Experimental and Computational Studies of the Novel Copper Borate Complexes [(NHC)Cu(HBR₃)] (R= Et, C₆F₅)


Abstract: The synthesis of the Cu-borate complexes [(6Mes)Cu(HBR₃)] featuring the unusual [HBEt₃] (5) and [H(BrC₆F₅)] (6) ligands is described. Experimental and computational studies show both compounds feature a direct Cu-H interaction, but while that 5 is two-coordinate, 6 displays an additional, stabilizing Cu-C(µ=H)₃ 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 [CuL] (L = phosphine, N-heterocyclic carbene (NHC)) remain hitherto unknown: for L = PR₃, species ranging from dimers up to octanuclear clusters have been characterized,[2,3] while even very bulky NHCs still give only dimers (I and II, Scheme 1).[5] The nearest example to an isolable monomeric [CuL] species reported to date is the three-coordinate [(CAAC)₃Cu(µ-3-BH₃)] complex III.[5] Herein, we report that during efforts to prepare mononuclear Cu-H species, we have instead isolated and structurally characterized two examples of mononuclear copper borate complexes featuring the highly unusual borate ligands [HBEt₃] and [H(BrC₆F₅)]

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

In recent work attempting to prepare [CuL] species stabilized by large six-membered ring carbene (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 alkylene to give 4.

We have now probed the reaction of 1 with alternative hydride sources. Addition of LiAlH₄ 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 ¹H NMR spectrum of the solution showed that 3 was the major species present. However, when LiAlH₄ 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 δ = 0.96 ppm, in good agreement with the shifts recently reported for [(6/7Dipp)Cu(µ-H)] species.[9,10] However, whereas [(6/7Dipp)Cu(µ-H)]: prove stable for days at 298 K, 2 was stable only below 209 K. Above this temperature, the ¹H NMR resonances began to broaden and at 255 K signals for 3 were present.[10]

Upon reacting (178 K) 1 with LiHBEt₃ instead of LiAlH₄, the rapid appearance of a yellow solution was again observed, but now resulting from the new monomeric complex [(6Mes)Cu(HBEt₃)] (5, Scheme 3) which features an intact [HBEt₃] moiety. The formation of 5 was unexpected since [HBEt₃] typically acts as a potent hydride source; indeed II was prepared from [(CAAC)₃Cu(µ-H)] and LiHBEt₃.[10] Unsurprisingly, examples of isolable triethylborohydride complexes are rare, being confined to few electropositive metals.[11]

The X-ray structure of 5 (Figure 1) showed the presence of a two-coordinate Cu centre attached to the carbene and a monodentate {HBEt₃} moiety. The hydrogen atom on B(1) was located and refined without restraint, yielding C₆Mes-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 III,[b] 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
H NMR spectrum featured a broad, low frequency signal (relative integral of 1)
| at δ = -2.60 ppm, assigned to the Cu-H. The
H coupled 13C NMR spectrum showed a 12 Hz doublet splitting of the carbonic carbon resonance (δ = 202 ppm), confirming C\textsubscript{4}atom-Cu-H connectivity.

The nature of the [Cu-H-BEt\textsubscript{3}]+ interaction in 5 was assessed via Quantum Theory of Atoms in Molecules (QTAIM) and Natural Bond
Orbital (NBO) analyses using the B3P86 functional and geometries based on the
crystallographically determined structure.[13] The QTAIM
molecular graph (Figure 3(a)) identifies Cu-H and B-H bond paths, as well as one for the Cu-C\textsubscript{4}atom 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 3. (a) Detail of the QTAIM molecular graph of 5 showing electron density contours in the (CuH-B plane). Bond critical points (BCPs) are shown as green
spheres and key values of ρ(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 ESI, along with equivalent ρ(r) values obtained with
a range of different functionals.

Figure 3(b) shows the computed QTAIM and NBO charges at the
c Cu, H and B centres in 5, the BP86-optimized free [(6Mes)Cu]+ and
[BHEt\textsubscript{3}]\textsuperscript{+} ions as well as the neutral [(6Mes)CuH] and BEt\textsubscript{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
Cu-H → Cu donation that a 2\textsuperscript{nd} order perturbation analysis
quantifies at 67.1 kcal/mol (see Figure S23 for NBO plots). The
computed evidence therefore indicates that 5 is a borate complex of a
{(6Mes)Cu}\textsuperscript{+} fragment, rather than a Lewis acid-stabilized Cu-hydride
(viz. [(6Mes)CuH--BEt\textsubscript{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\textsubscript{3} (1B;
δ = 73 ppm)).[14] H and H\textsubscript{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\textsubscript{3}]\textsuperscript{+} to [BEt\textsubscript{3}]\textsuperscript{+} and [H\textsubscript{2}BEt\textsubscript{3}].[15] This resulted in the formation of the [BEt\textsubscript{3}]\textsuperscript{+} salt of the known bis-carbene cation, [(6Mes)CuH\textsubscript{2}ESI],
and a second species believed to be [(6Mes)Cu(H\textsubscript{2}BEt\textsubscript{3})] 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\textsubscript{3}SiH in the presence
of B(C\textsubscript{2}F\textsubscript{5})\textsubscript{3}. A rapid reaction ensued in the case of Et\textsubscript{3}SiH to give
a mixture of [(6Mes)CuH(B(C\textsubscript{2}F\textsubscript{5}))\textsubscript{2}] (6) and [(6Mes)CuH[B(C\textsubscript{2}F\textsubscript{5})\textsubscript{3}]] (7)
(ESI).[16] Use of PhMe\textsubscript{3}SiH rather than Et\textsubscript{3}SiH gave only an 6. X-ray
crystal structure (Figure 2) showed that 6 was mononuclear like 5, but
that, in addition to a Cu-H interaction, there was also one short Cu-C\textsubscript{4} \textsubscript{exo} contact (2.183(17) Å) to the C\textsubscript{4} atom 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\textsubscript{exo} 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\textsubscript{4}atom-Cu-H angle of
146.5(8)° in 6 is notably more acute than that observed in 5 (162.8(14)°).

6 was more thermally stable than 5 and could be characterized at
room temperature. The 1\textsuperscript{B} NMR spectrum showed a resonance at δ =
-28.1 ppm, slightly upfield of the ion-separated species [X][HBC\textsubscript{2}F\textsubscript{5}]\textsuperscript{+}
(X = P\textsubscript{3}Bu\textsubscript{3}, δ = -25.5 ppm,[13] NBu\textsubscript{3}, δ = -25.4 ppm).[17] Moreover, the
1\textsuperscript{B}(H,H) doublet splitting in 6 was smaller (60 Hz) than in either
of these compounds (100 and 82 Hz, respectively) or any of the early metal
complexes (e.g. [C(SiMe\textsubscript{3})\textsubscript{2}]M(THF)\textsubscript{2}(HBC\textsubscript{2}F\textsubscript{5}))\textsuperscript{+} M = Ca: 76 Hz;
M = Yb: 73 Hz).[16] suggestive of a significant Cu-H-B interaction. This
was supported by IR spectroscopy (ν(ν-B-H): 2361 cm\textsuperscript{-1}[16] and the \textsuperscript{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 H NMR spectrum, \textsuperscript{1H} -\textsuperscript{1B} HMOC spectroscopy revealed
it at δ = 2.08 ppm. Over ca. 12 h in solution, 6 degraded to 7 and
deposited metallic Cu.
The QTAIM molecular graph for 6 (Figure 4(a)) 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 4(b)) and the reduced $d_{\text{CuH}} \rightarrow$ Cu interaction which the NBO 2nd order perturbation analysis quantifies as 42.9 kcal/mol. The similar charges at Cu, B and H in 6 and free \[([6\text{Mes}]\text{Cu}^+ \text{and } [\text{HB}(\text{CF}_3)])\] ions again suggest 6 is a borate complex. An additional feature, again consistent with a more electron deficient Cu centre, is the presence of a Cu-C$_{\text{ipso}}$ bond path which entails a ring critical point associated with the [CuHBC$_{\text{ipso}}$] unit. The lower value of $\rho(r)$ at the Cu-C$_{\text{ipso}}$ 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 0.071 kcal/mol corresponding to donation from the C$_{\text{ipso}}$-B $\sigma$-bond to Cu. NBO also suggests an additional stabilization occurs via donation from one of the C$_{\text{ipso}}$-C$_{\text{o ortho}}$ bonds of the CuF$_3$ ring ($\Delta E = -7.9$ kcal/mol, 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 green and magenta spheres respectively 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 ESI 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.[20] 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), i.e. 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 centre, 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.[21] 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 structural metrics is provided in the Supporting Information.

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$_{\text{ipso}}$ interaction makes the computed geometries less functional dependent, although B3LYP significantly overestimates both Cu-C$_{\text{ipso}}$ and Cu--B distances. Geometries derived from the periodic calculations are now in good agreement with experiment (see Figure S22).

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).

The isolation of the [HBEt$_3$] adduct 5 contrasts with the \([\text{CAAC}^3]^{+}\text{Cu[HBEt$_3$]}\) analogue that is (presumably) present as an (unseen) intermediate \textit{en route} to II (Scheme 1). We have assessed the stabilities of these species, along with 6 and \([\text{CAAC}^3]^{+}\text{Cu}^{2+}-\text{BH$_3$}]\) (III) by computing the free energy changes associated with borane loss and dimerization (Figure 6). These indicate a significantly stronger H-B(C$_3$F$_3$)$_2$ bond in 6 ($\Delta G_1 = +38.2$ kcal/mol) compared to the H-BEt$_3$ bond in 5 ($\Delta G_1 = +10.8$ kcal/mol). 5 may therefore be susceptible to BET$_3$ loss to form \([6\text{Mes}]\text{CuH}\), however, dimer formation is not thermodynamically accessible in this case ($\Delta G_1 = +6.8$ kcal/mol), and so alternative decomposition routes are apparently accessed, as seen experimentally. The BH$_3$ moiety in III is also strongly bound ($\Delta G_1 = +36.9$ kcal/mol), consistent with the isolation of the borohydride complex.[4] In contrast, BET$_3$ loss from \([\text{CAAC}^3]^{+}\text{Cu[HBEt$_3$]}\) is particularly facile ($\Delta G_1 = +5.8$ kcal/mol) and the subsequent dimerization energy is sufficiently exergonic to rationalize the formation of dimer II upon reaction of \([\text{CAAC}^3]^{+}\text{Cu(O\text{Bu})}]\) with LiHBEt$_3$.[38]
Keywords: heterocyclic carbene • copper • hydride ligand • Lewis acids • DFT calculations

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References


[7] References 8-11 provide examples which associate yellow colored solutions with [(NHC)Cu(η-H)]: dimers.


[9] 6Dipp = 1,3-bis(2,6-disopropylphenyl)-3,4,5,6-tetrahydroxypirimidine-2-ylidine; 7Dipp = 1,3-bis(2,6-disopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidine.

[10] All attempts to isolate 2 were unsuccessful. On occasion, crystalline material was isolated (ESI), but this proved to be [(6Mes)CuH]₂.


[12] Calculations on the isolated cations within 5 and 6 were run with Gaussian 09 while periodic DFT calculations were performed with CP2K. See ESI for full details.


Unusual Cu-borate complexes \([(6\text{Mes})\text{Cu}(HBR_3)] (R = \text{Et}, \text{C}_6\text{F}_5)\) 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-Cipso interaction to one Cipso substituent.