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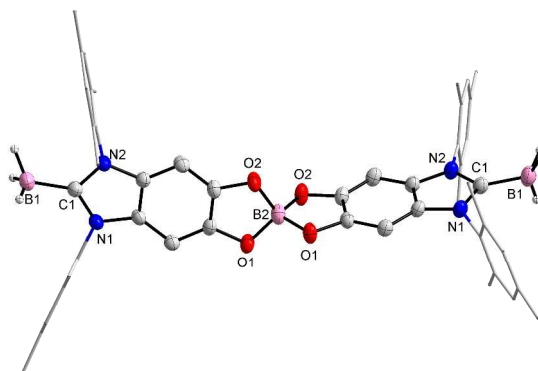
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A Spiroborate-Based Anionic Bis-*N*-Heterocyclic Carbene

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TOC



Abstract:

A twisted mono-cationic bis-benzimidazolium salt was serendipitously isolated from the dehydrative condensation of 5,6-dihydroxyl-1,3-dimesityl-benzimidazolium and 1,4-benzenediboronic acid. Subsequent deprotonation of the benzimidazolium salt led to the formation of a spiroborate linked free bis-NHC, which was further transformed into the corresponding diborane adduct and the di-Rh complex.

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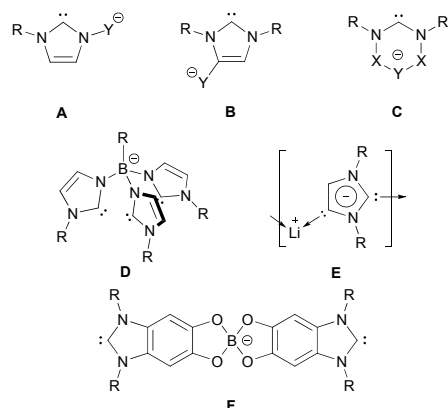
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A twisted mono-cationic bis-benzimidazolium salt was serendipitously isolated from the dehydrative condensation of 5,6-dihydroxyl-1,3-dimesityl-benzimidazolium and 1,4-benzenediboronic acid. Subsequent deprotonation of the benzimidazolium salt led to the formation of a spiroborate linked free bis-NHC, which was further transformed into the corresponding diborane adduct and the di-Rh complex.

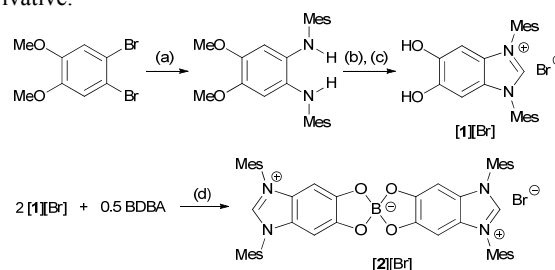
N-Heterocyclic carbenes (NHCs) have attracted considerable attention over the past two decades since the isolation of stable free carbene by Arduengo in 1991.¹ NHC ligands have become ubiquitous in organometallic catalysis due to their strong electron donating ability, which helps in stabilising active metal centres.²⁻⁸ Amongst the numerous ylidene molecules reported to date, increasing interest is focused on anionic NHCs, a subclass of NHCs that possesses negative charges.⁹ According to the position of the negative charge, anionic NHCs can be roughly categorised into three different types. The type A ligand features an anionic side arm on the nitrogen atoms and generally forms chelate complexes with metal centres.⁹ The type B ligand contains negative functionalities on the C4/C5 carbons,¹⁰⁻¹⁷ while the negative charge is delocalised over several ring atoms in the type C ligand.¹⁸⁻²³



In addition to anionic monotopic carbenes, anionic multi-dentate carbenes that feature more than one ylidene binding site have also been reported.^{24, 25} A representative example of a chelating anionic poly-NHC is the borate-linked scorpionate triscarbene ligand (type D), which was first reported by Fehlhammer and co-workers in 1996.²⁶⁻²⁸ Recently, Robinson's group demonstrated that by deprotonation of imidazol-2-ylidene, a bridging anionic dicarbene consisting of both normal and abnormal carbenes (type E) could be realised and structurally

characterised.^{29, 30} In this work, we report the synthesis and coordination chemistry of a twisted linear anionic bis-NHC (type F), an anionic version of linear "Janus-type" bis-NHC ligand,^{31, 32} produced by the deprotonation of a spiroborate-linked bis-benzimidazolium derivative, which was obtained from the dehydrative condensation of mono-functional benzimidazolium salt and 1,4-benzenediboronic acid (1,4-BDBA). We also experimentally investigated the unusual synthetic pathway of the bis-benzimidazolium salt.

As shown in Scheme 1, 5,6-dimethoxy-1,3-dimesityl-benzimidazolium was prepared from the Buchwald-Hartwig amination of 4,5-dibromo-1,2-dimethoxybenzene with 2,4,6-trimethylaniline to afford the *ortho*-phenylenediamine derivative, which was then cyclised in triethyl orthoformate in the presence of HBF₄. Double demethylation of the methoxyl derivative at low temperature with BBr₃ resulted in the desired compound [1][Br] as colourless solid, which was further purified via recrystallisation.[‡] The smooth transformation of the diamine to the benzimidazolium salt was a surprising finding because the formylative cyclisation of *N,N'*-dimesityl-*ortho*-phenylenediamine is notoriously difficult.³³⁻³⁵ The only exception is the triphenylene-based tris-azolium salt, which is prepared from the formylative cyclisation of the hexa-mesitylamine derivative.³⁶



Scheme 1 Synthetic procedures of [1][Br] and [2][Br]. Reaction conditions: (a) Pd(OAc)₂, NaO^tBu, IPr-HCl, MesNH₂, toluene, 110 °C, 16 h. (b) HC(OEt)₃, HBF₄·OEt₂, r.t., 16 h. (c) (i) BBr₃, DCM, -78 °C to r.t., 1 h. (ii) MeOH. (d) EtOH, 80 °C, 16 h.

Our initial goal was to develop an easy synthetic method for obtaining symmetrical poly-benzimidazolium salts, the apparent precursor for bridging-type poly-NHC ligands, via the dehydrative condensation of [1][Br] and appropriate poly-boronic acids. Such an assembly process has been used for constructing boronate ester-linked polymers^{37, 38} and covalent organic frameworks.^{39, 40} However, the reaction of [1][Br] and 1,4-BDBA did not afford the dicationic bis-benzimidazolium derivative;

instead, the unexpected mono-cationic salt $[2][Br]$ was obtained. The cleavage of the central benzene ring of 1,4-BDBA was first recognised in the 1H NMR spectrum of $[2][Br]$, which did not contain signals from the central phenylene group. Furthermore, the ^{11}B NMR resonance for $[2][Br]$ detected at 15 ppm was shifted considerably up-field relative to that observed for the boronate ester (32 ppm).⁴¹ Formation of the spiroborate moiety was confirmed with single crystal X-ray diffraction analysis of $[2][Br]$. As shown in Figure 1, $[2]^+$ consists of two benzimidazolium moieties connected by a tetra-coordinated borate unit. The distance between the two $[N=CH-N]^+$ carbon atoms is 13.2 Å. These two benzimidazolium rings are perpendicular to each other with a dihedral angle of 89° , suggesting the absence of electronic communication between the two units.

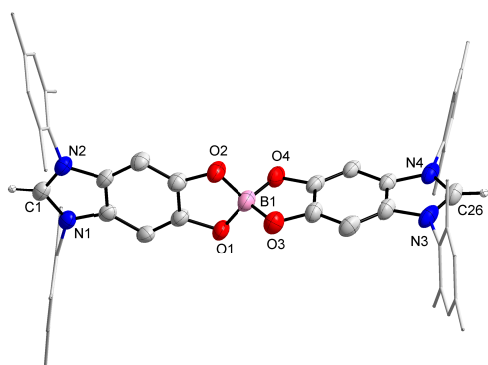
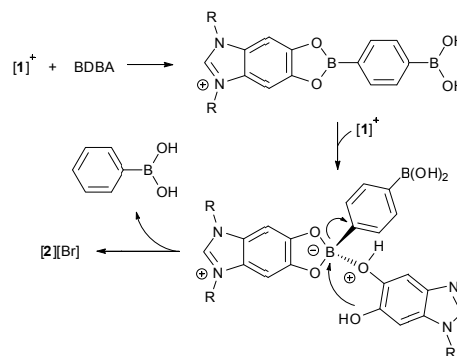


Figure 1 Molecular structure of $[2]^+$. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, the counter anion, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): N1-C1 1.349(6), N2-C1 1.333(6), N3-C26 1.330(7), N4-C26 1.346(6), B1-O1 1.480(7), B1-O2 1.490(7), B1-O3 1.488(7), B1-O4 1.499(8), N1-C1-N2 109.6(4), N3-C26-N4 109.5(4), O1-B1-O2 105.2(4), O3-B1-O4 104.0(4)

The isolation of $[2][Br]$ in high yield suggests that the boron-carbon bond cleavage occurred during the reaction. To understand the mechanism of the spiro compound formation, we varied the molar ratio of $[1][Br]$ and 1,4-BDBA from 1:1 to 2:1 and 4:1. The results are summarised in Table S1. Interestingly, when the yield of $[2][Br]$ was calculated based on the amount of $[1][Br]$ used, a similar yield for the isolated product was attained for each set of reaction conditions, suggesting that every 1,4-BDBA provided two boron atoms. In addition, the presence of phenylboronic acid was clearly identified in the 1H NMR spectra of the crude reaction mixture that contains either a 1:1 or 2:1 molar ratio of $[1][Br]$ and 1,4-BDBA, confirming the B-C bond cleavage of 1,4-BDBA during the reaction. To demonstrate that phenylboronic acid can serve as the boron source for $[2][Br]$, the reaction of $[1][Br]$ and phenylboronic acid was also examined. As expected, $[2][Br]$ was obtained in good yield.

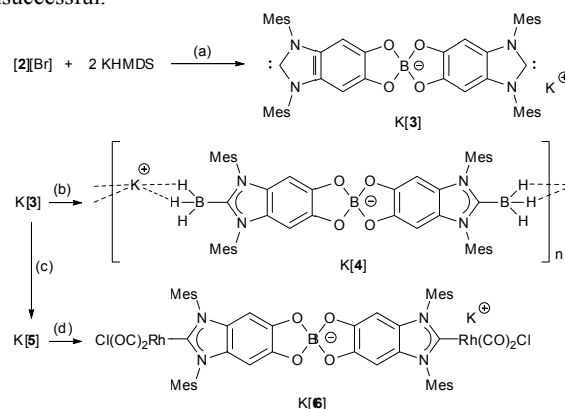
A proposed mechanism for the formation of $[2]^+$ is depicted in Scheme 2. After compound $[1]^+$ and 1,4-BDBA dehydratively condense to form the putative cationic boronate ester, the benzimidazolium-tethered boron centre is then attacked by another $[1]^+$ molecule. Subsequently, the resulting intermediate quickly undergoes B-C bond cleavage to yield phenylboronic acid and $[2]^+$. The large reactivity difference between the two boron centres is attributed to the positive charge-enhanced Lewis acidity of the benzimidazolium-tethered boron centre. Such increased Lewis acidity is well documented for cationic

triarylboranes, which show much stronger affinity towards anions than neutral boranes.^{42, 43}



Scheme 2 Proposed mechanism for the formation of $[2]^+$.

After this unusual bis-benzimidazolium salt was isolated and characterised, its corresponding free carbene ligand was prepared. Interestingly, the strained spiro-bicyclic structure of $[2]^+$ was found to be very stable, even in the presence of strong base or hydride species. Treating $[2]^+$ with two equivalents of potassium hexamethyldisilazide in THF led to the isolation of anionic bis-NHC $[3]^-$ in high yield. In the 1H NMR spectrum of $[3]^-$, the characteristic 1H resonance of the $[N=CH-N]^+$ moiety was absent. The ^{11}B resonance of $[3]^-$, detected at 15 ppm, was identical to that observed for $[2]^+$. The formation of ditopic anionic bis-NHC was further corroborated with the detection of a ^{13}C NMR signal at 224 ppm, a typical value for free benzimidazol-2-ylidenes.⁴⁴ Unfortunately, all attempts to structurally characterise $K[3]$ were unsuccessful.



Scheme 3 Synthetic procedures for anionic bis-NHC $K[3]$, di-borane adduct $K[4]$, and di-rhodium complex $K[6]$. Reaction conditions: (a) THF, r.t., 1 h. (b) i. $KOtBu$, THF, 15 min. ii. BH_3SMe_2 , r.t., 16 h. (c) i. $KOtBu$, THF, 15 min. ii. $[Rh(COD)Cl]_2$, THF, $80^\circ C$, 16 h. (d) CO, THF, 30 min.

To confirm that $[3]^-$ indeed functions as a di-carbene, we also prepared the corresponding diborane and the di-Rh complexes. Treating $K[3]$ with two equivalents of BH_3SMe_2 in THF resulted in the formation of the diborane adduct $K[4]$ in moderate yield. The coordination of BH_3 was evident in the ^{11}B NMR spectrum, where an addition signal was detected at -37 ppm.⁴⁵⁻⁴⁷ The observed chemical shift was comparable to the reported values of NHC- BH_3 adducts. The boron-decoupled proton NMR spectrum confirmed the chemical shift of the B-H hydrogen at 0.60 ppm.⁴⁶ The ^{13}C resonance of the ylidene centres was shifted from 224 ppm in $K[3]$ to 176.7 ppm in $K[4]$.⁴⁵ The structural connectivity

of K[4] was further corroborated by X-ray diffraction analysis (Figure 2). Single crystals were obtained from the methanol/diethyl ether solution of K[4] as colourless blocks. Structural analysis of K[4] revealed that the molecule exists as a linear polymer in the solid state via potassium-hydrogen interactions (Figure S2). Bond distances and angles of the central spiroborate core were reminiscent of those found in [2]⁺. The ylidene-boron bond distance of 1.589(5) Å was comparable to that observed for NHC-borane adducts.⁴⁵⁻⁴⁷

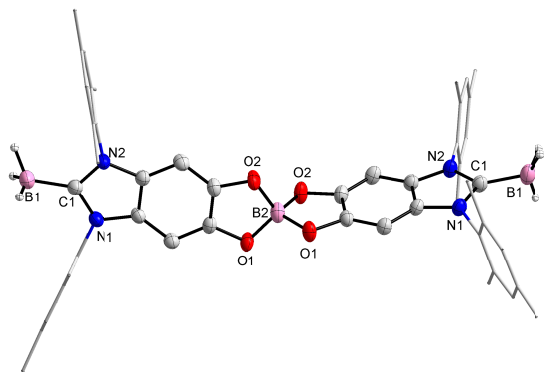


Figure 2 Molecular structure of [4]. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms, the counter cation, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): B1-C1 1.589(5), N1-C1 1.358(4), N2-C1 1.355(4), B2-O1 1.468(4), B2-O2 1.491(4), N1-C1-N2 105.8(2), O1-B2-O2 104.60(f11).

To evaluate the electron donating ability of [3][−], the di-rhodium complex K[6] was also synthesised. By treating K[3] with one equivalent of [Rh(COD)Cl]₂ in THF under refluxing conditions, the di-Rh complex K[5] was isolated in high yield. Complex K[5] was then converted into K[6] by bubbling CO into the THF solution of K[5] for 30 minutes. The $\bar{\nu}_{\text{CO}}$ bands for *cis* and *trans* isomers of [6] were observed at 1992 and 2073 cm^{−1}, respectively. The average $\bar{\nu}_{\text{CO}}$ value of 2032.5 cm^{−1} was relatively low compared to that obtained for neutral NHCs, confirming the stronger donating ability of [3][−].^{48, 49} However, this detected CO stretching frequency was not as low as that reported for monotopic anionic NHCs, indicating the dilution of the inductive effect of the borate anion over two identical carbene moieties.

In summary, we report the synthesis of a linear anionic bis-NHC from the corresponding spiroborate-linked bis-benzimidazolium salt. The formation of [2]⁺, involving the unexpected B-C bond cleavage of 1,4-BDBA, was investigated experimentally. Spectroscopic data and reactivity studies of [3][−] confirmed the di-carbene nature of [3][−]. The IR measurement of the di-Rh complex K[6] revealed that the electron donating ability of [3][−] was stronger than that of neutral NHC but lower than that of monotopic anionic NHC due to the dilution of the inductive effect of the borate anion over two electronically isolated NHC units.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and NMR spectra of all reported compounds. X-ray crystallographic data of [1][Br], [2][Br], and K[4]. CCDC 950338-950340. See DOI: 10.1039/b000000x/ ‡ Molecular structure of [1][Br] is included in ESI.

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