0.080 | 0.035 |
| $R 1$ [ $I>2 \sigma(I)]$ | 0.051 | 0.044 |
| wR2 (all data) | 0.122 | 0.122 |
| Goodness-of-fit | 1.09 | 1.04 |



Figure S14. Solid-state structure of 2 showing displacement ellipsoids at the 50\% probability level for non-H atoms. H -atoms, except those of $\mathrm{Al}-\mathrm{H}$ and $\mathrm{BH}_{4}{ }^{-}$, have been removed for clarity. Selected bond lengths (Å) and angles ( ${ }^{\circ}$ : $\mathrm{C}(2)-\mathrm{N}(1) 1.338(2), \mathrm{C}(4)-\mathrm{N}(2) 1.336(2), \mathrm{C}(2)-\mathrm{C}(3) 1.391(3), \mathrm{C}(3)-\mathrm{C}(4)$ $1.396(3), \mathrm{Al}(1)-\mathrm{N}(1) 1.8904(16), \mathrm{Al}(1)-\mathrm{N}(2) 1.8895(16), \mathrm{Al}(1)-\mathrm{H} 1.49(2), \mathrm{Al}(1)-\mathrm{T}-\mathrm{H} 1.72(3), 1.78(3), \mathrm{B}-\mathrm{H}$ $1.16(4)-1.25(3), \mathrm{N}(1)-\mathrm{Al}(1)-\mathrm{N}(2) 96.15(7), \mathrm{N}(1)-\mathrm{C}(2)-\mathrm{C}(3) 122.94(16), \mathrm{N}(2)-\mathrm{C}(4)-\mathrm{C}(3) 122.82(17), \mathrm{C}(2)-$ C(3)-C(4) 127.37(17).

## Section 4

## Computational Details

## 1) Methods

Geometry optimisation of compound $\mathbf{3}$ was carried out using the Gaussian package. ${ }^{3}$ The optimised structures were obtained employing the B3LYP ${ }^{4}$ functional in conjunction with a $6-31 \mathrm{~g}++(\mathrm{d}, \mathrm{p})^{5}$ basis set. Frequency calculations of the optimised structure, were utilised to prove the absence of imaginary frequencies. Natural bond orbital ${ }^{6}$ analysis and calculation of Wiberg bond indices ${ }^{7}$ were carried out employing the NBO program version $3 .{ }^{8}$ Calculations of the nucleus-independent chemical shifts were computed with the Gauge-Independent Atomic Orbital (GIAO) method. ${ }^{9}$ Molecular orbitals were visualised using the programme Avogadro. ${ }^{10}$

## 2) Results

To evaluate the aromatic character of the AI-N-B heterocycle, DFT calculations were carried out. Figure S15 shows the geometry optimised structure, with the heterocycle being planar. The calculated HOMO-LUMO gap of the system is 4.42 eV .


Figure S15. Geometry optimised structure of 3.

Table S1. Selected bond lengths and angles.

|  | Bond lengths $[\AA \AA]$ |  | Bond Angles [ ${ }^{\circ}$ ] |
| :--- | :--- | :--- | :--- |
| Al1-N1 | 1.84 | N1-Al1-N3 | 102.9 |
| Al1-N3 | 1.83 | Al1-N1-B1 | 123.2 |
| N1-B1 | 1.42 | Al1-N3-B2 | 122.9 |
| B1-N2 | 1.44 | B1-N2-B2 | 128.4 |
| N2-B2 | 1.44 |  |  |
| B2-N3 | 1.42 |  |  |

Figure S16 shows the calculated nucleus-independent chemical shifts (NICS), with a dummy atom placed in the middle of the AI-N-B ring unit for NICS( 0 ), and $1 \AA$ above the ring plane for NICS(1). The negative values indicate a weak aromatic character of the heterocycle. For comparison, at the same level of theory, values of $\operatorname{NICS}(0)=-8.3 \mathrm{ppm}$ and $\operatorname{NICS}(1)=-10.3 \mathrm{ppm}$ were obtained for benzene and $\operatorname{NICS}(0)=-2.0 \mathrm{ppm}$ and $\operatorname{NICS}(1)=-2.8 \mathrm{ppm}$ for borazine.


Figure S16. $\operatorname{NICS}(0)$ and $\operatorname{NICS}(1)$ values in ppm for the optimised structure of 3. Comparison benzene: $\operatorname{NICS}(0)=-8.3$ and $\operatorname{NICS}(1)=-10.3$; borazine: $\operatorname{NICS}(0)=-2.0$ and $\operatorname{NICS}(1)=-2.8$.

To further examine the bonding situation in compound 3, the Wiberg bond indices were determined. By looking at it, a very symmetrical distribution becomes obvious, with $B$ having a slightly higher total WBI in comparison to $N$. This can indicate different hybridisation states of the $N$ and $B$ atoms. ${ }^{11}$ For comparison, the WBI of the C-C bonds in the aromatic ring of the ligand backbone is about 1.4 with a total WBI per C atom of 3.9.

Table S2. Wiberg bond indices (WBI) for the bonds of the central $A I-N(1)-B(1)-N(2)-B(2)-N(3)$ unit.

| Bond X-Y | WBI | WBI per atom |  |
| :---: | :---: | :---: | :---: |
|  |  | $X$ | $Y$ |
| $\mathrm{Al}(1)-\mathrm{N}(1)$ | 0.42 | 1.67 | 2.45 |
| $\mathrm{Al}(1)-\mathrm{N}(3)$ | 0.44 | 1.67 | 2.82 |
| $\mathrm{~N}(1)-\mathrm{B}(1)$ | 1.10 | 2.45 | 3.11 |
| $\mathrm{~B}(1)-\mathrm{N}(2)$ | 0.97 | 3.11 | 2.82 |
| $\mathrm{~N}(2)-\mathrm{B}(2)$ | 0.97 | 2.82 | 3.11 |
| $\mathrm{~B}(2)-\mathrm{N}(3)$ | 1.10 | 3.11 | 2.45 |

The results of the natural bond orbital analysis are summarised in Tables S3 and S4. It becomes obvious that there are 2-center bonds between the N and B atoms, with N having a higher atomic contribution, probably due to its higher electronegativity. As mentioned before, from the WBI it is clear that B and N show different hybridisation states. This can be confirmed by the NBO analysis. Whereas $N(1)$ and $N(3)$ show a hybridisation close to $s p, B(1), B(2)$ and $N(2)$ are approximately $s p^{2}$ hybridised (Fig. S15).

Table S3. Results of natural bond orbital (NBO) analysis 2-center bonds (BD) for the central AI-N(1)-$\mathrm{B}(1)-\mathrm{N}(2)-\mathrm{B}(2)-\mathrm{N}(3)$ unit.

| NBO | Occupation | Atomic contribution | Orbital contribution |
| :---: | :---: | :---: | :---: |
| BD N(1)-B(1) | 1.97 | $\mathrm{~N}: 75.4$ | $\mathrm{~N}: 54.5 \mathrm{~s}, 45.5 \mathrm{p}$ |
|  |  | B: 24.6 | $\mathrm{~B}: 31.8 \mathrm{~s}, 68.0 \mathrm{p}$ |
| BD B(1)-N(2) | 1.98 | $\mathrm{~N}: 76.2$ | $\mathrm{~N}: 39.1 \mathrm{~s}, 60.9 \mathrm{p}$ |
|  |  | B: 23.8 | B: $30.0 \mathrm{~s}, 68.84 \mathrm{p}$ |
| BD N(2)-B(2) | 1.98 | $\mathrm{~N}: 76.3$ | $\mathrm{~N}: 38.9 \mathrm{~s}, 61.1 \mathrm{p}$ |
|  |  | B: 30.8 | $\mathrm{~B}: 30.8 \mathrm{~s}, 68.9 \mathrm{p}$ |
| BD B(2)-N(3) | 1.97 | $\mathrm{~N}: 75.4$ | $\mathrm{~N}: 54.3 \mathrm{~s}, 45.6 \mathrm{p}$ |
|  |  | B: 24.6 | B: $31.8 \mathrm{~s}, 68.0 \mathrm{p}$ |



Figure S17. Hybridization states.
Looking at the lone pairs of the atoms within the heterocyclic ring (Table S4), obtained from NBO analysis, it is clear that there are four empty orbitals on the Al centre, of which one is an s-orbital and the other three p-orbitals. On atoms $N(1)$ and $N(3)$ two lone pairs can be found, with different sand p-character. In contrast, on $N(2)$ there is only one p-type lone pair present. Each of the $B$ atoms exhibit one empty p-type orbital. Interestingly, the "empty" orbitals on the AI and B centres exhibit a small occupation of electrons ( $\leq 0.4$ ).

Table S4. Results of natural bond orbital (NBO) analysis 2-center bonds (BD) for the central AI-N(1)-$B(1)-N(2)-B(2)-N(3)$ unit.

| NBO | Occupation | Orbital contribution |
| :---: | :---: | :---: |
| $\mathrm{LP}^{*}(1) \mathrm{Al}(1)$ | 0.40 | 99.9 s |
| $\mathrm{LP}^{*}(2) \mathrm{Al}(1)$ | 0.19 | 99.2 p |
| $\mathrm{LP}^{*}(3) \mathrm{Al}(1)$ | 0.18 | 99.8 p |
| LP *(4) $\mathrm{Al}(1)$ | 0.17 | 99.3 p |
| $\mathrm{LP}(1) \mathrm{N}(1)$ | 1.79 | $19.1 \mathrm{~s}, 80.9 \mathrm{p}$ |
| $\mathrm{LP}(2) \mathrm{N}(1)$ | 1.72 | 100.0 p |
| LP *(1) B(1) | 0.38 | 99.9 p |
| $\mathrm{LP}(1) \mathrm{N}(2)$ | 1.68 | 100.0 p |
| $\mathrm{LP} *(1) \mathrm{B}(2)$ | 0.38 | 99.9 p |
| $\mathrm{LP}(1) \mathrm{N}(3)$ | 1.79 | $19.0 \mathrm{~s}, 81.1 \mathrm{p}$ |
| $\mathrm{LP}(2) \mathrm{N}(3)$ | 1.73 | 100.0 p |

From second-order perturbation analysis conclusions can be drawn about donor-acceptor interactions and therefore about the delocalisation of the system. These interactions can also explain the small occupation of the "empty" orbitals on the Al and B atoms, shown before. The results, summarised in Table S5, show that there is a donor-acceptor interaction between the filled lone pairs of $N(1)$ and $N(3)$ and the empty orbitals on Al. The lone pairs on atoms $N(1)$ and $N(3)$ also interact with the empty orbitals on $B(1)$ and $B(2)$. Furthermore, the lone pair of the middle nitrogen atom $N(2)$ donates some electron density into the empty $p$-orbital of the $B$ centres surrounding it.

Table S5. Results of the second-order perturbation theory analysis of fock matrix in NBO for the central $\mathrm{Al}-\mathrm{N}(1)-\mathrm{B}(1)-\mathrm{N}(2)-\mathrm{B}(2)-\mathrm{N}(3)$ unit.

| Donor | Acceptor | Stabilisation Energy [kcal/mol] |
| :--- | :--- | :--- |
| $\mathrm{LP}(1) \mathrm{N}(1)$ | LP *(1) $\mathrm{Al}(1)$ | 78.3 |
| $\mathrm{LP}(1) \mathrm{N}(1)$ | LP (2) $\mathrm{Al}(1)$ | 52.3 |
| $\mathrm{LP}(1) \mathrm{N}(1)$ | LP | $4.4 \mathrm{Al}(1)$ |
| $\mathrm{LP}(2) \mathrm{N}(1)$ | LP (3) $\mathrm{Al}(1)$ | 14.1 |
|  |  |  |
| $\mathrm{LP}(1) \mathrm{N}(3)$ | LP (1) $\mathrm{Al}(1)$ | 81.1 |
| $\mathrm{LP}(1) \mathrm{N}(3)$ | LP (2) $\mathrm{Al}(1)$ | 20.8 |
| $\mathrm{LP}(1) \mathrm{N}(3)$ | LP (4) $\mathrm{Al}(1)$ | 33.8 |
| $\mathrm{LP}(2) \mathrm{N}(3)$ | LP (3) $\mathrm{Al}(1)$ | 15.7 |
|  |  |  |
| $\mathrm{LP}(1) \mathrm{N}(2)$ | LP (1) $\mathrm{B}(1)$ | 66.8 |
| $\mathrm{LP}(1) \mathrm{N}(2)$ | LP (1) $\mathrm{B}(2)$ | 66.5 |
|  |  |  |
| $\mathrm{LP}(2) \mathrm{N}(1)$ | LP (1) $\mathrm{B}(1)$ | 67.9 |
| $\mathrm{LP}(2) \mathrm{N}(3)$ | LP (1) $\mathrm{B}(2)$ | 67.7 |

The aromatic character of the Al-N-B ring was further examined by looking at the $\pi$ orbitals of the system. Whereas HOMO-9 looks like an all in-phase combination, HOMO-2 and HOMO are bonding orbitals, which comprise one node. LUMO+17 in contrast, is anti-bonding, with two nodes.


Figure S18. Selected molecular orbitals of compound 3.

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