

# Preparation, reactivity and photoluminescence of copper(I) borohydride complexes with bis[(2-diphenylphosphino)phenyl] ether as chelating ligand

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## ABSTRACT

Bis[(2-diphenylphosphino)phenyl] ether (DPEphos) was used as chelating ligand to prepare the corresponding borohydride complex  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$ , whose structure was ascertained spectroscopically and by means of X-ray diffraction. The spectroscopic assignments related to the coordinated borohydride were confirmed by preparing the isotopologue  $[\text{Cu}(\kappa^2\text{-BD}_4)(\text{DPEphos})]$ . Reaction of  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$  with triflic acid afforded the dimer  $[\text{Cu}_2(\mu\text{-BH}_4)(\text{DPEphos})_2][\text{OTf}]$  (OTf = triflate). The borohydride complexes exhibited appreciable blue emission upon excitation with UV light at room temperature.  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$  revealed to be a suitable precursor for the preparation of luminescent heteroleptic copper(I) complexes having general formula  $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{DPEphos})]^+$  ( $\text{N}^{\wedge}\text{N}$  = 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine).

## 1. Introduction

Metal borohydride complexes were deeply investigated since the Sixties because of their possible use as solid-state ion conductors in batteries or in energy storage technology [1]. Another field of application of borohydride complexes is catalysis, for instance iron(II), zinc(II) and titanium(III) derivatives were successfully applied in the hydrogenation of aldehydes and ketones [2]. The zinc(II) complexes revealed to be active also in reductive amination reactions [3]. Rare earths-based borohydride complexes were recently applied as polymerization catalysts, and the borohydride ligand showed different behaviour depending upon the nature of the monomers considered [4].

Copper(I) complexes have been known from a long time [5], frequently in combination with mono- or bidentate phosphines, or phosphites [6]. The most common coordination mode for the borohydride ion is  $\kappa^2$  [7], but  $\kappa^1\text{-BH}_4$  derivatives were reported in a number of cases [7a,8]. The reactivity towards  $\text{CO}_2$  and heteroallenes was investigated [8b], wherein  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{PPh}_3)_2]$  and related compounds were widely used as selective reducing agents for carbonyl compounds [9]. The same species revealed to

be efficient catalysts for the photosensitized isomerization of dienes [10], while the formal replacement of the phosphine ligands with a bulky cyclic carbene afforded a complex which is able to catalyse the hydrolytic dehydrogenation of  $\text{BH}_3\text{NH}_3$  [11]. Intriguing catalytic activity was recently observed also for related hydridoborate species, such as  $\{[\text{IPr}]\text{Cu}(\text{HBPh}_3)\}$  (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-yl-idene) for carbonyl hydrosilations in aqueous solution [12].

The photophysical properties of metal borohydrides were less investigated. One of the most interesting examples is the Eu(II) borohydride coordination polymer reported by Roesky *et al.*, that exhibited blue luminescence with a quantum yield of 75% [13]. In the case of Cu(I) complexes, blue photoluminescence was observed for  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{PPh}_3)_2]$  and  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{dppp})_2]$  (dppp = 1,3-bis(diphenylphosphino)propane) after cooling down the samples at 77 K [14].

Our research group is currently investigating on first row transition metal complexes exhibiting peculiar luminescent properties that could be exploited in advanced technology [15]. The first copper complexes having bis[(2-diphenylphosphino)phenyl] ether (DPEphos) as P-donor ligand were reported by Venkateswaran *et al.* [16]. Several DPEphos complexes are of interest for their photophysical properties, despite the scarce luminescence of the free ligand [17]. In the case of Cu(I) species, the presence of a wide P–Cu–

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P angle improves the charge transfer processes and increases the emission lifetimes [18]. Copper(I) borohydride complexes were recently used by our research group as precursors to afford luminescent heteroleptic complexes with benzotriazole derivatives [15c]. Herein, we report the synthesis, characterization and single crystal X-ray structure determination of a new borohydride complex having formula  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$ . The compound was easily converted into the dimer  $[\text{Cu}_2(\mu\text{-BH}_4)(\text{DPEphos})_2][\text{OTf}]$  (OTf = triflate) by reaction with triflic acid. Both the borohydride complexes exhibited bright blue photoluminescence at room temperature.  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$  also revealed to be a suitable precursor for the preparation of luminescent heteroleptic complexes with chelating N-donor ligands in the coordination sphere [19].

## 2. Experimental section

### 2.1. Materials and methods

Commercial solvents (Merck) were purified following reported procedures [20]. The other reagents were Merck products used as received. CuCl was synthesized according to literature procedures using sodium sulphite as reducing agent and stored in a glove box to avoid decomposition [21]. The syntheses of the complexes were performed using common Schlenk techniques. Elemental analyses were carried out using an Elementar Unicube microanalyzer. The conductivity of acetone solutions of the complexes was measured with a Radiometer Copenhagen CDM83 instrument. Melting point measurements were carried out using a modified Falc 360 D apparatus equipped with a video recording device. TGA measurements were carried out under  $\text{N}_2$  atmosphere with a Linseis STA PT 1000 instrument. The heating rate was set at  $10\text{ }^\circ\text{C min}^{-1}$ . IR spectra were collected in the  $4000\text{--}400\text{ cm}^{-1}$  range using a PerkinElmer Spectrum One spectrophotometer. Nuclear magnetic resonance (NMR) spectra were collected at variable temperature employing Bruker Avance 300 and Avance 400 instruments operating respectively at 300.13 MHz and 400.13 MHz of  $^1\text{H}$  resonance.  $^1\text{H}$  and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra are referred to the partially non-deuterated fraction of the solvent, itself quoted to tetramethylsilane.  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR and  $^{11}\text{B}$  NMR resonances are respectively referred to 85%  $\text{H}_3\text{PO}_4$  in water and  $\text{BF}_3\cdot\text{Et}_2\text{O}$  complex in  $\text{CDCl}_3$ . The bandwidth of the  $^{31}\text{P}$  and  $^{11}\text{B}$  resonances is expressed as full width at half maximum (FWHM).  $^{19}\text{F}$  chemical shifts are referred to  $\text{CCl}_3\text{F}$ . UV-vis absorption spectra were collected for dichloromethane solutions using a PerkinElmer Lambda 40 spectrophotometer. Photoluminescence emission (PL) and excitation (PLE) measurements were carried out at room temperature on solid samples using a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer. A continuous-wave xenon arc lamp was used as source selecting the excitation wavelength using a double Czerny-Turner monochromator. A single grating monochromator coupled to a photomultiplier tube was used as detection system for optical emission measurements. Excitation and emission spectra were corrected for the instrumental functions. Time-resolved analyses were performed in Multi Channel Scaling mode (MCS) by using Horiba SpectralLED pulsed sources centred at 265, 290 and 445 nm, or in Time-Correlated Single Photon Counting mode (TCSPC), using a Horiba NanoLED pulsed source centred at 373 nm coupled with a 400 nm shortpass filter (declared pulse duration 1.3 ns). The experimental setup for measurements in the nanosecond range was checked using anthracene in methanol as standard (5 ns lifetime) and data were elaborated with the Horiba DAS6 software. The photoluminescence quantum yields ( $\Phi$ ) of the complexes (solid state, r.t.) were measured employing a OceanOptics HR4000CG UV-NIR detector, fiber-coupled to an integrating sphere connected to an OceanOptics LED source centred at 365 nm.

### 2.2. X-Ray structure determination

Crystallographic data were collected at CACTI (Universidade de Vigo) at 100 K (CryoStream 800) using a Bruker D8 Venture Photon II CMOS detector and Mo- $K\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) generated by a Incoatec Microfocus Source  $\mu\text{S}$ . The software APEX3 was used for collecting frames of data, indexing reflections, and the determination of lattice parameters [22], software SAINT for integration of intensity of reflections [22], and SADABS for scaling and empirical absorption correction [22]. The crystallographic treatment was performed with the Oscal program [23], solved using the SHELXT program [24]. The structure was subsequently refined by a full-matrix least-squares based on  $F^2$ , using the SHELXL program [25]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters, except those bonded to the boron atoms that were found in the final density map and refined isotropically. Other details concerning crystal data and structural refinement are given in Table S1. CCDC 2106874 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). PLATON (version 60720) was used to obtain some geometrical parameters of the cif file [26].

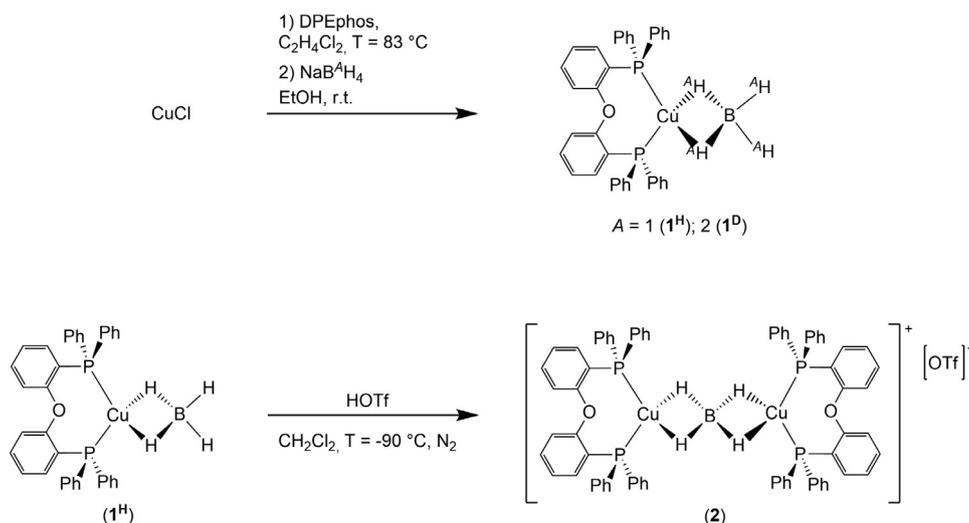
### 2.3. DFT calculations

The ground-state geometry optimizations of  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$  and  $[\text{Cu}_2(\mu\text{-BH}_4)(\text{DPEphos})_2]^+$  were carried out using the range-separated hybrid DFT functional  $\omega\text{B97X}$  [27]. The basis sets considered were Alhrichs' split-valence polarized def2-TZVP and def2-SVP, respectively for the mononuclear and the dinuclear complex [28]. The stationary points were characterized by IR simulation (harmonic approximation). The software used was Orca 4.2.0 [29].

### 2.4. Synthesis and characterization of $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$ (**1<sup>H</sup>**) and $[\text{Cu}(\kappa^2\text{-BD}_4)(\text{DPEphos})]$ (**1<sup>D</sup>**)

A stirred solution containing 0.500 g of CuCl (5.0 mmol) and 2.692 g of DPEphos (5.0 mmol) in dichloroethane was heated at  $83\text{ }^\circ\text{C}$  under  $\text{N}_2$  atmosphere for one hour. After allowing the reaction mixture to cool at room temperature, a solution of 10.0 mmol of  $\text{NaBH}_4$  or  $\text{NaBD}_4$  in ethanol was added dropwise to the previous one. The solution was left under stirring at room temperature overnight, then the solvents were evaporated under reduced pressure. The crude product separated as white solid by addition of 5 mL of ethanol and were collected by filtration and dried *in vacuo*. The purification was performed by dissolution in dichloromethane (20 mL), followed by filtration. Ethanol (20 mL) was then added and the solution was concentrated under reduced pressure until a white solid started to separate. After cooling at  $-20\text{ }^\circ\text{C}$  for one hour, the product was collected by filtration. Yield: 60% (1.856 g for **1<sup>H</sup>** and 1.845 g for **1<sup>D</sup>**) in both the cases. Crystals of **1<sup>H</sup>** suitable for X-ray diffraction were collected from dichloromethane and diethyl ether solutions.

*Characterization of  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$  (**1<sup>H</sup>**).* Anal. calcd for  $\text{C}_{36}\text{H}_{32}\text{BCuOP}_2$  (616.95  $\text{g mol}^{-1}$ ): C, 70.09; H, 5.23. Found (%): C, 69.81; H, 5.25. M.p. > 503 K (dec.). TGA mass loss > 570 K.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  7.53–7.43 (m, 8H, DPEphos), 7.40–7.27 (m, 12H, DPEphos), 7.20 (td, 2H,  $J_{\text{HH}} = 8.0\text{ Hz}$ ,  $J_{\text{HH}} = 1.5\text{ Hz}$ , DPEphos), 6.96–6.86 (m, 4H, DPEphos), 6.74–6.68 (m, 2H, DPEphos), 1.52–0.66 (m, 4H,  $\text{BH}_4$ ).  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  -15.48 (FWHM = 36 Hz).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 298 K)  $\delta$  157.86 (t,  $J_{\text{PC}} = 6.0\text{ Hz}$ ), 134.26, 134.16 (t,  $J_{\text{PC}} = 8.6\text{ Hz}$ ), 131.14, 129.99, 128.58 (t,  $J_{\text{PC}} = 5.0\text{ Hz}$ ), 124.44 (t,  $J_{\text{PC}} = 2.2\text{ Hz}$ ), 119.88 (t,  $J_{\text{PC}} = 1.9\text{ Hz}$ ).



**Scheme 1.** Synthesis of Cu(I) borohydride complexes.

P-bonded carbons not detected.  $^{11}B$  NMR ( $CDCl_3$ , 298 K)  $\delta$  -32.13 (quint, br,  $^1J_{BH} = 74$  Hz). IR (KBr,  $cm^{-1}$ ): 3050–3005 w (aromatic  $\nu_{C-H}$ ), 1690–1560 (aromatic  $\nu_{C-C}$ ), 2402 sh, 2371 m ( $\nu_{B-H,terminal}$ ), 1992 m, 1947 m ( $\nu_{B-H,bridging}$ ). UV-vis ( $CH_2Cl_2$ , 298 K)  $\lambda_{excitation} < 350$ , 250 (max), 273 (sh). PL (solid, r.t.,  $\lambda_{excitation} = 290$  nm, nm): 465 (FWHM =  $3400\text{ }cm^{-1}$ ). PLE (solid, r.t.,  $\lambda_{emission} = 470$  nm, nm)  $< 390$ .  $\tau$  (r.t.,  $\lambda_{excitation} = 373$  nm,  $\lambda_{emission} = 470$  nm, ns): 2.2.  $\Phi$  (solid, r.t.,  $\lambda_{excitation} = 365$  nm): 12%.

**Characterization of  $[Cu(\kappa^2-BD_4)(DPEphos)]\text{ (}^1D\text{)}$ .**  $^1H$  NMR ( $CDCl_3$ , 298 K)  $\delta$  7.55–7.40 (m, 8H, DPEphos), 7.40–7.27 (m, 12H, DPEphos), 7.21 (td, 2H,  $J_{HH} = 7.8$  Hz,  $J_{HH} = 1.4$  Hz, DPEphos), 6.95–6.85 (m, 4H, DPEphos), 6.78–6.69 (m, 2H, DPEphos).  $^{31}P$   $\{^1H\}$  NMR ( $CDCl_3$ , 298 K)  $\delta$  -15.44 (FWHM = 42 Hz).  $^{11}B$  NMR ( $CDCl_3$ , 298 K)  $\delta$  -32.37 (FWHM = 144 Hz). IR (KBr,  $cm^{-1}$ ): 3070–3000 w (aromatic  $\nu_{C-H}$ ), 1680–1560 m (aromatic  $\nu_{C-C}$ ), 1807 m, 1740 m ( $\nu_{B-D}$ ). PL (solid, r.t.,  $\lambda_{excitation} = 290$  nm, nm): 465. PLE (solid, r.t.,  $\lambda_{emission} = 470$  nm, nm)  $< 390$ .  $\tau$  (r.t.,  $\lambda_{excitation} = 373$  nm,  $\lambda_{emission} = 470$  nm, ns): 4.5.  $\Phi$  (solid, r.t.,  $\lambda_{excitation} = 365$  nm): 12%.

### 2.5. Synthesis and characterization of $[Cu_2(\mu-BH_4)(DPEphos)_2][OTf]$ ( $OTf = triflate$ ), (**2**)

The complex was prepared by adapting a reported procedure [30].  $[Cu(\kappa^2-BH_4)(DPEphos)]$  (0.617 g, 1.0 mmol) was dissolved in 20 mL dichloromethane. The solution was put under nitrogen atmosphere and frozen with a liquid nitrogen bath. Trifluoromethanesulfonic acid (HOTf, 44  $\mu L$ , 0.5 mmol) was added with a microsyringe and the mixture was allowed to warm at room temperature under stirring. After 30 min the solvent was evaporated under reduced pressure and the product was precipitated by addition of 10 mL of diethyl ether. The white solid was filtered, washed with diethyl ether and dried *in vacuo*. Yield: 60% (0.366 g).

**Characterization of  $[Cu_2(\mu-BH_4)(DPEphos)_2][OTf]$ , (**2**).** Anal. calcd for  $C_{72}H_{60}BCu_2O_2P_4$  (1219.07 g  $mol^{-1}$ ): C, 70.94; H, 4.96. Found (%): C, 70.66; H, 4.98. M.p.  $> 503$  K (dec.). TGA mass loss  $> 620$  K.  $\Lambda_M$  (acetone, 298 K):  $124\text{ }ohm^{-1}mol^{-1}cm^2$ .  $^1H$  NMR ( $CDCl_3$ , 298 K)  $\delta$  7.55–7.20 (m, 22H, DPEphos), 6.99 (t, 2H,  $J_{HH} = 7.5$  Hz, DPEphos), 6.89 (m, 2H, DPEphos), 6.78–6.71 (m, 2H, DPEphos), 1.87 (quart, 4H,  $^1J_{BH} = 76$  Hz,  $BH_4$ ).  $^{31}P$   $\{^1H\}$  NMR ( $CDCl_3$ , 298 K)  $\delta$  -13.96 (FWHM = 112 Hz).  $^{13}C$   $\{^1H\}$  NMR ( $CDCl_3$ , 298 K)  $\delta$  157.77, 134.20, 133.81 (t,  $J_{PC} = 6.7$  Hz), 131.89, 130.50, 128.83 (t,  $J_{PC} = 4.7$  Hz), 124.80, 119.74. P-bonded and  $CF_3$  carbons not detected.  $^{11}B$  NMR ( $CDCl_3$ , 298 K)  $\delta$  -30.38 (quint,  $^1J_{BH} = 76$  Hz).

$^{19}F$  NMR ( $CDCl_3$ , 298 K)  $\delta$  -77.78 (FWHM = 13 Hz). IR (KBr,  $cm^{-1}$ ): 3070–3005 w (aromatic  $\nu_{C-H}$ ), 2121 m ( $\nu_{B-H,bridging}$ ), 1590–1560 m/w (aromatic  $\nu_{C-C}$ ), 1030 m ( $\nu_{S=O}$ ). PL (solid, r.t.,  $\lambda_{excitation} = 350$  nm, nm): 476. PLE (solid, r.t.,  $\lambda_{emission} = 470$  nm, nm)  $< 390$ .  $\tau$  (r.t.,  $\lambda_{excitation} = 373$  nm,  $\lambda_{emission} = 470$  nm, ns): 5.0.  $\Phi$  (solid, r.t.,  $\lambda_{excitation} = 365$  nm): 14%.

## 3. Results and discussion

### 3.1. Synthesis and characterization of the complexes

The copper(I) borohydride complex  $[Cu(\kappa^2-BH_4)(DPEphos)]$  (**1<sup>H</sup>**) was prepared in two steps, first heating CuCl and DPEphos in dichloroethane at reflux for one hour, then by adding a solution of NaBH<sub>4</sub> in ethanol to the reaction mixture (Scheme 1). The synthetic procedure was extended to the isotopologue **1<sup>D</sup>**, using NaBD<sub>4</sub> as reactant, with the aim of unambiguously assigning the IR and NMR signals and to verify possible influences of the change of isotope on the luminescence features (*vide infra*).

Elemental analyses are in agreement with the proposed formulae and acetone solutions of **1<sup>H</sup>** and **1<sup>D</sup>** are non-conductive. TGA measurements on complex **1<sup>H</sup>** showed that the mass loss starts at 570 K, thus indicating good thermal stability (see Fig. S1). The  $^1H$  NMR spectrum of **1<sup>H</sup>** reported in Fig. 1 shows, besides the signals attributable to the phosphine in the region between 7.47 and 6.68 ppm, two broad multiplets of comparable intensity in the high-frequency region attributable to the borohydride moiety, broadened by quadrupolar relaxation. The  $^{13}C$   $\{^1H\}$  NMR and HSQC  $^1H$ - $^{13}C$  NMR spectra are reported in the Supporting Information for completeness (Fig. S2-S3). The  $^{31}P$   $\{^1H\}$  NMR and the  $^{11}B$  NMR spectra show respectively a singlet at -15.48 ppm and a broad quintet at -32.13 ppm with  $^1J_{BH}$  equal to 74 Hz (Fig. 1). The  $^1H$  and  $^{11}B$  NMR resonances related to the borohydride ligand are comparable to those of the known complex  $[Cu(\kappa^2-BH_4)(PPh_3)_2]$  and agree with  $\kappa^2$ -coordination mode. As expected, no signal in the 2.0–1.0 ppm range was detected in the  $^1H$  NMR spectrum of the **1<sup>D</sup>** isotopologue (Fig. S4), and no multiplicity was appreciated in the broad  $^{11}B$  NMR resonance of **1<sup>D</sup>** because of the lower gyromagnetic ratio of deuterium with respect to protium (Fig. S4).

Further confirmation of the presence of  $\kappa^2$ -BH<sub>4</sub> in the coordination sphere of the complex was given by the IR spectrum of **1<sup>H</sup>**, where two groups of signals are observable, one between 2240 and 2370  $cm^{-1}$  and the other one in 1940–1990  $cm^{-1}$  interval, respectively related to the asymmetric and symmetric stretchings of the

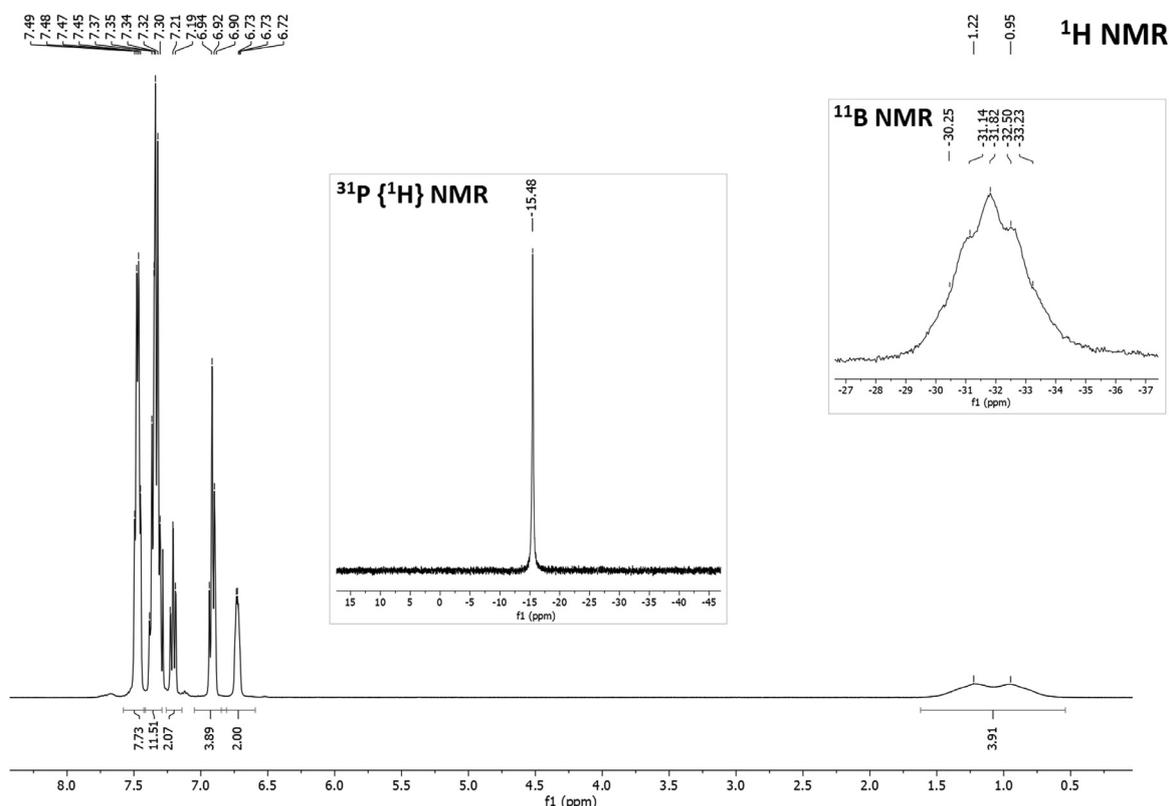


Fig. 1.  $^1\text{H}$  NMR,  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR and  $^{11}\text{B}$  NMR spectra of  $1^{\text{H}}$  in  $\text{CDCl}_3$  at 298 K.

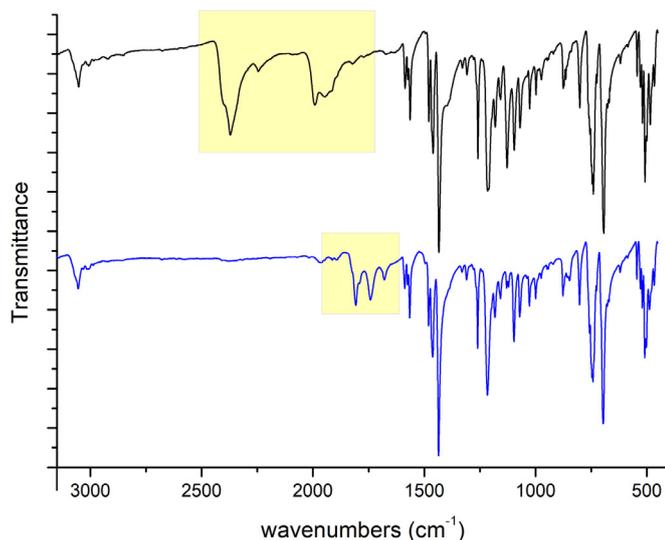


Fig. 2. IR of  $1^{\text{H}}$  (black line) and  $1^{\text{D}}$  (blue line). Bands related to B-H and B-D stretchings are highlighted in yellow.

terminal and bridging B-H bonds. As observable in Fig. 2, both the groups of signals are shifted at lower wavenumbers in the case of the  $1^{\text{D}}$  isotopologue.

Crystals of  $1^{\text{H}}$  suitable for X-ray diffraction were collected by slow diffusion of diethyl ether in dichloromethane solutions. Fig. 3 shows an ellipsoid plot of the two molecules found in the asymmetric unit [31]. The unit cell contents are shown in Figure S5 while crystal data and structure refinement are collected in Table S1. The two complexes do not show important differences in the geometrical parameters (see Table S2, where the values were carefully ordered). These values are not very different from the re-

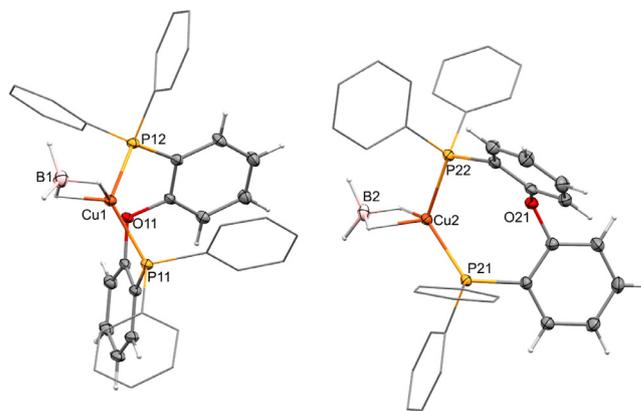
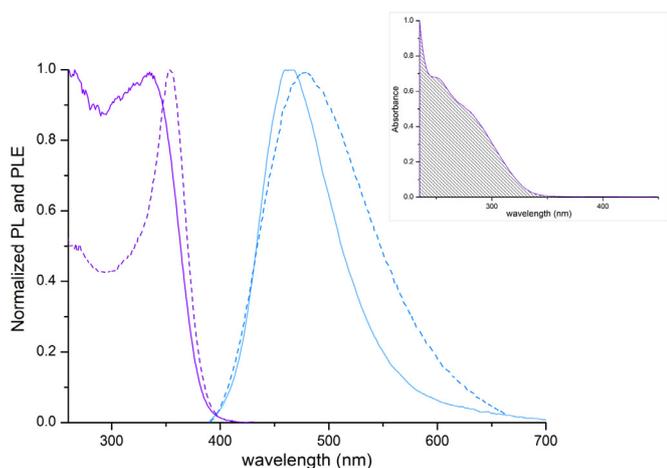


Fig. 3. Ellipsoid plot of the molecules in the asymmetric unit of  $1^{\text{H}}$ .

cently revised (tetrahydroborato)bis(triphenylphosphine)copper(I) [32] or related compounds such as  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{Cy}_3\text{P})_2]$ ,  $[\text{Cu}(\kappa^2\text{-BH}_4)(p\text{-tolyl}_3\text{P})_2]$  or  $[\text{Cu}(\kappa^2\text{-BH}_4)(p\text{-MeO-Ph}_3\text{P})_2]$  [33]. The average Cu-P bond lengths are 2.26 and 2.24 Å respectively in the first and second molecule of the asymmetric unit. The Cu-P distances are shorter than those reported for  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{PPh}_3)_2]$ , equal to 2.78 Å, but similar to those found in  $[\text{Cu}(\kappa^2\text{-BH}_4)(p\text{-MeO-Ph}_3\text{P})_2]$ , equal to 2.2462(9) Å. The P-Cu-P angles are 111.66(2) and 116.19(2)° in the two molecules of the asymmetric unit, similar to the values found in other Cu-DPEphos complexes [17d]. The P-Cu-B angles resulted to be asymmetric, being the values about 112° and 136° (see Table S2). The non-bonding Cu...B distances, 2.170(2) and 2.1564(18) Å in the two molecules, are shorter than the values in the 2.18–2.23 Å range reported for the above-mentioned compounds. The position of the hydrogen atoms bonded to the boron was found in the residual density and re-



**Fig. 4.** Normalized PL and PLE spectra (solid sample,  $\lambda_{\text{excitation}} = 290$  nm,  $\lambda_{\text{emission}} = 470$  nm, r.t.) of **1<sup>H</sup>** (solid line) and **2** (dashed line) Inset: absorption spectrum,  $10^{-5}$  M dichloromethane solution.

fined isotropically by using the usual procedure on SHELXL. Besides its typical inaccuracy [32b], the bridging hydrogen atoms are characterized by slightly longer B–H bonds with respect to the non-bridging ones. Moreover, the B–H bonds of the non-bridging hydrogen atoms are not identical between them, differently from the related compounds that exhibit in most of the cases crystallographic symmetry. In any case, these values are similar to those outlined for previously mentioned complexes [32b]. Instead, the Cu–H bonds, comprised between 1.67(3) and 1.75(2) Å, are only imperceptibly shorter. The most significant distinction between the two complexes in the asymmetric unit relies on the fact that the copper atoms lie at 0.031(1) and 0.116(1) Å from the plane defined

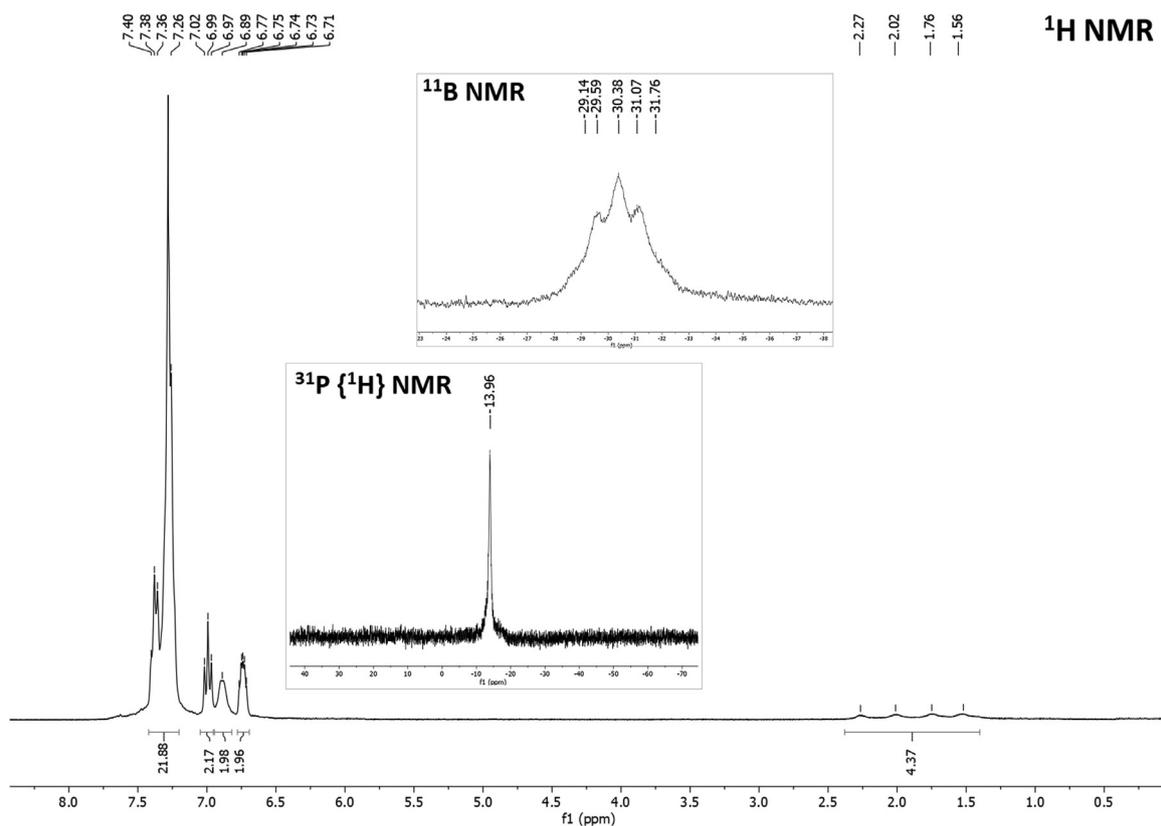
by the phosphorus and the boron atom, as observable from the superimposition depicted in Fig. S6.

In conclusion, the coordination of the copper atom resulted to be tetrahedral with  $\tau_4$  parameters respectively of 0.88 and 0.85 for the two molecules [34]. Noteworthy, the coordination of the  $\kappa$ -BH<sub>4</sub> to the copper ion is symmetrical in one of the molecules, while in the other one the Cu–H bond lengths show differences of around 0.05 Å (see Table S2). However, these differences are not enough to define the bond as asymmetric, if compared to values up to 0.15 Å found in Ni(II) borohydride complexes [35].

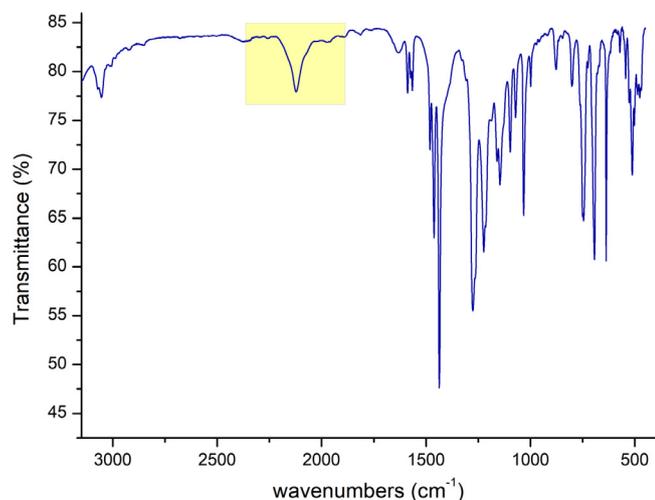
The  $\kappa^2$  coordination mode of borohydride was further confirmed by means of DFT calculations. The DFT-optimized structure of **1<sup>H</sup>** is shown in Fig. S7 (see Table S3 for the Cartesian coordinates). Experimental and computed bond lengths and angles are compared in Table S4. The most important difference is related to Cu–H and B–H distances, slightly longer in the DFT-optimized structure, a result attributable to the approximate localization of the hydrogen atoms by means of X-ray diffraction.

The frontier orbitals of the complex are depicted in Fig. S7. The HOMO is localized on the metal centre, the aromatic rings of DPEphos and also on the terminal B–H bonds. On the other hand, the LUMO is the combination of orbitals on Cu and DPEphos, with negligible participation of the borohydride ligand.

The complexes **1<sup>H</sup>** and **1<sup>D</sup>** are characterized by absorptions below 350 nm in dichloromethane solutions (inset of Fig. 4), in agreement with the bands reported for the free ligand and related to the  $\pi$ - $\pi^*$  transitions of the DPEphos [36]. The photoluminescence in solution is weak, but the excitation of solid samples in the UV region determined an emission in the blue region centred at 465 nm, as shown in Fig. 4 for **1<sup>H</sup>** (see also the CIE 1931 chromaticity diagram in Fig. S8). Emission in the same range was detected for the Cu(I) complex [Cu{BH(7-azaindolate)<sub>3</sub>}(PPh<sub>3</sub>)] in frozen dichloromethane [37].



**Fig. 5.** <sup>1</sup>H NMR, <sup>31</sup>P {<sup>1</sup>H} and <sup>11</sup>B NMR spectra of **2** in CDCl<sub>3</sub> at 298 K.



**Fig. 6.** IR spectrum of **2** in KBr pellets. Bands related to B-H stretchings are highlighted in yellow.

Quite surprisingly, the photoluminescence quantum yields of **1<sup>H</sup>** and **1<sup>D</sup>** are roughly the same, around 12%, this suggesting poor vibrational coupling of the emitting excited state with the borohydride ligand. It is worth noting that the free ligand is scarcely luminescent at solid state, characterized by an emission maximum at 443 nm and 3% of quantum yield [17e]. The radiative decays of **1<sup>H</sup>** and **1<sup>D</sup>** are fast processes. First attempts using MCS mode (see the Experimental section for details) indicated emission lifetimes below 500 ns. Further experiments in TCSPC mode revealed lifetimes for **1<sup>H</sup>** and **1<sup>D</sup>** in the nanoseconds range (see Fig. S9 for the luminescence decay curves). Such a result confirms that the luminescence is attributable to ligand-centred transitions, in line with the negligible difference between the photoluminescence quantum yields measured for **1<sup>H</sup>** and its deuterated isoanalogue.

### 3.2. Reactivity

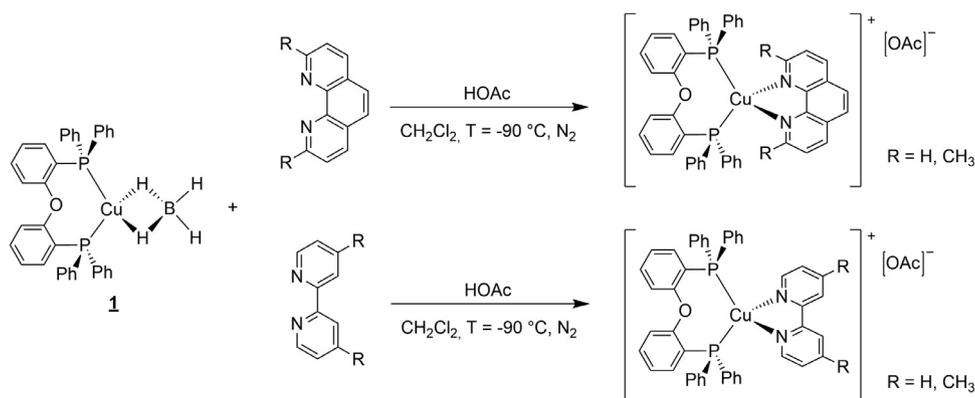
On the basis of a previously reported approach applied for  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{PPh}_3)_2]$  [27], the complex **1<sup>H</sup>** was initially reacted with trifluoromethanesulfonic acid (HOTf) in 2:1 ratio in dichloromethane solution at low temperature, thus obtaining the dimer  $[\text{Cu}_2(\mu\text{-BH}_4)(\text{DPEphos})_2][\text{OTf}]$  (**2**). Other synthetic approaches, such as the reaction of **1<sup>H</sup>** with a previously reacted mixture of CuCl and DPEphos in boiling 1,2-dichloroethane, were unsuccessful and afforded only insoluble materials [38]. The formation of a cationic complex was confirmed by conductivity measurements, indicating that **2** behaves as 1:1 electrolyte in acetone

solution. As for **1<sup>H</sup>**, TGA measurements on complex **2** indicated good thermal stability, with mass loss beginning at 620 K (see Figure S1). The presence of the counter-anion was confirmed both by the S=O stretching at  $1030\text{ cm}^{-1}$  in the IR spectrum and by the singlet at  $-77.78\text{ ppm}$  in the  $^{19}\text{F}$  NMR spectrum. The  $^1\text{H}$  NMR spectrum shows, besides the resonances of coordinated DPEphos, a quartet with 1:1:1:1 intensity ratio centred at 1.87 ppm, with  $^1J_{\text{BH}} = 76\text{ Hz}$ . The same coupling constant was detected for the  $^{11}\text{B}$  NMR quintet centred at  $-30.66\text{ ppm}$  (Fig. 5). The  $^{31}\text{P}\{^1\text{H}\}$  NMR showed only one singlet at  $-13.96\text{ ppm}$  (Fig. 5). The change of coordination mode of borohydride was further confirmed by the IR spectrum of **2**, where only one band at  $2121\text{ cm}^{-1}$  attributable to  $\mu\text{-BH}_4$  was detected, while no signal attributable to terminal B-H stretchings was observed (see Fig. 6).

The DFT-optimized structure of **2** is shown in Fig. S10 together with the frontier orbitals. Cartesian coordinates are collected in Table S5. The localization of HOMO and LUMO is somewhat similar to that of **1<sup>H</sup>**, and the borohydride ligand scarcely contributes to the LUMO only by a *p*-type orbital of boron.

The photophysical properties of **2** are roughly comparable to those of **1<sup>H</sup>**, with a red-shift of about 10 nm of the emission maximum that shifts the colour of the emission in the blue-green region of the CIE 1931 chromaticity diagram (Fig. S8). The absorption, PL and PLE spectra are reported in Fig. 4. The measured photoluminescence quantum yield of **2**, 14%, is in line with the values obtained for **1<sup>H</sup>** and **1<sup>D</sup>**, confirming a scarce participation of the borohydride ligand in the non-radiative decay routes of the excited states. As for **1<sup>H</sup>** and **1<sup>D</sup>**, the luminescence lifetime of **2** is in the nanoseconds range. It can be tentatively concluded, also on the basis of the comparison with literature data [17e], that the photoluminescence of **1<sup>H</sup>**, **1<sup>D</sup>** and **2** is attributable to transitions of DPEphos, enhanced by the rigidity due to coordination. The interaction with Cu(I) causes a red shift of the emission maxima, more pronounced in the cationic complex **2**.

The ease of conversion of **1<sup>H</sup>** into **2** prompted us to extend the reactivity study of **1<sup>H</sup>** with acids. The investigation was also motivated by the air stability of **1<sup>H</sup>**, that makes it a promising precursor for the synthesis of other Cu(I) complexes. In particular, compound **1<sup>H</sup>** was reacted with acetic acid (HOAc) in combination with 1,10-phenanthroline (phen), 2,9-dimethyl-1,10-phenanthroline (dmp), 2,2'-bipyridine (bpy) and 4,4'-dimethyl-2,2'-bipyridine (dmbpy), to obtain previously reported luminescent complexes having general formula  $[\text{Cu}(\text{N}^*\text{N})(\text{DPEphos})]^+$  [16], isolated as acetate salts (see Scheme 2). The compounds were prepared in high yields and purity using mild reaction conditions. Details about the synthetic procedure are reported in the Supporting Information (Table S6), together with  $^1\text{H}$  NMR and  $^{31}\text{P}\{^1\text{H}\}$  NMR data and spectra (Figs. S11-S14). The characterization of the



**Scheme 2.** Synthesis of  $[\text{Cu}(\text{N}^*\text{N})(\text{DPEphos})][\text{OAc}]$  ( $\text{N}^*\text{N}$  = phen, dmp, bpy, dmbpy).

neocuproine complex  $[\text{Cu}(\text{dmp})(\text{DPEphos})][\text{OAc}]$  was corroborated by the determination of the luminescence lifetime, 33  $\mu\text{s}$ , in line with literature data [39]. The luminescence decay curve is shown in Fig. S15.

#### 4. Conclusion

In this work we described the preparation of mono- and dinuclear Cu(I) borohydride complexes having bis[(2-diphenylphosphino)phenyl] ether (DPEphos) as bidentate P-donor ligand. The coordination to Cu(I) enhanced the photoluminescence of DPEphos and the isolated compounds showed bright emissions in the blue-green region. Differently from CuCl and  $[\text{Cu}(\text{NCCH}_3)_4][\text{BF}_4]$ , the borohydride complex  $[\text{Cu}(\kappa^2\text{-BH}_4)(\text{DPEphos})]$  proved to be air stable and also a viable precursor for the synthesis of heteroleptic complexes with chelating N-donor ligands, isolated in high yields and purity using very mild reaction conditions and minimal work-up. The decomposition of the borohydride ligand with an acid avoids the possibility that acetonitrile or chloride remain in the Cu(I) coordination sphere. Thanks to this feature, we are successfully obtaining new Cu(I)-DPEphos complexes with unusual azoles in the coordination sphere, that will be submitted for publication in the next future.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRedit authorship contribution statement

**Valentina Ferraro:** Formal analysis, Investigation, Validation, Writing – original draft. **Jesús Castro:** Formal analysis, Investigation, Supervision, Writing – original draft. **Enrico Trave:** Investigation, Formal analysis. **Marco Bortoluzzi:** Conceptualization, Formal analysis, Funding acquisition, Supervision, Writing – original draft.

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#### References

[1] (a) T.J. Marks, J.R. Kolb, Covalent transition metal, lanthanide, and actinide tetrahydroborate complexes, *Chem. Rev.* 77 (1977) 263–293, doi:10.1021/cr60306a004; (b) L.H. Jepsen, M.B. Ley, Y.-S. Lee, Y.W. Cho, M. Dornheim, J.O. Jensen, Y. Filinchuk, J.E. Jørgensen, F. Besenbacher, T.R. Jensen, Boron-nitrogen based hydrides and reactive composites for hydrogen storage, *Mater. Today* 17 (2014) 129–135, doi:10.1016/j.mattod.2014.02.015; (c) L.H. Jepsen, M.B. Ley, Y. Filinchuk, F. Besenbacher, T.R. Jensen, Tailoring the properties of ammine metal borohydrides for solid-state hydrogen storage, *ChemSusChem* 8 (2015) 1452–1463, doi:10.1002/cssc.201500029; (d) Q. Lai, M. Paskevicius, D.A. Sheppard, C.E. Buckley, A.W. Thornton, M.R. Hill, Q. Gu, J. Mao, Z. Huang, H.K. Liu, Z. Guo, A. Banerjee, S. Chakraborty, R. Ahuja, K.-F. Aguey-Zinsou, Hydrogen storage materials for mobile and stationary applications: current state of the art, *ChemSusChem* 8 (2015) 2789–2825, doi:10.1002/cssc.201500231;

(e) I. Dovgaliuk, Y. Filinchuk, Aluminium complexes of B- and N-based hydrides: Synthesis, structures and hydrogen storage properties, *Inter. J. Hydrogen Energ.* 41 (2016) 15489–15504, doi:10.1016/j.ijhydene.2016.05.196; (f) R. Mohtadi, S.-I. Orimo, The renaissance of hydrides as energy materials, *Nat. Rev. Mater.* 2 (2017) 16091, doi:10.1038/natrevmats.2016.91; (g) M. Paskevicius, L.H. Jepsen, P. Schouwink, R. Černý, D.B. Ravnsbæk, Y. Filinchuk, M. Dornheim, F. Besenbacher, T.R. Jensen, Metal borohydrides and derivatives – synthesis, structure and properties, *Chem. Soc. Rev.* 46 (2017) 1565–1634, doi:10.1039/C6CS00705H; (h) H.-W. Li, Y. Yan, S.-I. Orimo, A. Züttel, C.M. Jensen, Recent progress in metal borohydrides for hydrogen storage, *Energies* 4 (2011) 185–214, doi:10.3390/en4010185; (i) S.-I. Orimo, Y. Nakamori, J.R. Eliseo, A. Züttel, C.M. Jensen, Complex hydrides for hydrogen storage, *Chem. Rev.* 107 (2007) 4111–4132, doi:10.1021/cr0501846.

[2] (a) R. Langer, M.A. Iron, L. Konstantinovski, Y. Diskin-Posner, G. Leitun, Y. Ben-David, D. Milstein, Iron borohydride pincer complexes for the efficient hydrogenation of ketones under mild, base-free conditions: synthesis and mechanistic insight, *Chem. Eur. J.* 18 (2012) 7196–7209, doi:10.1002/chem.201200159; (b) S. Chakraborty, P.O. Lagaditis, M. Förster, E.A. Bielinski, N. Hazari, M.C. Holthausen, W.D. Jones, S. Schneider, Well-defined iron catalysts for the acceptorless reversible dehydrogenation-hydrogenation of alcohols and ketones, *ACS Catal.* 4 (2014) 3994–4003, doi:10.1021/cs5009656; (c) T. Zell, Y. Ben-David, D. Milstein, Highly efficient, general hydrogenation of aldehydes catalyzed by PNP iron pincer complexes, *Catal. Sci. Technol.* 5 (2015) 822–826, doi:10.1039/C4CY01501K; (d) S. Mohammadi, D. Setamdidah, Acridine)(tetrahydroborato)zinc complex  $[\text{Zn}(\text{BH}_4)_2(\text{acr})]$ : a new stable and efficient reducing agent, *Orient. J. Chem.* 31 (2015) 2395–2399, doi:10.13005/ojc/310470; (e) F. Abdollahpour, D. Setamdidah, Caffeine)(tetrahydroborato)zinc complex  $[\text{Zn}(\text{BH}_4)_2(\text{caf})]$ : a new stable and efficient reducing agent, *Orient. J. Chem.* 31 (2015) 1787–1792, doi:10.13005/ojc/310361; (f) K.S. Ravikummar, S. Sinha, S. Chandrasekaran, Diastereoselectivity in the reduction of acyclic carbonyl compounds with diisopropoxytitanium(iii) tetrahydroborate, *J. Org. Chem.* 64 (1999) 5841–5844, doi:10.1021/jo9902906.

[3] (a) S. Bhattacharyya, A. Chatterjee, J.S. Williamson, Reductive amination with zinc borohydride. Efficient, safe route to fluorinated benzylamines, *Synthetic Commun.* 27 (1997) 4265–4274, doi:10.1080/00397919708005050; (b) H. Alinezhad, M. Tajbakhsh, R. Zamani, One-pot reductive amination of aldehydes and ketones using N-methylpiperidine zinc borohydride (ZBN-MPP) as a new reducing agent, *Synlett* 3 (2016) 0431–0434, doi:10.1055/s-2006-926230; (c) H. Firouzabadi, N. Iranpoor, H. Alinezhad, Micellar media catalyzed highly efficient reductive amination of carbonyl compounds with bis(triphenylphosphine)(tetrahydroborato)zirconium(II),  $[\text{Zr}(\text{BH}_4)_2(\text{Ph}_3\text{P})_2]$ , as a new and a highly water tolerant tetrahydroborate reducing agent, *J. Iran. Chem. Soc.* 6 (2009) 177–186, doi:10.1007/BF03246518.

[4] M. Visseaux, F. Bonnet, Borohydride complexes of rare earths, and their applications in various organic transformations, *Coord. Chem. Rev.* 255 (2011) 374–420, doi:10.1016/j.ccr.2010.09.016.

[5] (a) S.J. Lippard, K.M. Melmed, Transition metal borohydride complexes. I. The solid-state structure of borohydridobis(triphenylphosphine)copper(I), *Inorg. Chem.* 6 (1967) 2223–2228, doi:10.1021/ic50058a021; (b) S.J. Lippard, D. Ucko, Transition metal borohydride complexes. II. The reaction of copper(I) compounds with boron hydride anions, *Inorg. Chem.* 7 (1968) 1051–1056, doi:10.1021/ic50064a002; (c) S.J. Lippard, K.M. Melmed, Transition metal borohydride complexes. III. Structure of octahydrotriborato-bis(triphenylphosphine)copper(I), *Inorg. Chem.* 8 (1969) 2755–2762, doi:10.1021/ic50082a043.

[6] M.S. Balakrishna, *Copper(I) Chemistry of Phosphines, Functionalized Phosphines and Phosphorus Heterocycles*, 1st edn., Elsevier, Chennai, 2019.

[7] (a) J.C. Bommer, K.W. Morse, Temperature-dependent phosphite complex equilibria observable with NMR and IR techniques, *Inorg. Chem.* 20 (1981) 1731–1734, doi:10.1021/ic50220a023; (b) V.D. Makhaev, A.P. Borisov, É.B. Lobkovskii, V.B. Polyakova, K.N. Semenenko, Preparation of hydroborate complexes of copper and an investigation of the dependence of their structure on the nature of the organophosphorus ligands, *Russ. Chem. Bull.* 34 (1985) 1731–1736, doi:10.1007/BF00948527; (c) Z. Xi, D. Jin, Preliminary study on the syntheses and structures of copper complexes with bidentate phosphine ligands, *Chinese J. Inorg. Chem.* 9 (1993) 379–383; (d) V. Makhaev, A. Borisov, N.K. Baranetskaya, V.D. Vil'chevskaya, Y.Y. Gorelikova, A.I. Krylova, D.N. Kravtsov, Complexes of copper(I) tetrahydroborate with organometallic and polydentate phosphine ligands, *Russ. J. Coord. Chem.* 18 (1992) 416–420; (e) M.M. Taqui, K. Parimal, P.K. Venkatasubramanian, Synthesis and structural characterization of  $[\alpha, \alpha'$ -bis(bis(2-(diphenylphosphino)ethyl)amino)ethane] bis(tetrahydroborato)dipropylidene. Hydrogen bridge attachment of the tetrahydroborate group, *Polyhedron* 10 (1991) 1827–1829, doi:10.1016/S0277-5387(00)83806-1; (f) É.B. Lobkovskii, V.D. Makhaev, A.P. Borisov, Crystal and molecular structure of (tetrahydroborato)bis(diphenylbutylphosphine)copper(I), *J. Struct. Chem.* 25 (1984) 496–498, doi:10.1007/BF00749355; (g) V.D. Makhaev, A.P. Borisov, S. Antsyshkina, G.G. Sadikov, M.A. Porai-Koshits, N.S. Kedrova, N.N. Mal'tseva, S. Ya. Istomin, Synthesis and crystal structure of (1,10-phenanthroline)(triethylphosphite)copper(I) tetrahydroborate, *Russ. J. Coord. Chem.* 19 (1993) 858–863; (h) B.E. Green, C.H.L. Kennard, G. Smith, M.M. Elcombe, F.H. Moore, B.D. James, A.H. White, Crystal structures of  $\alpha$ - and  $\beta$ -(1,10-phenanthroline)tetrahydroborato(triphenylphosphine)copper(I) and (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)tetrahydroboratocopper(I), *Inorg. Chim. Acta* 83 (1984) 177–189, doi:10.1016/S0020-1693(00)82389-0; (i) J.C. Bommer, K.W. Morse,  $[(\text{MePh}_2\text{P})_3\text{CuBH}_4]$ : a single M–H bridged

- tetrahydroborate, *J. Chem. Soc., Chem. Commun.* (1977) 137–138, doi:[10.1039/C39770000137](https://doi.org/10.1039/C39770000137); (j) M. Besora, A. Lledós, Coordination modes and hydride exchange dynamics in transition metal tetrahydroborate complexes, *Struct. Bond.* 130 (2008) 149–202, doi:[10.1007/430\\_2007\\_076](https://doi.org/10.1007/430_2007_076); (k) N.V. Belkova, I.E. Golub, E.I. Gutsul, K.A. Lyssenko, A.S. Peregodov, V.D. Makhaev, O.A. Filippov, L.M. Epstein, A. Rossin, M. Peruzzini, E.S. Shubina, Binuclear copper(I) borohydride complex containing bridging bis(diphenylphosphino) methane ligands: polymorphic structures of  $[(\mu^2\text{-dppm})_2\text{Cu}_2(\eta^2\text{-BH}_4)_2]$  dichloromethane solvate, *Crystals* 7 (2017) 318, doi:[10.3390/cryst7100318](https://doi.org/10.3390/cryst7100318).
- [8] (a) I.E. Golub, O.A. Filippov, N.V. Belkova, L.M. Epstein, A. Rossin, M. Peruzzini, E.S. Shubina, Two pathways of proton transfer reaction to (triphos)Cu( $\eta^1\text{-BH}_4$ ) via a dihydrogen bond [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane], *Dalton Trans* 45 (2016) 9127–9135, doi:[10.1039/C6DT01104G](https://doi.org/10.1039/C6DT01104G); (b) C. Bianchini, C.A. Ghilardi, A. Meli, S. Midollini, A. Orlandini, Reactivity of copper(I) tetrahydroborates toward carbon dioxide and carbonyl sulfide, *Inorg. Chem.* 24 (1985) 924–931, doi:[10.1021/ic00200a025](https://doi.org/10.1021/ic00200a025).
- [9] (a) G.W.J. Fleet, P.J.C. Harding, Convenient synthesis of bis(triphenylphosphine) copper(I) tetrahydroborate and reduction of acid chlorides to aldehydes, *Tetrahedron Lett* 20 (1979) 975–978, doi:[10.1016/S0040-4039\(01\)86066-4](https://doi.org/10.1016/S0040-4039(01)86066-4); (b) W.J. Fleet, P.J.C. Harding, M.J. Whitcombe, Bis(triphenylphosphine)copper tetrahydroborate in the reduction of -toluenesulphonylhydrazones and 2,4,6-triisopropylbenzenesulphonyl hydrazones (trisyl hydrazones) to alkanes, *Tetrahedron Lett* 21 (1980) 4031–4034, doi:[10.1016/S0040-4039\(00\)92863-6](https://doi.org/10.1016/S0040-4039(00)92863-6); (c) T.N. Sorrell, P.S. Pearlman, Preparation of aldehydes from acid chlorides using copper tetrahydroborate complexes, *J. Org. Chem.* 45 (1980) 3449–3451, doi:[10.1021/jo01305a015](https://doi.org/10.1021/jo01305a015); (d) G.W.J. Fleet, P.J.C. Harding, Selectivity in the acid catalysed reduction of carbonyl compounds to alcohols by bis(triphenylphosphine)copper(I) tetrahydroborate: Reduction of aldehydes in the presence of ketones, *Tetrahedron Lett* 22 (1981) 675–678, doi:[10.1016/S0040-4039\(01\)92520-1](https://doi.org/10.1016/S0040-4039(01)92520-1); (e) M.J. Bhanushali, N.S. Nandurkar, M.D. Bhor, B.M. Bhanage, Direct reductive amination of carbonyl compounds using bis(triphenylphosphine) copper(I) tetrahydroborate, *Tetrahedron Lett* 48 (2007) 1273–1276, doi:[10.1016/j.tetlet.2006.12.037](https://doi.org/10.1016/j.tetlet.2006.12.037).
- [10] (a) P.A. Grutsch, C. Kotal, Use of copper(I) phosphine compounds to photosensitize the valence isomerization of norbornadiene, *J. Am. Chem. Soc.* 99 (1977) 6460–6463, doi:[10.1021/ja00461a059](https://doi.org/10.1021/ja00461a059); (b) P.A. Grutsch, C. Kotal, Photobehavior of copper(I) compounds. Role of copper(I)-phosphine compounds in the photosensitized valence isomerization of norbornadiene, *J. Am. Chem. Soc.* 101 (1979) 4228–4233, doi:[10.1021/ja00509a031](https://doi.org/10.1021/ja00509a031); (c) B. Liaw, S.W. Orchard, C. Kotal, Photobehavior of copper(I) compounds. 4. Role of the triplet state of aryl(phosphine)copper(I) complexes in the photosensitized isomerization of dienes, *Inorg. Chem.* 27 (1988) 1311–1316, doi:[10.1021/ic00281a002](https://doi.org/10.1021/ic00281a002).
- [11] X. Hu, M. Soleilhavou, M. Melaimi, J. Chu, G. Bertrand, Air-stable (CAAC)CuCl and (CAAC)CuBH<sub>4</sub> complexes as catalysts for the hydrolytic dehydrogenation of BH<sub>3</sub>NH<sub>3</sub>, *Angew. Chem. Int. Edit.* 54 (2015) 6008–6011, doi:[10.1002/ange.201500224](https://doi.org/10.1002/ange.201500224).
- [12] F. Ritter, D. Mukherjee, T.P. Spaniol, A. Hoffmann, J. Okuda, A masked cuprous hydride as a catalyst for carbonyl hydrosilylation in aqueous solutions, *Angew. Chem. Int. Edit.* 58 (2019) 1818–1822, doi:[10.1002/anie.201811890](https://doi.org/10.1002/anie.201811890).
- [13] S. Marks, J.G. Heck, M.H. Habicht, P. Oña-Burgos, C. Feldmann, P.W. Roesky, [Ln(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub>] (Ln = Eu, Yb)—A highly luminescent material. Synthesis, properties, reactivity, and NMR studies, *J. Am. Chem. Soc.* 134 (2012) 16983–16986, doi:[10.1021/ja308077t](https://doi.org/10.1021/ja308077t).
- [14] D.P. Segers, M.K. DeArmond, P.A. Grutsch, C. Kotal, Multiple luminescence from borohydridobis(triphenylphosphine)copper(I), *Inorg. Chem.* 23 (1984) 2874–2878, doi:[10.1021/jc00186a032](https://doi.org/10.1021/jc00186a032).
- [15] (a) M. Bortoluzzi, J. Castro, M. Giroto, F. Enrichi, A. Vomiero, Luminescent copper(I) coordination polymer with 1-methyl-1H-benzotriazole, iodide and acetonitrile as ligands, *Inorg. Chem. Commun.* 102 (2019) 141–146, doi:[10.1016/j.inoche.2019.02.016](https://doi.org/10.1016/j.inoche.2019.02.016); (b) V. Ferraro, M. Bortoluzzi, J. Castro, A. Vomiero, S. You, Luminescent Cu(I) complex with bis(indazol-1-yl)phenylmethane as chelating ligand, *Inorg. Chem. Commun.* 116 (2020) 107894, doi:[10.1016/j.inoche.2020.107894](https://doi.org/10.1016/j.inoche.2020.107894); (c) V. Ferraro, J. Castro, L. Agostinis, M. Bortoluzzi, Luminescent heteroleptic copper(I) complexes with polydentate benzotriazolyl-based ligands, *Transition Met. Chem.* 46 (2021) 391–402, doi:[10.1007/s11243-021-00458-4](https://doi.org/10.1007/s11243-021-00458-4); (d) M. Bortoluzzi, J. Castro, F. Enrichi, A. Vomiero, M. Busato, Green-emitting manganese(II) complexes with phosphoramidate and phenylphosphonic diamide ligands, *Inorg. Chem. Commun.* 92 (2018) 145–150, doi:[10.1016/j.inoche.2018.04.023](https://doi.org/10.1016/j.inoche.2018.04.023); (e) M. Bortoluzzi, J. Castro, E. Trave, D. Dallan, S. Favaretto, Orange-emitting manganese(II) complexes with chelating phosphine oxides, *Inorg. Chem. Commun.* 90 (2018) 105–107, doi:[10.1016/j.inoche.2018.02.018](https://doi.org/10.1016/j.inoche.2018.02.018); (f) M. Bortoluzzi, J. Castro, Dibromomanganese(II) complexes with hexamethylphosphoramide and phenylphosphonic bis(diamide) ligands, *J. Coord. Chem.* 72 (2019) 309–327, doi:[10.1080/00958972.2018.1560430](https://doi.org/10.1080/00958972.2018.1560430); (g) M. Bortoluzzi, J. Castro, A. Gobbo, V. Ferraro, L. Pietrobon, S. Antoniutti, Tetrahedral photoluminescent manganese(II) halide complexes with 1,3-dimethyl-2-phenyl-1,3-diazaphospholidine-2-oxide as a ligand, *New J. Chem.* 44 (2020) 571–579, doi:[10.1039/C9NJ05083C](https://doi.org/10.1039/C9NJ05083C); (h) M. Bortoluzzi, J. Castro, A. Gobbo, V. Ferraro, L. Pietrobon, Light harvesting indolyl-substituted phosphoramidate ligand for the enhancement of Mn(II) luminescence, *Dalton Trans* 49 (2020) 7525–7534, doi:[10.1039/D0DT01659D](https://doi.org/10.1039/D0DT01659D); (i) M. Bortoluzzi, V. Ferraro, J. Castro, Synthesis and photoluminescence of manganese(II) naphthylphosphonic diamide complexes, *Dalton Trans* 50 (2021) 3132–3136, doi:[10.1039/D1DT00123J](https://doi.org/10.1039/D1DT00123J); (j) M. Bortoluzzi, J. Castro, A. Di Vera, A. Palù, V. Ferraro, Manganese(II) bromo- and iodo-complexes with phosphoramidate and phosphonate ligands: synthesis, characterization and photoluminescence, *New J. Chem.* 45 (2021) 12871–12878, doi:[10.1039/D1NJ02053F](https://doi.org/10.1039/D1NJ02053F).
- [16] R. Venkateswaran, M.S. Balakrishna, S.M. Mobin, H.M. Tuononen, Copper(I) complexes of bis(2-(diphenylphosphino)phenyl) ether: synthesis, reactivity, and theoretical calculations, *Inorg. Chem.* 46 (2007) 6535–6541, doi:[10.1021/ic7005474](https://doi.org/10.1021/ic7005474).
- [17] (a) A.R. Cabrera, I.A. Gonzalez, D. Cortés-Arriagada, M. Nalati, H. Berke, C.G. Daniliuc, M.B. Camarada, A. Toro-Labbé, R.S. Rojas, C.O. Salsola, Synthesis of new phosphorescent imidoyl-indazol and phosphine mixed ligand Cu(I) complexes – structural characterization and photophysical properties, *RSC Adv* 6 (2016) 5141–5153, doi:[10.1039/C5RA20450J](https://doi.org/10.1039/C5RA20450J); (b) K. Kubiček, S.T. Veedu, D. Storozhuk, R. Kia, S. Techert, Geometric and electronic properties in a series of phosphorescent heteroleptic Cu(I) complexes: Crystallographic and computational studies, *Polyhedron* 124 (2017) 166–176, doi:[10.1016/j.poly.2016.12.035](https://doi.org/10.1016/j.poly.2016.12.035); (c) C. Bizzarri, C. Fléchon, O. Fenwick, F. Cacialli, F. Polo, M.D. Gálvez-López, C.H. Yang, S. Scintilla, Y. Sun, R. Fröhlich, L. De Cola, Luminescent neutral Cu(I) complexes: synthesis, characterization and application in solution-processed OLED, *ECS J. Solid State Sci. Technol.* 5 (2016) R83–R90, doi:[10.1149/2.0021606jss](https://doi.org/10.1149/2.0021606jss); (d) G.U. Mahoro, E. Fresta, M. Elie, D. di Nasso, Q. Zhang, J.-F. Lohier, J.-L. Renaud, M. Linares, R. Wannemacher, J. Cabanillas-Gonzales, R.D. Costa, S. Gaillard, Towards rainbow photo/electro-luminescence in copper(I) complexes with the versatile bridged bis-pyridyl ancillary ligand, *Dalton Trans* 50 (2021) 11049–11060, doi:[10.1039/D1DT01689J](https://doi.org/10.1039/D1DT01689J); (e) J. Yuasa, M. Dana, T. Kawai, Phosphorescent properties of metal-free diphosphine ligands and effects of copper binding, *Dalton Trans* 42 (2013) 16096–16101, doi:[10.1039/C3DT51390D](https://doi.org/10.1039/C3DT51390D).
- [18] T. McCormick, W.-L. Jia, S. Wang, Phosphorescent Cu(I) complexes of 2-(2'-pyridylbenzimidazolyl)benzene: impact of phosphine ancillary ligands on electronic and photophysical properties of the Cu(I) complexes, *Inorg. Chem.* 45 (2006) 147–155, doi:[10.1021/ic051412h](https://doi.org/10.1021/ic051412h).
- [19] (a) S.-M. Kuang, D.G. Cuttall, D.R. McMillin, P.E. Fanwick, R.A. Walton, Synthesis and structural characterization of Cu(I) and Ni(II) complexes that contain the bis[2-(diphenylphosphino)phenyl]ether ligand. Novel emission properties for the Cu(I) species, *Inorg. Chem.* 41 (2002) 3313–3322, doi:[10.1021/ic0201809](https://doi.org/10.1021/ic0201809); (b) L. Yang, J.-K. Feng, A.-M. Ren, M. Zhang, Y.-G. Ma, X.-D. Liu, Structures, electronic states and electroluminescent properties of a series of Cu<sup>I</sup> complexes, *Eur. J. Chem.* (2005) 1867–1879, doi:[10.1002/ejic.200400941](https://doi.org/10.1002/ejic.200400941); (c) I. Andrés-Tomé, J. Fyson, F.B. Dias, A.P. Monkman, G. Iacobellis, P. Coppo, Copper(I) complexes with bipyridyl and phosphine ligands: a systematic study, *Dalton Trans* 41 (2012) 8669–8674, doi:[10.1039/C2DT30698K](https://doi.org/10.1039/C2DT30698K).
- [20] W.L.F. Armarego, D.D. Perrin, *Purification of laboratory chemicals*, Butterworth-Heinemann, 4th edn., Oxford, 1996.
- [21] R.N. Keller, H.D. Wycoff, L.E. Marchi, Copper(I) chloride, *Inorg. Synth.* 2 (1946) 1–4, doi:[10.1002/9780470132333.ch1](https://doi.org/10.1002/9780470132333.ch1).
- [22] Bruker APEX3, SMART, SAINT, Bruker AXS Inc., Madison, Wisconsin, USA, 2015.
- [23] P. McArdle, *Oscail*, a program package for small-molecule single-crystal crystallography with crystal morphology prediction and molecular modelling, *J. Appl. Crystallogr.* 50 (2017) 320–326, doi:[10.1107/S16005767160181](https://doi.org/10.1107/S16005767160181).
- [24] G.M. Sheldrick, *SHELXT* – Integrated space-group and crystal-structure determination, *Acta Crystallogr. A71* (2015) 3–8, doi:[10.1107/S2053273314026370](https://doi.org/10.1107/S2053273314026370).
- [25] G.M. Sheldrick, Crystal structure refinement with *SHELXL*, *Acta Crystallogr. C71* (2015) 3–8, doi:[10.1107/S205329614024218](https://doi.org/10.1107/S205329614024218).
- [26] A.L. Spek, *checkCIF validation ALERTS: what they mean and how to respond*, *Acta Crystallogr. E76* (2020) 1–11.
- [27] (a) Y. Minenkov, Å. Singstad, G. Occhipinti, V.R. Jensen, The accuracy of DFT-optimized geometries of functional transition metal compounds: a validation study of catalysts for olefin metathesis and other reactions in the homogeneous phase, *Dalton Trans* 41 (2012) 5526–5541, doi:[10.1039/C2DT12232D](https://doi.org/10.1039/C2DT12232D); (b) J.-D. Chai, M. Head-Gordon, Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections, *Phys. Chem. Chem. Phys.* 10 (2008) 6615–6620, doi:[10.1039/B810189B](https://doi.org/10.1039/B810189B); (c) I.C. Gerber, J.G. Ángyán, Hybrid functional with separated range, *Chem. Phys. Lett.* 415 (2005) 100–105, doi:[10.1016/j.cplett.2005.08.060](https://doi.org/10.1016/j.cplett.2005.08.060).
- [28] F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.* 7 (2005) 3297–3305, doi:[10.1039/B508541A](https://doi.org/10.1039/B508541A).
- [29] (a) F. Neese, The ORCA program system, *WIREs Comput. Mol. Sci.* 2 (2012) 73–78, doi:[10.1002/wcms.81](https://doi.org/10.1002/wcms.81); (b) F. Neese, Software update: the ORCA program system, *WIREs Comput. Mol. Sci.* 8 (2018) e1327, doi:[10.1002/wcms.1327](https://doi.org/10.1002/wcms.1327).
- [30] (a) F. Cariati, L. Naldini,  $\mu$ -tetrahydridoborato-bis(triphenylphosphine)copper salts, *J. Nucl. Inorg. Chem.* 28 (1966) 2243–2246, doi:[10.1016/0022-1902\(66\)80112-4](https://doi.org/10.1016/0022-1902(66)80112-4); (b) E.E. Green, C.H.L. Kennard, G. Smith, B.D. James, P.C. Healy, A.H. White, Crystal and molecular structure of  $\mu$ -tetrahydroborato-bis[bis(triphenylphosphine)copper(I)] perchlorate, *Inorg. Chim. Acta* 81 (1984) 147–150, doi:[10.1016/S0020-1693\(00\)88750-2](https://doi.org/10.1016/S0020-1693(00)88750-2).
- [31] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, *Mercury CSD 2.0* – new features for the visualization and investigation of crystal structures, *J. Appl. Cryst.* 41 (2008) 466–470, doi:[10.1107/S0021889807067908](https://doi.org/10.1107/S0021889807067908).
- [32] (a) J. Moncol, M. Gembicky, P. Coppens, Tetrahydro-borato-bis(triphenylphosphine)copper(I): a redetermination at 90 K, *Acta Cryst. E61* (2005) m242–m243, doi:[10.1107/S1600536804030314](https://doi.org/10.1107/S1600536804030314); (b) M. Woźnińska, S. Grabowsky, P.M. Dominiak, K. Woźniak, D. Jayatilaka, Hydrogen atoms can be located accurately and precisely by x-ray crystallography, *Sci. Adv.* 2 (2016) e1600192, doi:[10.1126/sciadv.1600192](https://doi.org/10.1126/sciadv.1600192).

- [33] M. Lueckheide, N. Rothman, B. Ko, J.M. Tanski,  $\pi$ -Stacking motifs in the crystal structures of bis(phosphine) copper(I)  $\eta^2$ -tetrahydroborate complexes, *Polyhedron* 58 (2013) 79–84, doi:[10.1016/j.poly.2012.08.003](https://doi.org/10.1016/j.poly.2012.08.003).
- [34] L. Yang, D.R. Powell, R.P. Houser, Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index,  $\tau_4$ , *Dalton Trans* (2007) 955–964, doi:[10.1039/B617136B](https://doi.org/10.1039/B617136B).
- [35] S. Murugesan, B. Stöger, M. Weil, L.F. Veiros, K. Kirchner, Synthesis, structure, and reactivity of Co(II) and Ni(II) PCP pincer borohydride complexes, *Organometallics* 34 (2015) 1364–1372, doi:[10.1021/acs.organomet.5b00075](https://doi.org/10.1021/acs.organomet.5b00075).
- [36] (a) C. Wen, G. Tao, X. Xu, X. Feng, R. Luo, A phosphorescent copper(I) complex: Synthesis, characterization, photophysical property, and oxygen-sensing behavior, *Spectrochim. Acta A* 79 (2011) 1345–1351, doi:[10.1016/j.saa.2011.04.067](https://doi.org/10.1016/j.saa.2011.04.067); (b) R. Czerwieniec, J. Yu, H. Yersin, Blue-light emission of Cu(I) complexes and singlet harvesting, *Inorg. Chem.* 50 (2011) 8293–8301, doi:[10.1021/jc200811a](https://doi.org/10.1021/jc200811a) ; (c) C. Zhou, Q. Wang, Synthesis, characterization, photophysical and oxygen-sensing properties of a copper(I) complex, *Transition Met. Chem.* 35 (2010) 605–611, doi:[10.1007/s11243-010-9370-1](https://doi.org/10.1007/s11243-010-9370-1).
- [37] D. Song, W.L. Jia, G. Wu, S. Wang, Cu(I) and Zn(II) complexes of 7-azaindole-containing scorpionates: Structures, luminescence and fluxionality, *Dalton Trans* (2005) 433–438, doi:[10.1039/B414328K](https://doi.org/10.1039/B414328K).
- [38] M.-W. Hong, L. Song, Y. Zhao, L.-S. Qin, C.-Y. Wang, H.-S. Shi, J.-Y. Guo, X.-D. Tao, K.-Y. Shu, W.-X. Chai, Synthesis and characterizations of strongly phosphorescent copper(I) halide complexes with bridged bis[2-(diphenylphosphino)phenyl]ether ligand, *J. Clust. Sci.* 25 (2014) 1627–1640, doi:[10.1007/s10876-014-0762-9](https://doi.org/10.1007/s10876-014-0762-9).
- [39] D.G. Cuttell, S.-M. Kuang, P.E. Fanwick, D.R. McMillin, R.A. Walton, Simple Cu(I) complexes with unprecedented excited-state lifetimes, *J. Am. Chem. Soc.* 124 (2002) 6–7, doi:[10.1021/ja012247h](https://doi.org/10.1021/ja012247h).