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Phosphanylboranes | *Very Important Paper* |

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The Coordination Chemistry of the Phosphanylborane $(C_6H_5)_2PBH_2{\cdot}N(CH_3)_3$ towards Copper(I) Salts

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Dedicated to Professor T. Marder on the occasion of his 65th birthday

Abstract: The reactions of the phosphinoborane $Ph_2PBH_2{\cdot}NMe_3$ with $Cu^{(I)}$ halides [CuCl, CuBr, CuI] and $[Cu(CH_3CN)_4BF_4]$, respectively, were studied. Depending on the ratio of the reactants used, the former reaction allowed for the synthesis of eight neutral coordination compounds with the general formula $[Cu_nX_n(Ph_2PBH_2{\cdot}NMe_3)_m]$ (X = Cl, Br, I; n = 1, 2, 4, 5; m = 2, 4) (**4–11**). The latter reaction, however, led to the formation of the homoleptic complex $[Cu(Ph_2PBH_2{\cdot}NMe_3)_3][BF_4]$ (**13**). The structures of the products **4**–**11** and **13** were compared to related complexes possessing the well-known Ph_3P ligand. All compounds were characterized by single crystal X-ray structure analysis, multinuclear NMR spectroscopy, IR spectroscopy and mass spectrometry.

Introduction

In the recent past, phosphines have been gaining in importance among the most widely studied L-type ligands in coordination chemistry.[1] Specifically, phosphine-copper(I) complexes emerged as cheap and effective candidates for a variety of applications such as antitumor activities, enantioselective catalysis and luminescence properties.[2] By varying the stabilizing phosphine ligand, rational control of the structure and property of the copper complex is attainable. Phosphine-boranes are a common class of phosphines which are mainly used as precursors for the synthesis of inorganic polymers by dehydrocoupling reactions.[3] Our group contributed to this field by investigating the synthesis and reactivity of Lewis base stabilized pnictogenylboranes of the type $R_2E–BH_2{\cdot}NMe_3$ (E = P, As; R = H, alkyl, aryl).[4] The reactivity of these adducts towards main group Lewis acids as well as their oxidation with chalcogens[5] and their use as building blocks for the synthesis of oligomeric[6] and polymeric compounds[7] were studied thoroughly. However, their coordination chemistry towards Lewis-acidic metal compounds was only examined to a limited extent.[8]

Another major direction of our research is devoted to the use of organometallic polyphosphorus (P_n) ligand complexes as connectors between metal ions. In this respect, the utilization of $Cu^{(I)}$ salts, mainly $Cu^{(I)}$ halides, plays an important role. Such reactions have allowed for the synthesis of 1D, 2D and 3D coordination polymers (CPs) as well as fullerene-like inorganic nanospheres.[9] Therefore, we became interested in extending this research area towards the use of monomeric pnictogenylboranes in the coordination chemistry of copper. We had previously reported primary results of the reaction of $H_2P–BH_2{\cdot}NMe_3$ with copper iodide affording two Cu-I-P clusters.[8b] According to the CSD database, only six coordination complexes, including one homoleptic complex, of phosphine-borane ligands and $Cu^{(I)}$ ions have been structurally characterized to date.[8b,10] Therefore, we decided to study the coordination potential of the phosphanylborane $Ph_2P–BH_2{\cdot}NMe_3$ (**L**) towards $Cu^{(I)}$ salts and compare it with that of Ph_3P-containing complexes. Herein, we report on the study of the reaction of **L** with $Cu^{(I)}$ halides in defined stoichiometries resulting in a series of complexes of the type $[Cu_nX_n(Ph_2PBH_2{\cdot}NMe_3)_m]$ (X = Cl, Br, I; n = 1, 2, 4, 5; m = 2, 4) (**4–11**), whereas its reaction with $[Cu(MeCN)_4][BF_4]$ afforded the homoleptic complex $[Cu(Ph_2PBH_2{\cdot}NMe_3)_3][BF_4]$ (**13**).

Results and Discussion

In a first approach, the phosphanylborane **L** was treated with $Cu^{(I)}$ halides {CuX; X = Cl (**1**), X = Br (**2**), X = I (**3**)} and the dependence of the product composition on the stoichiometry of the used reactants studied (Scheme 1). The reaction of two equivalents of **L** with the $Cu^{(I)}$ salts **1**–**3** in CH_2Cl_2 afforded the complexes $[CuX(Ph_2PBH_2{\cdot}NMe_3)_2]$ {X = Cl (**4**), X = Br (**5**), X = I

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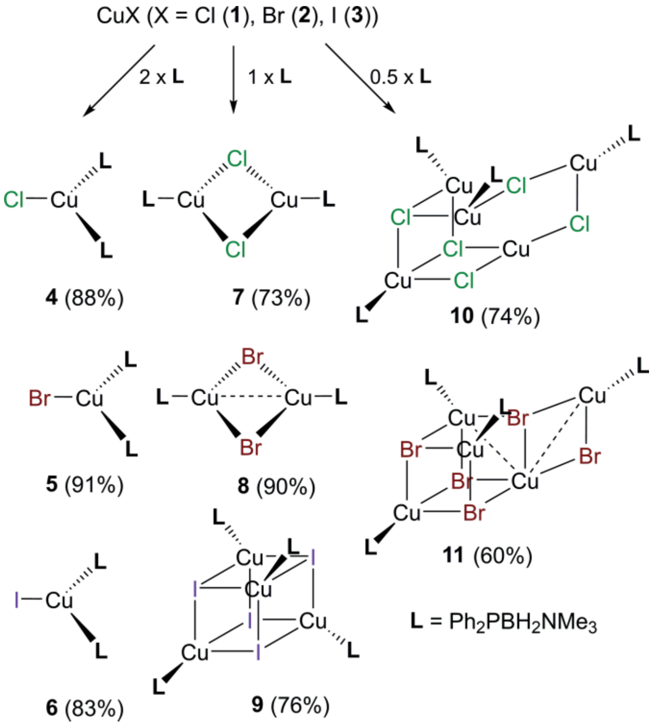
(**6**)} (Scheme 1) in good yields as polycrystalline powders (**4**: 88 %; **5**: 91 %; **6**: 83 %). Crystals of **4**–**6** grown by layering CH_2Cl_2 solutions of the crude reaction mixtures with *n*-hexane were examined by X-ray structure analysis (Figure 1). Their crystal structures reveal that the obtained coordination complexes are isomorphous to each other and show solid-state structures that are comparable to $[CuX(Ph_3P)_2]$.[11] In each case, the $Cu^{(I)}$ atom possesses a trigonal coordination sphere consisting of two P atoms from two ligands **L** and one halide ion. The P–Cu bond lengths in **4**, **5** and **6** are 2.2482(8) Å, 2.2486(4) Å and 2.2564(11) Å, respectively. The P–B bond lengths of 1.980(4), 1.976(2) and 1.979(5) Å for **4**, **5** and **6**, respectively, are nearly identical to that of the free ligand **L** [1.975(3) Å].[7]



Scheme 1. Reaction of **L** with the $Cu^{(I)}$ salts **1**–**3**: synthesis of the coordination compounds **4**–**11**. All reactions are performed under similar experimental conditions: CH_2Cl_2, 18 h, r.t. Yields are given in parentheses.

Compounds **4**–**6** are well soluble in common organic solvents such as CH_2Cl_2, THF and CH_3CN and insoluble in *n*-hexane. Their room temperature ^{31}P NMR spectra in CD_2Cl_2 show in each case a broad singlet centered at ca. $\delta = -42.8$ ppm that is slightly upfield shifted relative to that of the free ligand **L** (–39.5 ppm).[7] Their room temperature ^{1}H NMR spectra show the expected signals attributable to the H atoms of the ligand **L** (for further details, see the Supporting information). FD-MS spectra of **4**–**6** reveal peaks assignable to the fragments $[Cu_lX_m(L)_n]$ ($l = 1$–3; $m = 0$–3; $n = 1$–3) in which an increasing cluster size is realized associated with the increasing atomic number of the halogen atom.

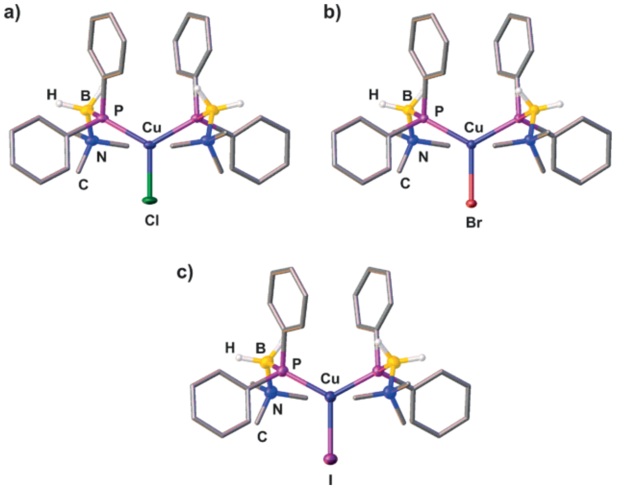


Figure 1. Molecular structures of the neutral $Cu^{(I)}$ complexes (a) **4**, (b) **5** and (c) **6** in the solid state. Hydrogen atoms on carbon atoms are omitted for clarity.

In a second step, the ligand **L** was treated with the CuX (**1**–**3**) in a 1:1 ratio. These reactions afforded the products $[CuX(Ph_2PBH_2{\cdot}NMe_3)]_n$ (**7**: X = Cl, $n = 2$; **8**: X = Br, $n = 2$; **9**: X = I, $n = 4$) (Scheme 1) in good isolated yields (**7**: 73 %; **8**: 90 %; **9**: 76 %). Single crystal X-ray structure analyses of $[CuCl(Ph_2PBH_2{\cdot}NMe_3)]_2$ (**7**) and $[CuBr(Ph_2PBH_2{\cdot}NMe_3)]_2$ (**8**) (Figure 2) reveal similar dinuclear complexes with trigonally coordinated $Cu^{(I)}$ centers bearing one phosphine ligand **L** and two halide ions in μ_2-bridging coordination modes (Figure 2). On the other hand, $[CuI(Ph_2PBH_2{\cdot}NMe_3)]_4$ (**9**) shows a cubane-like structure with a Cu_4I_4 core and one phosphine ligand **L** coordinating to each $Cu^{(I)}$ center. As a consequence, each $Cu^{(I)}$ atom in **9** adopts a tetrahedral coordination sphere with one P atom and three iodide ions in μ_3-caping modes. The P–Cu bond lengths in **7** [2.1915(2) Å], and **8** [2.2024(7)–2.2139(7) Å] are slightly shorter than those in **9** [2.2427(16)–2.2540(15) Å]. The P–B bond lengths in **7**–**9** amounting to between 1.973(3) and 2.006(8) Å are within the same range as those of the compounds **4**–**6** and the free ligand **L**. The Cu•••Cu distances in **7** (3.103 Å) and **9** (3.166–3.455 Å) are larger than the sum of their van der Waals radii (2.80 Å), revealing no Cu•••Cu interactions.[12] There are two Cu•••Cu distances in **8** (2.784 and 2.913 Å) due to

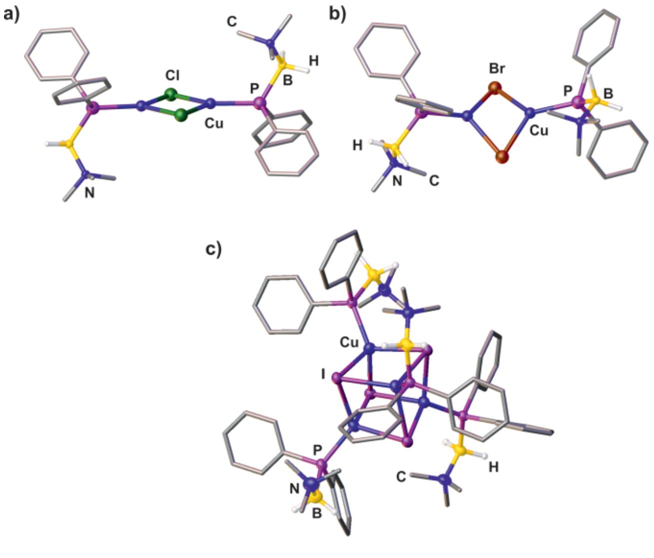


Figure 2. Molecular structures of the $Cu^{(I)}$ complexes (a) **7**, (b) **8** and (c) **9** in the solid state. Hydrogen atoms on carbon atoms are omitted for clarity.

the presence of two independent units of the same molecule of **8** in the solid state structure. Despite the fact that these values lie below and at the upper limit of the sum of the van der Waals radii of two adjacent Cu$^{(I)}$ atoms, the discussion of Cu•••Cu interactions is beyond the scope of this article. To date, no structures similar to those of the compounds **7** and **8** were reported for Ph_3P and Cu$^{(I)}$ halides. However, $[CuI(Ph_3P)]_4$ was described to display a cubane-like structure similar to **9**.[13]

The room temperature ^{31}P NMR spectra of **7** and **8** in CD_2Cl_2 reveal broad singlets at δ = –34.7 and –37.2 ppm, respectively. These signals are downfield shifted compared to those of the free ligand **L** and the complexes **4**–**6**. In comparison, the ^{31}P NMR spectrum of **9** shows an upfield shifted singlet at δ = –42.4 ppm. In the FD-MS spectra of the complexes **7**–**9**, peaks assignable to the fragments $[Cu_lX_m(L)_n]$ (l = 1–5; m = 0–4; n = 1–4) are detected showing variable cluster compositions some of which are even bigger (e.g: $[Cu_3Cl_2\mathbf{L}_3]^+$ for **7**; $[Cu_3Br_3\mathbf{L}_3]^+$ for **8**; and $[Cu_5I_4\mathbf{L}_4]^+$ for **9**; for further information see ESI) than those observed in the solid state. Note that solids of the CuI-containing complexes $[CuI(Ph_2PBH_2{\cdot}NMe_3)_2]$ (**6**) and $[CuI(Ph_2PBH_2{\cdot}NMe_3)]_4$ (**9**) perceive by the human eye orange emission under an UV lamp at room temperature. These compounds do not reveal any short intermetallic distances, so their emission is likely to be caused by some other effects, which will be the subject of future investigations.

Comparing the compositions of complexes **7**–**9** with those of **4**–**6** shows that by increasing the ratio of the CuX/**L** used as starting material, complexes of higher nuclearity are formed in the solid state. Thus, the question arose whether a further increase in the amount of Cu$^{(I)}$ halides used would lead to coordination compounds with even higher nuclearity. Consequently, two equivalents of the copper salts CuX (**1**–**3**) were treated with one equivalent of **L** in CH_2Cl_2. These reactions led to the formation of the complexes **9**, $[Cu_5Cl_5(Ph_2PBH_2{\cdot}NMe_3)_4]$ (**10**) and $[Cu_5Br_5(Ph_2PBH_2{\cdot}NMe_3)_4]$ (**11**) (Scheme 1, Figure 3) in good yields as polycrystalline powders (**10**: 74 %; **11**: 60 % based on **L**). The crystal structures of **10** and **11** reveal that these two complexes have a ratio of **L**/CuX (4:5) differing from that initially used in the reactions (1:2). These compounds can be viewed as edge-open cubanes with an additional **L**CuX (X = Cl, Br) fragment attached to the Cu_4X_4 core. Thus, each of the molecules **10** and **11** consist of four ligands **L** and five CuX {X = Cl (**10**), Br(**11**)} moieties. All Cu$^{(I)}$ ions within compound **10** possess a trigonal coordination sphere, with the exception of the tetrahedral coordinated Cu4 atom. However, one of them (Cu2) is coordinated to three Cl$^-$ ions while the others are each coordinated to two Cl$^-$ ions and one P atom from a ligand **L** (Figure 3b). On the other hand, there are three types of coordination spheres for the Cu$^{(I)}$ ions in compound **11**. Cu3 adopts a threefold-coordinated geometry possessing two Br$^-$ ions and one P atom. The atoms Cu1 and Cu4 are each tetracoordinated by three Br$^-$ ions and one P atom. Cu5 is also tetracoordinated by two Br$^-$ ions and one P atom in addition to a possible weak interaction towards the Cu2 atom forming a short Cu5•••Cu2 distance [2.7218(10) Å]. Cu2 is pentacoordinated by four Br$^-$ ions and a possible weak interaction towards Cu5. The P–Cu and P–B bond lengths in **10** and **11** are in the range of 2.196(2)–2.227(7) Å and [1.961(10)–2.031(18) Å], respectively. With the exception of the short Cu2–Cu5 distance in **11**, all Cu•••Cu distances [2.9301(18)–2.9563(13) Å] in **10** and **11** are longer than the sum of the van der Walls radii of two neighbouring Cu$^{(I)}$ atoms. Although a large number of coordination compounds based on Cu$^{(I)}$ halides were synthesized and structurally characterized, to the best of our knowledge, none of these possesses a solid state structure similar to the compounds **10** and **11**.

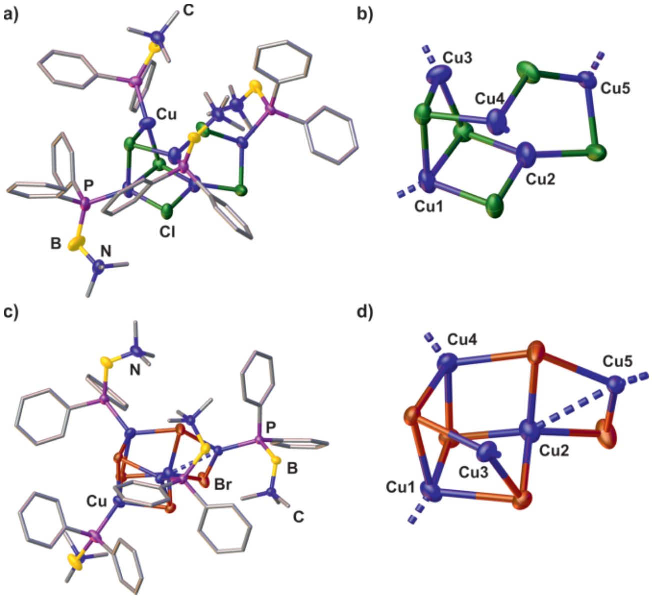


Figure 3. Molecular structures of the Cu$^{(I)}$ complexes (a) **10** and (c) **11** in the solid state. Hydrogen atoms are omitted for clarity. Core structures of complexes (b) **10** and (d) **11**.

The room temperature ^{31}P NMR spectra of **10** and **11** display similarly broad signals centered at δ = –33.6 ppm and –34.7 ppm, respectively, which are upfield shifted compared to that of the free ligand **L** (–39.5 ppm).[7] FD-MS spectra of **10** and **11** show fragments of $[Cu_lX_m(L)_n]$ (l = 1–5; m = 0–4; n = 1–4), similar to those observed from the ESI-MS spectra of complexes **7**–**9**.

The obtained results motivated us to increase the challenge by studying the possibility to synthesize homoleptic complexes of the ligand **L** and Cu$^{(I)}$ ions. Accordingly, **L** was treated with $[Cu(MeCN)_4][BF_4]$ (**12**) in CH_3CN using two different ratios of **L**/**12** (3:1, 4:1). Both reactions allowed the selective synthesis of the complex $[Cu(Ph_2PBH_2{\cdot}NMe_3)_3][BF_4]$ (**13**) in good yields (63–65 %; Figure 4). Complex **13** exhibits a distorted trigonal planar coordination environment [Σ(P–Cu–P) angles = 359.84°], with P–Cu–P angles ranging from 111.45(2) to 124.84(3)°. The P–Cu [2.3072(5) - 2.3292(5) Å] and the P–B [1.982(3) to 1.992(2) Å] bond lengths in **13** are slightly longer than those measured for the complexes **4**–**11**. In the solid state, each boranyl group of **13** adopts a different orientation; one lies within the P_3Cu plane while the others are positioned above and below (Figure 4b). In contrast, the Cu$^{(I)}$ center in the complex $[Cu(Ph_3P)_3][BF_4]$ is also coordinated by the BF_4^- group, resulting in a pseudotetrahedral coordination geometry.[14]

In the room temperature ^{31}P NMR spectra of **13**, a single broad signal is detected at –42.9 ppm, which is upfield shifted

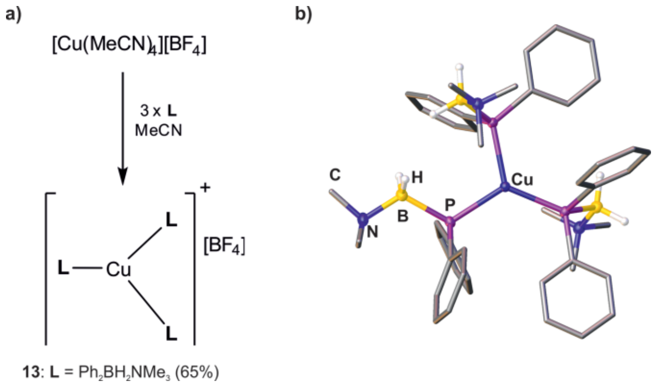


Figure 4. (a) Reaction of **L** with the $[Cu(CH_3CN)_4][BF_4]$: synthesis of the homoleptic coordination compound **13**. Yield is given in parentheses. (b) Molecular structure of **13** in the solid state. Hydrogen atoms on carbon atoms are omitted for clarity.

compared to that of the free ligand **L** (δ = –39.5 ppm). In the FD-MS spectrum, the two fragments $(Ph_2PBH_2{\cdot}NMe_3)^+$ and $[Cu(Ph_2PBH_2{\cdot}NMe_3)_2]^+$ are detected indicating a partial dissociation of complex **13** in CH_2Cl_2.

Conclusions

In summary, it was shown for the first time that the phosphanylborane $Ph_2PBH_2{\cdot}NMe_3$ (**L**) can be used as a building block for the synthesis of complexes of a new class of $Cu^{(I)}$ coordination compounds. The reaction of **L** with $Cu^{(I)}$ halides gave rise to a series of neutral complexes of the type $[Cu_nX_n(Ph_2PBH_2{\cdot}NMe_3)_m]$ (X = Cl, Br, I; n = 1,2,4,5; m = 2,4) (**4**–**11**), while its reaction with $[Cu(MeCN)_4][BF_4]$ yields the cationic homoleptic complex $[Cu(Ph_2PBH_2{\cdot}NMe_3)_3][BF_4]$ (**13**). The coordination complexes **4**–**6** and **9** possess solid-state structures comparable to those based on PPh_3 ligands, however, no such resemblance is found for the products **7**, **8**, **10** and **11**. Furthermore, according to the CSD database, the cluster compounds **10** and **11** possess solid-state structures unprecedented within the class of $Cu^{(I)}$ halide coordination compounds. These results open the door to the further use of new phosphine–borane adducts in $Cu^{(I)}$ coordination chemistry to access new structural types of compounds, thus enlarging the library of this promising research area. Current investigations in this field involve reactions based on the pnictogenylboranes $Ph_2E–BH_2{\cdot}NMe_3$ (E = P, As) towards: *i*) a variety of $Cu^{(I)}$ salts to design clusters with possible Cu•••Cu interactions and study their luminescence properties, and *ii*) $Ag^{(I)}$ salts which will allow the synthesis of the first examples of $Ag^{(I)}$-stabilized pnictogenylborane coordination compounds.

Supporting Information (see footnote on the first page of this article): NMR spectroscopy data, elemental analysis, mass spectrometry, as well as crystal-structure refinement data for complexes **4**–**11** and **13**.

CCDC 1990538 (for **4**), 1992539 (for **5**), 1990540 (for **6**), 1990541 (for **7**), 1990542 (for **8**), 1990543 (for **9**), 1990544 (for **10**), 1990545 (for **11**), and 1990546 (for **13**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Keywords: Phosphorus · Boron · Copper · Coordination chemistry · Cubane

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