

**Supplementary Preparation and Characterization data in support of Chem Comm Manuscript ‘Reversible C-C bond formation: Solid state structure of the aldol-like addition product of adamantanone to a 1,5-diazapentadienyllithium, and its solution state retro-aldol dissociation.’**

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## **Experimental**

All manipulations requiring dry conditions were carried out under a protective argon blanket, either in a double manifold argon/vacuum line or argon-filled recirculating glovebox. Argon was dried over phosphorus pentoxide supported on vermiculite. Toluene and n-hexane were used freshly distilled under argon from sodium-benzophenone ketyl. 2-isopropylaniline was distilled from potassium hydroxide prior to use. CDCl<sub>3</sub>, C<sub>6</sub>D<sub>6</sub> and C<sub>6</sub>D<sub>14</sub> were stored over 4 Å molecular sieves. The hexane solution of nBuLi was used as received and standardised using N-benzylbenzamide. All other reagents were obtained from standard commercial vendors and used as received.

Melting points were determined in sealed glass capillaries under argon. Elemental analyses were performed by the microanalytical group in the Chemistry Department at UMIST.

<sup>1</sup>H NMR spectra were recorded on Bruker DPX 200MHz, 300 MHz and 400 MHz NMR spectrometers. <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker DPX 300MHz spectrometer operating at 75 MHz. Chemical shifts are given in ppm and referenced to residual H solvent shifts or <sup>13</sup>C-NMR solvent shifts. Assignments were made with the aid of DEPT and HMQC experiments. Solid State CP-MAS NMR was performed on a Bruker 400MHz instrument.

Infrared spectra were recorded on a Nicolet Nexus-FTIR/Raman spectrometer using NaCl plates and nujol mulls. Raman spectra were recorded from powdered samples in Lindemann capillaries.

### **2-(2-isopropyl)phenylamino-4-(2-isopropyl)phenylimino-pent-2-ene, (1)**

A solution of 2,4-pentanedione (9.48 ml, 92.03 mmol), 2-isopropylaniline (25.50 ml, 184.07 mmol) and toluene (ca. 120 ml) was prepared. A catalytic amount of p-toluene sulfonic acid was added and the resultant mixture was heated under reflux for 7 h. The water (~ 3.3 ml) produced in the reaction was collected in a Dean - Stark apparatus as a toluene azeotrope. The majority of the toluene (~ 100 ml) was then removed from the reaction by distillation into the Dean - Stark arm and the remaining mixture was triturated with methanol and filtered to yield a cream crystalline solid, **1**. Cooling the toluene/methanol filtrate to -25 °C yielded further cream crystals. M.p.: 105-108 °C. Combined yield: 17.65 g, 57 %. <sup>1</sup>H NMR (200MHz; CDCl<sub>3</sub>): δ 1.22 (12H, d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, *MeCHMe*); 1.95 (6H, s, *NCMeCHCMeN*); 3.25 (2H, septet, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, *MeCHMe*); 4.96 (1H, s, *NCMeCHCMeN*); 6.92-7.38 (8H, non-first-order m, aromatic protons); 12.53 (1H, bs, *NH*). <sup>13</sup>C NMR (75MHz; CDCl<sub>3</sub>): δ 21.2 (*NCMeCHCMeN*); 23.6 (*MeCHMe*); 28.5 (*MeCHMe*); 96.6 (*NCMeCHCMeN*); 124.3, 124.7, 125.9 and 126.2 (aromatic CH); 142.0 (*C(CH(Me)<sub>2</sub>*, aromatic C); 143.7 (*C-NH*, aromatic C); 160.4 (*C=N*). Elemental analysis, Calcd. for C<sub>23</sub>H<sub>30</sub>N<sub>2</sub>: C, 82.6 %; H, 9.0 %; N, 8.4 %. Found: C, 82.6 %; H, 9.1 %; N, 8.4 %. IR: 1628 cm<sup>-1</sup> (s, ν(C=N)), 1557 cm<sup>-1</sup> (s, ν(C=C, aromatic)).

### **Lithium{2-[2-(2-isopropyl)phenylimino-1-(1-(2-isopropyl)phenylimino-ethyl)-propyl-adamantan-2-olate] (3)}**

To a stirred suspension of **1** ( 2.44 g, 7.3 mmol) in hexane (8 mL) in a Schlenk tube at 0 °C was added nBuLi (4.86 mL of a 1.51 M solution in hexanes, 7.3 mmol). Heat

and butane were evolved. The resultant pale yellow solution was re-cooled to 0°C with stirring, causing a pale cream fine precipitate to form. To this was added adamantan-2-one (1.095 g, 7.3 mmol), which caused momentary dissolution of the precipitate, but solid re-precipitated upon stirring for 5 min. The suspension was evacuated to remove butanes and concentrated *in vacuo* to approximately 8mL, then briefly heated to boiling to re-dissolve the precipitate. A crop of pale yellow blocks was deposited after standing overnight. These were isolated by filtration to yield 2.42 g (4.93 mmol, 68%) of **3**. M. p. 76-78°C. <sup>1</sup>H NMR (400MHz; C<sub>6</sub>D<sub>6</sub>, 300K): δ 1.2-1.5 (24H, overlapping m, *MeCHMe* and adamantyl resonances); 1.85 (2H, apparent br s, adamantyl OC(CH)<sub>2</sub>); 2.14 (6H, s, N*CMeCH*(Ad)*CMeN*); 3.68 (2H, sept, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, *MeCHMe*); 5.20 (1H, s, N*CMeCH*(Ad)*CMeN*); 7.1-7.4 (8H, non-first-order m, aromatic protons). <sup>1</sup>H NMR in deuterohexane was also recorded. Though it was not possible to lock on the signal, and some field drift was present, the peaks were essentially the same. The diagnostic alkenyl resonance (N*CMeCH*(Ad)*CMeN*) shifted slightly upfield to 4.85 ppm, still firmly in the alkenyl region. Solubility was low, such that collection of <sup>13</sup>C NMR data failed, and low temperature data was unobtainable. <sup>13</sup>C NMR (100MHz; C<sub>6</sub>D<sub>6</sub>, 300K): δ 23.8 (*MeCHMe*); 24.2 (N*CMeCH*(Ad)*CMeN*); 27.5 (*MeCHMe*); 28.3 (adamantyl CH); 36.1, 39.5 (adamantyl CH<sub>2</sub>) 47.3 (adamantyl OC(CH)<sub>2</sub>), 94.7 (N*CMeCH*(Ad)*CMeN*); 122.8, 125.0, 126.0 and 126.4 (aromatic CH); 141.8 (C(CH(Me)<sub>2</sub>), aromatic C); 153.3 (aromatic C-N); 163.7 (C=N); 227 (CO). Elemental analysis, Calcd. for C<sub>33</sub>H<sub>43</sub>N<sub>2</sub>OLi: C, 80.8 %; H, 8.8 %; N, 5.7 %. Found: C, 79.6 %; H, 9.2 %; N, 5.4 %. IR: 1650, 1626 cm<sup>-1</sup> (s, ν(C=N), *syn* and *anti*), 1596 cm<sup>-1</sup> (s, ν(C=C, aromatic)). Raman showed the same vibrations. On exposure of the IR plates to moist air, 3566 (sharp, LiOH), 1720 (C=O) 1628, 1556 (free **1**) cm<sup>-1</sup>. Attempts to collect data by

dissolving **3** in freshly distilled hexane and injecting the solution into a pre-dried and flushed IR solution cell were thwarted by hydrolysis, as indicated by peaks in the 1720, 1628 and 1555  $\text{cm}^{-1}$  regions.

**Cryoscopy:** Spectrograde benzene was dried with freshly activated molecular sieves 3A and standardised using benzil to an experimental cryoscopic constant of 5.04. Measurements were made under argon in an air-jacketed Schlenk tube fitted with a Beckman thermometer and placed in a cooling bath held at 0°C. Addition of 0.182 g of **3** to 25mL of benzene (0.0148 M solution, expressed as monomer) depressed its freezing point by  $0.092 \pm 2$ , corresponding to an average molecular weight of 456.3. This corresponds to an aggregation state of 0.93, i.e. 100% monomer, perhaps with some dissociation of free adamantanone, or perhaps some adventitious hydrolysis. Similar measurement on a 0.041 M solution showed no evidence of monomer-dimer equilibria, giving an value of RMM in solution of 452.4, indistinguishable from the more dilute result. This is approximately the concentration range that the NMR measurements were undertaken in, so it can be inferred that the observed shifts correspond to monomeric species in solution.

**Solid State CP-MAS NMR:** A powdered sample of **3** was packed into a spinner in the glovebox, and  $^{13}\text{C}\{^1\text{H}\}$  spectra were recorded in portions over a time period of 12h to check for decay. There was none, and so all datasets were combined to give a low-noise spectrum. Resolution was good, with symmetry inequivalent/chemically equivalent peaks often being resolved, though in some cases the two (or four) resonances overlapped with other groups of resonances, obscuring assignments:  $\delta$  20.5, 21.1 (*MeCHMe*); 24.5 (*NCMeCH(Ad)CMeN*); 25.1, 26.2, 26.6, 27.3, 28.8 (*MeCHMe*, adamantyl CH); 34.7, 36.3, 38.4, 41.1 (adamantyl  $\text{CH}_2$ , adamantyl  $\text{OC}(\text{CH}_2)_2$ ); 62.5, 63.4 (*NCMeCH(Ad)CMeN*); 85.6, 91.4 (CO) 121.5, 122.0, 123.2,

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124.3, 124.7, (aromatic CH); 136.1, 137.3, 138.2, 138.8 ( $C(\text{CH}(\text{Me})_2)$ , aromatic C);  
148.6, 149.8 (aromatic C-N); 169.0, 170.6 ( $C=N$ ); 180-230 ppm region totally silent.

**Quenching experiments:** Samples of **3** were taken up in hexane and washed with distilled water. The organic phase was separated, dried in vacuo and subjected to NMR analysis. Peaks corresponding to **1** and adamantanone were observed. Using saturated aqueous  $\text{NH}_4\text{Cl}$  in place of pure water produced identical results.