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COMMUNICATION

Stepwise and selective synthesis of chelating, multimetallic and mixed-metal π-diborene complexes

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The reaction of a pyridyl-substituted, doubly Lewis base-stabilised diborene with different amounts of copper(I) precursors led to the formation of the first chelating π-diborene complexes, the first π-diborene complexes in which metals are bound to both faces of the B=B bond, and the first mixed-metal π-diborene species.

In recent years, a wide range of Lewis-base stabilised diborene compounds containing B=B π-bonding have been isolated using different synthetic protocols.[1-7] The doubly Lewis-base stabilised diborenes, RLB=BLR (L = Lewis base and R = anionic substituent) are isoelectronic and isolobal with alkenes. However, their energetically high-lying HOMO and relatively low-lying LUMO make them undergo facile [2+2] cycloaddition and 1,2-addition reactions, unlike most olefins.[6] TM alkene π-complexes are well documented in the literature,[8, 9] however, in comparison, TM π-complexes of non-carbon homodiatomics are very limited.[10-20] Metal π-diborene complexes are rarer still, but exhibit surprising structural variety (Fig. 1). Since our reports of the first π-complexes of doubly base-stabilised and non-stabilised diborenes (types **I**[21, 22] and **III**[23]; Fig. 1), we and others have expanded this family of complexes to include cyclic diborenes (**II**[24], **VIII**[25]), clusters with bridging diborene units (**VI**[26], **VII**[27]), complexes with unsymmetrical diborene ligands (**II**, **IV**[28-30], **VIII**), cationic diborene complexes (**VIII**), and complexes containing metals of Groups 2 (**IV^a**), 6 (**VII**), and 12 (**IV^b**, **V**[31]).

Our recent discovery of the intermolecular *o*-C–H borylation of pyridine by the diboryne species $[(SIDep)B{\equiv}B(SIDep)]$[32] (SIDep = 1,3-bis(2,6-diethylphenyl)-imidazolin-2-ylidene) provided the doubly NHC-stabilised 1-(2-pyridyl)-2-hydrodiborene $[(SIDep)(H)B{=}B(2\text{-}NC_5H_4)(SIDep)]$[33] **1** (Scheme 1) in good yield, for which we envisioned the possibility of interesting coordination chemistry due to its additional pyridyl donor. Herein we describe the use of this ditopic diborene ligand to

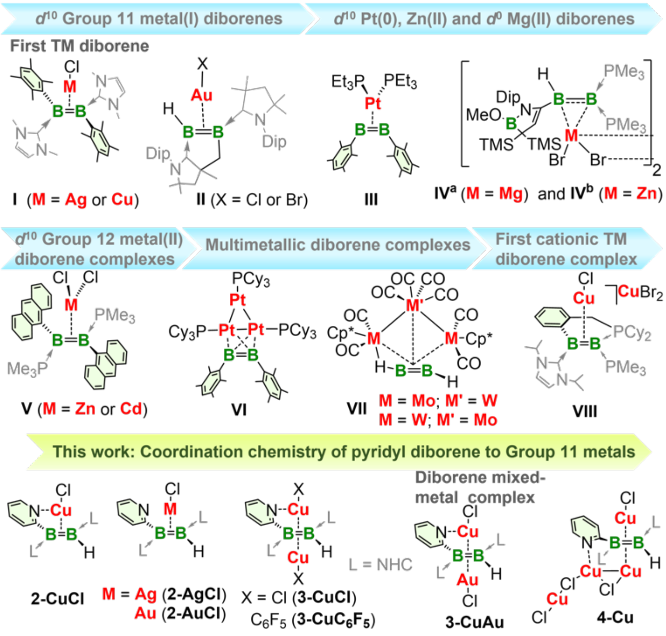

Fig. 1 Coordination chemistry of diborene ligands to main-group and transition metals.

construct the first examples of chelating and mixed-metal π-diborene complexes of Group 11 metals, via a range of stepwise metalations and transmetalation processes. The bonding between the metal centres and the B_2 and pyridyl donors is analysed via their solid-state structures and quantum-chemical calculations, and the presence of the secondary coordination of the pyridyl unit (only present in copper-containing complexes) is implicated in the construction of π-diborene complexes of higher nuclearity.

As shown in Scheme 1, the room-temperature reaction of **1** with 1.0 equivalent of $[CuCl(SMe_2)]$ exclusively yielded an orange solid (**2-CuCl**) in 46% yield. The $^{11}B\{^1H\}$ NMR spectrum of **2-CuCl** revealed signals at δ 23.9 and 5.1 ppm, both considerably upfield-shifted relative to those of **1** (δ 35 and 25 ppm), suggesting the complexation of the diborene unit to copper based on similar observations made in the syntheses of previous Group 11 metal(I) diborene complexes.[22, 25] The presence of one pyridine, one terminal B–H and two carbene

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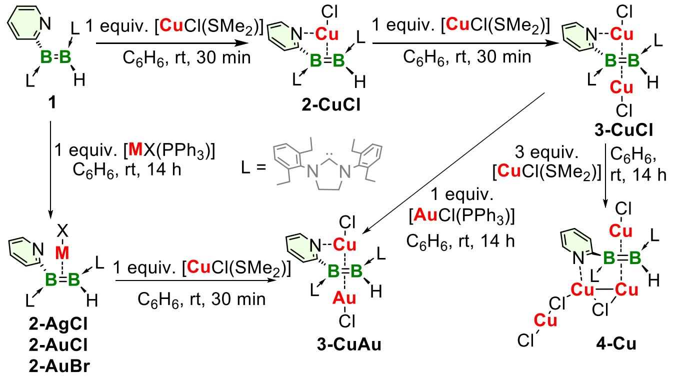

Scheme 1 Syntheses of Group 11 metal π-diborene complexes.

units in **2-CuCl** was confirmed by signals observed in the ^{1}H{^{11}B} and ^{13}C{^{1}H,^{11}B} NMR spectra. A single-crystal X-ray diffraction (SCXRD) study on **2-CuCl** (Fig. 2a) revealed it to be the expected π-diborene complex, with B–Cu and B–B distances in line with those of other π-diborene complexes of copper (d(B–Cu): 2.1744(16), 2.1479(17) Å; d(B–B): 1.628(2) Å). In addition, the pyridyl group was found to engage in a distinct but distorted bonding interaction with the copper centre (d(N–Cu): 2.335(1) Å) that is relatively long compared to those of related pyridyl copper complexes (e.g. [CuCl(py)$_3$];[34] d(N–Cu): 2.036(3), 2.058(8) Å). This N–Cu bond is bent significantly away from the central axis of the pyridyl group (∡(Cu–N^1–C^4): 148.80(7)°) and causes a bending of the CuCl axis to one side of the B=B unit (∡(Cl–Cu–centroid(B=B)): 165°).

Diborynes (LB≡BL) have shown a marked propensity to bind multiple independent Group 11 metal-halide units,[35] however, analogous multiple coordination behaviour has thus far not been observed with neutral diborenes. In order to test this limitation, we treated **2-CuCl** with a further equivalent of [CuCl(SMe$_2$)], resulting in a colour change of the reaction mixture from orange to red and the isolation of a red solid (**3-CuCl**) in 46% yield (Scheme 1). Alternatively, **3-CuCl** can be synthesised directly by the reaction of **1** with two equivalents of [CuCl(SMe$_2$)] (Scheme S1). In a similar manner, the pentafluorophenyl analogue of **3-CuCl**, **3-CuC$_6$F$_5$**, was synthesised from the reaction of **1** with a half equivalent of [Cu(C$_6$F$_5$)]$_4$ (Scheme S2). Although the B–H resonance could not be observed in the ^{1}H{^{11}B} NMR spectra of these complexes due to broadening, the presence of boron atoms was confirmed by signals at δ 10.2, 0.0 ppm (**3-CuCl**) and 13.9, 6.5 ppm (**3-CuC$_6$F$_5$**) in their ^{11}B{^{1}H} NMR spectra. That these signals for **3-CuCl** are found further upfield of those of **2-CuCl** suggested the possibility of coordination of a second Cu(I) centre. The ^{1}H{^{11}B} and ^{13}C{^{1}H,^{11}B} NMR spectra revealed the presence of two carbene units and one pyridyl ring in both **3-CuC$_6$F$_5$** and **3-CuCl**. Interestingly, three ^{19}F NMR signals at δ −110.3, −161.3, and −162.7 ppm were observed for **3-CuC$_6$F$_5$** in a 2:1:2 ratio at room temperature, indicating the equivalency of the two Cu(C$_6$F$_5$) units and suggesting that no Cu–N$_{py}$ interaction persists in solution. The solid-state structure of **3-CuCl** was confirmed by SCXRD (Fig. 2b) to have CuCl units bound on each side of the B=B plane, one of which is loosely bound to the nitrogen atom of the pyridyl unit. Disorder in this unit precludes confident determination of the bonding metrics in the vicinity of the pyridyl unit, however, the B–Cu and Cu–Cl bonds are all slightly longer in the pyridyl-bound CuCl unit (d(B–Cu): 2.142(4), 2.138(4) Å; d(Cu–Cl): 2.185(1) Å) than the non-pyridyl-bound CuCl unit (d(B–Cu): 2.111(4), 2.118(4) Å; d(Cu–Cl): 2.134(1) Å), while the pyridyl-bound B$_2$CuCl axis is bent as in **2-CuCl** (∡(Cl–Cu–centroid(B=B)): 163° (bound), 178° (unbound)). In line with the additional metalation of the B–B bond in **3-CuCl**, its B=B distance (d(B–B): 1.687(4) Å) is significantly longer than that of **2-CuCl** (d(B–B): 1.628(2) Å).

Inspired by the above results, we were motivated to test the limits of the cupration of diborene **1**. Thereby, the reaction of **3-CuCl** with three equivalents of CuCl·SMe$_2$ over 14 hours led to complete consumption of the diborene starting material and provided a yellow solid (**4-Cu**) in 56% yield (Scheme 1). The very similar ^{11}B NMR signals of **4-Cu** (δ 16.5 and 0.3 ppm) to those of **3-CuCl** suggested that the coordination of further metal centres to the B=B bond had not taken place. Unlike the complexes described above, a ^{1}H{^{11}B} NMR signal for the boron-bound hydrogen nucleus of **4-Cu** was identified at δ 3.20 ppm (broad), slightly upfield shifted relative to that of **1** (δ 3.35 ppm). An SCXRD study of **4-Cu** (Fig. 2c) revealed it to be an unusual tetracopper π-diborene complex in which the two original CuCl units bound to the B$_2$ unit are retained, but one of which is now bound to a Cu–Cl–Cu–Cl chain via a chloride-bridged Cu–Cu bond. Accordingly, the pyridyl unit has switched coordination to the first Cu atom of this chain, resulting in a far less distorted py–Cu interaction (∡(Cu–N^1–C^4): 171.8(3), 171.0(4)°; two molecules in the unit cell) and a far shorter N–Cu bond (1.941(6), 1.942(6) Å).

In an effort to extend this chemistry to the heavier coinage metals, room-temperature reactions of diborene **1** with equimolar amounts of [MX(PPh$_3$)] (MX = AgCl, AuCl, AuBr) were carried out, providing the monometallic π-diborene complexes **2-AgCl**, **2-AuCl** and **2-AuBr**, respectively, in moderate yields (54%, 50% and 38%, respectively) (Scheme 1). Unfortunately, all

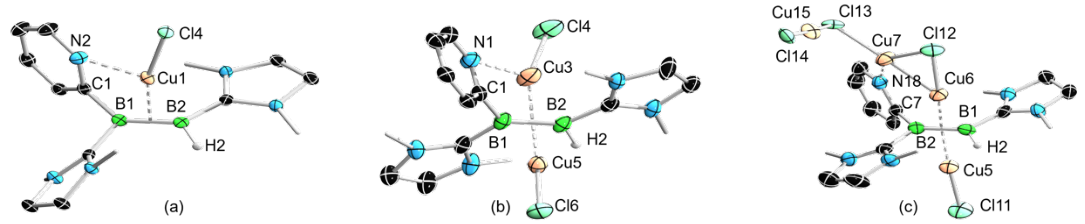

Fig. 2 Crystallographically-derived structures of (a) **2-CuCl**, (b) **3-CuCl**, and (c) **4-Cu**. Ellipsoids are shown at the 50% probability level. Aryl groups of the NHC units and all hydrogen atoms except that bound to the boron are omitted for clarity.

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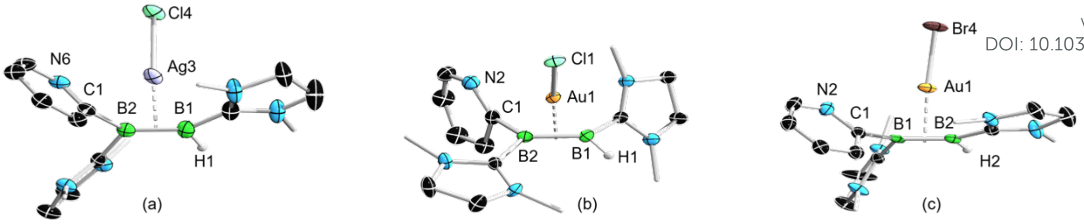

Fig. 3 Crystallographically-derived structures of (a) **2-AgCl**, (b) **2-AuCl** and (c) **2-AuBr**. Ellipsoids are shown at the 80% probability level. Aryl groups of the NHC units, solvent molecule/s and all hydrogen atoms except that bound to the boron are omitted for clarity.

efforts to prepare multimetallic complexes analogous to **3-CuCl** or **4-Cu** by treating **1** with multiple equivalents of the metal halides were unsuccessful. The monomeric silver and gold diborene complexes **2-AgCl**, **2-AuCl** and **2-AuBr** were fully characterised by ^{1}H{^{11}B}, ^{11}B{^{1}H} and ^{13}C{^{1}H,^{11}B} NMR spectroscopy, mass spectrometry, and SCXRD. The ^{31}P{^{1}H} NMR spectra of these three complexes did not show any appreciable signals, indicating the absence of phosphine ligands. The silver diborene complex **2-AgCl** showed somewhat distinct ^{11}B NMR spectra (δ 27.0, 4.1 ppm) to the two gold complexes (**2-AuCl**: 15.0, 6.3 ppm; **2-AuBr**: 15.5, 6.6 ppm), the former having much more disparate resonances than the latter. SCXRD studies disclosed the solid-state structures of **2-AgCl**, **2-AuCl** and **2-AuBr** (Fig. 3), all of which resemble previously-reported π-diborene complexes of Ag[21, 25] and Au[24] and possess no metal-pyridyl interactions.

We saw the diborene **1** as a promising platform for the synthesis of as-yet unknown mixed-metal π-diborene complexes, given its propensity to bind two metal centres. Treatment of **2-CuCl** with [AuCl(PPh$_3$)] led only to replacement of the single CuCl unit by AuCl and formation of **2-AuCl** (Scheme S4). However, when **3-CuCl** was treated with one equivalent of AuCl(PPh$_3$), transmetalation of just one CuCl unit occurred, providing mixed-metal π-diborene complex **3-CuAu** (Scheme 1) as red needles in 52% yield. Alternatively, this complex can also be prepared by addition of [CuCl(SMe$_2$)] to **2-AuCl** in slightly higher yield. It should also be noted that all attempts to prepare the silver/copper analogue of **3-CuAu** proved unsuccessful. The ^{11}B{^{1}H} NMR spectrum of **3-CuAu** showed the most upfield-shifted signals of all complexes prepared herein (4.7, –3.4 ppm) and a SCXRD study (Fig. 4) showed the complex to have the longest B=B bond (1.735(12) Å), both suggesting that this combination of metals results in the greatest influx of electron density to the B=B unit. Interestingly, the Cu centre forms a distinct interaction with the pyridyl unit, with a Cu–N distance (2.227(9), 2.282(9) Å) that is slightly shorter than that of **2-CuCl** (2.335(1) Å).

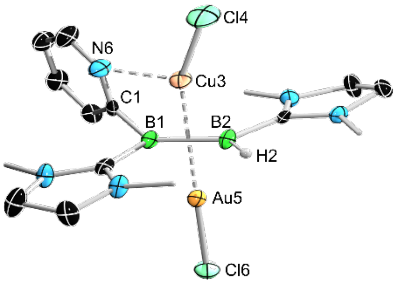

Fig. 4 Crystallographically-derived structure of mixed-metal complex **3-CuAu**. Ellipsoids are shown at the 50% probability level. Aryl groups of the NHC units, solvent molecule, and all hydrogen atoms except that bound to the boron are omitted for clarity.

The bonding scenarios in these coinage-metal-containing diborene complexes were evaluated by DFT studies (for details see SI). The geometry of **2-AuCl** was optimised using the ωB97X-D/Def2-SVP level of theory. The HOMO of this complex is mostly localised on the π-orbital of the B=B bond and donates electron density to a vacant orbital of the gold atom, whereas the LUMO is localised in the B–C$_{NHC}$ bonds and the carbene ligand. The nature of the B$_2$–Au bond was analysed by energy decomposition analysis combined with natural orbitals for chemical valence theory (EDA-NOCV) and the results indicated that the bonding in **2-AuCl** is mostly dominated by electrostatics (68%) with a minor orbital interaction (28%). The B$_2$–Au interaction can be most accurately described as an electron-sharing bond (for more details, see Table S1). To our surprise, the dissimilar Mayer bond orders (MBOs) of B1–Au1 (0.46) and B2–Au1 (0.20) indicate an unsymmetrical bonding of the gold centre towards the boron atoms. This could be due to the differing arrangement of the two NHC ligands with respect to the B$_2$ unit; one is roughly coplanar, while the other is more twisted, suggesting differing amounts of π interaction. Analysis of the intrinsic bond orbitals (IBOs) revealed the same relevant orbital interactions as in the EDA-NOCV analysis. The B–Au bond is dominated by interaction of the π orbital of the B=B bond with the d_z orbital of the Au (Fig. 5, left). The electron participation in the bond is almost equally distributed among all the atoms, which leads to the assumption that the B$_2$ ligand is not a pure σ-donor, and that a significant electronic contribution from the gold atom exists. Another IBO shows the presence of significant π-backbonding from the d_{xz} orbital of the gold atom to the B$_2$ unit (Fig. 5, right). The aforementioned complexes **3-CuCl** and**3-CuAu** and the hypothetical complexes **3-AuCl** ([{(SIDep)HB=B(2-

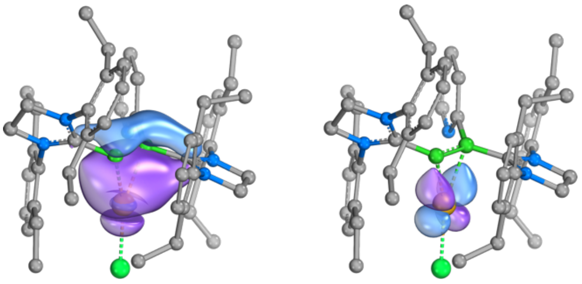

Fig. 5 IBOs of the interaction between the boron and the gold atom of **2-AuCl**. Hydrogen atoms are omitted for clarity.

$\mathrm{C_5H_4N)(SIDep)\}(AuCl)_2]}$) and **3-AuCu** (analogous to **3-CuAu** but with the pyridyl nitrogen atom proximal to the Au centre) were also optimised. DFT results indicate that while the $M{-}N_{py}$ interaction is absent in the hypothetical complexes **3-AuCu** and **3-AuCl**, it provides significant additional stability in complexes **3-CuCl** and **3-CuAu**, with MBOs of 0.30 and 0.31 and stabilisation energies (computed via natural bonding orbital (NBO) analysis) of 13.8 and 12.2 $\mathrm{kcal\ mol^{-1}}$, respectively.

In conclusion, the addition of coinage metal halides to a doubly base-stabilised 1-pyridyl-2-hydrodiborene led to isolation of a series of coinage metal π-diborene complexes. The additional 2-pyridyl binding site enabled the synthesis of the first chelating π-diborene complexes, the first π-diborene complexes in which metals are bound to both faces of the B=B bond, and the first mixed-metal π-diborene species. Notably, only the copper chloride unit enables binding of the pyridyl site, while multimetallic complexes are only observed when one of the metals is copper, suggesting that the copper-pyridyl interaction may be critical for the construction of higher nuclearity complexes. These results add a number of new coordination patterns for boron-containing π-ligands, highlighting the great potential of diborenes to produce novel coordination chemistry in the future.

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Conflicts of interest

There are no conflicts to declare.

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