

## Supporting Information

for

### ***Structural diversity in donor free alkali metal complexes of a sterically demanding triazenide***

Alasdair I. McKay and Marcus L. Cole

*School of Chemistry, University of New South Wales, Sydney,  
NSW 2052, Australia*

E-mail: [alasdair.mckay@unimelb.edu.au](mailto:alasdair.mckay@unimelb.edu.au)

#### Table of Contents

|  |     |
|--|-----|
| Experimental   | S2  |
| General Synthetic Procedures   | S2  |
| [Li(N <sub>3</sub> Dmp <sub>2</sub> )] ( <b>1</b> )                                    | S2  |
| [Na(N <sub>3</sub> Dmp <sub>2</sub> )] ( <b>2</b> )                                    | S3  |
| [K(N <sub>3</sub> Dmp <sub>2</sub> )] ( <b>3</b> )                                     | S3  |
| [Rb(N <sub>3</sub> Dmp <sub>2</sub> )] ( <b>4</b> )                                    | S4  |
| [Cs(N <sub>3</sub> Dmp <sub>2</sub> )] ( <b>5</b> )                                    | S4  |
| [Li <sub>2</sub> (N <sub>3</sub> Dmp <sub>2</sub> )( <sup>n</sup> Bu)] ( <b>6</b> )    | S5  |
| [Li(N <sub>3</sub> Dmp <sub>2</sub> )(THF) <sub>2</sub> ] ( <b>1·THF<sub>2</sub></b> ) | S5  |
| [K(N <sub>3</sub> Dmp <sub>2</sub> )(DME)] ( <b>3·DME</b> )                            | S6  |
| X-ray Crystallography  | S7  |
| General Procedures   | S7  |
| <i>Variata</i>   | S7  |
| Molecular Structures   | S8  |
| Crystallographic Data  | S10 |
| Assignment of M···π-Arene Hapticities  | S12 |
| References   | S15 |

## Experimental

### General Synthetic Procedures

All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity argon in flame-dried glassware. Reaction yields are unoptimized. Diethyl ether, THF, dimethoxyethane, toluene and *n*-hexane were dried over sodium wire and purged with nitrogen prior to distillation from sodium benzophenone ketyl. Benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) was dried over sodium and freeze-thaw degassed prior to use. Dmp<sub>2</sub>N<sub>3</sub>H<sup>S1</sup> and *n*-butylsodium<sup>S2</sup> were prepared according to the literature procedures, all other reagents were purchased from Sigma-Aldrich and used as received. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Avatar 320 FTIR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopic characterisations were recorded on Bruker spectrometers (see below for MHz) at 298 K unless otherwise stated, with chemical shifts referenced to the residual <sup>1</sup>H and <sup>13</sup>C resonances of benzene-*d*<sub>6</sub> (δ 7.16 and 128.06 ppm respectively).<sup>S3</sup> Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were conducted at the Microanalytical unit of the Australian National University, Canberra, Australia or the Campbell Microanalytical Lab of the University of Otago, P.O. Box 56, Dunedin, New Zealand.

### [Li(N<sub>3</sub>Dmp<sub>2</sub>)] (1)

*n*-Butyllithium (1.6 M in hexanes, 0.34 mL, 0.54 mmol) was added dropwise to a solution of Dmp<sub>2</sub>N<sub>3</sub>H (360 mg, 0.54 mmol) in toluene (30 mL), the solution immediately changed color from pale yellow to golden yellow. Stirring was continued for *ca.* 3 h followed by solvent removal *in vacuo*. The resultant yellow solid was extracted with hexane (60 mL), concentrated to insipient crystallization and cooled to -2 °C overnight afforded bright yellow prisms suitable for X-ray diffraction structure determination (130 mg, 36%); m.p. 174-176°C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.90 (s, 24H, *o*-CH<sub>3</sub>), 2.17 (s, 12H, *p*-CH<sub>3</sub>), 6.73 (s, 8H, *m*-Ar'*H*), 6.78 (s, 2H, *p*-Ar*H*), 6.90 (s, 4H, *m*-Ar*H*). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ 21.1 (*p*-CH<sub>3</sub>), 21.2 (*o*-CH<sub>3</sub>), 122.0, 128.8, 129.5 (ArCH), 132.5, 135.9, 136.0, 140.2, 145.8 (ArC). IR (Nujol, cm<sup>-1</sup>) 1611 (w), 1495 (w), 1401 (w), 1277 (w), 1260 (m), 1227 (w), 1093 (w), 1031 (w), 849 (m), 801 (w), 765 (w), 754 (w), 735 (w). Crystalline samples repeatedly gave microanalyses

low in carbon which presumably emanates from the high oxygen and moisture sensitivity of this complex.

### **[Na(N<sub>3</sub>Dmp<sub>2</sub>)] (2)**

Method A: Hexane (20 mL) was added to a mixture of Dmp<sub>2</sub>N<sub>3</sub>H (268 mg, 0.40 mmol) and *n*-butylsodium (40 mg, 0.50 mmol). Gas evolution was immediately observed, with the formation of a bright yellow solid and a dark orange solution. The resultant mixture was stirred for 16 h. Filtration followed by concentration to insipient crystallization *in vacuo* and cooling to -25°C overnight afforded bright yellow octahedra. Further concentration *in vacuo* afforded two additional crops. Yield of combined crops (270 mg, 97%).

Method B: Toluene (40 mL) was added to a mixture of Dmp<sub>2</sub>N<sub>3</sub>H (340 mg, 0.50 mmol) and sodium bis(trimethylsilyl)amide (93 mg, 0.50 mmol). The resultant golden solution was stirred at ambient temperature for a further 8 h. The solvent was then removed *in vacuo*. The resultant yellow solid was extracted with hexane (50 mL), concentrated to insipient crystallization and cooling to -25°C overnight afforded bright yellow octahedra (155 mg, 45%); m.p. 170°C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.93 (s, 24H, *o*-CH<sub>3</sub>), 2.15 (s, 12H, *p*-CH<sub>3</sub>), 6.70 (s, 8H, *m*-Ar'H), 6.87-6.90 (m, 6H, *m*- and *p*-Ar'H). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ 21.1 (*p*-CH<sub>3</sub>), 21.3 (*o*-CH<sub>3</sub>), 121.1, 127.7, 129.6 (ArCH), 132.0, 134.8, 136.2, 141.3, 147.6 (ArC). IR (Nujol, cm<sup>-1</sup>) 1612 (m), 1496 (s), 1463 (s), 1414 (w), 1261 (s), 1230 (w), 1202 (w), 1142 (m), 1092 (w), 1076 (w), 1013 (w), 849 (s), 899 (s), 766 (s), 754 (w), 741 (w), 665 (w). Anal. Calc. for C<sub>48</sub>H<sub>50</sub>N<sub>3</sub>Na: C, 83.32; H, 7.28; N, 6.07. Found: C, 82.74; H, 7.30; N, 6.09%.

### **[K(N<sub>3</sub>Dmp<sub>2</sub>)] (3)**

Method A: A solution of Dmp<sub>2</sub>N<sub>3</sub>H (1.05 g, 1.57 mmol) in toluene (50 mL), was added to a potassium mirror (250 mg, 6.39 mmol). The resultant mixture was stirred for 24 h at 80°C, during this period the color changed from pale yellow to gold. Filtration followed by solvent removal *in vacuo* afforded a golden yellow powder. Extraction with fresh toluene, concentration to insipient crystallization and cooling to -25°C overnight afforded bright yellow octahedra suitable for X-ray diffraction structure determination (902 mg, 81%).

Method B: Toluene (30 mL) was added to a mixture of Dmp<sub>2</sub>N<sub>3</sub>H (340 mg, 0.50 mmol) and potassium bis(trimethylsilyl)amide (100 mg, 0.50 mmol). The resultant

golden solution was stirred at ambient temperature for a further 8 h, followed by solvent removal *in vacuo*. The resultant yellow residue was then extracted with hexane (50 mL), concentrated to insipient crystallization and cooling to -25°C overnight to afford bright yellow prisms suitable for X-ray diffraction structure determination (202 mg, 58%), m.p. 226-230°C (dec.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.97 (s, 24H, *o*-CH<sub>3</sub>), 2.15 (s, 12H, *p*-CH<sub>3</sub>), 6.72 (s, 8H, *m*-Ar'*H*), 6.75-6.88 (m, 6H, *m*-Ar*H* and *p*-Ar*H*). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ 21.2 (*p*-CH<sub>3</sub>), 21.6 (*o*-CH<sub>3</sub>), 120.7, 127.9, 129.8 (ArCH), 132.0, 134.4, 136.1, 141.8, 149.6 (ArC). IR (Nujol, cm<sup>-1</sup>) 2728 (w), 1607 (w), 1580 (m), 1486 (m), 1398 (s), 1277 (s), 1260 (s), 1240 (w), 1213 (br s), 1192 (s), 1073 (w), 1031 (w), 1015 (w), 952 (w), 858 (m), 850 (s), 801 (w), 784 (m), 761 (s), 740 (s), 660 (w). Anal. Calc. for C<sub>48</sub>H<sub>50</sub>N<sub>3</sub>K: C, 81.43; H, 7.18; N, 5.93. Found: C, 81.84; H, 7.66; N, 5.87%.

#### **[Rb(N<sub>3</sub>Dmp<sub>2</sub>)] (4)**

A solution of Dmp<sub>2</sub>N<sub>3</sub>H (340 mg, 0.50 mmol) in hexane (60 mL), was added to a rubidium mirror (150 mg, 1.76 mmol). The resultant mixture was stirred for 4 h at ambient temperature, during this period the color changed from pale yellow to gold. Filtration followed by concentration to insipient crystallization and cooling to -25°C overnight afforded golden yellow prisms (247 mg, 65%); m.p. 218-220°C (dec.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.98 (s, 24H, *o*-CH<sub>3</sub>), 2.15 (s, 12H, *p*-CH<sub>3</sub>), 6.75 (s, 8H, *m*-Ar'*H*), 6.81-6.89 (m, 6H, *m*-Ar*H* and *p*-Ar*H*). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>) δ 21.2 (*p*-CH<sub>3</sub>), 21.7 (*o*-CH<sub>3</sub>), 120.4, 127.9, 129.8 (ArCH), 131.7, 134.3, 136.1, 142.0, 149.7 (ArC). IR (Nujol, cm<sup>-1</sup>) 2729 (m), 2028 (m), 1723 (w), 1603 (m), 1574 (w), 1276 (m), 1259 (m), 1195 (w), 1156 (w), 1074 (w), 1013 (m), 849 (s), 800 (m), 780 (w), 763 (w), 739 (w), 722 (m), 665 (w). Anal. Calc. for C<sub>48</sub>H<sub>50</sub>N<sub>3</sub>Rb: C, 76.42; H, 6.68; N, 5.57. Found: C, 76.61; H, 6.82; N, 5.60%.

#### **[Cs(N<sub>3</sub>Dmp<sub>2</sub>)] (5)**

A solution of Dmp<sub>2</sub>N<sub>3</sub>H (170 mg, 0.25 mmol) in hexane (50 mL), was added to a cesium mirror (150 mg, 1.13 mmol). The resultant mixture was stirred for 2 h at ambient temperature, during this period the color changed from pale yellow to gold. Filtration followed by concentration to insipient crystallization and cooling to -25°C overnight afforded golden yellow prisms suitable for X-ray diffraction structure

determination (100 mg, 50%); 244-246°C (dec.).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  2.00 (s, 24H, *o*- $\text{CH}_3$ ), 2.16 (s, 12H, *p*- $\text{CH}_3$ ), 6.76 (s, 8H, *m*-Ar'*H*), 6.79-6.83 (m, 2H, *p*-Ar*H*), 6.87-6.89 (m, 4H, *m*-Ar*H*).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  21.2 (*p*- $\text{CH}_3$ ), 21.9 (*o*- $\text{CH}_3$ ), 120.2, 128.1, 129.8 (ArCH), 131.4, 134.2, 136.2, 142.2, 150.0 (ArC). IR (Nujol,  $\text{cm}^{-1}$ ) 2724 (w), 1780 (w), 1744 (w), 1607 (w), 1579 (m), 1485 (w), 1398 (s), 1276 (s), 1257 (s), 1208 (br s), 1075 (m), 1027 (w), 1014 (w), 960 (w), 851 (s), 833 (w), 801 (w), 781 (m), 763 (s), 754 (s), 740 (m), 665 (w). Anal. Calc. for  $\text{C}_{48}\text{H}_{50}\text{N}_3\text{Cs}$ : C, 71.90; H, 6.29; N, 5.25. Found: C, 71.78; H, 6.78; N, 4.88%.

### **[Li<sub>2</sub>( $\mu$ - $\kappa^1$ -N<sub>3</sub>Dmp<sub>2</sub>)( $\mu$ -*n*Bu)] (6)**

*n*Butyllithium (1.6 M in hexanes, 0.65 mL, 1.0 mmol) was added dropwise to a solution of Dmp<sub>2</sub>N<sub>3</sub>H (338 mg, 0.50 mmol) in hexane (60 mL) at ambient temperature. The color of the solution immediately changed from pale yellow to golden yellow. Stirring was continued for a further 12 h. Concentration to ca. 20 mL *in vacuo*, followed by cooling to -25°C overnight afforded bright yellow prisms suitable for X-ray diffraction structure determination (244 mg, 66%); m.p. 143-145°C.  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -1.46 (br t,  $^3J_{\text{HH}} = 8.2$  Hz, 2H, Li- $\text{CH}_2$ ), 1.10-1.20 (br m, 5H, Li- $\text{CH}_2\text{CH}_2$  and  $\text{CH}_2\text{CH}_3$ ), 1.34-1.42 (br m, 2H,  $\text{CH}_2\text{CH}_3$ ), 1.96 (s, 24H, *o*- $\text{CH}_3$ ), 2.15 (s, 12H, *p*- $\text{CH}_3$ ), 6.75-7.82 (m, 6H, *m*- and *p*-Ar*H*), 6.86 (s, 8H, *m*-Ar'*H*). IR (Nujol,  $\text{cm}^{-1}$ ) 1609 (w), 1582 (w), 1484 (w), 1413 (w), 1277 (m), 1257 (s), 1226 (s), 1078 (w), 1032 (w), 854 (w), 802 (w), 783 (w), 764 (w), 744 (w). Anal. Calc. for  $\text{C}_{52}\text{H}_{59}\text{N}_3\text{Li}_2$ : C, 84.41; H, 8.04; N, 5.68. Found: C, 84.44; H, 8.13; N, 5.74%.

### **[Li(N<sub>3</sub>Dmp<sub>2</sub>)(THF)<sub>2</sub>] (1·THF<sub>2</sub>)**

*n*Butyllithium (1.6 M hexane solution, 0.55 mL, 0.85 mmol) was added dropwise to a stirred solution of Dmp<sub>2</sub>N<sub>3</sub>H (500 mg, 0.85 mmol) in THF (50 mL) at ambient temperature, the solution immediately changed color from pale to dark yellow. After 2 h, the volatiles were removed *in vacuo* and the yellow solid was extracted with THF (80 mL), concentration to ca. 30 mL followed by cooling to -25°C afforded large yellow plates (260 mg, 38%), m.p. 176-177°C.  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  1.34 (m, 8H,  $\beta$ - $\text{CH}_2$  THF), 1.99 (s, 24H, *o*- $\text{CH}_3$ ), 2.18 (s, 12H, *p*- $\text{CH}_3$ ), 3.19 (m, 8H,  $\alpha$ - $\text{CH}_2$  THF), 6.80 (s, 8H, *m*-Ar'*H*), 6.85 (s, 6H, *m*- and *p*-Ar*H*).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  21.2 (*p*- $\text{CH}_3$ ), 21.7 (*o*- $\text{CH}_3$ ), 25.6 ( $\beta$ - $\text{CH}_2$  THF), 67.9 ( $\alpha$ - $\text{CH}_2$  THF), 121.9, 128.1,

130.1 (ArCH), 132.9, 134.5, 135.9, 140.5, 147.4 (ArC). IR (Nujol,  $\text{cm}^{-1}$ ) 1612 (w), 1261 (m), 1201 (w), 1149 (br w), 1075 (w), 1031 (br w), 974 (w), 845 (w), 799 (w), 766 (w), 753 (w). Anal. Calc. for  $\text{C}_{56}\text{H}_{66}\text{N}_3\text{LiO}_2$ : C, 82.02; H, 8.11; N, 5.12. Found: C, 81.90; H, 7.88; N, 5.60%.

### **[K(N<sub>3</sub>Dmp<sub>2</sub>)(DME)] (3·DME)**

A solution of potassium bis(trimethylsilyl)amide (50 mg, 0.25 mmol) in 1,2-dimethoxyethane (10 mL) was added dropwise to a solution of  $\text{Dmp}_2\text{N}_3\text{H}$  (168 mg, 0.25 mmol) in hexane (30 mL) at ambient temperature, the solution immediately changed color from pale yellow to gold. Stirring was continued for ca. 4 h, during which time a yellow precipitate formed (75 mg). The supernatant was decanted and the solvent concentrated *in vacuo* (ca. 10 mL), cooling to  $-25^\circ\text{C}$  afforded large yellow plates overnight. Yield: 137 mg, 69%; m.p.  $232\text{--}234^\circ\text{C}$  (dec.).  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  2.01 (s, 24H, *o*- $\text{CH}_3$ ), 2.17 (s, 12H, *p*- $\text{CH}_3$ ), 2.89 (br m, 6H,  $\text{OCH}_3$ ), 3.06 (br m, 4H,  $\text{OCH}_2$ ), 6.77 (s, 8H, *m*-ArH), 6.84-6.92 (m, 6H, *m*-ArH and *p*-ArH).  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  21.2 (*p*- $\text{CH}_3$ ), 21.7 (*o*-Ar $\text{CH}_3$ ), 58.5 ( $\text{OCH}_3$ ), 71.7 ( $\text{OCH}_2$ ), 120.5, 127.9, 129.8 (ArCH), 132.0, 134.2, 136.0, 141.9, 149.7 (ArC). IR (Nujol,  $\text{cm}^{-1}$ ) 1610 (w), 1579 (w), 1486 (w), 1401 (m), 1281 (m), 1256 (s), 1240 (s), 1210 (br s), 1173 (w), 1126 (w), 1085 (s), 1029 (w), 1013 (w), 852 (s), 804 (w), 783 (w), 762 (s), 754 (m), 742 (m), 665 (w). Anal. Calc. for  $\text{C}_{52}\text{H}_{60}\text{N}_3\text{KO}_2$ : C, 78.25; H, 7.58; N, 5.26. Found: C, 77.91; H, 7.65; N, 5.20%.

## X-ray Crystallography

### General details

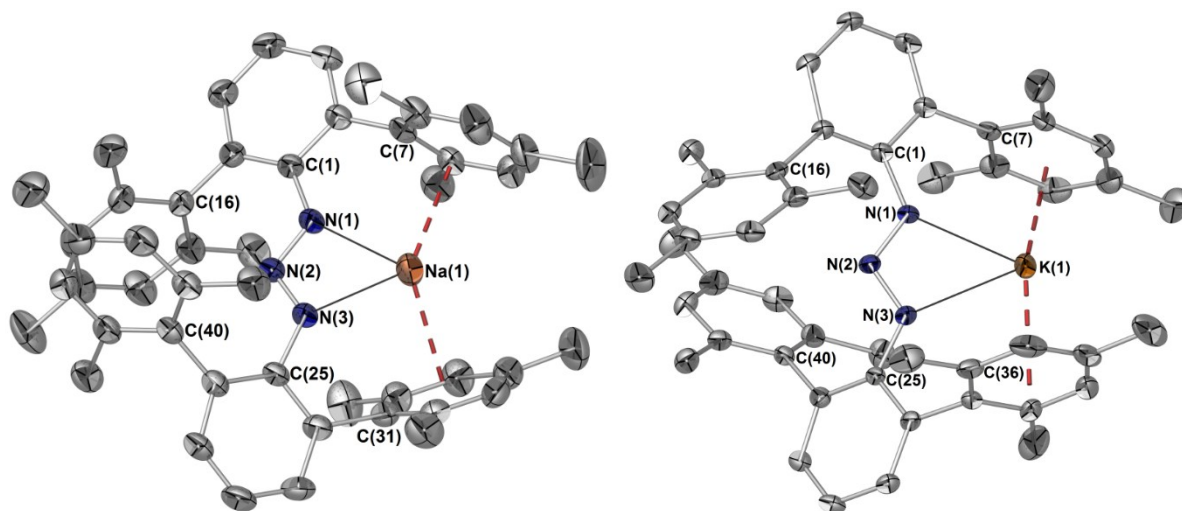
Crystalline samples of were mounted on MiTeGen micromounts in type NVH immersion oil at 150(2) K. Data were collected using a Bruker Quazar Multilayer Optics Mo $\kappa\alpha$  X-ray micro source ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker Apex II CCD diffractometer, and were corrected for absorption using SADABS.<sup>S4</sup> Unit cell parameters were determined for collection employing software defaults and optimized upon completion of data collection using all collected frames. The structure were solved with SHELXT<sup>S5</sup> and refined with SHELXL<sup>S6</sup> using the interface OLEX2.<sup>S7</sup> Hydrogen atoms were refined in calculated positions (riding model) for all compounds. A summary of crystallographic data can be found in Tables S1 and S2.

### *Variata*

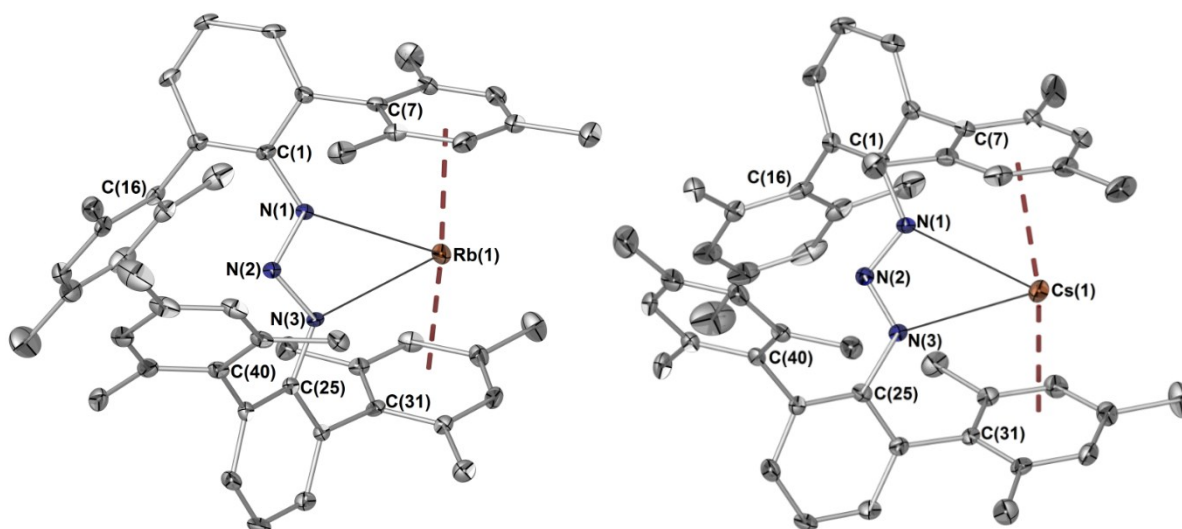
Several reflections were found to be affected by the beamstop, these were omitted from the final refinement.

Disorder of the <sup>n</sup>Bu group in [Li<sub>2</sub>(N<sub>3</sub>Dmp<sub>2</sub>)(<sup>n</sup>Bu)] (**6**) was modelled over two sites with occupancies 66:34.

## Molecular Structures

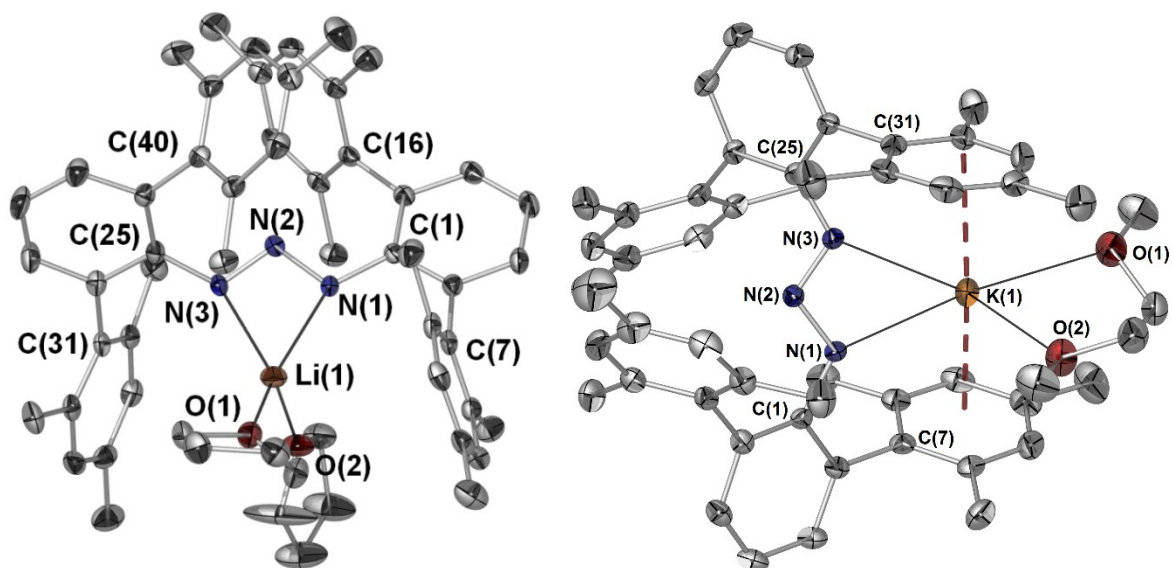


**Figure S1.** Molecular structures (50% displacement ellipsoids) of **2** (left) and **3** (right). All hydrogen atoms removed for clarity.



**Figure S2.** Molecular structures (50% displacement ellipsoids) of **4** (left) and **5** (right). All hydrogen atoms removed for clarity.





**Figure S3.** Molecular structure (50% displacement ellipsoids) of **1(THF)<sub>2</sub>** (left) and **3(DME)** (right). All hydrogen atoms and lattice solvent molecules removed for clarity. Selected bond lengths (Å) and angles (°) for **1(THF)<sub>2</sub>** and **3(DME)** (in braces): M(1)-N(1) 2.064(4) {2.702(2)}, M(1)-N(3) 2.068(4) {2.794(2)}, M(1)-O(1) 1.951(4) {2.789(2)}, M(1)-O(2) 1.966(4) {2.629(2)}, N(1)-N(2) 1.315(2) {1.311(3)}, N(2)-N(3) 1.319(2) {1.307(3)}, N(1)-M(1)-N(3) 62.40(12) {45.64(6)}, N(1)-N(2)-N(3) 102.58(17) {109.15(19)}.

**Table S1.** Summary of crystallographic data for compounds **1-5**.

|   | <b>1</b>   | <b>2</b>   | <b>3</b>  | <b>4</b>   | <b>5</b>   |
|---|--|--|---|--|--|
| <b>empirical formula</b>                          | C <sub>48</sub> H <sub>50</sub> LiN <sub>3</sub> | C <sub>48</sub> H <sub>50</sub> NaN <sub>3</sub> | C <sub>48</sub> H <sub>50</sub> KN <sub>3</sub> | C <sub>48</sub> H <sub>50</sub> RbN <sub>3</sub> | C <sub>48</sub> H <sub>50</sub> CsN <sub>3</sub> |
| <b>formula weight</b>                             | 675.85   | 691.90   | 708.01  | 754.38   | 801.82   |
| <b>crystal system</b>                             | monoclinic                                       | monoclinic                                       | monoclinic                                      | monoclinic                                       | monoclinic                                       |
| <b>space group</b>                                | <i>P</i> 2 <sub>1</sub> / <i>c</i>               | <i>P</i> 2 <sub>1</sub> / <i>n</i>               | <i>P</i> 2 <sub>1</sub>                         | <i>P</i> 2 <sub>1</sub>                          | <i>P</i> 2 <sub>1</sub>                          |
| <b>a (Å)</b>                                      | 10.6536(9)                                       | 14.2522(19)                                      | 10.6705(4)                                      | 11.1579(18)                                      | 11.0720(4)                                       |
| <b>b (Å)</b>                                      | 22.3187(17)                                      | 19.794(3)  | 15.6826(8)                                      | 15.707(2)  | 15.5491(5)                                       |
| <b>c (Å)</b>                                      | 17.0499(12)                                      | 14.8684(18)                                      | 12.3438(7)                                      | 11.9335(18)                                      | 12.1161(5)                                       |
| <b>α (deg)</b>                                    | 90   | 90   | 90  | 90   | 90   |
| <b>β (deg)</b>                                    | 92.052(3)  | 109.082(6)                                       | 93.288(2)                                       | 100.237(7)                                       | 99.4860(10)                                      |
| <b>γ (deg)</b>                                    | 90   | 90   | 90  | 90   | 90   |
| <b>V (Å<sup>3</sup>)</b>                          | 4051.4(5)  | 3964.1(9)  | 2062.23(18)                                     | 2058.2(5)  | 2057.38(13)                                      |
| <b>Z</b>  | 4  | 4  | 2   | 2  | 2  |
| <b>μ (mm<sup>-1</sup>)</b>                        | 0.064  | 0.076  | 0.164   | 1.238  | 0.935  |
| <b>ρ(calcd) (g cm<sup>-3</sup>)</b>               | 1.108  | 1.159  | 1.140   | 1.217  | 1.294  |
| <b>F(000)</b>                                     | 1448   | 1480   | 756   | 792  | 828  |
| <b>reflections collected</b>                      | 33461  | 61415  | 17379   | 29557  | 15794  |
| <b>unique reflections</b>                         | 8926   | 8755   | 8586  | 8392   | 7596   |
| <b>R<sub>int</sub></b>                            | 0.0735   | 0.0741   | 0.0574  | 0.0670   | 0.0470   |
| <b>R<sub>1</sub> [<i>I</i> &gt; 2σ(<i>I</i>)]</b> | 0.0589   | 0.0531   | 0.0551  | 0.0386   | 0.0279   |
| <b>wR<sub>2</sub> (all data)</b>                  | 0.1724   | 0.1600   | 0.1286  | 0.0704   | 0.0663   |
| <b>Goof</b>                                       | 1.032  | 1.025  | 1.029   | 0.924  | 1.042  |
| <b>largest peak and hole (e Å<sup>-3</sup>)</b>   | 0.20/-0.23                                       | 0.20/-0.23                                       | 0.22/-0.31                                      | 0.25/-0.42                                       | 0.27/-0.38                                       |
| <b>Flack parameter</b>                            | -  | -  | -0.01(4)  | 0.009(6)   | 0.049(13)  |
| <b>Hoofst parameter</b>                           | -  | -  | 0.02(3)   | 0.012(5)   | 0.077(9)   |
| <b>CCDC no.</b>                                   | 1838338  | 1838339  | 1838340   | 1838341  | 1838342  |

**Table S2.** Summary of crystallographic data for compounds **6**, **1(THF)<sub>2</sub>** and **3(DME)**.

|   | <b>6</b>   | <b>1(THF)<sub>2</sub>·THF</b>                                   | <b>3(DME)·DME</b>  |
|---|--|---|--|
| <b>empirical formula</b>                          | C <sub>52</sub> H <sub>59</sub> Li <sub>2</sub> N <sub>3</sub> | C <sub>60</sub> H <sub>74</sub> LiN <sub>3</sub> O <sub>3</sub> | C <sub>56</sub> H <sub>70</sub> KN <sub>3</sub> O <sub>4</sub> |
| <b>formula weight</b>                             | 739.90   | 892.16  | 888.25   |
| <b>crystal system</b>                             | monoclinic   | monoclinic  | monoclinic   |
| <b>space group</b>                                | <i>P2<sub>1</sub>/n</i>  | <i>P2<sub>1</sub>/c</i>   | <i>P2<sub>1</sub>/c</i>  |
| <b>a (Å)</b>                                      | 11.4916(4)   | 11.9250(4)  | 16.857(3)  |
| <b>b (Å)</b>                                      | 30.8596(12)  | 17.6801(5)  | 13.948(2)  |
| <b>c (Å)</b>                                      | 13.3457(5)   | 24.5702(7)  | 23.240(4)  |
| <b>α (deg)</b>                                    | 90   | 90  | 90   |
| <b>β (deg)</b>                                    | 110.931(2)   | 97.2130(10)   | 108.738(9)   |
| <b>γ (deg)</b>                                    | 90   | 90  | 90   |
| <b>V (Å<sup>3</sup>)</b>                          | 4420.4(3)  | 5139.5(3)   | 5174.6(15)   |
| <b>Z</b>  | 4  | 4   | 4  |
| <b>μ (mm<sup>-1</sup>)</b>                        | 0.063  | 0.070   | 0.149  |
| <b>ρ(calcd) (g cm<sup>-3</sup>)</b>               | 1.112  | 1.153   | 1.140  |
| <b>F(000)</b>                                     | 1592   | 1928  | 1912   |
| <b>reflections collected</b>                      | 65307  | 40773   | 34744  |
| <b>unique reflections</b>                         | 9767   | 12255   | 11431  |
| <b>R<sub>int</sub></b>                            | 0.0688   | 0.0559  | 0.0624   |
| <b>R<sub>1</sub> [<i>I</i> &gt; 2σ(<i>I</i>)]</b> | 0.0558   | 0.0546  | 0.0623   |
| <b>wR<sub>2</sub> (all data)</b>                  | 0.1466   | 0.1581  | 0.1831   |
| <b>GooF</b>                                       | 1.021  | 1.027   | 1.053  |
| <b>largest peak and hole (e Å<sup>-3</sup>)</b>   | 0.34/-0.21   | 0.48/-0.41  | 0.86/-0.68   |
| <b>CCDC no.</b>                                   | 1838343  | 1838344   | 1838345  |

### Assignment of M $\cdots$ $\pi$ -Arene Hapticities

The assignment of the hapticities of the metal $\cdots$  $\pi$ -arene interactions in **1-6** and **3(DME)** is based on the method introduced by Niemeyer.<sup>S8</sup> The M-centroid ( $X_n$ ) distance ( $d$ ) and the angle ( $\alpha$ ) between the M-centroid vector and the normal of the arene plane are calculated. The best description is that with the smallest values of  $d$  and  $\alpha$ .

**Table S3.** Evaluation of Li $\cdots$  $\pi$ -arene hapticities in **1**.

| $X_n$                 | $d$ (Ar <sub>C(7)</sub> ) | $\alpha$ (Ar <sub>C(7)</sub> ) | $d$ (Ar <sub>C(31)</sub> ) | $\alpha$ (Ar <sub>C(31)</sub> ) |
|-----------------------|---------------------------|--------------------------------|----------------------------|---------------------------------|
| <b>X<sub>6</sub></b>  | 2.501                     | 9.6                            | 3.023                      | 15.5                            |
| <b>X<sub>5</sub></b>  | 2.472                     | 4.0                            | 3.007                      | 14.4                            |
| <b>X<sub>4</sub></b>  | 2.479                     | 5.2                            | 2.954                      | 9.6                             |
| <b>X<sub>3</sub></b>  | 2.522                     | 12.2                           | 2.924                      | 3.0                             |
| <b>X<sub>2</sub></b>  | 2.596                     | 18.3                           | 2.976                      | 10.8                            |
| <b>X<sub>5</sub>'</b> | 2.485                     | 6.8                            | 2.963                      | 10.4                            |
| <b>X<sub>4</sub>'</b> | 2.501                     | 10.0                           | 2.941                      | 6.8                             |

**Table S4.** Evaluation of Na $\cdots$  $\pi$ -arene hapticities in **2**.

| $X_n$                 | $d$ (Ar <sub>C(7)</sub> ) | $\alpha$ (Ar <sub>C(7)</sub> ) | $d$ (Ar <sub>C(31)</sub> ) | $\alpha$ (Ar <sub>C(31)</sub> ) |
|-----------------------|---------------------------|--------------------------------|----------------------------|---------------------------------|
| <b>X<sub>6</sub></b>  | 2.761                     | 2.4                            | 2.866                      | 15.7                            |
| <b>X<sub>5</sub></b>  | 2.771                     | 3.5                            | 2.801                      | 13.1                            |
| <b>X<sub>4</sub></b>  | 2.812                     | 10.2                           | 2.773                      | 6.6                             |
| <b>X<sub>3</sub></b>  | -                         | -                              | 2.763                      | 3.9                             |
| <b>X<sub>2</sub></b>  | -                         | -                              | 2.813                      | 11.7                            |
| <b>X<sub>5</sub>'</b> | 2.767                     | 4.5                            | 2.829                      | 13.1                            |
| <b>X<sub>4</sub>'</b> | 2.817                     | 10.7                           | 2.802                      | 9.9                             |

**Table S5.** Evaluation of K $\cdots$  $\pi$ -arene hapticities in **3**.

| $X_n$  | $d(\text{Ar}_{C(7)})$ | $\alpha(\text{Ar}_{C(7)})$ | $d(\text{Ar}_{C(31)})$ | $\alpha(\text{Ar}_{C(31)})$ |
|--------|-----------------------|----------------------------|------------------------|-----------------------------|
| $X_6$  | 3.059                 | 12.6                       | 3.001                  | 9.1                         |
| $X_5$  | 3.015                 | 7.9                        | 2.998                  | 4.2                         |
| $X_4$  | 2.985                 | 2.7                        | 2.976                  | 4.0                         |
| $X_3$  | 3.007                 | 6.9                        | 3.006                  | 9.0                         |
| $X_5'$ | 3.022                 | 9.4                        | 2.990                  | 6.9                         |
| $X_4'$ | 3.037                 | 10.1                       | 2.999                  | 7.9                         |

**Table S6.** Evaluation of Rb $\cdots$  $\pi$ -arene hapticities in **4**.

| $X_n$  | $d(\text{Ar}_{C(7)})$ | $\alpha(\text{Ar}_{C(7)})$ | $d(\text{Ar}_{C(31)})$ | $\alpha(\text{Ar}_{C(31)})$ |
|--------|-----------------------|----------------------------|------------------------|-----------------------------|
| $X_6$  | 3.279                 | 3.3                        | 3.243                  | 7.7                         |
| $X_5$  | 3.276                 | 1.6                        | 3.314                  | 3.3                         |
| $X_4$  | 3.306                 | 8.0                        | 3.220                  | 3.4                         |
| $X_5'$ | 3.284                 | 4.5                        | 3.227                  | 5.2                         |
| $X_4'$ | 3.319                 | 7.8                        | 3.247                  | 8.1                         |

**Table S7.** Evaluation of Cs $\cdots$  $\pi$ -arene hapticities in **5**.

| $X_n$  | $d(\text{Ar}_{C(7)})$ | $\alpha(\text{Ar}_{C(7)})$ | $d(\text{Ar}_{C(31)})$ | $\alpha(\text{Ar}_{C(31)})$ |
|--------|-----------------------|----------------------------|------------------------|-----------------------------|
| $X_6$  | 3.371                 | 1.7                        | 3.372                  | 8.9                         |
| $X_5$  | 3.374                 | 3.0                        | 3.344                  | 5.6                         |
| $X_4$  | 3.409                 | 8.9                        | 3.328                  | 1.4                         |
| $X_3$  | -                     | -                          | 3.370                  | 8.8                         |
| $X_5'$ | 3.379                 | 4.5                        | 3.345                  | 5.3                         |
| $X_4'$ | 3.415                 | 8.6                        | 3.377                  | 9.3                         |

**Table S8.** Evaluation of Li $\cdots$  $\pi$ -arene hapticities in **6**.

| $X_n$  | $d(\text{Ar}_{C(7)})$ | $\alpha(\text{Ar}_{C(7)})$ | $d(\text{Ar}_{C(31)})$ | $\alpha(\text{Ar}_{C(31)})$ |
|--------|-----------------------|----------------------------|------------------------|-----------------------------|
| $X_6$  | 2.489                 | 21.7                       | 2.521                  | 23.6                        |
| $X_5$  | 2.397                 | 15.5                       | 2.424                  | 17.7                        |
| $X_4$  | 2.361                 | 12.0                       | 2.360                  | 11.8                        |
| $X_3$  | 2.309                 | 0.3                        | 2.320                  | 4.8                         |
| $X_2$  | 2.386                 | 14.9                       | 2.441                  | 19.0                        |
| $X_1$  | 2.361                 | 11.7                       | 2.351                  | 11.0                        |
| $X_5'$ | 2.452                 | 19.4                       | 2.464                  | 20.4                        |
| $X_4'$ | 2.363                 | 12.2                       | 2.406                  | 16.20                       |

**Table S9.** Evaluation of K $\cdots$  $\pi$ -arene hapticities in **3(DME)**.

| $X_n$  | $d(\text{Ar}_{C(7)})$ | $\alpha(\text{Ar}_{C(7)})$ | $d(\text{Ar}_{C(31)})$ | $\alpha(\text{Ar}_{C(31)})$ |
|--------|-----------------------|----------------------------|------------------------|-----------------------------|
| $X_6$  | 3.148                 | 5.8                        | -                      | -                           |
| $X_5$  | 3.131                 | 1.6                        | -                      | -                           |
| $X_4$  | 3.146                 | 5.6                        | -                      | -                           |
| $X_3$  | 3.194                 | 11.4                       | 3.676                  | 22.7                        |
| $X_2$  | 3.259                 | 16.1                       | 3.659                  | 21.9                        |
| $X_1$  | -                     | -                          | 3.534                  | 15.6                        |
| $X_5'$ | 3.140                 | 4.2                        | -                      | -                           |
| $X_4'$ | 3.148                 | 5.8                        | -                      | -                           |

## References

- S1 Hinz, A.; Schulz, A.; Villinger, A.; Wolter, J.-M. *J. Am. Chem. Soc.* **2015**, *137*, 3975.
- S2 Bertz, S. H.; Gibson, C. P.; Dabbagh, G. *Organometallics* **1988**, *7*, 227.
- S3 Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176.
- S4 SADABS, A program for area detector absorption correction, Sheldrick, G. M., Bruker Analytical X-Ray Division, Madison, Wisconsin, USA, **2008**.
- S5 Sheldrick, G. M. *Acta. Cryst.* **2015**, *A71*, 3.
- S6 Sheldrick, G. M. *Acta. Cryst.* **2015**, *C71*, 3.
- S7 Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339.
- S8 Lee, H. S.; Niemeyer, M. *Inorg. Chem.* **2006**, *45*, 6126.