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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 [HBE₄]²⁻ (5) and [HBr(C₆F₅)]⁻ (6) ligands is described. Experimental and computational studies show both compounds feature a direct Cu-H interaction, but while 5 is two-coordinate, 6 displays an additional, stabilizing Cu-C(ipso)(C₆F₅) 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 = 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).[4] The nearest example to an isolable monomeric [LCuH] species reported to date is the three-coordinate [(CAAC)₃Cu(H₂)] complex III.[5,6] 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 [HBE₄]⁻ and [HBr(C₆F₅)]⁻.

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

In recent work attempting to prepare [LCuH] species stabilized by large six-membered ring carbene ligands (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 'H 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] 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 'H NMR resonances began to broaden and at 255 K signals for 3 were present.[10]

Upon reacting (178 K) 1 with LiHBE₄ instead of LiAlH₄, the rapid appearance of a yellow solution was again observed, but now resulting from the new monomeric complex [(6Mes)Cu(HBE₄)] (5, Scheme 3) which features an intact [HBE₄]⁻ moiety. The formation of 5 was unexpected since [HBE₄]⁻ typically acts as a potent hydride source; indeed II was prepared from [(CAAC)₃Cu(O'Bu)] and LiHBE₄.[10] Unsurprisingly, examples of isolable triethylborohydride complexes are rare, being confined to very electropositive metals.[11]

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


The X-ray structure of 5 (Figure 1) showed the presence of a two-coordinate Cu centre attached to the carbene and a monodentate {HBE₄}⁻ 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 II, (9) 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 1H NMR spectrum featured a broad, low frequency signal (relative integral of 1) at δ = -2.60 ppm, assigned to the Cu-H. The 1H coupled 13C NMR showed a 12 Hz doublet splitting of the carbenic carbon resonance (δ = 202 ppm), confirming C_{6Mes}-Cu-H connectivity.

The nature of the [Cu-H-BEt₄] interaction in 5 was assessed via Quantum Theory of Atoms in Molecules (QTAIM) and Natural Bond Orbital (NBO) analyses using the BP86 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_{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. Molecular structure of 6. Ellipsoids are shown at the 30% level. Hydrogen atoms (except for Cu-H-B) are removed for clarity.

Figure 3. (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 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 Cu, H and B centres in 5, the BP86-optimized free [6(Mes)Cu]⁺ and [HBEt₄]⁺ ions as well as the neutral [(6Mes)CuH] and BEt₄ 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 σ_{Cu-H} → Cu donation that a 2nd 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 [6(Mes)Cu]⁺ fragment, rather than a Lewis acid-stabilized Cu-hydride (viz: [6(Mes)CuH···B(Et)]).
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 ρ(r) (0.083 au, cf. 0.092 au) indicating a weaker interaction, and this is complemented by the higher ρ(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 εCu → 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 [(6Mes)Cu]⁺ and [HB(C₂F₅)₂] 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-C₆B₆ bond path which entails a ring critical point associated with the [CuHBC₆B₆] unit. The lower value of ρ(r) at the Cu-C₆B₆ 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 0.1 au corresponding to donation from the C₆B₆ σ-bond to Cu. NBO also suggests an additional stabilization occurs via donation from one of the C₆B₆-C₆B₆ bonds of the C₆F₆ ring (ΔE = 7.9 kcal/mol, see Figure S24).

**Figure 4.** (a) Detail of the QTAIM molecular graph for 6 showing electron density contours for the [CuH/B plane]. Bond critical points (BCPs) and ring critical points (RCPs) are shown as green and magenta spheres respectively and ρ(r) values of key BCPs 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 ρ(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(HBEt₃)] moieties 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.⁹ 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.³⁸ 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.

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···C₆B₆ interaction makes the computed geometries less functional dependent, although B3LYP significantly overestimates both Cu···C₆B₆ 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 [HBEt₃]⁻ adduct 5 contrasts with the [(CAAC⁵⁺)Cu(HBEt₃)] 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 [(CAAC⁵⁺)Cu(C₂F₅H)₂] (III) by computing the free energy changes associated with borane loss and dimerization (Figure 6). These indicate a significantly stronger H-B(C₂F₅) bond in 6 (ΔG = +38.2 kcal/mol) compared to the H-BEt₃ bond in 5 (ΔG = +10.8 kcal/mol). 5 may therefore be susceptible to BEt₃ loss to form [6MesCuH], however, dimer formation is not thermodynamically accessible in this case (ΔG = +6.8 kcal/mol), and so alternative decomposition routes are apparently accessed, as seen experimentally. The BH₃ moiety in III is also strongly bound (ΔG = +36.9 kcal/mol), consistent with the isolation of the borohydride complex.⁴ In contrast, BEt₃ loss from [(CAAC⁵⁺)Cu(HBEt₃)] is particularly facile (ΔG = +5.8 kcal/mol) and the subsequent dimerization energy is sufficiently exergonic to rationalize the formation of dimer II upon reaction of [(CAAC⁵⁺)Cu(O’Bu)] with LiHBEt₃.[⁴]
Computational studies show that the
reduction of the alkyne had occurred.
In conclusion, the synthesis of the novel Cu-borate complexes
([6Mes]CuHBr₃) shows a similar coordination to one C₆F₅ substituent.
Both species possess a direct Cu-H interaction, neither can be considered as Lewis acid stabilized forms of [6MesCuH].
The isolation of a monomeric [NHC]CuH species, therefore, still remains an elusive target.

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Keywords: heterocyclic carbone • copper • hydride ligand • Lewis acids • DFT calculations

[7] References a)-h) provide examples which associate yellow colored solutions with (NHC)[Cu(κ²-H)] dimers.
[9] 6Dipp = 1,3-bis(2,6-diisopropylphenyl)-3,4,5,6-tetrahydroxymimidin-2-ylidene; 7Dipp = 1,3-bis(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-1,3-diazepin-2-ylidene.
[10] All attempts to isolate 2 were unsuccessful. On occasion, crystalline material was isolated (ESI), but this proved to be ([6Mes]AH)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 [(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.