Copper Borates

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Experimental and Computational Studies of the Copper Borate Complexes [(NHC)Cu(HBEt$_3$)] and [(NHC)Cu(HB(C$_6$F$_5$)$_3$)]

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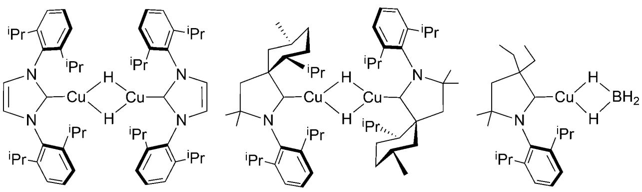
Abstract: *The synthesis of the Cu-borate complexes [(6Mes)Cu(HBR$_3$)] featuring the unusual [HBEt$_3$]$^-$ (**5**) and [HB(C$_6$F$_5$)$_3$]$^-$ (**6**) ligands is described. Experimental and computational studies show both compounds feature a direct Cu–H interaction, but that while **5** is two-coordinate, **6** displays an additional, stabilizing Cu–C$_{ipso}$(C$_6$F$_5$) interaction.*

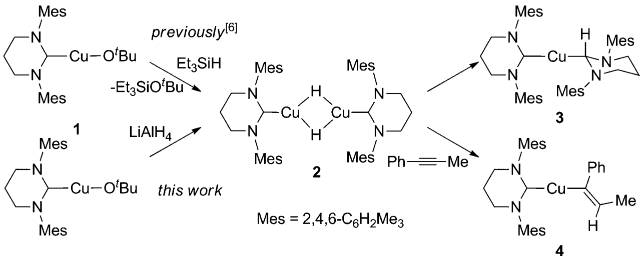
There is considerable interest in mononuclear copper hydride species because of their proposed importance as intermediates in copper-catalyzed reductive transformations.[1] However, simple monomeric [LCuH] complexes (L = phosphine, N-heterocyclic carbene (NHC)) remain hitherto unknown: for L = PR$_3$, species ranging from dimers up to octanuclear clusters have been characterized,[1h,2] while even very bulky NHCs still give only dimers (**I** and **II**, Scheme 1).[3] The nearest example to an isolable monomeric [LCuH] species reported to date is the three-coordinate [(CAAC^{Et})Cu(κ^2-BH$_4$)] complex **III**.[4,5] Herein, we report that during efforts to prepare mononuclear Cu–H species, we have instead isolated and structurally characterized two new examples of mononuclear copper borate complexes featuring the highly unusual borate ligands [HBEt$_3$]$^-$ and [HB(C$_6$F$_5$)$_3$]$^-$.

In recent work attempting to prepare [LCuH] species stabilized by large six-membered ring carbenes (e.g. from the reaction of **1** with tertiary silanes, Scheme 2), we showed that migratory insertion (MI) products such as **3** formed under mild conditions.[6] This MI process thwarted efforts to spectroscopically characterize any putative Cu-H intermediates (e.g. **2**); however, Cu-H formation was implied through trapping with alkyne to give **4**.



I [(IPr)Cu(μ-H)]$_2$ **II** [(CAAC^{Cy})Cu(μ-H)]$_2$ **III** (CAAC^{Et})Cu(κ^2-BH$_4$)

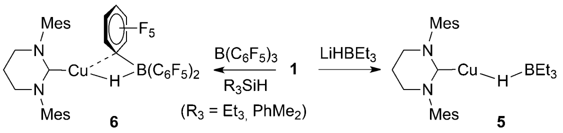
Scheme 1. Cu–H complexes prepared using IPr and CAAC ligands.



Scheme 2. Synthesis and reactivity of [(6Mes)Cu(μ-H)]$_2$ (**2**).

We have now probed the reaction of **1** with alternative hydride sources. Addition of LiAlH$_4$ to a THF solution of **1** at room temperature brought about the instantaneous formation of a yellow solution, indicative of a Cu-H-containing species. Within minutes, this yellow color faded and Cu metal was deposited. A ^{1}H NMR spectrum of the solution showed that **3** was the major species present. However, when LiAlH$_4$ addition was carried out at 178 K, the Cu-H product (**2**) proved to be stable. DOSY measurements showed that it was dimeric (Scheme 2).[7,8] The complex exhibited a low frequency Cu-H resonance at $\delta = 0.96$ ppm, in good agreement with the shifts recently reported for [(6/7Dipp)Cu(μ-H)]$_2$ species.[3d,9] However, whereas [(6/7Dipp)Cu(μ-H)]$_2$ prove stable for days at 298 K, **2** was stable only below 209 K. Above this temperature, the ^{1}H NMR resonances began to broaden and at 255 K signals for **3** were present.[10]

Upon reacting (178 K) **1** with LiHBEt$_3$ instead of LiAlH$_4$, the rapid appearance of a yellow solution was again observed, but now resulting from the new monomeric complex [(6Mes)Cu(HBEt$_3$)] (**5**, Scheme 3) which features an intact {HBEt$_3$} moiety. The formation of **5** was unexpected since [HBEt$_3$]$^-$ typically acts as a potent hydride source; indeed **II** was prepared from [(CAAC^{Cy})Cu(O^{t}Bu)] and LiHBEt$_3$.[3b] Unsurprisingly, examples of isolable triethyl-borohydride



Scheme 3. Synthesis of [(6Mes)Cu(HBR$_3$)] complexes **5** and **6**.

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complexes are rare, being confined to very electropositive metals.[11]

The X-ray structure of **5** (Figure 1) showed the presence of a two-coordinate Cu center attached to the carbene and a monodentate {HBEt$_3$} moiety. The hydrogen atom on B(1) was located and refined without restraint, yielding C$_{6Mes}$-Cu-H and Cu-H-B angles of 162.4(13) and 110.2(18)°, respectively, and B–H and Cu–H distances of 1.22(3) and 1.56(3) Å, respectively. The latter is comparable to the shortest Cu–H distance in **II**,[3b] but much shorter than either of the Cu–H bond lengths in **III** (1.679(2) Å, 1.717(18) Å). Additional characterization of **5** was performed in solution at low temperature (209 K). The ^{1}H NMR spectrum featured a broad, low frequency signal (relative integral of 1) at $\delta = -2.60$ ppm, assigned to the Cu–H. The ^{1}H-coupled ^{13}C NMR spectrum showed a 12 Hz doublet splitting of the carbenic carbon resonance ($\delta = 202$ ppm), confirming C$_{6Mes}$-Cu-H connectivity.

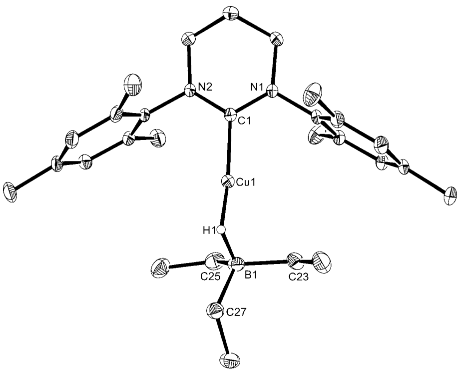


Figure 1. Molecular structure of **5**. Ellipsoids are shown at the 30% level. Hydrogen atoms (except for Cu-H-B) are removed for clarity.

The nature of the {Cu-H-BEt$_3$} interaction in **5** was assessed by QTAIM (quantum theory of atoms in molecules) and NBO (natural bond orbital) analyses using the BP86 functional and geometries based on the crystallographically determined structure.[12] The QTAIM molecular graph (Figure 2a) identifies Cu–H and B–H bond paths, as well as one for the Cu–C$_{6Mes}$ bond. No further bonding interactions involving Cu (e.g. to any atoms of the Et substituents) are seen, thereby supporting the assignment of **5** as a two-coordinate complex.

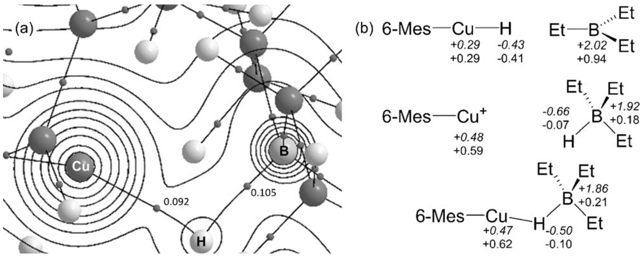


Figure 2. a) Detail of the QTAIM molecular graph of **5** showing electron density contours in the {Cu/H/B plane}. Bond critical points (BCPs) are shown as small gray spheres and key values of $\rho(r)$ (the associated BCP electron densities) are indicated in au. b) Computed atomic charges for **5** and selected comparator species (QTAIM charges in italics; NBO charges in plain text). Full QTAIM metrics are provided in the Supporting Information, along with equivalent $\rho(r)$ values obtained with a range of different functionals.

Figure 2b shows the computed QTAIM and NBO charges at the Cu, H and B centers in **5**, the BP86-optimized free [(6Mes)Cu]$^+$ and [HBEt$_3$]$^-$ ions as well as the neutral [(6Mes)CuH] and BEt$_3$ species. Significantly, the charge distribution in **5** more closely resembles that in the free ions, rather than the neutral species. NBO analysis also highlights a $\sigma_{B\text{-}H} \rightarrow$Cu donation that a 2nd order perturbation analysis quantifies at 67.1 kcal mol^{-1} (see Figure S23 in the Supporting Information for NBO plots). The computed evidence therefore indicates that **5** is a borate complex of a {(6Mes)Cu}$^+$ fragment, rather than a Lewis acid-stabilized Cu-hydride (viz. [(6Mes)CuH···BEt$_3$]).

Experimentally, complex **5** was found to be stable both in THF solution and the solid state for several days below ca. 243 K, but started to decompose within hours upon warming above this temperature through B–H bond cleavage (apparent from the appearance of BEt$_3$ (^{11}B: $\delta = 73$ ppm)).[11c] **3** and H$_2$ were also formed, alongside deposition of Cu metal. Interestingly, in contrast to the quantitative formation of the migratory insertion product **3** from **2** (Scheme 1), **5** converted at room temperature to **3** in only ca. 5% yield due to the transformation of [HBEt$_3$]$^-$ to [BEt$_4$]$^-$ and [H$_2$BEt$_2$]$^-$.[13] This resulted in the formation of the [BEt$_4$]$^-$ salt of the known bis-carbene cation, [(6Mes)$_2$Cu]$^+$ (ESI), and a second species believed to be [(6Mes)Cu(H$_2$BEt$_2$)] as the ultimate products of the reaction.

The formation of **5** and its formulation as a Cu-borate complex prompted us to consider the formation of related species with properties modulated by the nature of the B-substituents. Taking a lead from the reactions of s-block, early transition metal and lanthanide complexes with Lewis acidic boranes,[14] **1** was treated with R$_3$SiH in the presence of B(C$_6$F$_5$)$_3$. A rapid reaction ensued in the case of Et$_3$SiH to give a mixture of [(6Mes)Cu(HB(C$_6$F$_5$)$_3$)] (**6**) and [(6Mes)$_2$Cu][B(C$_6$F$_5$)$_4$]$^-$ (**7**) (ESI).[15] Use of PhMe$_2$SiH rather than Et$_3$SiH gave only **6**. An X-ray crystal structure (Figure 3) showed that **6** was mononuclear like **5**, but that, in addition to a Cu–H interaction, there was also one short Cu–C$_{ipso}$ contact (2.2183(17) Å) to the C$_6$F$_5$ ring based on C29.[16] The nature of this interaction differs noticeably from those found with more electropositive metals, which invariably involve *ortho*-C–F bond contacts. In particular, the Cu–C$_{ipso}$ interaction in **6** was seen to be concomitant with lengthening of the B(1)–C(29) distance to 1.657(3) Å, relative to the B(1)–C(23) and B1–C(35) distances of 1.624(3) and 1.628(3) Å, respectively. Additionally, the C$_{6Mes}$-Cu-H angle of 146.5(8)° in **6** is notably more acute than that observed in **5** (162.8(14)°). The Cu–H and B–H distances are each comparatively similar in both structures.

6 was more thermally stable than **5** and could be characterized at room temperature. The ^{11}B NMR spectrum showed a resonance at $\delta = -28.1$ ppm, slightly upfield of the ion-separated species [X][HB(C$_6$F$_5$)$_3$] (X = P^{t}Bu$_3$H, $\delta = -25.5$ ppm;[17a] NBu$_4$, $\delta = -25.4$ ppm).[17b] Moreover, the ^1J-(B,H) doublet splitting in **6** was smaller (60 Hz) than in either

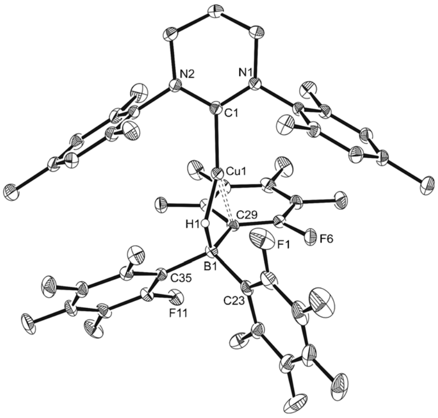


Figure 3. Molecular structure of **6**. Ellipsoids are shown at the 30% level. Hydrogen atoms (except for Cu-H-B) are removed for clarity.

of these compounds (100 and 82 Hz, respectively) or any of the early metal complexes (e.g. $[(C(SiMe_2H)_3)M(THF)_2(HB(C_6F_5)_3)]$, M = Ca: 76 Hz; M = Yb: 73 Hz),[14c] suggestive of a significant Cu-H-B interaction. This was supported by IR spectroscopy (ν(B–H): 2361 cm^{-1})[14c] and the ^{19}F NMR chemical shift difference of 5.4 Hz between the *meta*- and *para*-fluorine atoms.[18] Although we could not observe the Cu–H resonance directly in the ^1H NMR spectrum, ^1H-^{11}B HMQC spectroscopy revealed it at $\delta = 2.08$ ppm. Over ca. 12 h in solution, **6** degraded to **7** and deposited metallic Cu.

The QTAIM molecular graph for **6** (Figure 4a) confirmed the presence of Cu–H and H–B bond paths. Compared to **5**, the Cu–H BCP has a lower $\rho(r)$ (0.083 au, cf. 0.092 au) indicating a weaker interaction, and this is complemented by the higher $\rho(r)$ of the B–H BCP (0.135 au, cf. 0.105 au). Weaker donation to Cu in **6** is also manifest in a higher computed positive charge at Cu (Figure 4b) and the reduced $\sigma_{B\text{-}H}\rightarrow$Cu interaction which the NBO 2nd order perturbation analysis quantifies as 42.9 kcal mol^{-1}. The similar charges at Cu, B and H in **6** and the free $[(6Mes)Cu]^+$ and $[HB(C_6F_5)_3]^-$ ions again suggest **6** is a borate complex. An additional feature, again consistent with a more electron deficient Cu center, is the presence of a Cu–C_{ipso} bond path which entails a ring critical point associated with the $\{CuHBC_{ipso}\}$ unit. The lower value of $\rho(r)$ at the Cu–C_{ipso} BCP (0.055 au) indicates a weaker interaction than the Cu–H bond and the NBO 2nd order perturbation analysis confirms this, providing an interaction energy of only 7.1 kcal mol^{-1} corresponding to donation from the C_{ipso}–B σ-bond to Cu. NBO also suggests an additional stabilization occurs via donation from one of the C_{ipso}–C_{ortho} bonds of the C_6F_5 ring ($\Delta E = -7.9$ kcal mol^{-1}, see Figure S24).

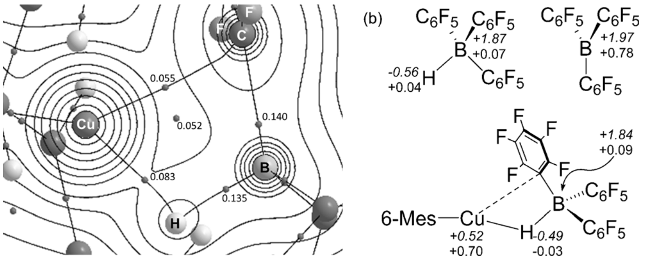


Figure 4. a) Detail of the QTAIM molecular graph for **6** showing electron density contours for the {Cu/H/B plane}. Bond critical points (BCPs) and ring critical points (RCPs) are shown as small gray spheres, and $\rho(r)$ values of key CPs are indicated in au. b) Computed atomic charges for **6** and selected comparator species (QTAIM charges in italics; NBO charges in plain text). Full QTAIM metrics are provided in the Supporting Information along with equivalent $\rho(r)$ values obtained with a range of different functionals.

Reproducing the molecular geometries of **5** and **6** presented a challenge to theory; in particular the structure of the $\{Cu(HBEt_3)\}$ moiety in **5** was very sensitive to functional choice. Given this, we also investigated the role of the chemical model used in the calculations by computing the extended solid-state structure of **5** with periodic DFT calculations. Such an approach has been shown to be important in correctly describing ambiguous bonding situations.[19] Figure 5 shows deviations from experiment for the Cu···B and Cu···C(25) distances computed in **5** with different functionals, where the latter is a proxy for any additional Cu···H interactions involving the Et substituents. For the molecular calculations, BP86 provides the best agreement for the Cu···B distance, but underestimates Cu···C(25) by 0.15 Å. PBE gives somewhat poorer agreement, and this deteriorates further with PBE(D3), that is, when a dispersion correction is included in the optimization. These geometries imply the presence of a Cu···H-C(25) agostic interaction and thus a three-coordinate Cu center, at odds with the observed two-coordinate geometry. In contrast, BLYP and B3LYP overestimate both distances, a result that has parallels in the description of agostic interactions.[20] B3LYP(D3) improves the situation but this relatively good net performance probably reflects a cancellation of errors, due to the poor B3LYP geometry and an overestimation of intramolecular dispersion effects in the isolated molecular model. Of these molecular calculations, M06 provides the best overall result, with both Cu···B and Cu···C(25) being underestimated by ca. 0.05 Å. A wider comparison of computed structural metrics is provided in the Supporting Information.

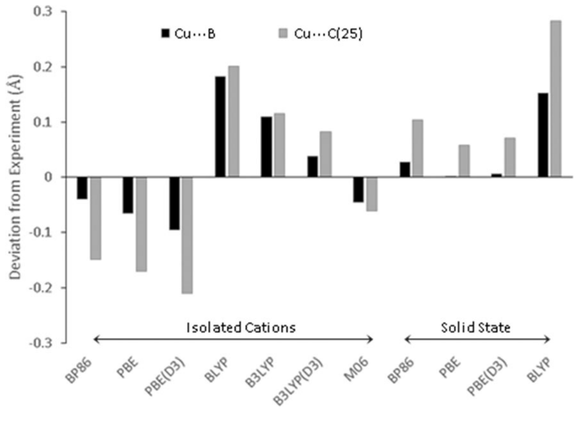
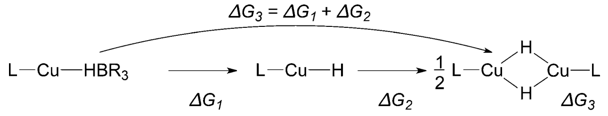


Figure 5. Cu···B and Cu···C(25) distances in **5** computed with various functionals and displayed as deviations from the experimental values of 2.283(3) Å and 2.619(3) Å respectively. Calculations employed either the isolated molecule (Gaussian) or the extended solid state via periodic boundary conditions (CP2K).

Full optimization of the extended solid-state structure of **5** under periodic boundary conditions with BP86 and (particularly) PBE provided improved geometries; moreover, the results are now far less sensitive to the inclusion of dispersion, reflecting how the full solid-state environment can balance the intramolecular dispersion that was overestimated in the calculations using molecular models. Use of an extended model does not guarantee good agreement, however, with BLYP still giving a poor geometry, even with the solid-state model. An equivalent set of calculations was performed for **6** and similar trends were obtained. In this case, the stronger Cu–C_{ipso} interaction makes the computed geometries less functional dependent, although B3LYP significantly overestimates both Cu–C_{ipso} and Cu···B distances. Geometries derived from the periodic calculations are now in good agreement with experiment (see Figure S22).

The isolation of the $[HBEt_3]^-$ adduct **5** contrasts with the $[(CAAC^{Cy})Cu(HBEt_3)]$ analogue that is (presumably) present as an (unseen) intermediate en route to **II** (Scheme 1). We have assessed the stabilities of these species, along with **6** and $[(CAAC^{Et})Cu(\kappa^2\text{-}BH_4)]$ (**III**) by computing the free energy changes associated with borane loss and dimerization (Figure 6). These indicate a significantly stronger H–$B(C_6F_5)_3$ bond in **6** ($\Delta G_1 = +38.2$ kcal mol^{-1}) compared to the H–BEt_3 bond in **5** ($\Delta G_1 = +10.8$ kcal mol^{-1}). **5** may therefore be susceptible to BEt_3 loss to form [(6Mes)CuH], however, dimer formation is not thermodynamically accessible in this case ($\Delta G_3 = +6.8$ kcal mol^{-1}), and so alternative decomposition routes are apparently accessed, as seen experimentally.



	ΔG1	ΔG2	ΔG3
L = 6Mes; R = Et (**5**)	+10.8	-4.0	+6.8
L = 6Mes; R = C_6F_5 (**6**)	+38.2	-4.0	+34.2
L = $CAAC^{Et}$; R = H (**III**)	+36.9	-4.1	+32.8
L = $CAAC^{Cy}$; R = Et	+5.8	-6.5	-0.7 (**II**)

Figure 6. Computed free energy changes (kcal mol^{-1}; BP86-optimised with corrections for dispersion (D3) and THF solvent) for borane loss and dimerization of different $[LCu(HBR_3)]$ complexes.

The BH_3 moiety in **III** is also strongly bound ($\Delta G_1 = +36.9$ kcal mol^{-1}), consistent with the isolation of the borohydride complex.[4] In contrast, BEt_3 loss from $[(CAAC^{Cy})Cu(HBEt_3)]$ is particularly facile ($\Delta G_1 = +5.8$ kcal mol^{-1}) and the subsequent dimerization energy is sufficiently exergonic to rationalize the formation of dimer **II** upon reaction of $[(CAAC^{Cy})Cu(O^tBu)]$ with $LiHBEt_3$.[3b]

The computational findings that **5** and **6** are not simple Lewis acid stabilized forms of [(6Mes)CuH] were reinforced by probing their reactivity with PhC≡CMe. In neither case was the hydrocupration product **4** (Scheme 1) formed. Addition of PhC≡CMe (2 equiv) to **5** at 225 K resulted in no reaction until ca. 288 K, at which point the presence of multiplets in the $\delta = 4$–6 ppm region of the ^1H NMR spectrum suggested that some reduction of the alkyne had occurred. However, none of the signals matched those of **4**.[6] The ^{11}B NMR spectrum showed resonances at $\delta = 60$, 52 and −14 ppm suggestive of multiple boron-containing species being produced. There was no reaction between **6** and the alkyne over days at room temperature, with only the transformation to the homoleptic cationic bis-carbene complex **7** apparent from the ^{11}B NMR spectrum.

In conclusion, the synthesis of the novel Cu-borate complexes $[(6Mes)Cu(HBR_3)]$ (R = Et (**5**), C_6F_5 (**6**)) has been reported. Experimental and computational studies show that **5** features a two-coordinate Cu center, while **6** exhibits a further stabilizing Cu–C_{ipso} interaction to one C_6F_5 substituent. Although both species possess a direct Cu–H interaction, neither can be considered as Lewis acid stabilized forms of [(6Mes)CuH]. The isolation of a monomeric [(NHC)CuH] species, therefore, still remains an elusive target.

Acknowledgements

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Keywords: copper · DFT calculations · hydride ligand · Lewis acids · N-heterocyclic carbene

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[7] References [3a,c–d] provide examples which associate yellow colored solutions with [$(NHC)Cu(\mu\text{-}H)$]$_2$ dimers.

[8] DOSY measurements gave a value for r_H of 6.2 Å. Based on previous studies of diamidocarbene copper chloride complexes (L. R. Collins, J. P. Lowe, M. F. Mahon, R. C. Poulten, M. K. Whittlesey, *Inorg. Chem.* **2014**, *53*, 2699 – 2707), the value is consistent with a dimeric structure.

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[10] All attempts to isolate **2** were unsuccessful. On occasion, crystalline material was isolated (Supporting Information), but this proved to be [$(6Mes)AlH_3$].

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Communications

Copper Borates

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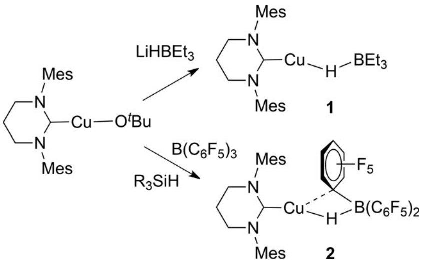
Experimental and Computational Studies of the Copper Borate Complexes [(NHC)Cu(HBEt$_3$)] and [(NHC)Cu(HB(C$_6$F$_5$)$_3$)]



Unusual Cu-borate complexes [(6Mes)Cu(HBR$_3$)] (R = Et (**5**), C$_6$F$_5$ (**6**)) are described. Experimental and computational studies show both species exhibit a direct Cu—H interaction with **5** featuring a two-coordinate Cu while **6** has a further Cu—C$_{ipso}$ interaction to one C$_6$F$_5$ substituent.