

# Stabilization of two coordinate tetrylene by borylamide ligand

Michal Aman, Ondřej Mrózek, Libor Dostál, Zdenka Růžicková, Roman Jambor\*

Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 95, CZ-532 10, Pardubice, Czech Republic

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## ABSTRACT

Here we report the synthesis of aminoborane  $\text{HN}(\text{BCy}_2)$  ( $\text{C}_6\text{H}_3$ -2,6-Me<sub>2</sub>) (**1**) (Cy = cyclohexyl), that was successfully deprotonated and its lithium salt  $\{\text{LiN}(\text{BCy}_2)$  ( $\text{C}_6\text{H}_3$ -2,6-Me<sub>2</sub>)<sub>2</sub> (**2**) has been characterised. The borylamide ligand  $-\text{N}(\text{BCy}_2)$  ( $\text{C}_6\text{H}_3$ -2,6-Me<sub>2</sub>) was used for the preparation of N→Sn coordinated stannylene  $[\text{2,6}-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{Sn}[\text{N}(\text{BCy}_2)$  ( $\text{C}_6\text{H}_3$ -2,6-Me<sub>2</sub>) (**3**) and two coordinate tetrylenes  $\{\text{N}(\text{BCy}_2)$  ( $\text{C}_6\text{H}_3$ -2,6-Me<sub>2</sub>)<sub>2</sub> (E = Sn (**4**), Pb (**5**)). Experimental and theoretical studies suggested  $\sigma$  character of E-N bonds without additional N(p)→E(p) donation as the result of the preference of N(p)→B(p) donation in **4** and **5**. DFT studies on **4** and **5** also reveal their HOMO to exhibit E lone pair character and their LUMO to include p-orbital character located on metal atoms E.

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## 1. Introduction

Low coordinate group 14 compounds are studied extensively, because it has been recognised that they can behave similarly to transition metal complexes. Therefore, this field is attractive since these complexes can be possible alternatives to late transition metal complexes in homogeneous catalytic transformations [1–7]. The majority of developments in the field of two coordinate group 14 compounds were mainly achieved by the kinetic stabilization of the metal centre using sterically bulky terphenyl ligands  $\text{C}_6\text{H}_3(\text{C}_6\text{H}_2$ -2,6-*i*Pr<sub>2</sub>)<sub>2</sub>-2,6 and  $\text{C}_6\text{H}_3(\text{C}_6\text{H}_2$ -2,4,6-*i*Pr<sub>3</sub>)<sub>2</sub>-2,6 [8–13]. Nevertheless, it has been also reported, that the utilization of the bulky amides  $-\text{N}(\text{SiMe}_3)_2$  [14],  $-\text{N}(\text{SiMe}_3)$  (Dip) (Dip =  $\text{C}_6\text{H}_3$ -2,6-*i*Pr<sub>2</sub>) [15–17],  $-\text{N}(\text{SiMe}_3)\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2$ -2,4,6-Me<sub>3</sub>)<sub>2</sub>-2,6} [18], or  $-\text{N}(\text{SiMe}_3)\{\text{C}_6\text{H}_2\{\text{C}(\text{H})\text{Ph}_2\}_2\text{Me}$ -2,6,4} [19] *etc.* may be successful concept for the stabilization of low coordinated group 14 elements (Fig. 1A).

Another approach in this field was developed by the group of Power, who successfully synthesized low coordinated transition metal derivatives by the help of borylamides  $-\text{NRBMe}_2$  (R = Ph, Mes, Mes = mesityl) (Fig. 1B) [20,21]. Later on, Linti reported on monomeric gallium borylamide  $\text{Et}_2\text{GaN}(\text{tBu})\text{BMe}_2$  with rather long Ga-N bond length (1.937 (3) Å) [22]. These ligands have nitrogen atom less basic due to the B-N multiple bond and as the

result, the  $-\text{NRBMe}_2$  entities do not behave as bridging ligands. Here, we extended the family of these compounds and we prepared simple aminoborane  $\text{HN}(\text{BCy}_2)$  ( $\text{C}_6\text{H}_3$ -2,6-Me<sub>2</sub>) (**1**), that was successfully used for the stabilization of two coordinate tetrylenes.

## 2. Experimental part

### 2.1. General methods

The starting compound  $[\text{2,6}-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{SnCl}$  [23] was prepared according to the literature and 1.6 M hexane solution of *n*BuLi, (2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)NH<sub>2</sub>, Cy<sub>2</sub>BCl, SnCl<sub>2</sub> and PbCl<sub>2</sub> were purchased from Sigma Aldrich. Solvents were dried under the argon over sodium benzofenone and distilled prior to use. The <sup>1</sup>H, <sup>7</sup>Li{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H}, <sup>119</sup>Sn{<sup>1</sup>H}, <sup>207</sup>Pb{<sup>1</sup>H} NMR spectra were recorded on a Bruker Avance500 spectrometer at 300 K in C<sub>6</sub>D<sub>6</sub>. The <sup>1</sup>H, <sup>7</sup>Li{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H}, <sup>13</sup>C{<sup>1</sup>H}, <sup>119</sup>Sn{<sup>1</sup>H}, <sup>207</sup>Pb{<sup>1</sup>H} NMR chemical shifts  $\delta$  are given in ppm and referenced to external Me<sub>4</sub>Sn (<sup>119</sup>Sn), LiCl (<sup>7</sup>Li), BF<sub>3</sub>·OEt<sub>2</sub> (<sup>11</sup>B), Me<sub>4</sub>Si (<sup>13</sup>C, <sup>1</sup>H) and Me<sub>4</sub>Pb (<sup>207</sup>Pb). UV/Vis spectra were recorded with UV/Vis spectrophotometer Evolution 201. Elemental analyses were performed on a LECO-CHNS-932 analyser but we were not able to get satisfactory analysis for 2–5 due to their hydroscopic non-stability.

### 2.2. Synthesis of $\text{HN}(\text{BCy}_2)$ ( $\text{C}_6\text{H}_3$ -2,6-Me<sub>2</sub>) (**1**)

1.6 M solution of *n*BuLi (9.34 ml, 15.0 mmol) and (2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)

\* Corresponding author.

E-mail address: [roman.jambor@upce.cz](mailto:roman.jambor@upce.cz) (R. Jambor).

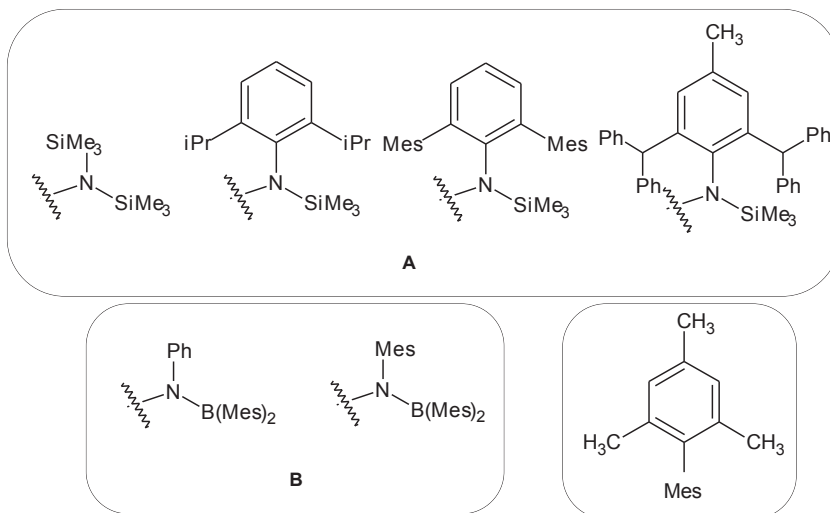


Fig. 1. Bulky amides (A) and borylamides (B) used for stabilization of low coordinated species.

NH<sub>2</sub> (1.81 g, 14.9 mmol) was stirred in hexane for 1 h at 0 °C and 1.0 M hexane solution of Cy<sub>2</sub>BCl (14.90 ml, 14.9 mmol) was added to this suspension at 0 °C and stirred for addition 4 h at room temperature. The white solid was filtrated, the hexane solution was concentrated and crystallized at –20 °C to yield colourless crystals of **1**. Yield 3.77 g (85%). MW: 297.29 g/mol. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.12 (m, 5H, CyH), 1.34 (m, 7H, CyH), 1.58 (m, 5H, CyH), 1.71 (m, 5H, CyH), 2.09 (s, 6H, CH<sub>3</sub>), 4.71 (s, 1H, NH), 7.08 (t, 1H, ArH), 7.22 (s, 2H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 18.2 (CH<sub>3</sub>), 27.3, 27.5, 27.8, 28.0, 28.1, 28.6 (CyC), 29.2, 29.8 (BC<sub>ipso</sub>), 125.1, 128.3, 134.4, 140.7 (ArC). <sup>11</sup>B{<sup>1</sup>H} (160.57 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 46.6.

### 2.3. Synthesis of {LiN(BCy<sub>2</sub>)(C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)}<sub>2</sub> (**2**)

1.6 M solution of *n*BuLi (0.44 ml, 0.7 mmol) in hexane was added to a toluene solution of **1** (0.17 g, 0.6 mmol) at room temperature and stirred for 24 h at room temperature. Toluene solution was concentrated and crystallized at 4 °C to yield colourless crystals of **2**. Yield 0.16 g (95%). MW: 303.22 g/mol. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.11 (m, 8H, CyH), 1.23 (m, 12H, CyH), 1.54 (m, 6H, CyH), 1.60 (m, 6H, CyH), 1.69 (m, 6H, CyH), 1.91 (m, 6H, CyH), 2.12 (s, 12H, CH<sub>3</sub>), 6.38 (t, 2H, ArH), 6.85 (d, 4H, ArH). <sup>7</sup>Li (193.75 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ –4.2. <sup>11</sup>B{<sup>1</sup>H} (160.57 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 46.7.

### 2.4. Synthesis of [2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]Sn[N(BCy<sub>2</sub>)(C<sub>6</sub>H<sub>3</sub>-2,6-Me<sub>2</sub>)] (**3**)

1.6 M solution of *n*BuLi (1.05 ml, 1.7 mmol) in hexane was added to a toluene solution of **1** (0.48 g, 1.6 mmol) and stirred for 24 h at room temperature. Resulting white suspension was added to a toluene solution of [2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]SnCl (0.56 g, 1.6 mmol) and stirred for 24 h at room temperature. White solid material was filtrated, organic filtrate was concentrated and crystallized at –20 °C to yield colourless crystals of **3**. Yield 0.64 g (66%). MW: 606.28 g/mol. Mp. 121.2–122.5 °C. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.22 (m, 2H, CyH), 1.43 (m, 2H, CyH), 1.61 (m, 4H, CyH), 1.82 (m, 4H, CyH), 1.94 (m, 4H, CyH), 2.11 (m, 4H, CyH), 2.39 (d, 2H, CyH), 2.01 (s, 12H, NCH<sub>3</sub>), 2.11 (s, 6H, CH<sub>3</sub>), 2.92 (AB spin system, 4H, CH<sub>2</sub>N, <sup>2</sup>J(1H, 1H) = 8 Hz), 6.86 (m, 3H, ArH), 7.05 (d, 2H, ArH), 7.11 (t, 1H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 20.4 (CH<sub>3</sub>), 27.4, 27.6, 28.6, 28.6, 29.9, 30.3 (CyC), 33.3, 35.1 (BC<sub>ipso</sub>), 45.3 (NCH<sub>3</sub>), 66.5 (CH<sub>2</sub>N), 121.4, 123.8, 127.2, 127.9, 133.5, 147.6, 151.9,

170.7 (ArC). <sup>11</sup>B{<sup>1</sup>H} (160.57 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K) δ 46.8. <sup>119</sup>Sn{<sup>1</sup>H} (186.49 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 202.8.

### 2.5. Synthesis of [(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)(Cy<sub>2</sub>B)N]<sub>2</sub>Sn (**4**)

1.6 M solution of *n*BuLi (10.63 ml, 17.0 mmol) in hexane was added to a toluene solution of **1** (4.81 g, 16.2 mmol) and stirred for 24 h at room temperature. The resulting white suspension was added to a THF solution of SnCl<sub>2</sub> (1.53 g, 8.1 mmol) at 0 °C and stirred for 24 h at room temperature. The organic solvents were evaporated, remaining residue was extracted by hexane and an orange hexane solution was concentrated to 5 ml. Crystallization at 4 °C provided yellow crystals of **4**. Yield 3.1 g (30%). MW: 711.27 g/mol. Mp. 199–205 °C. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.03 (m, 10H, CyH), 1.21 (m, 6H, CyH), 1.33 (m, 8H, CyH), 1.65 (m, 20H, CyH), 2.19 (s, 12H, CH<sub>3</sub>), 6.81 (t, 2H, ArH), 7.01 (d, 4H, ArH). <sup>13</sup>C{<sup>1</sup>H} NMR (125.77 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 20.8 (CH<sub>3</sub>), 28.0, 28.1, 28.1, 28.2, 29.0, 30.6 (CyC), 38.1, 41.9 (BC<sub>ipso</sub>), 123.4, 128.6, 133.0, 147.4 (ArC). <sup>11</sup>B{<sup>1</sup>H} (160.57 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 46.5. <sup>119</sup>Sn{<sup>1</sup>H} (186.49 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 527.7. UV/VIS (n-hexane): λ<sub>max</sub> (nm) 285, 356 (shoulder).

### 2.6. Synthesis of [(2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)(Cy<sub>2</sub>B)N]<sub>2</sub>Pb (**5**)

1.6 M solution of *n*BuLi (11.10 ml, 17.8 mmol) in hexane was added to a toluene solution of **1** (5.03 g, 16.9 mmol) and stirred for 24 h at room temperature. The resulting white suspension was added to a toluene suspension of PbCl<sub>2</sub> (2.35 g, 8.5 mmol) at 0 °C and stirred for 24 h at room temperature. The organic solvents were evaporated, remaining residue was extracted by hexane and an orange hexane solution was concentrated to 5 ml. Crystallization at 4 °C yielded orange crystals of **5**. Yield 4.4 g (32%). MW: 799.76 g/mol. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 1.24 (m, 4H, CyH), 1.32 (m, 24H, CyH), 1.71 (m, 16H, CyH), 2.51 (s, 12H, CH<sub>3</sub>), 6.79 (t, 2H, ArH), 7.08 (d, 4H, ArH). <sup>13</sup>C{<sup>1</sup>H} (125.77 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 14.1 (CH<sub>3</sub>), 28.3, 28.4, 28.7, 29.3, 31.3, 31.8 (CyC), 36.4, 39.1 (BC<sub>ipso</sub>), 123.8, 127.6, 133.9, 147.7 (ArC). <sup>11</sup>B{<sup>1</sup>H} (160.57 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 46.3. <sup>207</sup>Pb{<sup>1</sup>H} (104.61 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ 3537 ppm. UV/VIS (n-hexane): λ<sub>max</sub> (nm) 283, 360 (shoulder).

### 2.7. X-ray structure determination

Compound **2** was dissolved in toluene and the X-ray quality material was received from the saturated solutions at room

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