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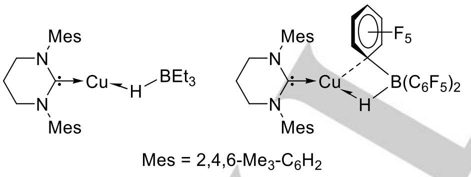
A Masked Cuprous Hydride as a Catalyst for Carbonyl Hydrosilylation in Aqueous Solutions

Florian Ritter, Debabrata Mukherjee, Thomas P. Spaniol, Alexander Hoffmann and Jun Okuda*

Abstract: Redox-unstable cuprous hydridotriphenylborate was isolated as an N-heterocyclic carbene adduct [(IPr)Cu(HBPh$_3$)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with good thermal stability. Despite a contact ion-pair structure, a Cu(I)H-like catalytic activity was envisaged in carbonyl hydrosilylation. Sufficient moisture stability allowed the catalysis in aqueous/organic media. Mechanistic study further showed a phenyl group abstraction by [(IPr)Cu]$^+$ from a borate anion to give a cationic organocopper complex [(IPr)$_2$Cu$_2$(μ-Ph)][BPh$_4$].

Molecular cuprous hydrides are important as mild and selective reducing agents, as intermediates in hydrofunctionalization, and in many other catalytic reactions.[1] They are difficult to isolate as a monomer due to the inherent redox-instability and pronounced aggregation tendency.[1f] Phosphines[2] and N-heterocyclic carbenes (NHCs)[3] are known to stabilize cuprous hydrides of lower nuclearity, but a monomeric "Cu(I)H" species has only been detected spectroscopically in solution.[4]

Recently Whittlesey et al. reported cuprous hydridoborates such as [(6Mes)Cu(HBR$_3$)] [6Mes = 1,3-dimesitylhexahydropyrimidine-2-ylidene; R = Et (**A**), C$_6$F$_5$ (**B**)], which may be regarded as surrogates for monomeric "Cu(I)H" (Fig. 1).[5] However, **A** is stable only below −30 °C, while **B** persists for ca. 12 h at room temperature. Computational studies identified them as contact ion-pairs consisting of [(6Mes)Cu]$^+$ and [HBR$_3$]$^-$ rather than as a borane adduct of monomeric cuprous hydrides [(6Mes)CuH•BR$_3$], despite the presence of Cu⋯H interactions.

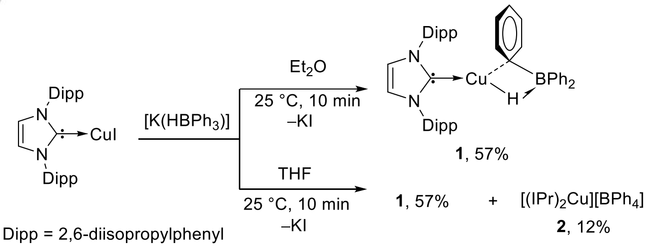


A **B**

Figure 1: NHC-bonded Cu(HBR$_3$); R = Et, B(C$_6$F$_5$)$_3$.[5]

Recently, we established hydridotriphenylborate [HBPh$_3$]$^-$ complexes of electropositive metals (Li, Na, K, Mg, Zn, Al) as chemoselective hydroboration catalysts for various polar substrates including CO$_2$.[6] Cu$^+$ has the same size as Li$^+$ [(r_{ionic} = 0.6 Å (Cu$^+$ for CN 4), 0.59 Å (Li$^+$ for CN 4)] but is more electronegative [χ_{Pauling} = 1.90 (Cu), 0.98 (Li)] and softer.[7] Given the stability difference between **A** and **B** and the increasing order of hydridicity ([HB(C$_6$F$_5$)$_3$]$^-$ < [HBPh$_3$]$^-$ < [HBEt$_3$]$^-$),[8] an NHC-bonded "Cu(HBPh$_3$)" may be compelling for further exploitation. Here we describe the synthesis, structure, and catalytic carbonyl hydrosilylation activity of an NHC-bonded "Cu(HBPh$_3$)" species.

Salt metathesis of [(IPr)CuI][9] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)[10] with K(HBPh$_3$)[6a] in Et$_2$O gave the NHC-bonded cuprous hydridotriphenylborate [(IPr)Cu(HBPh$_3$)] (**1**) in 57% yield (Scheme 1). **1** can be purified by recrystallization (see SI). Use of THF instead of Et$_2$O resulted in an unwanted side product [(IPr)$_2$Cu][BPh$_4$] (**2**) via carbene and phenyl ligand exchange (see below). **2** was independently synthesized from [(IPr)CuI] with [(IPr)H•BPh$_4$] and fully characterized including a crystal structure analysis (see SI). Whereas **A** or **B** were prepared by treating [(6Mes)CuO*t*Bu] with LiHBEt$_3$ or with PhMe$_2$SiH in the presence of B(C$_6$F$_5$)$_3$, respectively,[5] compound **1** was not accessible *via* any of these methods. The synthesis of **B** using Et$_3$SiH instead of PhMe$_2$SiH gave the by-product [(6Mes)$_2$Cu][B(C$_6$F$_5$)$_4$] that has a similar composition as **2**.[5]



Scheme 1: Synthesis of **1** by salt metathesis of IPrCuI with [K(HBPh$_3$)].

Dimeric NHC- and CAAC (cyclic amino alkyl carbene)-bonded cuprous hydrides are intensely colored (yellow to orange).[4, 11] **1** is colorless like **A** and **B**, soluble in aromatic hydrocarbons and stable for at least two days at 25 °C, or for several hours at 40 ˚C. It decomposes immediately at 60 ˚C. Dissolving **1** in THF or acetonitrile led to a complex mixture of **1**, **2**, and other minor species. An ancillary ligand-free "Cu(HBPh$_3$)" would be redox-unstable and decompose into Cu(0), BPh$_3$ and H$_2$, rendering this compound inaccessible like [Zn(HBPh$_3$)$_2$].[6d] Strong σ-donation and appropriate steric protection from IPr is

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critical for kinetic stabilization, since the corresponding [(IMes)Cu(HBPh$_3$)] (IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) was not isolable.

The crystal structure determined by X-ray diffraction shows the monomeric contact ion pair structure for **1**, similar to that of **A** and of **B**.[5] The anion [HBPh$_3$]$^-$ is bonded to [(IPr)Cu]$^+$ through the Cu···H–B interaction and an additional Cu···C$_{ipso}$ coordination from one of the three phenyl rings. The hydride position was located from a Fourier difference map and was refined. The Cu···H distance of 1.59(3) Å is similar to 1.55(3) Å in both **A** and **B**, but the Cu–C$_{ipso}$ contact of 2.166(2) Å is slightly shorter than 2.2183(17) Å found in **B**. The ∠IPr–Cu–H angle of 136.1(11)° is more acute than 162.8(14)° and 146.5(8)° in **A** and **B**, respectively.

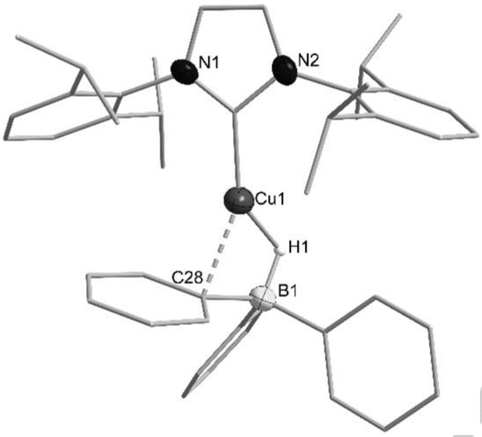


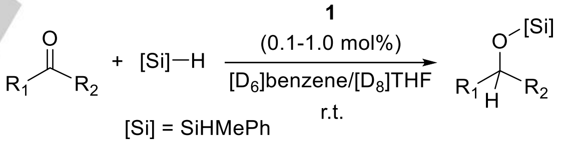
Figure 2: Molecular structure of **1**. Displacement parameters are set at 50% probability level; solvent molecules and hydrogen atoms except of H1 are omitted for clarity. Selected bond distances [Å] and angles [°]: Cu1–C1 1.888(3), Cu1–H1 1.59(3), B1–H1 1.17(3), Cu1–C28 2.166(2), ∠C1–Cu1–H1 136.1(11).

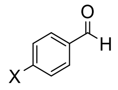
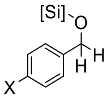
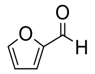
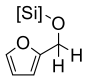
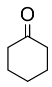
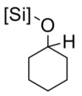
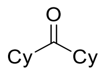
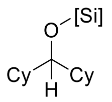
The ^{1}H NMR spectrum of **1** in [D$_6$]benzene shows the characteristic resonances of a coordinated IPr carbene and a [HBPh$_3$]$^-$ anion, but unlike the alkali metal salts, the $^1J_{BH}$ coupling is not apparent due to the broad *H*B (δ = 3.42 ppm). Signals for *B*H (δ = −10.5 ppm) in the ^{1}H and ^{11}B NMR spectra, were not resolved even at −60 °C. This suggests that a significant Cu···H–B interaction is maintained in solution. This may also explain the solubility difference between **1** and the alkali metal salts which are not soluble in aromatic hydrocarbons. The *H*B resonances of **A** (δ = −2.60 ppm at −64 °C) and **B** (δ = 2.08 ppm) are quite different.[5] The solid state IR (KBr) spectrum shows a broad absorption at ν_{BH} = 1693 cm^{-1}.

The extent of Cu···H···B interaction in **1** was probed by DFT calculations on the basis of the NBO analysis, the Wiberg bond indices and of the quantum theory of atoms in molecules (QTAIM) analysis.[12] The Wiberg bond indices (as implemented in Gaussian 09) show a high covalency of the B–H bond. The QTAIM analysis (see SI) detects an additional bond critical point between the Cu and H atoms but the interaction is weaker than the B–H bond. Second-order perturbation theory as implemented in NBO 6.0 gave four donor-acceptor interactions around copper. The C$_{ipso}$-Cu interaction is stabilized by 18.3 kcal/mol, the σC$_{carbene}$ → Cu donation amounts to 80.4 kcal/mol, and the σB-H → Cu donation to 26.3 kcal/mol. Additionally, the σB-C$_{ipso}$ bond donates to Cu by 9.9 kcal/mol. Comparing the NBO and the QTAIM charges of the whole complex with two hypothetical fragment pairs [(carbene)Cu]$^+$[HBPh$_3$]$^-$ or [(carbene)CuH] and [BPh$_3$] agreed better with the hydridoborate formulation.

The fair stability of **1** prompted us to test its activity in carbonyl hydrosilylation catalysis. [1d] The reduction of carbonyl groups with PhMeSiH$_2$ was catalyzed by 0.1-1.0 mol% of **1** under mild conditions in both benzene and THF (Table 1). Polymethylhydrosiloxane (PMHS) as reductant gave lower conversions. Aldehydes were expectedly easier to reduce and required less catalyst than ketones. Various *para*-substituted benzaldehydes containing electron donating and withdrawing groups (Table 1, entry 1) as well as furfural (Table 1, entry 2) were hydrosilylated with equal efficiency. The aliphatic cyclohexanone and dicyclohexylketone (Table 1, entry 3 and 4) were more reactive than acetophenone or benzophenone (Table 1, entry 5 and 6). The cinnamaldehyde and 2-cyclohexen-1-one were hydrosilylated in 1,2-fashion with 97% regioselectivity (Table 1, entry 7 and 8). The current system shows a better activity for carbonyl hydrosilylation when compared to other “NHC-Cu” catalysts reported in the literature.[13]

Table 1: Carbonyl hydrosilylation catalyzed by **1** using PhMeSiH$_2$.[a]



Entry	Substrate	Product	Cat. mol%	% Conv.[b]	Time (h)
1[c]			0.1	>95	<0.2
2			0.1	>95	<0.2
3			0.1	>95	4
4			1.0	>95	<0.2

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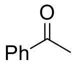
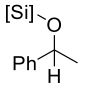
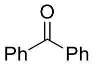
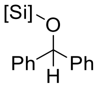
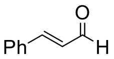
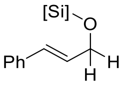
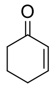
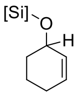
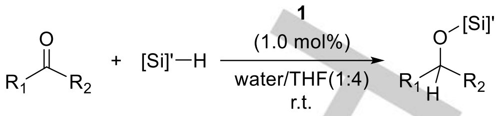
5			1.0	>95	16.5
6			1.0	>95	44
7[d]			0.1	>95	0.7
8[d]			1.0	>95	<0.2

(a) $n(PhMeSiH_2)$ = 0.18 mmol, n(substrate) = 0.18 mmol, 0.5 mL of [D$_6$]benzene. (b) % Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene (0.03 mM) as an internal standard. (c) X = H, Br, F, OMe, NO_2, Me, CN. (d) Trace amounts of C=C double bond reduction.

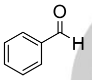
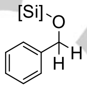
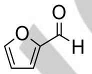
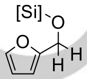
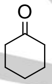
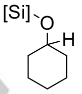
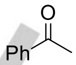
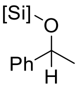
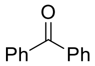
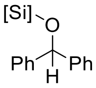
Complex **1** is surprisingly robust against moisture. A [D$_8$]THF solution containing 10% (v/v) of water remained visibly and spectroscopically unchanged at room temperature for at least 6 h. Standing for 24 h led to only ca. 10% decomposition. Catalysis in aqueous or aqueous/organic media by NHC-supported transition metal complexes including copper is of current interest.[14] Due to the poor solubility of **1**, the substrates, and tetramethyldisiloxane $(Me_2SiH)_2O$ in neat water, a H_2O/THF (1:4) mixture was used as solvent. As summarized in Table 2, the reaction time is significantly longer, likely due to inhomogeneity of the system. **1** can be generated in situ for catalysis by mixing [(IPr)CuI] and $KHBPh_3$ under N_2, followed by adding the THF/H_2O solvent mixture and a mixture of substrate and hydrosilane. However, a bench-top experiment run in open air did not lead to conversion.

Air- and moisture-sensitivity of cuprous hydrides vary with nuclearity and ligand encapsulation. Polymeric [CuH]▯ is produced in water, but dry [CuH]▯ is pyrophoric.[15] The hexameric Stryker's reagent $[(PPh_3)CuH]_6$ is also air-sensitive, but water-stable.[2] Dimeric cuprous hydrides are thermally unstable as well as against air and moisture.[4, 11, 16] Some chalcogen-stabilized polyhydrido copper clusters over a wide range of nuclearities (Cu_7 to Cu_{32}) on the other hand exhibit exceptional air and moisture stability.[17] Catalytically active cuprous hydrides including those supported by NHCs are often generated *in situ* during hydrosilylation.[1c, 1h, 3b, 3c] Protic reagents such as *t*-BuOH are used on many such instances to enhance reaction rates without impeding the catalyst's activity.[1c, 1h, 3b, 3c] The sensitivity of **A** and **B** against air and moisture were not reported, but both compounds are thermally less stable than **1**.[5]

Table 2: Carbonyl hydrosilylation catalyzed by **1** in a 4:1 water/THF mixture.



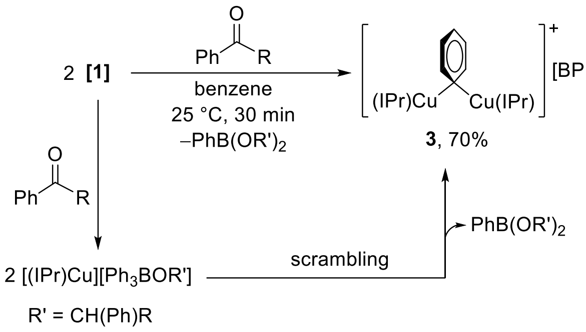
[Si]' = $SiMe_2$-O-$SiHMe_2$

Entry	Substrate	Product	% Conv.[b]	Time (h)
1			>95	19
2			78	24
3			58	26
4			>95	19
5			74	26

(a) $n((Me_2SiH)_2O)$ = 0.18 mmol, n(substrate) = 0.18 mmol, 0.2 mL of D_2O and 0.8 mL of THF (1:4). (b) % Conversion determined by ^{1}H NMR spectroscopy using hexamethylbenzene (0.03 mM) as an internal standard.

Complex **1** also catalyzed the carbonyl hydroboration with pinacolborane (HBpin). Similar to the alkali metal salts,[6a] **1** did not react with polar and nonpolar functional groups such as imine, amide, ester, nitrile, olefin, and internal alkyne under stoichiometric as well as catalytic conditions. Reaction with pyridine led to decomposition.

Reaction between **1** and PhC(O)R (R = H, Ph) in benzene/[D$_6$]benzene unexpectedly precipitated an ionic complex identified as $[(IPr)_2Cu_2(\mu\text{-}Ph)][BPh_4]$ (**3**) in 70% yield (Scheme 3). The same outcome was obtained using THF or Et_2O, except that **3** remained soluble. Monitoring the reactions in [D$_6$]benzene by ^{1}H NMR spectroscopy revealed fast carbonyl insertion to give $[(IPr)Cu][Ph_3BOR']$ (R' = CHPhR), followed by phenyl and alkoxy group migrations to ultimately precipitate **3** (Scheme 3). The actual scrambling process is complicated as signals of several other boranes and borates were detected by ^{11}B NMR spectroscopy. Intriguingly, **1** is stable toward such exchange process in benzene or Et_2O, but the more polar solvents like THF or acetonitrile trigger the formation of **2**.



Scheme 2: Formation of **3** via phenyl abstraction by [(IPr)Cu]$^+$.

Organocopper(I) chemistry is dominated by cuprates $[CuR_2]^-$ and neutral clusters $[CuR]_n$,[18] whereas cationic complexes with bridging aryl groups are rare. Apart from **3**, few other examples include $[Cu_3Ph_2(pmdta)_2][Cu_5Ph_6]$ (PMDTA = *N*,*N*,*N*',*N*",*N*"-pentamethyldiethylenetriamine)[19] and $[Cu_2(\mu\text{-}\eta^1{:}\eta^1\text{-Ar})(DPFN)]X$ (Ar = C_6H_5, 3,5-$(CF_3)_2$-C_6H_3, and C_6F_5; DPFN = 2,7-bis(fluoro-di(2-pyridyl)methyl)-1,8-naphthyridine; X = BAr_4^- and NTf_2^-; Tf = SO_2CF_3).[20] These DPFN complexes were obtained in a similar manner from the dicationic $[Cu_2(\mu\text{-}\eta^1{:}\eta^1\text{-}NCCH_3)(DPFN)]X_2$ (X = PF_6^- and NTf_2^-) by aryl group abstraction from $[BAr_4]^-$ anions. This was explained by the constrained geometry of the $[Cu_2(DPEN)]^{2+}$ motif and the cooperative electrophilic effect exhibited by the two Cu^+ centers in close proximity. Aryl group transfer from boron to copper centers is also common in copper mediated C–C coupling reactions.[21] The same carbene IPr stabilizes a μ-hydrido dicopper cation as $[(IPr)_2Cu_2(\mu\text{-}H)][A]$ (A = BF_4^-, OTf^-).[22] Interestingly, the cationic μ-aryls react with acidic alkynes under protonation to give cationic μ-alkynyl dicopper complexes,[23] while the μ-hydride reacts with the alkynes under insertion to give μ-vinyl derivatives.[22b]

The solid-state structure of **3** exhibits two IPr-bonded copper centers with three-coordinate geometry, bridged symmetrically by a phenyl ligand [Cu1−C55: 1.964(2) Å; Cu2−C55: 1.962(2) Å]; the phenyl moiety shows no preferential inclination toward either copper center. The Cu···Cu distance of 2.5373(4) Å is longer than 2.3927(5) Å in $[Cu_2(\mu\text{-}\eta^1{:}\eta^1\text{-Ph})(DPFN)][BPh_4]$.[20b] The ^1H NMR spectrum of **3** in $[D_8]$THF shows the characteristic resonances of a coordinated IPr and $[BPh_4]^-$ anion in 2:1 ratio. Signals of the bridging phenyl group appeared broad, likely due to free rotation across the Cu···Cu motif which was not the case for $[Cu_2(\mu\text{-}\eta^1{:}\eta^1\text{-Ph})(DPFN)]BPh_4$ due to its rigid geometry.[20b]

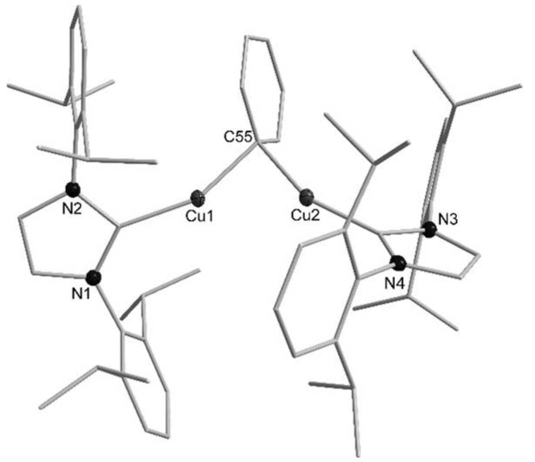


Figure 3: Molecular structure of **3.** Displacement parameters are set at 50% probability level; solvent molecules, hydrogen atoms and the $[BPh_4]^-$ anion are omitted for clarity. Selected bond distances [Å] and angles [°]: Cu1-C1 1.908(2), Cu1-Cu2 2.5373(4), Cu1-C55 1.964(2), Cu2-C55 1.962(2), C1-Cu1-C55 154.32(9), C28-Cu2-C55 156.89(8).

The reaction between **1** and PhCHO (1:1) with an excess of $PhMeSiH_2$ in $[D_6]$benzene gave only $PhMeSiHOCH_2Ph$ and regenerated **1**. Conversely, the reaction of **1** and $PhMeSiH_2$ (1:1) with an excess of PhCHO gave the silyl ether and **3**. Thus, the formation of **3** depends on the reaction stoichiometry and is not operative under catalytic condition as long as hydrosilane is present. Complex **3** is a much poorer catalyst than **1** for carbonyl hydrosilylation (see SI). Free BPh_3 is also incapable of hydrosilylation catalysis under this condition.[24]

In conclusion, the redox-unstable "$Cu(HBPh_3)$" has been stabilized by the N-heterocyclic carbene IPr as a contact ion-pair **1**, whose thermal and moisture stability is notable. It shows catalytic carbonyl hydrosilylation activity in aqueous media. Formation of the cationic cuprous aryl complex **3** by phenyl abstraction highlights the electrophilicity of Cu^+, despite being coordinated to the strong σ-donor IPr.

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Keywords: Copper • Hydridotriphenylborate • Carbonyl reduction • Hydrosilylation • Catalysis in water

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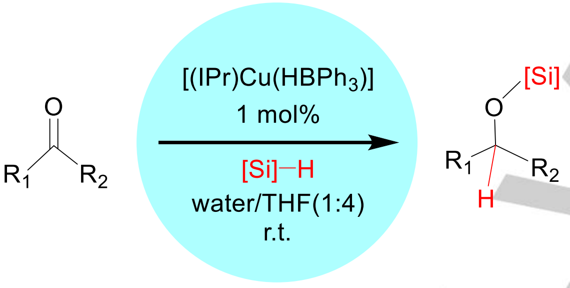
COMMUNICATION

Monomeric Cu($HBPh_3$) supported by an N-heterocyclic carbene catalyzed the carbonyl hydrosilylation in water as a co-solvent.



Catalysis by "CuH"

*Florian Ritter, Debabrata Mukherjee, Thomas P. Spaniol, Alexander Hoffmann, Jun Okuda**

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A Masked Cuprous Hydride as a Catalyst for Carbonyl Hydrosilylation in Aqueous Solutions