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Experimental and Computational Studies of the Novel Copper Borate Complexes [(NHC)Cu(HBR$_3$)] (R= Et, C$_6$F$_5$)

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Abstract: The synthesis of the Cu-borate complexes [(6Mes)Cu(HBR$_3$)] featuring the unusual [HBEt$_3$] (5) and [HBCF$_3$]$_2$ (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$_F$)$_3$ 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 [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,[1b,2] while even very bulky NHCs still give only dimers (I and II, Scheme 1). The nearest example to an isolable monomeric [LCuH] species reported to date is the three-coordinate [CAAC$_2$Cu($κ^2$-BH$_3$)] complex III.[3] 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 [HBCF$_3$]$_2$.

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 carbenes (e.g. from the reaction of I with tertiary silanes, Scheme 2), we showed that migratory insertion (MI) products such as 3 formed under mild conditions.[4] 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 I with alternative hydride sources. Addition of LiAlH$_4$ to a THF solution of I 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).[3,4] 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)$_2$] 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) I 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)CuH(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$_2$Cu(O'Bu)]$_2$ and LiHBEt$_3$.[3b] Unsurprisingly, examples of isolable triethyl-borohydride complexes are rare, being confined to very electropositive metals.[3b]


The X-ray structure of 5 (Figure 1) showed the presence of a two-coordinate Cu centre attached to the carbene and a monodentate [HBEt$_3$] moiety. The hydrogen atom on B(1) was located and refined without restraint, yielding C$_{683}$-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 \[ \text{III} \] (1.679(2) Å, 1.717(18) Å). Additional characterization of \( \text{Cu} \) was performed in solution at low temperature (209 K). The \(^1H\) NMR spectrum featured a broad, low frequency signal (relative integral of 1) at \( \delta = -2.60 \) ppm, assigned to the Cu-H. The \(^1H\) coupled \(^1C\) NMR spectrum showed a 12 Hz doublet splitting of the carbenic carbon resonance (\( \delta = 202 \) ppm), confirming Cu\(_{\text{Me}}\)-Cu-H connectivity.

The nature of the \([\text{Cu-H-BEt}_3]\) interaction in \( \text{Cu} \) 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.\(^{[12]}\) The QTAIM molecular graph (Figure 3(a)) identifies Cu-H and B-H bond paths, as well as one for the Cu-C\(_{\text{Me}}\) bond. No further bonding interactions involving \( \text{Cu} \) (e.g., to any atoms of the Et substituents) are seen, thereby supporting the assignment of \( \text{Cu} \) as a two-coordinate complex.

Experimentally, complex \( \text{Cu} \) 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\(_3\) \((\text{H}: \delta = 73 \) ppm))\(^{[14]}\) \( \text{Cu} \) and \( \text{H} \) were also formed, alongside deposition of \( \text{Cu} \) 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 \([\text{HBEt}_3]^+\) to \([\text{BEt}_3]^+\) and \([\text{H}:\text{BEt}_3]\).\(^{[13]}\) This resulted in the formation of the \([\text{BEt}_3]^+\) salt of the known bis-carbene cation, \([6\text{Mes}]\text{Cu}^[\text{6}]\) (ESI), and a second species believed to be \([6\text{Mes}]\text{Cu}(\text{HBEt}_3]\) 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\(_2\)SiH in the presence of B(C\(_3\)F\(_5\)). A rapid reaction ensued in the case of Et\(_2\)SiH to give a mixture of \([6\text{Mes}]\text{Cu}(\text{HBEt}_3]\) (6) \( \text{Cu} \) and \([6\text{Mes}]\text{Cu}(\text{H}:\text{BEt}_3]\) (7) (ESI).\(^{[15]}\) Use of Ph\(_2\)SiH rather than Et\(_2\)SiH gave only 6. An 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\(_{\text{Me}}\) bond (2.183(17) Å) to the C\(_3\)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\(_{\text{Me}}\) 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\(_{\text{Me}}\)-C-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 \(^1B\) NMR spectrum showed a resonance at \( \delta = -28.1 \) ppm, slightly upfield of the ion-separated species \([\text{X}][\text{HB(C\(_3\)F\(_5\))}]\) (X = Ph\(_2\)Bu, \( \delta = -25.5 \) ppm)\(^{[17]}\) NBEt\(_3\), \( \delta = -25.4 \) ppm)\(^{[18]}\). Moreover, the \(^1J(\text{B}\_\text{H})\) 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., \([\text{C(SiMe\(_3\))}]\text{M}(\text{THF})_2[\text{HB(C\(_3\)F\(_5\))}]\), M = Ca: 76 Hz; M = Yb: 73 Hz)\(^{[19]}\) suggestive of a significant Cu-H-B interaction. This was supported by IR spectroscopy (v(B-H): 2361 cm\(^{-1}\))\(^{[19]}\) 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-1B HMBC 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 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 ρ(r) = -7.9 kcal/mol. The similar charges at Cu, B and H in 6 and free \([6Mes]Cu\) and \([HB(Fe)]\) 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_Bond path which entails a ring critical point associated with the \(\{\text{CuHBC}_{\text{sp}}\}\) unit. The lower value of ρ(r) at the Cu-C_Bond 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. NBO also suggests an additional stabilization occurs via donation from one of the \(\text{C}_{\text{sp}}\text{-Cu}\_\text{C}_{\text{sp}}\) bonds of the \(\text{CdF}_3\) ring (ΔE = -7.9 kcal/mol, see Figure S24).

Reproducing the molecular geometries of 5 and 6 presented a challenge to theory; in particular the structure of the \(\{\text{CuHBEt}\}\) 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. 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. 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.

The isolation of the extended solid-state structure of 5 under periodic boundary conditions with BP86 and (particularly) PBE provides 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_Bond interaction makes the computed geometries less functional dependent, although B3LYP significantly overestimates both CuC_Bond and Cu–B distances. Geometries derived from the periodic calculations are now in good agreement with experiment (see Figure S22).
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\(_4\) signals matched those of that some reduction of the alkyne had occurred. However, none of the multiplets in the \(\text{^1H NMR}\) spectrum suggested that some reduction of the alkyne had occurred. Hence, none of the signals matched those of \(6\). The \(\text{^{18}B NMR}\) 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 alkyn over days at room temperature, with only the transformation to the homoleptic cationic bis-carbene complex \(\text{[(6Mes)Cu(HBR\_5)]}\) (\(R = \text{Et}\) (7)) has been reported. Experimental and computational studies show that 5 features a two-coordinate Cu\(_2\) interaction at \(\text{^1H NMR}\) region, which is not consistent with a dimeric structure. The stability of 3 contrasts markedly with that of the phosphine analogue \(\text{[(PPh\_3)Cu(\text{^3}H\_4)]}\); R. K. Hertz, R. Goetz, Shore, Inorg. Chem. 1979, 28, 2813-2816.

References 33a-33d provide examples which associate yellow colored solutions with [(NHC)Cu(\text{^3}H\_4)] dimers.

DOSY measurements gave a value for \(r_0\) of 6.2 Å. Based on previous studies of diamidocarbene copper chloride complexes (L. R. Collins, J. P. Lowe, M. P. Mahon, R. C. Poullent, M. K. Whittlesey, Inorg. Chem. 2014, 53, 2699-2707), the value is consistent with a dimeric structure.

6Dipp = 1,3-bis(2,6-disopropylphenyl)-4,5,6-tetraydropyrimidin-2-ylidene; 7Dipp = 1,3-bis(2,6-disopropylphenyl)-4,5,6,7-tetraydro-1,3-diazepin-2-ylidene.

All attempts to isolate 2 were unsuccessful. On occasion, crystalline material was isolated (ESI), but this proved to be [(6Mes)AlH\(_2\)].


[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.


Copper Borates

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Experimental and Computational Studies of the Novel Copper Borate Complexes [(NHC)Cu(HBR)][(R = Et, C$_6$F$_5$)]

Unusual Cu-borate complexes [(6Mes)Cu(HBR)] (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$_{ipp}$ interaction to one C$_6$F$_5$ substituent.