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ARTICLE TYPE

# Anionic *N*-Heterocyclic Carbenes (NHCs): A Versatile Route to Saturated NHCs Bearing Pendant Weakly Coordinating Anions

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A versatile methodology is reported for the synthesis of anionic NHCs featuring a 5-, 6-, or 7-membered saturated heterocyclic core. Lewis acid promoted exocyclic ring closure generates systems in which the pendant borate functionality is incorporated via a CH<sub>2</sub> linker, allowing for electronic and steric isolation of the anionic component. Hence, a library of NHCs can be accessed which incorporate metal binding environments essentially identical to the neutral parent donors, but with significantly altered solubility profiles.

*N*-heterocyclic carbenes (NHCs) are neutral, strongly  $\sigma$ -donating ligands which have been widely exploited in the stabilisation of cationic metal species implicated in homogenous catalysis.<sup>1,2</sup> In recent years, NHC ligands have been reported incorporating pendant anionic groups, thereby removing the need for a separate counter-ion in mono-cationic systems (Fig. 1). The resulting zwitterions have markedly enhanced solubility in apolar solvents, thereby enabling catalytic processes to be effected in non-donor media.<sup>3</sup> Thus, Tamm and co-workers have reported the synthesis of imidazolyl NHCs featuring a weakly coordinating anionic component in the backbone C4 position (e.g. [L<sup>2</sup>], Fig. 1).<sup>3(i)</sup> Subsequently derived complexes of the type (L<sup>2</sup>)Ir(COD) (COD = 1,5-cyclooctadiene) represent neutral counterparts to Crabtree's hydrogenation catalyst, [(Cy<sub>3</sub>P)Ir(COD)(py)][PF<sub>6</sub>], which are soluble and active in neat alkene media.<sup>4,5</sup>

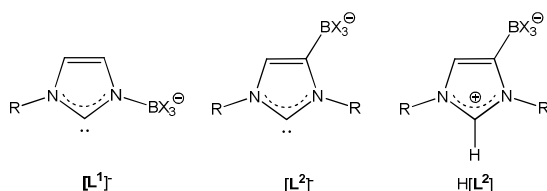
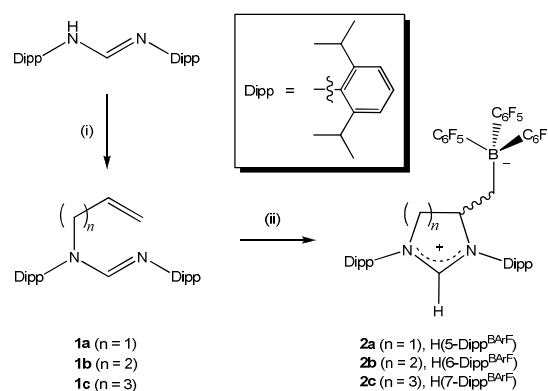


Fig. 1 Previously reported classes of borate-functionalized NHC.<sup>3(a-d,h,j)</sup>

Interestingly, however, zwitterionic C2-protonated systems of the type H[L<sup>2</sup>] are stable with respect to deprotonation.<sup>3(i)</sup> As a result, the synthesis of systems of the type [L<sup>2</sup>] necessitates metallation (typically lithiation) at the C4 position of the corresponding *free* NHC, followed by borane capture. Consequently, this methodology is limited to NHCs capable of backbone lithiation. With a view to exploiting a wider range of carbene donors in zwitterionic late metal catalysts (including saturated and expanded ring NHCs)<sup>6</sup> we targeted alternative routes for incorporation of the weakly coordinating anion (WCA)

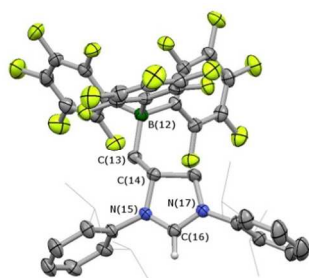
component. Herein we report a general synthetic method for the formation of NHCs incorporating pendant WCA functions, offering systematic variation in the heterocycle size.



Scheme 1 General method for the synthesis of the zwitterionic NHC precursors 2a-c. Reagents and conditions: (i) Br(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub> (1 equiv.), K<sub>2</sub>CO<sub>3</sub> (0.5 equiv.), MeCN, 50 °C, 2 h (n = 1), 90 °C, 3 d (n = 2, 3), 26-68% yield; (ii) B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1 equiv.), toluene, 1 h, 20 °C, 59-66% yield.

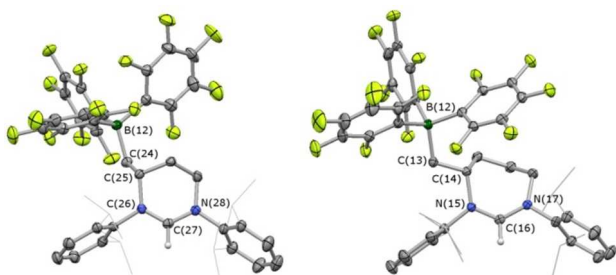
We have previously reported that the acyclic system *N,N'*-bis(diisopropylphenyl)-*N*-allylformamidine (**1a**) undergoes ring closure in the presence of sources of the potent electrophile “[{(6-Dipp)Au}]<sup>+</sup>”.<sup>7</sup> Given their inherently strong Lewis acidity, we hypothesized that triarylboranes, such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, might also facilitate ring closure, thereby generating a heterocycle featuring a pendant (anionic) borate group. Accordingly, addition of one equivalent of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to **1a** leads to the appearance of a signal in the <sup>11</sup>B NMR spectrum at  $\delta_B = -14.7$  ppm, characteristic of an anionic system of the type [RB(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>-</sup> (Scheme 1).<sup>8,9</sup> The formation of a single alkyltriarylborane species suggests high regioselectivity in the ring closure step, and subsequent crystallographic studies support a 5-exo-trig mechanism rather than a 6-endo-trig pathway.<sup>7,10</sup> Thus, the major product is confirmed as the zwitterionic 5-membered heterocycle H(5-Dipp<sup>BArF</sup>) (**2a**; Fig. 2) featuring a borate function appended via a CH<sub>2</sub> linker. In contrast to the structure of H[L<sup>2</sup>],<sup>11</sup> the two endocyclic N–C bonds in **2a** are identical in length {1.311(3), 1.309(3) Å *cf.* 1.336(3), 1.414(3) Å for H[L<sup>2</sup>]} suggesting that the steric and/or electronic influence of the borate is more remote in **2a**.

The systematic application of this ring closure methodology in heterocycle synthesis can readily be demonstrated. Thus, alkene-functionalised formamidine species **1b** and **1c** can be viewed as



**Fig. 2** Molecular structure of **2a** ( $C_6H_5CH_3$ ) as determined by X-ray crystallography with most H atoms and toluene solvate molecule omitted and <sup>1</sup>Pr groups shown in wireframe format for clarity; thermal ellipsoid set at 50% probability level. Key bond lengths (Å) and angles (°): B(12)–C(13) 1.664(4), N(15)–C(16) 1.311(3), C(16)–N(17) 1.309(3), N(15)–C(16)–N(17) 114.0(2).

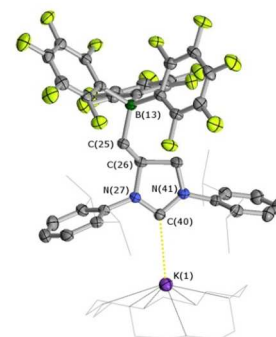
precursors to the corresponding 6- and 7-membered heterocycles (Scheme 1). Treatment of each with  $B(C_6F_5)_3$  gives rise to species characterized by <sup>11</sup>B signals at  $\delta_B = -14.5$  and  $-14.3$  ppm respectively, and exo-trig ring closure to give H(6-Dipp<sup>BArF</sup>) (**2b**) and H(7-Dipp<sup>BArF</sup>) (**2c**) is verified crystallographically (Fig. 3). As with **2a**, both expanded ring systems feature a  $CH_2$ -tethered borate function and statistically identical endocyclic N–C distances. The N–C–N angles for **2b** and **2c** are somewhat wider than in **2a** [ $124.9(1)^\circ$  and  $127.0(1)^\circ$  vs.  $114.0(2)^\circ$ ] mirroring the trend observed for the parent (non borate-functionalized) systems.<sup>6(a)</sup>



**Fig. 3** Molecular structures of (left) **2b** and (right) **2c2**( $Et_2O$ ) as determined by X-ray crystallography with most H atoms and ether solvate molecules omitted (for **2c2**( $Et_2O$ )), and <sup>1</sup>Pr groups shown in wireframe format for clarity; thermal ellipsoid set at 50% probability level. Key bond lengths (Å) and angles (°): (for **2b**) B(12)–C(24) 1.661(2), N(26)–C(27) 1.314(2), C(27)–N(28) 1.322(2), N(26)–C(27)–N(28) 124.9(1); (for **2c2**( $Et_2O$ )) B(12)–C(13) 1.666(2), N(15)–C(16) 1.319(2), C(16)–N(17) 1.323(1), N(15)–C(16)–N(17) 127.0(1).

Due to the electronic separation of the borate and formamidinium moieties in **2a–c** enforced by the saturated  $CH_2$  linker, it was hypothesized that the acidities of the NC(H)N protons would be comparable to those of the parent NHC salts. Consistently, deprotonation can be effected by the use of an appropriately strong base (e.g. <sup>n</sup>BuLi or  $K[N(SiMe_3)_2]$ ) to generate the corresponding alkali metal complex. Thus, addition of one equivalent of  $K[N(SiMe_3)_2]$  to **2a** leads to the disappearance of the NC(H)N resonance at  $\delta_C = 155.6$  ppm and the growth of a carbenic signal at  $\delta_C = 165.5$  ppm. Addition of 18-crown-6 yields single crystals of  $[K(18\text{-crown-6})][(5\text{-Dipp}^{BArF})]$  (**3**), the structure of which is confirmed crystallographically (Fig. 4). In comparison to its conjugate acid **2a**, **3** has a narrower N–C–N angle [ $104.7(2)^\circ$  cf.  $114.0(2)^\circ$ ] and elongated N–C bonds [1.353(4), 1.353(2) Å cf. 1.311(3), 1.309(3) Å], a trend mirroring that observed for the corresponding borate-free 5-

Mes system.<sup>12</sup> The  $C_{NHC}\cdots K$  separation in **3** [3.234(3) Å] is indicative of a weak interaction, being markedly longer than other potassium NHC complexes {e.g. 3.00 Å for  $[(6\text{-}^i\text{Pr})KN(SiMe_3)_2]_2$  and 3.029(2) Å for  $[(6\text{-Dipp})KN(SiMe_3)_2]_2$ },<sup>13</sup> and is significantly outside the sum of the respective covalent radii (2.76 Å).<sup>14</sup>

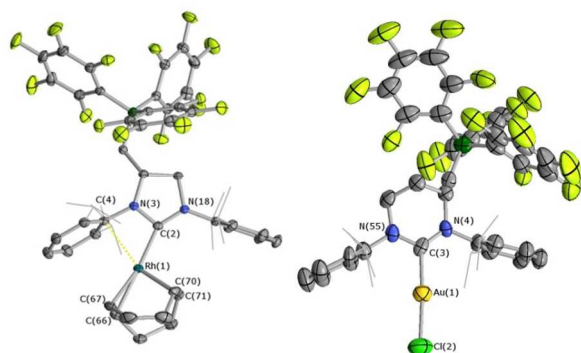


**Fig. 4** Molecular structure of **3** as determined by X-ray crystallography with H atoms omitted, and <sup>1</sup>Pr groups and 18-crown-6 shown in wireframe format for clarity; thermal ellipsoid set at 50% probability level. Key bond lengths (Å) and angles (°): B(13)–C(25) 1.669(4), N(27)–C(40) 1.353(4), C(40)–N(41) 1.353(3), C(40)–K(1) 3.234(3), B(13)–C(25)–C(26) 115.9(2), N(27)–C(40)–N(41) 104.7(2).

While the synthesis of **3** demonstrates the ready accessibility of the respective alkali metal NHC salts, more convenient transfer protocols exploit *in situ* deprotonation with <sup>n</sup>BuLi.<sup>15</sup> Thus, transmetalation of *in situ* lithiated NHCs was probed with archetypal late transition metal electrophiles, with a view to comparing the donor properties of this new ligand class (i) with the parent charge-neutral expanded ring NHCs; and (ii) with systems of the type  $[L_2]^-$  in which the borate is more closely linked (both physically and electronically) to the carbene heterocycle.

Lithiation of **2a** *in situ* and subsequent addition to  $[Rh(COD)Cl]_2$  results in the appearance of a downfield-shifted <sup>13</sup>C NMR signal with a doublet splitting pattern, suggesting coordination to rhodium ( $\delta_C = 176.9$  ppm,  $^1J_{RhC} = 40.9$  Hz). The structure of the isolated (hydrocarbon soluble) product was confirmed by X-ray crystallography as the zwitterion (5-Dipp<sup>BArF</sup>)Rh(COD) (**4**; Fig 5). Superficially at least, **4** is similar to  $(L^2)Rh(COD)$  reported by Tamm *et al.* (for  $X = C_6F_5$ ,  $R = Dipp$ ) in which the Rh<sup>+</sup> centre receives secondary stabilisation from a flanking aryl ring;<sup>5</sup> closer inspection shows that the Rh– $C_{NHC}$  distance in **4** is somewhat shorter [ $Rh(1)–C(2) = 2.005(2)$  Å cf.  $2.027(2)$  Å], consistent with the stronger donor capabilities of the saturated backbone NHC.<sup>1(d)</sup> As a consequence, there is a reduced interaction between the rhodium centre and the aryl *ipso*-carbon in **4** [ $Rh(1)\cdots C(4) 2.509(2)$  Å cf.  $2.466(2)$  Å], and less distortion is demanded of the NHC framework [e.g.  $C(2)–N(3)–C(4) 113.7(1)^\circ$  cf.  $109.8(2)^\circ$ ].

Transmetalation was also investigated with  $(THT)AuCl$  (THT = tetrahydrothiophene): reaction of *in situ* lithiated **2b** was probed using THF as the solvent in the hope of generating an anionic counterpart to Cavell's (6-Dipp)AuCl system,<sup>6(e)</sup> to allow for direct structural comparison. In the event, the isolated product displays no coordinated THT by <sup>1</sup>H NMR, but does reveal signals corresponding to bound THF. Consistently, X-ray crystallographic analysis reveals the product to be  $[Li(THF)_4][(6\text{-Dipp}^{BArF})AuCl]$  (**5**) in which the Au–Cl bond has been retained within an overall negatively charged complex. This contrasts with chemistry reported for systems of the type  $[L_2]^-$  in which chloride



**Fig. 5** Molecular structures of (left) **4** ( $C_6H_{14}$ ) and (right) **5**, with H atoms, hexane solvate molecule (for **4** ( $C_6H_{14}$ )) and  $[Li(THF)_4]^+$  cation omitted (for **5**) and 'Pr groups shown in wireframe format for clarity; thermal ellipsoids set at 50% probability level. Key bond lengths (Å) and angles ( $^\circ$ ): (for **4** ( $C_6H_{14}$ )) Rh(1)–C(2) 2.005(2), Rh(1)–C(4) 2.509(2), C(2)–N(3) 1.335(2), C(2)–N(18) 1.330(2), Rh(1)–C(66) 2.253(2), Rh(1)–C(67) 2.200(2), Rh(1)–C(70) 2.104(2), Rh(1)–C(71) 2.100(2), N(3)–C(2)–N(18) 108.7(1), C(2)–N(3)–C(4) 113.7(1); (for **5**) Au(1)–Cl(2) 2.277(3), Au(1)–C(3) 2.000(8), C(3)–N(4) 1.31(1), C(3)–N(55) 1.35(1), C(3)–Au(1)–Cl(2) 176.3(3), N(55)–C(3)–N(4) 118.7(7).

is displaced to generate charge neutral systems of the type  $(L^2)Au(THT)$ . The use of THF (rather than toluene) as the reaction medium presumably favours the formation of the salt **5** in our case. Interestingly, the structural metrics determined for the  $[(6-Dipp)^{BArF}AuCl]^-$  component of **5** are statistically identical to those reported for the corresponding neutral complex  $(6-Dipp)AuCl$  [Au(1)–Cl(2) 2.277(3) Å, Au(1)–C(3) 2.000(8) Å, C(3)–Au(1)–Cl(2) 176.3(3) $^\circ$ , cf. 2.281(12), 2.004(8) and 175.6(3) $^\circ$  for  $(6-Dipp)AuCl$ ].<sup>6(e)</sup> This observation (plus that of near identical percentage buried volumes,  $\%V_{bur}$ , for the two ligands),<sup>16,17</sup> supports the notion that this new family of anionic NHCs offers steric and electronic properties which are essentially unaffected by the incorporation of the borate anion.

## Conclusions

We have developed a versatile method for the synthesis of a library of anionic NHCs in which the borate component is tethered to the heterocycle by a  $CH_2$  linker. In contrast to previously reported examples of borate-functionalized NHCs, inclusion of this saturated tether provides (i) electronic isolation from the donor site, and (ii) sufficient conformational flexibility that the steric effects of the bulky borate function are also negligible. This leads to a binding environment analogous to the neutral parent NHCs but with an altered solubility profile provided by the zwitterionic nature of the resulting complex. Applications of these ligands in novel hydrocarbon soluble metal systems are currently under investigation and will be reported in due course.

## Notes and references

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† Electronic Supplementary Information (ESI) available: characterizing data for all new compounds; CIFs for **2a** ( $C_6H_5CH_3$ ), **2b**, **2c** ( $Et_2O$ ), **3**, **4** and **5** (CCDC refs: 1006573–1006578). See DOI: 10.1039/b000000x/

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15. *In situ* NMR monitoring of the deprotonation of **2b** in  $thf-d_8$  is consistent with the formation of  $[Li(thf)_n][6-Dipp^{BArF}]^-$  (see ESI). The carbenic  $^{13}C$  NMR shift (243.1 ppm) is indicative of a 'free' (i.e. non-coordinated) carbene ligand.
16. The percentage buried volumes,  $\%V_{bur}$ , determined for  $[(6-Dipp)^{BArF}]^-$  and 6-Dipp based on their respective  $Au^+Cl^-$  complexes are 50.4 and 50.8, respectively.<sup>6(e),17,18</sup>
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