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Bis(σ -B–H) complexes of copper(i): precursors to a heterogeneous amine–borane dehydrogenation catalyst†

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A series of bis(σ -B–H) complexes of copper(i) have been prepared by displacement of arene solvent from a β -diketiminate copper(i) complex by four-coordinate boranes, H_3B-L ($L = NMe_3$, lutidine). In the presence of the same copper arene complex, the secondary amine–borane H_3B-NMe_2H undergoes dehydrogenation. We provide evidence for formation of a heterogeneous catalyst from decomposition of the solution species.

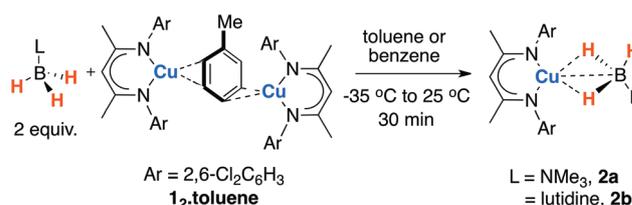
Since Hartwig and co-workers reported the isolation and characterisation of $[Cp_2Ti(\eta^2-HBcat)_2]$ ($HBcat = catecholborane$),¹ our understanding of the coordination chemistry of boranes has flourished.² Contrasting studies have investigated the interaction of 3- and 4-coordinate boranes with transition metal centres.^{3,4} Regardless of the environment at boron and the mode of coordination to the metal, σ -borane complexes have become synonymous with B–H bond activation. These species are invoked as intermediates in the catalytic borylation of C–H bonds,⁵ the hydroboration of alkenes and alkynes,⁶ and the dehydrogenation of amine–boranes.⁷ For example, Shimoi and co-workers studied the coordination of H_3B-NMe_3 to a series of group 6 carbonyl complexes and demonstrated dehydrogenation of H_3B-NHR_2 under photochemical conditions.⁸ In related studies, Weller, Sabo–Etienne, Aldridge, Manners, Schneider, and others have conducted extensive investigations into the coordination of H_3B-NR_3 , $H_2B=NR_2$ and $[H_2B-NR_2]_2$ fragments to a series of late transition metals, including ruthenium, rhodium and iridium complexes.^{7,9–12} A detailed understanding of not only the electronic structure of a clutch of σ -borane complexes but also the mechanisms of amine–borane dehydrogenation has emerged.

Despite a growing interest in the catalytic applications of the 1st row transition metals, little is known about σ -complexes of copper. The coordination of σ -bonds to Cu(i) may fore-

shadow oxidative addition to Cu(III) and play an unappreciated role in catalysis. In line with these expectations, Bourissou and coworkers have reported the *intramolecular* coordination of Si–Si and Si–H bonds within carefully designed ligand frameworks to Cu(i). In the case of an Sn–Sn analogue, oxidative addition of the tin–tin bond was observed allowing isolation of the corresponding Cu(III) distannyl complex.¹³ Stack, Ribas and co-workers have provided EPR and computational support for an agostic interaction in a Cu(II) metallocycle.¹⁴ Recently we reported the reversible, *intermolecular*, coordination of Al–H and Zn–H bonds to a two-coordinate copper(i) fragment generated *in situ* from **1**–**toluene** (Scheme 1).^{15,16} Here we disclose that amine–boranes coordinate reversibly to Cu(i), and demonstrate an effective pre-catalyst for amine–borane dehydrogenation.

The reaction of **1**–**toluene**¹⁵ with H_3B-L ($L = NMe_3$, lutidine) in a 1 : 2 stoichiometry C_6D_6 resulted in a minor perturbation of the resonances of **1** and the borane as evidenced by line-broadening and chemical shift changes in both the 1H and $^{11}B\{^1H\}$ NMR spectra. Despite the weak and potentially reversible nature of the interaction, preparative scale reactions allowed the isolation of the corresponding σ -borane complexes **2a–b** as yellow crystalline solids in 63–85% yield (Scheme 1).

Single crystals of **2a–b** could be grown from toluene or toluene/hexane mixtures at -35 °C (Fig. 1). Compound **2a** crystallises with a mirror plane that passes through the metal centre and bisects the N–Cu–N angle, necessitating that the BH_3NMe_3 unit be disordered (see ESI†). Due to this disorder, the hydride atoms could not be located. The Cu–B distances



Scheme 1 Synthesis of σ -borane complexes of copper(i).

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† Electronic supplementary information (ESI) available: Full experimental procedures, VT NMR data, crystallographic data, and details of the DFT calculations. CCDC 1048449–1048450. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02144h



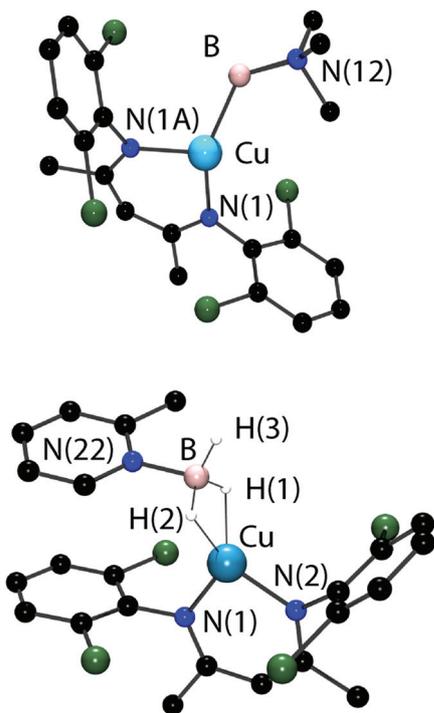


Fig. 1 The crystal structure of **2a** (top) and **2b** (bottom). H-atoms with the exception of experimentally identified B–H units omitted for clarity. Selected bond lengths (Å) and bond angles (°) **2a**, Cu–B 2.191(6), B–N(12) 1.549(11), N(1)–Cu–N(1A) 97.08(14); **2b**, Cu–B 2.152(3), B–N(22) 1.590(3), N(3)–Cu–N(1) 98.58(7).

(**2a**, 2.191(6) Å; **2b**, 2.152(3) Å) are longer than the 2.002(3) Å Cu–B bond of the copper-boryl complex [(IPr)Cu(Bpin)] (IPr = 1,3-bis(2,6-di-iso-propylphenyl)imidazol-2-ylidene; HBpin = pinacolborane). In contrast, the quality of data acquired on **2b** allowed the location of the hydride positions from a difference electron density map. It is apparent that the ligand coordinates in an $\eta^2:\eta^2$ -mode forming a bis(σ -B–H) complex. The two Cu–H distances of 1.81(2) and 1.79(2) Å are within experimental error of one another. The B–H bond lengths of the bridging hydrides (1.15(1) and 1.16(2) Å) are both significantly longer than that to the terminal hydride (1.04(2) Å).

The $\eta^2:\eta^2$ -coordination of a borane ligand in [Ru(H)₂(PCy₃)₂($\eta^2:\eta^2$ -H₂BMes)] was reported by Sabo-Etienne and co-workers.¹⁷ There is also direct precedent for this type of interaction in amine–borane chemistry and Weller and co-workers have reported a series of rhodium, iridium and ruthenium complexes in which amine–boranes coordinate through two hydride sites.⁹ In contrast, Shimoi and co-workers proposed the $\eta^2:\eta^2$ -mode as a transition state for the fast exchange of geminal B–H units of η^2 -coordinated amine–boranes within metal carbonyl complexes.¹⁸ It is worth noting that, two cationic complexes in which chelating diboranes, [H₂B(PMe₃)₂]₂ and [HB(hpp)]₂ (hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]-pyrimidine), coordinate to copper(i) *via* vicinal B–H bonds are known.¹⁹ Inspection of the solid-state structure of **2b** reveals π - π stacking between the electron-rich lutidine and

electron-poor 2,6-dichlorophenyl moieties; a secondary, non-covalent, interaction that undoubtedly contributes to the stabilisation of **2b**.

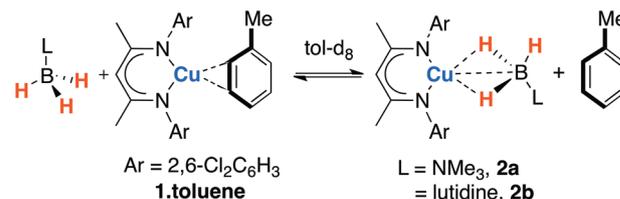
Infrared data are consistent with the formulation of these species as weakly coordinated boron hydrides and reveal broad B–H stretches (**2a**, 2423 cm⁻¹; **2b**, 2403 cm⁻¹) in the range expected for terminal boron hydrides with no clear differentiation between the (σ -B–H) and B–H vibrations.

¹H and ¹¹B NMR spectroscopy show that, upon dissolution in toluene-d⁸, isolated crystalline samples of the Cu(i) σ -complexes establish an equilibrium between **2** + toluene and **1**·toluene + amine–borane (Scheme 2). We have previously shown that **1**·toluene forms **1**·toluene by solvation, and the latter is the predominant species in toluene solution.¹⁵

For complex **2b** at 298 K in toluene-d⁸ the BH₃ unit of the amine–borane is observed as a single resonance at δ = -15.5 ppm in the ¹¹B{¹H} NMR and as a broad quartet at δ = 3.27 ppm in the ¹H NMR. The resonances are assigned to a time-averaged contribution from bound and unbound amine–borane; consistent with fast chemical exchange. Upon cooling, decoalescence of a series of resonances assigned to both the amine–borane and the β -diketiminato ligand occurs. At 193 K the slow exchange regime is reached and a mixture of **1**·toluene, amine–borane and **2b** is observed in solution (ESI, Fig. S1 and S2[†]).²⁰ While at this temperature B–H resonances were apparent as broad signals in the ¹H{¹¹B} NMR between δ = 2.5 and 3.5 ppm, we have been unable to resolve terminal B–H and (σ -B–H) resonances. We suggest that even at 193 K fast exchange between the terminal B–H and (σ -B–H) units within **2b** occurs.

The observation of a weak and reversible coordination of the B–H bond to Cu(i) parallels that reported for analogous Al–H and Zn–H σ -complexes.¹⁵ This fluxional process was observed for not only **2b** (*vide supra*) but also **2a**. VT NMR on toluene-d⁸ samples of **2a** across the 193 to 353 K range allowed quantification of the equilibrium depicted in Scheme 2. Van't Hoff analysis gave $\Delta H_{\text{rxn}} = -1.40(4)$ kcal mol⁻¹, $\Delta S_{\text{rxn}} = -5.87(2)$ cal K⁻¹ mol⁻¹ and $\Delta G_{\text{rxn}} = +0.17(3)$ kcal mol⁻¹. The data suggest that binding of H₃B–NMe₃ to **1**·toluene is slightly endergonic.

In order to gain a deeper understanding of the strength and nature of the bonding within the bis(σ -B–H) complexes, a series of DFT calculations were undertaken. A minimum on the potential energy surface with a bis(σ -B–H) coordination mode was obtained for the series of complexes presented in



Scheme 2 Reversible σ -complex formation with copper(i).



Scheme 1. All attempts to optimise mono(σ -B-H) geometries led to this structure. The calculated B-H bond lengths are significantly longer than those determined in **2b** by X-ray crystallography and range from 1.20–1.23 Å. Furthermore, across a choice of functionals, and in contrast to the X-ray data, the (σ -B-H) lengths were determined to be only slightly longer than the terminal B-H bond in these calculations ($\Delta = 0.03$ Å). Based on the known difficulty in assigning the position of the hydrogen atoms in X-ray diffraction experiments, the calculated B-H bond lengths represent a more realistic description of the ground-state structure.

NBO calculations suggest only a minor perturbation of borane within the coordination complexes **2a** and **2b**. The Wiberg Bond Indices (WBIs) for the (σ -B-H) bonds are similar to that of the terminal B-H. Furthermore, both the Cu-H and Cu-B WBIs are low, suggestive of a weak interaction (Fig. 2). Second order perturbation analysis allows a quantification of the donor-acceptor interactions, donation of electrons from each of the two B-H σ -bonds occurs to the 4s orbital of copper (**2a**, 21.7 + 22.3 kcal mol⁻¹; **2b**, 15.6 + 16.8 kcal mol⁻¹), significant back-donation from Cu(I) to the B-H σ^* -orbitals is not recorded for either **2a** or **2b**.

These data were further underscored by a quantum theory atoms-in-molecules (QTAIM) calculation on **2a** which revealed bond critical points (BCPs) between the Cu/B and H atoms, but not between Cu and B. These data show a bending of the (σ -B-H) bond critical paths toward Cu and are consistent with two 3-centre,2-electron interactions (Fig. 2). In line with the NBO analysis, the QTAIM data for coordinated ($\rho_{\text{bcp}} = 0.154$; $\nabla\rho_{\text{bcp}}^2 = -0.14$) and non-coordinated B-H bonds ($\rho_{\text{bcp}} = 0.171$; $\nabla\rho_{\text{bcp}}^2 = -0.20$) within **2a** suggests small changes of the bonding in the B-H bond upon coordination to Cu(I).

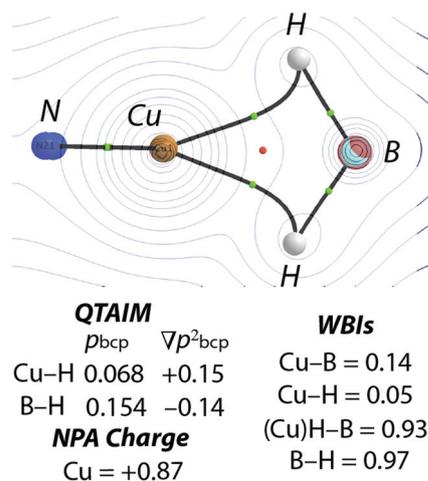
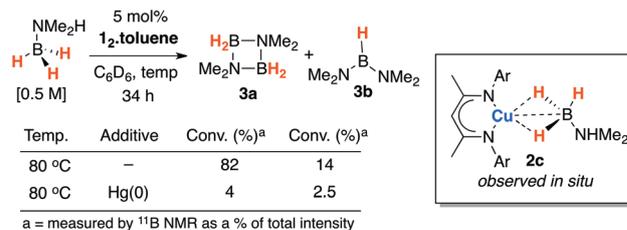


Fig. 2 QTAIM electron density contour plot for **2a**. Molecule presented in the {CuHB} plane. Figure annotated with selected data from QTAIM and NBO calculations. Green dots are bond critical points, red dots are ring critical points, bond critical paths are represented by thick solid lines.



Scheme 3 Amine-borane dehydrogenation.

Further modification of the amine-borane to a substrate that contained both hydridic and acidic protons resulted in facile dehydrogenation and boron-nitrogen bond formation. While reaction of H₃B-NHMe₂ with **1,2-toluene** resulted in the generation of the corresponding σ -complex, compound **2c** was short-lived and only observed *in situ*. All attempts to isolate this latter species resulted in dehydrogenation of H₃B-NHMe₂ (Scheme 3).

In line with these expectations, **1,2-toluene** catalysed the dehydrogenation of H₃B-NHMe₂ in 5 mol% loading at 80 °C in C₆D₆ solution (Scheme 2). Notably **2c** was observed as an intermediate in solution by ¹H NMR spectroscopy. In this case, at 298 K the ¹J_{11B-1H} coupling can be resolved and the ¹J_{11B-1H} for the equilibrium mixture of **1-toluene**, **2c** and H₃B-NMe₂H (90.4 Hz) is slightly smaller than that of the independent amine-borane (96.4 Hz). Monitoring catalytic reactions by ¹H and ¹¹B NMR spectroscopy revealed the formation of known products [H₂B-NMe₂]₂ (**3a**) and HB(NMe₂)₂ (**3b**). The reaction proceeded with concomitant formation of a Cu(0) mirror on the interior of the reaction vessel. Following a catalytic run, re-exposure of the Cu(0) mirror to the reaction conditions reestablished amine-borane dehydrogenation. An Hg(0) drop experiment resulted in a significant inhibition of catalysis. In this instance, data are consistent with **2c** acting as a homogeneous precursor to a heterogeneous species.²¹

These data contrast those found by Philips and co-workers for the dehydrogenation of ammonia-borane catalysed by a ruthenium analogue of **1-benzene** and by Bertrand and co-workers using a CAAC-stabilised copper borohydride complex.^{22,23}

Conclusions

In summary, we have reported the first examples of isolable and crystallographically characterised σ -borane complexes of Cu(I). While in the solid-state amine-boranes coordinate *via* an η^2 : η^2 -mode, in solution displacement of this ligand by arene solvent is both fast and reversible. Inclusion of both hydridic and protic hydrogen atoms on the ligand leads to a decomposition of the coordination compound and production of a heterogeneous copper catalyst that is capable of the dehydrogenation of an amine-borane.



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