Copper–Ligand Cooperativity in H_2 Activation Enables the Synthesis of Copper Hydride Complexes

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Abstract

Copper(I) complexes of a new participative triphosphane ligand (2^H) have been prepared and structurally characterized, in particular [Cu(2^H)I] and [Cu(**2**)]$_2$. Hydrogenation of the latter species afforded the trimetallic hydride species [Cu$_3$(**2**)$_2$(μ-H)] or in the presence of BEt$_3$, [Cu(2^H)(HBEt$_3$)]. Their formation evidences transient formation of [Cu(2^H)H] formed by hydrogenolysis of the Cu–N bond of [Cu(**2**)]$_2$. [Cu(2^H)(HBEt$_3$)] behaves like a hydride complex and inserts CO$_2$ to yield the formate product [Cu(2^H)(O$_2$CH)]. QTAIM analysis of the Cu–H–BEt$_3$ interaction indicates a hydride complex stabilized by the Lewis acid BEt$_3$.
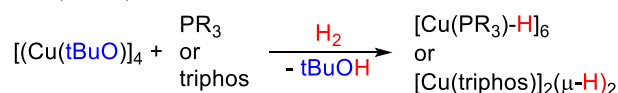
Introduction

The development of efficient catalysts for the hydrogenation and cleavage of C–O bonds is an active area of research, in particular for the production of fuels and chemicals from renewable feedstocks such as CO$_2$ or biomass.[1] While complexes of noble metals (Ru, Ir…) favor such hydrogenation reactions, economic and environmental reasons incite for the use of catalysts involving base metals (Fe, Co, Mo, Cu…).[2] Among them, solid materials based on copper are well known catalysts for hydrogenation of C=O bonds in carboxylic acids, esters and CO$_2$ but proceed under harsh conditions and with low selectivity.[1b] A handful of molecular copper complexes were reported to activate H$_2$ and catalyze the hydrogenation of more reactive substrates such as ketones or aldehydes.[3] Two of them, [Cu(triphos)(MeCN)]$^+$ and Cu(OAc)$_2$, catalyzed the hydrogenation of CO$_2$ to formic acid in the presence of an external base, thus evidencing the potential of copper species in catalytic hydrogenation reactions.[4]
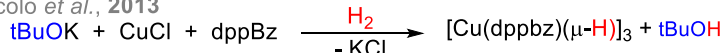
The generally proposed mechanism for the hydrogenation of C=O bonds involves a transient metal-hydride species generated from the activation of H$_2$. In the case of copper, however, while a number of Cu–H intermediates were proposed, for example in hydroelementation reactions as described by Buchwald,[3a, 4a, 5] only a few have been fully characterized.[6] The synthesis of the hexameric complex [(Ph$_3$P)CuH]$_6$ by Osborn in 1971 led to the characterization of a number of polymetallic hydrido clusters or complexes,[7] mostly obtained through the reaction of copper halide or alkoxide complexes with borohydrides, boranes or silanes.[8] The groups of Caulton, Ruccolo, Appel and Broere reported efficient procedures that involve the hydrogenolysis of Cu–OR bonds (Scheme 1).[9] No terminal copper hydride has ever been isolated in the solid state but recently Bertrand *et al.* demonstrated that, by using a highly congested carbene ligand, a monomeric copper hydride could exist in solution, in equilibrium with its dimeric form.[6b]
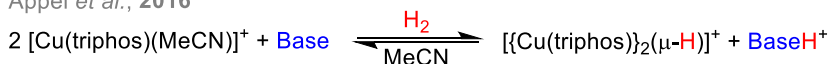
Previous work:

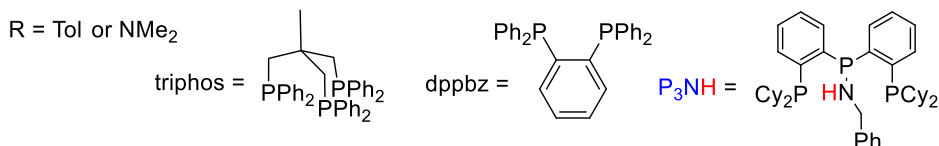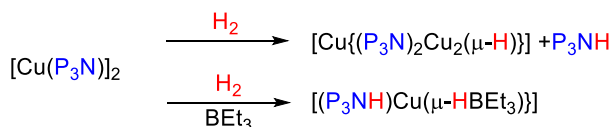Caulton *et al.*, **1981**, **1985** and **1986**

$$[(Cu(tBuO)]_4 \ + \ \begin{array}{c} PR_3 \\ or \\ triphos \end{array} \ \xrightarrow[\ -\ tBuOH\ ]{\ H_2\ } \ \begin{array}{c} [Cu(PR_3)\text{-}H]_6 \\ or \\ [Cu(triphos)]_2(\mu\text{-}H)_2 \end{array}$$

Ruccolo *et al.*, **2013**

$$tBuOK \ + \ CuCl \ + \ dppBz \ \xrightarrow[\ -\ KCl\ ]{\ H_2\ } \ [Cu(dppbz)(\mu\text{-}H)]_3 \ + \ tBuOH$$

Appel *et al.*, **2016**

$$2\ [Cu(triphos)(MeCN)]^+ \ + \ Base \ \underset{MeCN}{\overset{H_2}{\rightleftharpoons}} \ [\{Cu(triphos)\}_2(\mu\text{-}H)]^+ \ + \ BaseH^+$$

This work:

$$[Cu(P_3N)]_2 \quad \xrightarrow{\ H_2\ } \ [Cu\{(P_3N)_2Cu_2(\mu\text{-}H)\}] \ + P_3NH$$

$$\xrightarrow[\ BEt_3\ ]{\ H_2\ } \ [(P_3NH)Cu(\mu\text{-}HBEt_3)\}]$$

- -

R = Tol or NMe$_2$

triphos = PPh$_2$ | PPh$_2$ PPh$_2$

dppbz = Ph$_2$P PPh$_2$

P$_3$NH = Cy$_2$P HN PCy$_2$ / Ph

Scheme 1. Copper(I) hydride complexes obtained by hydrogenation methods

In recent years, metal-ligand cooperation in amino phosphine pincer complexes has led to the successful synthesis of many hydride complexes with Ru, Ir, Fe and Mn ions, through heterolytic cleavage of H_2, and was associated with increased hydrogenation performances.[10] Yet, this strategy has never been applied to copper. As tripodal phosphine ligands are well suited to stabilize four-coordinate copper(I) complexes,[4a, 11] we have designed a novel triphosphine P$_3$NH ligand (**2^H**) featuring an aminophosphine moiety, as possible participative group (schemes 1 and 2). We report here the preparation of reactive copper(I) complexes of the ligands **2^H** and **2**, their use in the activation of H_2 and further reactivity with CO_2 and HCO_2H. These results demonstrate, for the first time, how a participative ligand can facilitate the splitting of H_2 in the coordination sphere of copper.

Results and Discussion

Syntheses of ligand **2^H** and its potassium derivative **2^K** are described in Scheme 2. Lithium halogen exchange between (2-bromophenyl)dicyclohexylphosphine and ^{n}BuLi at -78 °C in diethylether gave [Cy$_2$PC$_6$H$_5$]Li (non-isolated) which upon addition of 0.5 equivalent of phosphorus trichloride afforded **1** in 93% yield. Addition of benzylamine to a toluene solution of **1** in the presence of an excess of triethylamine led to the formation of the targeted aminophosphine **2^H** isolated as a white solid in 69 % yield. Compound **2^H** was characterized by X-ray diffraction (see SI for details) and by multinuclear NMR experiments, exhibiting ^{31}P NMR shifts at 32.6 (dd, $^3J_{PP}$ = 145, 149 Hz) and −12.6 ppm (d, $^3J_{PP}$ = 147 Hz, average of two overlapping doublets) for the P–NH and the two Cy$_2$P fragments, respectively. While the NH signal is masked by the cyclohexyl protons in benzene, it appears as a multiplet at 2.62 ppm in d$_8$-TDF. However, the multiplicity of the CH$_2$ signal of the benzylic N–CH$_2$Ph group can be

used to probe the protonation of the N center. Indeed, in the presence of an NH functionality, the CH_2 benzylic signal is a pseudo-triplet as observed in 2^H, which displays a signal at 4.27 ppm ($^3J_{HP} \approx {}^3J_{HH} = 6.5$ Hz). In compound 2^K, obtained from the reaction between 2^H and one equivalent of $PhCH_2K$, deprotonation of the amine changed the CH_2 signal to a doublet at 4.02 ppm with a unique coupling constant $^3J_{HP} = 11.9$ Hz.
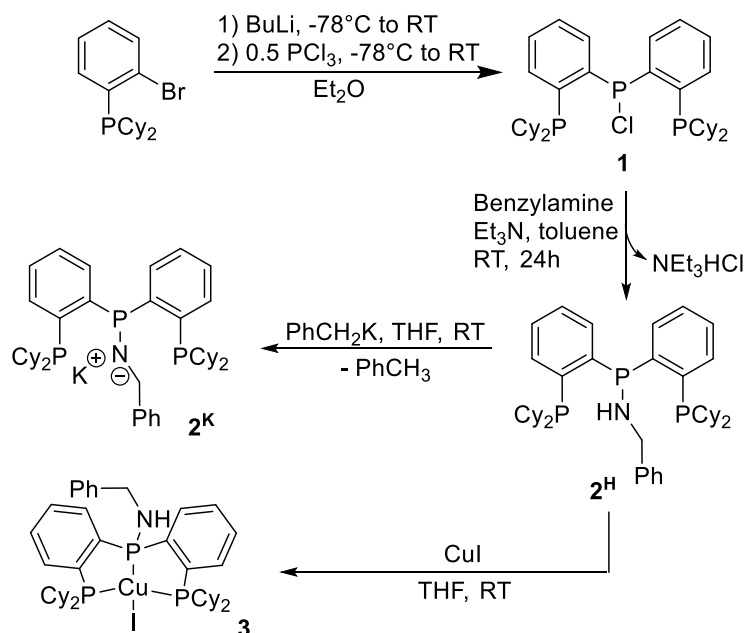
Scheme 2. *Syntheses of ligand 2^H, 2^K, and of the iodide complex 3*
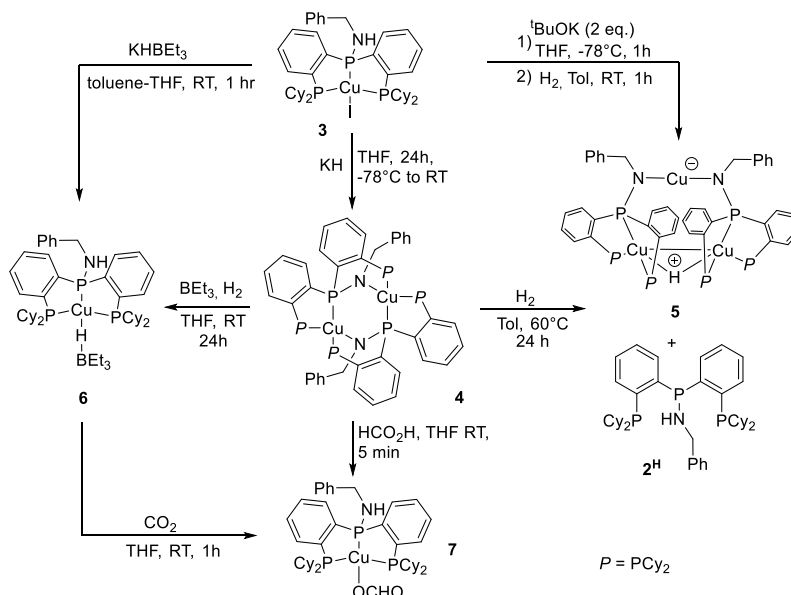
Scheme 3. *Synthesis of the copper complexes*

Reaction of 2^H with one equivalent of copper(I) iodide in THF led to the quantitative formation of the yellow complex [(2^H)CuI] (**3**) isolated in 95% yield after washing with pentane and crystallized as the orange-yellow solvate $3 \cdot C_6H_6$ in refluxing benzene. Complex **3** was characterized by X-ray diffraction and multinuclear NMR (see ESI and Fig. 1). The $^{31}P\{^1H\}$

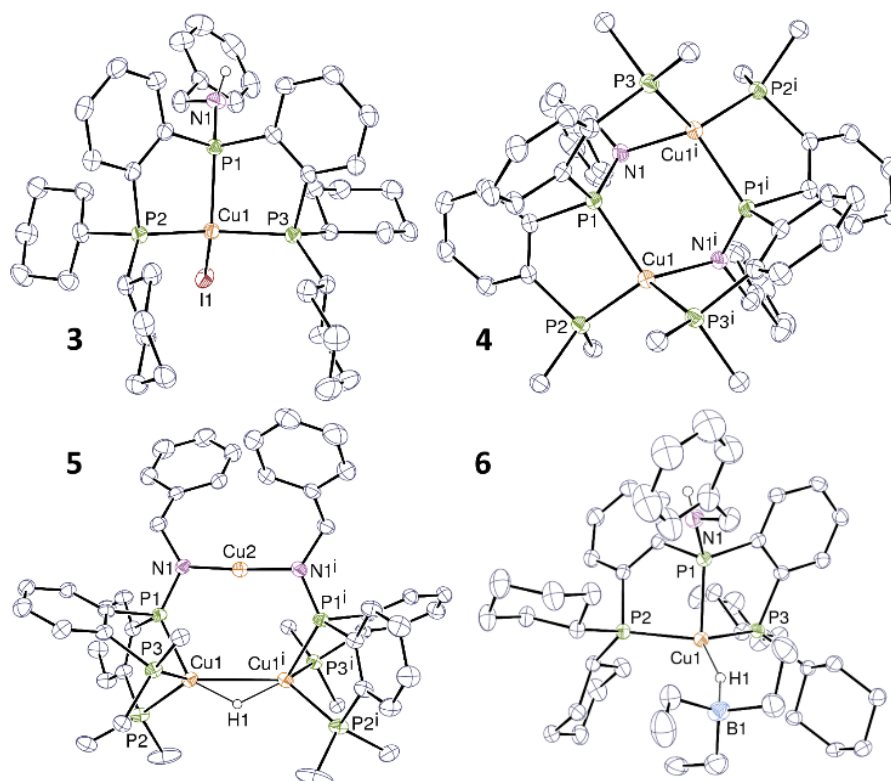NMR spectrum displayed two signals at 26.1 and 5.8 ppm, broadened due to coupling to the copper nucleus.

**Figure 1**. *ORTEP views for complexes 3-6. Displacement ellipsoids are drawn at the 40% probability level. Solvent molecules and carbon bound hydrogen atoms are omitted. The cyclohexyl rings in 4 and 5 are omitted for clarity. For 6, only one position of the disordered aromatic ring is represented. Selected bond distances (Å) and angles (°): 3: Cu1–I1 2.6098(3), < Cu-P> 2.27(1); 4: Cu1–N1 2.0634(16), < Cu-P> 2.31(1); 5: Cu1–H1 1.66(3), Cu2–H1 1.61(3), Cu3–N1 1.862(3), Cu3–N2 1.858(3), <Cu1-P> 2.31(6), <Cu2-P> 2.27(1); Cu1–H1–Cu2 106.5(14), N1–Cu3–N2 176.60(12); 6: Cu1–H1 1.66(3), H1–B1 1.35(3), <Cu-P> 2.30(1), Cu1–H1–B1 159(2).*

In order to form either a [Cu(2$^\mathbf{H}$)H] (**6'**) hydride species or the amido derivative [Cu(**2**)], reaction of **3** with potassium hydride was attempted in THF. Deprotonation of **3** and loss of KI occurred with formation of the dimeric amido species [Cu(**2**)]$_2$ (**4**) which was isolated after extraction in diethyl ether as an orange powder (73% yield) while it crystallized as yellow platelets upon slow diffusion of pentane into a THF solution. The dimeric nature of **4** was revealed by single crystal X-ray diffraction. The doublet for the N–CH$_2$ group at 5.27 ppm (d, $^3J_{HP}$ = 25 Hz) in the ^{1}H NMR spectrum confirms deprotonation of the amine. The ^{31}P{^{1}H} NMR spectrum evidenced three broad signals at 55.2, −1.9 and –4.3 ppm for the P–N and the Cy$_2$P moieties, respectively. The structure of **4** possesses a crystallographic C2 symmetry axis passing at the center of the (CuPN)$_2$ ring found in a boat configuration with the two N atoms outside the plane. The ligand is bridging in a μ-κ^2-P,P-κ^2-P,N mode and bound by two P atoms (of the P–N and one of the PCy$_2$ moieties) to a Cu$^+$ ion and by the second PCy$_2$ unit and the N atom to another Cu$^+$ ion so that the copper atom adopts a pseudo-tetrahedral arrangement (Figure 1). The Cu–P and Cu–N can be compared to those found in the rare other amido triphosphine complexes such as [Cu{PN}(PMe$_3$)$_2$] ({PN} = *p*-PhN-C$_6$H$_4$-P^{i}Pr$_2$), 2.25(2) and

2.086(1) Å.[12] The P1–N1 bond length of 1.6370(17) is notably shorter than the P–NH bond in **3** (1.6849(19) Å) or in the free ligand **2^{H}** (1.691(2) Å) (See ESI).

Complex **4** can be viewed as a relevant precursor to the targeted monometallic copper(I) hydride [Cu(**2^{H}**)(H)] (**6'**) through hydrogenolysis of the Cu–N bond. Exposure of **4** to 1 atm of H$_2$ in benzene or toluene led, after 24 h at 60 °C, to the formation of **5** and free **2^{H}** as the major species with 70 % conversion. Complex **5** (Figure 1) was unambiguously identified as the trimetallic monohydride [Cu$_3$(**2**)$_2$(μ–H)] by X-ray diffraction on orange-yellow crystalline platelets of **5** (and its solvate **5'**·2 C$_6$H$_6$, see ESI) grown in refluxing benzene. The ^{31}P{^{1}H} and ^{1}H NMR spectra of **5** present a characteristic Cu–H signal at −1.99 ppm and the two magnetically inequivalent protons in the PNCH$_2$ moieties appear as two pseudo triplets at 4.62 and 4.37 ppm ($^2J_{HH} \approx {}^3J_{HP}$ = 14.7 Hz). The negative chemical shift of the hydride resembles that of −1.46 ppm in the 4-coordinate phosphine complex [{Cu(κ^3-triphos)}$_2$(μ^2-H)]$^+$ which has a linear cationic [Cu(μ^2-H)Cu]$^+$ core distinct from that in **5**.[9e] The structure of **5** is composed of a triangular Cu$_2$H core with Cu1, Cu2 and a symmetric μ^2-bridging hydride (Figure 1, bottom left). Each of these Cu atoms is coordinated in a κ^3-P,P,P fashion to a ligand **2**, while the two nitrogen atoms of the amide groups bind the third, two-coordinate Cu3 copper ion in trans positions. The Cu–H distances compare well with those reported for neutral or cationic copper complexes containing bridging μ^2–hydride.[6, 8b, e, 9c, d] Treatment of a chilled toluene solution of **3** with 2 equiv. KO^{t}Bu, followed by addition of H$_2$ (1 atm.) similarly led to the quantitative formation of **5** and free **2^{H}** after only 1 hour at room temperature. This is the most straightforward way to obtain **5** which was isolated in good yield (69%) after washing with pentane to eliminate free **2^{H}**.
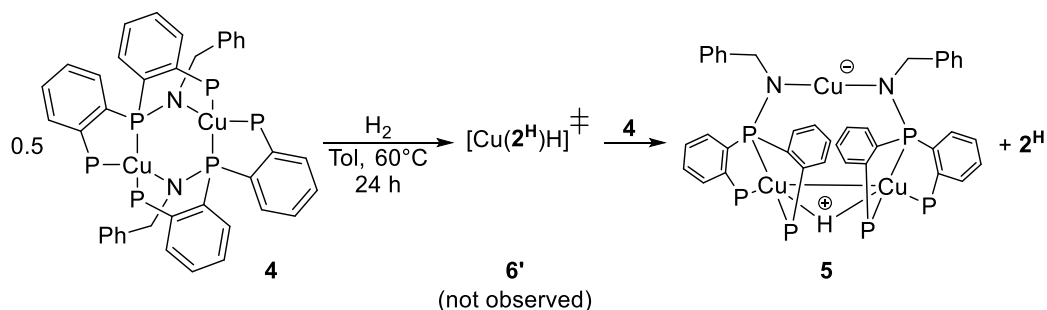

Scheme 4. *Formation of **5** through activation of H$_2$ on **4** and putative generation of a copper hydride intermediate*

In the hydrogenolysis of dimer **4**, the concomitant formation of a copper hydride entity and free protonated ligand strongly suggests formation of the putative [Cu(**2^{H}**)(H)] species that would be immediately trapped by the precursor **4** to give **5** with loss of one equivalent of **2^{H}** (Scheme 4). To further support the transient formation of [Cu(**2^{H}**)(H)] in the above reactions, we sought to deliberately trap this species with a Lewis acid, e.g. BEt$_3$, in order to bring kinetic stability as previously reported for the stabilization of a Ca–H bond.[13] Hydrogenation (1 atm.) of a THF solution of **4** in the presence of one equivalent of BEt$_3$ cleanly afforded, after 24h at room temperature, the new complex **6**. The conversion never exceeded 20% yield, but no side reaction was observed. Complex **6** was characterized in ^{31}P{^{1}H} NMR by two broad signals (at 33.7 and 10.8 ppm) and in the ^{1}H NMR spectrum by a signal at −1.39 ppm typical for a Cu–H bond as well as a pseudo-triplet for the benzylic CH$_2$ at 4.25 ppm ($^3J_{HH} \approx {}^3J_{HP}$ = 7.3 Hz). The ^{11}B{^{1}H} NMR spectroscopy in benzene revealed a very broad singlet at −15.4 ppm, in the usual

region for a [HBEt$_3$]$^-$ ligand.[14] Complex **6** was formed alternatively by the direct reaction of **3** with 1 equivalent of potassium triethylborohydride for 1 hour in toluene. After evaporation of the solvent and dissolution in Et$_2$O, **6** could be isolated as a yellow powder. Complex **6** is the second example of an isolable triethyl-borohydride copper complex after [Cu(NHC)(μ-H–BEt$_3$)] (NHC = N-N'(2,4,6-C$_6$H$_2$Me$_3$)C$_6$H$_6$N$_2$C).[15] The latter complex features notably a downfield shift for the hydride compared to that in **6**, -2.6 ppm. Such stable species are very unusual because of their extreme reactivity and propensity to loose BEt$_3$. Only a handful of such compounds have been described, mostly with strongly electropositive metals.[16] When compared to [Cu(NHC)(HBEt$_3$)], which decomposes above 243 K with loss of borane, **6** is stable and doesn't degrade after five days at RT.

Yellow crystals of the adduct **6**, obtained in refluxing ether and suitable for X-ray diffraction, definitively evidenced formation of the borate [Cu(**2^H**)(μ-H–BEt$_3$)]. Its structure (Figure 1, bottom right) is very similar to that of **3** and reveals a tetrahedral Cu$^+$ center κ^3-coordinated by the tridentate ligand **2^H** and by a monodentate [Et$_3$BH]$^-$ anion through the H atom. The Cu–H and B–H distances, respectively 1.66(3) Å and 1.35(3) Å, are longer than in the two-coordinate [Cu(NHC)(μ-HBEt$_3$)] complex (1.56(3) and 1.22(3) Å) in line with the different coordination numbers of the complexes (triphosphane vs NHC). The angle Cu–H–B is also more linear (159(2)° vs 110.2(18)°).

Copper hydrides are reactive species in catalytic and stoichiometric reduction reactions of unsaturated oxygenated substrates. We thus investigated the behavior of **6** as a stable substitute of the putative hydride [Cu(**2^H**)(H)] in the reduction of CO$_2$.[17] Exposure of **6** to 1 atm of CO$_2$ led to the formation of the corresponding formate complex **7** with complete conversion after 1 hour at room temperature. The ^{31}P{^{1}H} NMR spectrum of **7** shows two broad signals at 26.9 and 7.3 ppm while the ^{1}H NMR spectrum reveals the presence of a HCOO$^-$ ligand at 8.72 ppm and the characteristic triplet for the CH$_2$–(NH) group at 4.08 ppm. A peak at 167.6 ppm in the ^{13}C{^{1}H} NMR spectrum was also observed and assigned to the formate moiety. Complex **7** was also immediately obtained from the reaction of **4** with two equivalents of formic acid in THF, and isolated in 89 % yield. In the infra-red spectrum, the ν(CO$_2$)$_{asym}$ and ν(CO$_2$)$_{sym}$ frequencies are found at 1595 and 1377 cm^{-1}, respectively.[18]
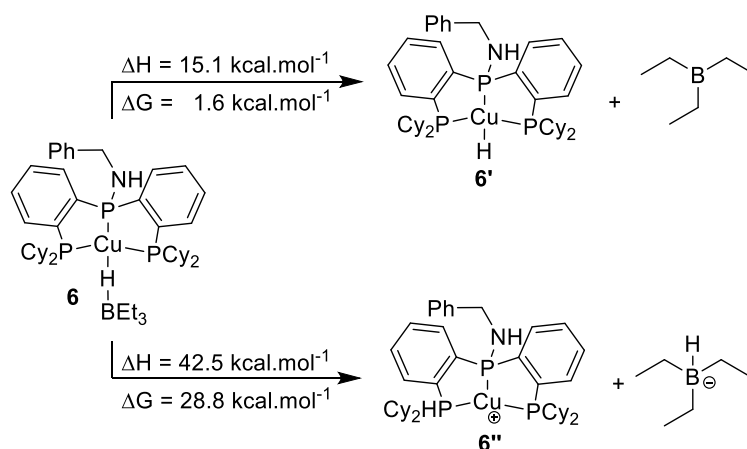
Scheme 5. *Analysis of the bond enthalpies and energies in **6**. Calculations were performed with Gaussian09, using: PBE0 as a functional; Def2TZVP for Cu, 6-311+G(d,p) for the bridging H, and 6-31G(d) for other atoms as a basis set. Solvent effects in benzene were accounted for with the SMD model.*

Table 1. Results of QTAIM Analysis.

	ρBCP	∇2ρBCP	HBCP	GBCP/ρBCP
Cu–H in **6'**	0.090	0.126	-0.104	0.809
Cu–H in **6**	0.081	0.175	-0.116	0.897
B–H in **6**	0.095	-0.064	-0.030	0.485
B–H in HBEt$_3^-$	0.116	-0.206	0.006	0.389

BCP: Bond Critical Point. Decreasing ρ values indicates lower interaction. $\nabla^2\rho_{BCP}$ is more positive for greater ionic character. G_{BCP} is the kinetic energy density and H_{BCP} the local energy density.

In order to gain a deeper understanding of the nature of **6**, and especially of its hydridic character, its electronic structure was studied by QTAIM analysis. The topology of the electron density and its gradient was thus interpreted in terms of chemical bonding, to map the chemical bonds and their critical points (BCP), that can be characterized thanks to the values of the density itself ρ_{BCP} and its Laplacian $\nabla^2\rho_{BCP}$.[19] Further analysis of these values through an Abramov gradient decomposition then leads to two values, G_{BCP} and H_{BCP}, that can be interpreted as the kinetic energy density and the local energy density respectively.[20] The interpretation of both values then allows creating a classification of bonds in covalent, ionic or dative groups. This analysis was performed on **6** and the putative terminal hydride complex [(**2^H**)CuH] (**6'**) as well as on the anion HBEt$_3^-$, the results are displayed Table 1. As expected, the Cu–H and B–H bonds in **6** display an ionic character ($\nabla^2\rho_{BCP}$ more positive, smaller ρ_{BCP}) greater than in **6'** and free HBEt$_3^-$, which is coherent with the presence of a three-center-two-electrons bond in **6**. Comparing the G/ρ and H values at the BCPs suggests that the Cu–H bond in **6** retains the character of a terminal Cu–H bond, as in **6'**. On the other hand, the B–H bond in **6** is significantly disturbed compared to the HBEt$_3^-$ borohydride. The change in sign of H is particularly indicative, as well as the relative differences in the values of G/ρ. To further investigate the nature of **6**, we calculated the energy required to cleave the Cu–H and the B–H bonds in **6** (Scheme 5). While the loss of BEt$_3$ from **6** is slightly endothermic (15.1 kcal.mol^{-1}), splitting the Cu–H bond to form **6''** requires 42.5 kcal.mol^{-1}, pointing to a much weaker B–H bond. This is also reflected in the free energy values for these reactions: +1.6 vs. +28.8 kcal.mol^{-1} for the formation of **6'** vs. **6''**, respectively. This is in line with the energies computed for [Cu(NHC)(HBEt$_3$)], (for which dissociation of BEt$_3$ has a ΔG of +10.8 kcal.mol^{-1}) and which describe a weaker Cu–H bond compared to **6**.[15] Overall, these data show that complex **6** features an electronic structure closer to a borane-stabilized copper hydride complex, that may behave as its terminal hydride close congener.

Conclusion

In conclusion, we have reported the synthesis and characterization of the new P$_3$N neutral and anionic ligands $\mathbf{2^H}$ and $\mathbf{2^K}$ and their copper(I) complexes **3** and **4**. Due to the close proximity to the metal center of the amide group in **4**, metal-ligand cooperativity was exploited for the first time with copper, as a new route to prepare hydride species by H$_2$ activation. Complex **4** reacted with H$_2$, in smooth conditions, to give either the trimetallic monohydride hydride **5** or the borate complex **6**, when BEt$_3$ is initially present in the reaction mixture. Complex **6**, a rare example of a stable M(μ-H–BEt$_3$) complex, behaves like a hydride complex with CO$_2$ and has an electronic structure close to the hydride complex [($\mathbf{2^H}$)Cu–H⋯(BEt$_3$)], where the terminal hydride copper complex is stabilized by a Lewis acid.

Acknowledgements

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