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Synthesis of the dinuclear bis(acetonitril)adduct 1 (L = CH₃CN).

The best results of our structural investigations of the dinuclear complex were obtained with the carbastanna-closo-dodecaborate counterion. This heteroborate shows not enough nucleophilicity to coordinate at copper and the complex crystallizes as the solvent adduct (Fig. 1). In complex 1 the copper atoms exhibit a Cu–Cu distance of more than 5 Å and we have found aggregation of coinage metals silver and gold caused by coordination of strong donor ligands like Group 14 heteroborates.
each copper centre is coordinated by one phosphorus atom, two
dimethylamino substituents and one solvent molecule in a
nearly tetrahedral arrangement. Coordination of the PN-moiety
of the dmapm ligand can be compared with published PN-
chelate ligands.\textsuperscript{63,64} The acetonitrile coordination at copper is
also known from complexes present in the literature.\textsuperscript{38, 39, 41, 46,}

The copper complex

two Cu(I) atoms: the germanium ligand shows a short
Ge1–Cu2 bond [2.2838(7) Å] and a longer bond [Ge1–Cu1 2.7229(7) Å]
NMR spectroscopy. The copper complex

In the solid state structure of the crystals of

dinuclear copper complex

Ge, Sn) and were interested to study the reaction between the
all four cases the acetonitrile adduct

We have investigated the aggregation reaction of co inage
metals coordinated at germanium or tin donors [EB\textsubscript{1}H\textsubscript{1}]\textsuperscript{2} (E =
Ge, Sn) and were interested to study the reaction between the
dinuclear copper complex 1 and the nucleophilic ligands
[GeB\textsubscript{12}H\textsubscript{11}]\textsuperscript{2}–, [SnB\textsubscript{12}H\textsubscript{11}]\textsuperscript{2}–, [GeB\textsubscript{13}H\textsubscript{13}]\textsuperscript{2}– and
[SnB\textsubscript{13}H\textsubscript{13}]\textsuperscript{2}–. In all four cases the acetonitrile adduct 1 was reacted with one
equivalent of heteroborate at room temperature (Scheme 2, 3, 5,
6). The products were purified by crystallization and characterized by elemental analysis, NMR spectroscopy, single
crystal structure analysis and in the case of the SnB\textsubscript{11}H\textsubscript{11} reaction product 3 by \textsuperscript{119}Sn Mößbauer and \textsuperscript{117}Sn solid state
NMR spectroscopy. The copper complex 1 reacts with the four
different nucleophiles to give four different products (Scheme 2,
3, 5, 6 and Fig. 2, 3, 6, 7).

In the solid state structure of the crystals of 2 obtained from the
reaction with germa-closo-dodecaborate (Scheme 2) both
ligands, the germanium nucleophile [GeB\textsubscript{11}H\textsubscript{11}]\textsuperscript{2}– and the
chelating PN-ligand, are unsymmetrically coordinated at the
two Cu(I) atoms: the germanium ligand shows a short Ge–Cu2
bond [2.2838(7) Å] and a longer bond [Ge1–Cu1 2.7229(7) Å] to
the copper atom which is also coordinated by a BH-unit. The
shorter Cu–Ge distances lies within the range of published bond
lengths.\textsuperscript{70-72} In these molecules the germanium atom is further
coordinated by other germanium atoms,\textsuperscript{70} a $\beta$-diketiminate ligand\textsuperscript{73} or silylamides.\textsuperscript{74} Besides a Cu–Cu distance of 2.7910(8)
Å, which is comparable with other phosphine bridged dinuclear
Cu-Cu units, both transition metals show bonds with four donor
ligands.\textsuperscript{73, 74} The coordination of Cu1 can be described as a
capped trigonal planar arrangement and in the case of Cu2 as
distorted tetrahedral. As a consequence of the BH-coordination
one dimethylamino group remains uncoordinated at Cu1
(Figure 2). This unsymmetrical coordination could not be
verified by NMR spectroscopy: in the solution NMR spectra at
room temperature the signals in the $^1$H, $^{13}$C\{\textit{H}\} and $^{31}$P\{\textit{H}\} spectra indicate symmetrical coordination of the PN-ligand.
The signals in the $^1$B\{\textit{H}\} NMR spectra of 2 (−1.8, −10.6, −
13.8 ppm) are a good indicator for coordination of the cluster
($^1$B NMR of uncoordinated cluster: −5.4, −10.0, −11.5 ppm),
however the ratio and the number of the signals are not a proof
for the unsymmetrical structure. Moreover, the $^{31}$P\{\textit{H}\} NMR spectrum in solution shows only one resonance even at −80°C.

Even the $^{31}$P VACP/MAS NMR spectrum features one broad
Lorentzian (Δν\textsubscript{1/2} = 600 Hz) instead of the characteristic
multiplet anticipated for spin-spin interactions with $^{63,65}$Cu
(vide infra) (VACP: variable amplitude crosspolarization).\textsuperscript{75}

![Fig. 1 ORTEP plot of the molecular structure of the dinuclear copper complex 1a. Counteranions have been omitted; ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: Cu1–Cu2 5.524(1), Cu1–P1 2.169(1), Cu1–N1 2.258(3), Cu1–N2 2.229(4), Cu1–N5 1.891(4), Cu2–P2 2.179(1), Cu2–N3 2.189(4), Cu2–N4 2.241(4), Cu2–N6 1.917(4); P1–C1–P2 111.2(2), P1–Cu1–N1 85.46(10), P1–Cu1–N2 84.58(10), P1–Cu1–N5 149.47(12), N1–Cu1–N2 112.97(13) Å, P2–Cu2–N3 86.45(9), P2–Cu2–N4 87.00(9), P2–Cu2–N6 143.32(11), N3–Cu2–N4 111.08(13) Å.](image1)

![Scheme 2 Reaction of the copper complex 1 with [GeB\textsubscript{12}H\textsubscript{11}]\textsuperscript{2}–.](image2)

![Fig. 2 ORTEP plot of the molecular structure of the dinuclear copper complex 2. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: Ge1–Cu1 2.2838(7), Ge1–
Cu1 2.7229(7), Cu1–N2 2.205(4), Cu1–P1 2.240(1), Cu1–Cu2 2.7910(8), Cu2–P2 2.172(1), Cu2–N4 2.198(4), Cu2–N3 2.387(5), Cu1–B2 2.334(6), Ge1–B2 2.141(5), Ge1–B6 2.145(5),
Ge1–B5 2.154(5), Ge1–B6 2.154(5), Ge1–B3 2.154(5), Ge1–B4 2.170(5), P2–C1–
P1 107.6(2).](image3)
Stanna-closo-dodecaborate reacts with the copper electrophile 1 to give a neutral coordination compound exhibiting a hitherto unprecedented coordination mode for this heteroborate (Scheme 3). The copper coordination complex 3 is on the basis of NMR spectroscopy the only product of this reaction and was isolated in a yield of 73%. The molecular structure in the solid state, determined by X-ray crystallography, is shown in Fig. 3. The phosphorus ligand shows coordination at the copper atoms with distances of 2.2287(4) and 2.1932(4) Å. These bond lengths are comparable with the values in complex 2 and starting material 1. On both sides of the chelating ligand only one Me₂N₄-group is coordinated at the Cu(I) metal centre with bond lengths of 2.272(1) and 2.244(1) Å. The cluster is side on coordinated via symmetric interaction of three BH₄-units of the upper boron belt with the copper atoms. The B–Cu interatomic distances can be compared with a variety of Cu₄borane complexes. Both copper atoms show coordination number five which can be explained as a tetrahedral coordination of the P, N donor and two BH₄-units plus a long interaction with the tin vertex of the borate. Due to this cluster copper interaction the Cu–Sn interatomic distance is with 3.0118(3) Å longer than the interaction found in the germanium complex 2. Side on coordination of stanna-closo-dodecaborate is a known structural motif with the BH₄-units of the upper and lower belt coordinating at ruthenium or iron transition metal fragments. These complexes show a reversible coordination mode rearrangement between η₁(BH) and η₁(Sn) coordination.

Table 1  Selected interatomic distances and angle

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<td>2.179(1)</td>
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<td>2.1853(8)</td>
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<td>2.258(3)</td>
<td>2.205(4),</td>
<td>2.272(1)</td>
<td>2.191(3)</td>
<td>2.208(3)</td>
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<td>2.229(4)</td>
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<td>2.244(1)</td>
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<td>2.227(3)</td>
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<td>Cu–Cu</td>
<td>5.524(1)</td>
<td>2.791(1)</td>
<td>3.012(1)</td>
<td>3.530(1)</td>
<td>4.499(1)</td>
<td>2.663(1)</td>
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<td>2.3017(5)</td>
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<td>(E = Ge, Sn)</td>
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<td>2.8363(2)</td>
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<td>2.3049(5)</td>
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<tr>
<td>Cu–B</td>
<td>2.145(5)</td>
<td>2.276(2)</td>
<td>2.284(4)</td>
<td>2.234(4)</td>
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<td>2.154(5)</td>
<td>2.196(2)</td>
<td>2.275(4)</td>
<td>2.542(3)</td>
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<td>2.163(5)</td>
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<td>2.273(4)</td>
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<td>2.251(2)</td>
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<td>P–C–P</td>
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<td>107.6(2)</td>
<td>115.6(1)</td>
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<td>109.7(1)</td>
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Scheme 3  Reaction of the copper complex 1 with [SnB₁₁H₁₁]²⁻.
B–H–Cu-interaction at the upper boron belt. Presumably a rotation of the borate in the Cu$_2$-sphere is responsible for the $^1$B-NMR spectroscopic findings. In the $^{31}$P($^1$H) NMR solution spectrum the resonance for the phosphorus atoms can be found at $-40.6$ ppm and can be compared to the signals found at $-34.9$ and $-42.8$ ppm in the solid state $^{31}$P VACP/MAS NMR spectrum. Both crystallographically nonequivalent phosphorus atoms exhibit spin-spin coupling interactions with $^{63,65}$Cu with non-equidistant intra-multiplet spacings due to the $^{63,65}$Cu nuclear quadrupolar interaction. Detailed analysis (see Supporting Information) of the multiplets reveals spin-spin coupling constants, $J(^{65}$Cu,$^{31}$P), of 1650 and 1670 Hz, respectively. Since we have characterized a variety of coordination modes of the heteroborate ligand via crystal structure analysis and $^{119}$Sn NMR spectroscopy in solution as well as in the solid state we interpret the results of the $^{119}$Sn NMR spectroscopy for complex 3 (solution $-601$ ppm, solid state $-623$ ppm) as a further proof for side on coordination.

In order to investigate the influence of the side on coordination of the two copper atoms on the tin atom of the heteroborate $^{119}$Sn Mößbauer spectroscopy was carried out. The experimental and simulated $^{119}$Sn Mößbauer spectrum of [Cu$_2$(dmapm)(SnB$_{11}$H$_{11}$)] at 78 K is presented in Fig. 4 together with a transmission integral fit. The spectrum was well reproduced with a signal at an isomer shift of $\delta = 2.68(1)$ mm/s which is subjected to significant quadrupole splitting of $\Delta E_Q = 1.55(1)$ mm/s. The experimental line widths is $\Gamma = 0.88(1)$ mm/s. The isomer shift value obtained for [Cu$_2$(dmapm)(SnB$_{11}$H$_{11}$)] is indicative for divalent tin and the large quadrupole splitting parameter reflects the asymmetric coordination of the tin atom due to the lone-pair activity. The refined isomer shift and quadrupole splitting can be compared with the values published for the side on coordinated cluster in the iron complex [Fe(SnB$_{11}$H$_{11}$)(triophos)] ($\delta = 2.71$, $\Delta E_Q = 1.54$ mm/s) and are therefore significant for the BH-coordinated cluster. A second spectral component with an approximate amount of 8% occurs at $\delta = 0.50(5)$ mm/s; most likely a hydrolysis product containing tetravalent tin. The latter signal was included as a simple Lorentzian in the fit.

The nucleophilicity of the side on coordinated cluster was investigated by means of reaction with the electrophile [Mo(CO)$_2$(CH$_3$CN)$_3$] (Scheme 4). This type of reaction is known for the side-on coordinated clusters in $[2,7,8-(\mu-H)]$-{Fe(triophos)}-$\text{E}B_3$H$_2$ (E = Ge, Sn). In these cases the $\eta^3$-coordinated tin or germanium clusters show enough nucleophilicity to react with the transition metal electrophiles [M(CO)$_2$(thf)] (M = Cr, Mo, W) under formation of a Mo–Ge or Mo–Sn bond. The presented dicopper-stanna-closo-dodecaborate coordination compound 3 exhibits also enough reactivity at the tin vertex and forms a Sn–Mo bond in reaction with the acetonitrile adduct [Mo(CO)$_2$(CH$_3$CN)$_3$]. Interestingly a carbonyl transfer has also taken place. Carbonyl transfer reactions with [Mo(CO)$_2$(CH$_3$CN)$_3$] are known in the literature. The best proof for coordination at the tin vertex can be found in the $^{119}$Sn NMR spectra of complex 4: in the solution NMR spectra we can detect a shift to high frequency upon coordination at the tin vertex [3: $-601$ ppm, 4: $-218$ ppm]. The discussed shift of the $^{119}$Sn NMR resonance is a general trend in stanna-closo-dodecaborate coordination chemistry. However in the $^{31}$P NMR spectrum of complexes 3 and 4 although presenting different coordination modes of the cluster both complexes exhibit a resonance close to $-41$ ppm.
Scheme 4 Reaction of the stanna-closo-dodecaborate complex 3 with [Mo(CO)$_3$(CH$_3$CN)$_3$] (n = 1.7).

Fig. 5 ORTEP plot of the molecular structure of the dinuclear copper complex 4. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: Sn1–B2 2.374(4), Sn1–B3 2.336(4), Sn1–B4 2.358(4), Sn1–B5 2.346(4), Sn1–B6 2.358(4), Cu1–B2 2.284(4), Cu1–B7 2.275(4), Cu2–B3 2.273(4), Cu2–B8 2.256(4), Sn1–Mo 2.759(1), Cu1–P1 2.193(1), Cu2–P2 2.199(1), Cu1–N2 2.191(3), Cu2–N3 2.188(4), Cu1–Cu2 3.530(1), Mo–C1 1.979(4), Mo–C2 2.054(4), Mo–C3 2.035(4), Mo–C4 2.054(5), Mo–C5 2.038(5), C1–O1 1.145(6), C2–O2 1.130(5).

The molecular structure in the solid state of complex 4 determined by X-ray crystallography is shown in Fig. 5. Like in starting material the chelating ligand is coordinated at each copper atom with two nitrogen and one phosphorus donor sites. The Cu–N and Cu–P interatomic distances are listed in Table 1 and can be compared with the values found in the acetonitrile adduct 1. Both Cu(I) atoms show a tetrahedral coordination and the fourth bond is formed with the germanium atoms of the cluster to construct a seven membered ring. The found Cu–Ge interatomic distances of 2.3017(5) and 2.3049(5) Å lie in the range of published bond lengths with germanium, which is further coordinated by other germanium atoms, a β-diketiminate ligand or silylamides (2.214–2.446 Å). The molecular structure of the Cu–Ge coordination compound in the solid state is shown in Fig. 6. Like in starting material the chelating ligand is coordinated at each copper atom with two nitrogen and one phosphorus donor sites. The Cu–N and Cu–P interatomic distances are listed in Table 1 and can be compared with the values found in the acetonitrile adduct 1. Both Cu(I) atoms show a tetrahedral coordination and the fourth bond is formed with the germanium atoms of the cluster to construct a seven membered ring. The found Cu–Ge interatomic distances of 2.3017(5) and 2.3049(5) Å lie in the range of published bond lengths with germanium, which is further coordinated by other germanium atoms, a β-diketiminate ligand or silylamides (2.214–2.446 Å). Fig. 6 ORTEP plot of the molecular structure of the dinuclear copper complex 5. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: N1–Cu1 2.208(3), N2–Cu1 2.209(3), N3–Cu2 2.209(3), N4–Cu2 2.209(3), C1–O1 1.145(6), C2–O2 1.130(5).
Since we were interested about the effect of the change to the higher homologue of $[\text{Ge}_2\text{B}_{10}\text{H}_{10}]^{2-}$ on the structure with the dicopper electrophile we reacted distanna-closo-dodecaborate with the coordination compound 1 (Scheme 6). However in this case, although four transition metal complexes of the di-tin nucleophile have already been isolated so far, the tin coordination was not found. Instead we lost the Sn$_2$-unit and the remaining decaborate cluster $[\text{B}_{10}\text{H}_{10}]^{2-}$ occupies the di-copper pocket. The fate of the tin is so far unclear to us. Decaborate coordination of copper was intensively investigated also with respect to chemical bonding.

Scheme 6 Reaction of the copper complex 1 with $[\text{Sn}_2\text{B}_{10}\text{H}_{10}]^{2-}$.

A small amount of single crystals of 6 were obtained after slow diffusion of diethyl ether into the acetonitrile reaction mixture. The molecular structure is depicted in Fig. 7 and selected interatomic distances are listed. Each copper atom is coordinated at one nitrogen and phosphorus atom with distances in the range of the presented copper coordination compounds. The copper atoms exhibit coordination at a BH$_4$ unit with short Cu–B bonds: B1–Cu1 2.214(3), B2–Cu2 2.201(3). Another feature of complex 6 is a relatively short Cu(I)–Cu(I) interaction [2.6631(5) Å]. Including this Cu–Cu interaction the copper atoms exhibit coordination number four in a distorted tetrahedral arrangement. In the presented series of di-copper complexes the decaborate coordination results to give the shortest interaction between the metals.

Conclusions

In summary, we herein describe the synthesis of a new dinuclear copper electrophile by using the hexadentate dmapm ligand. Coordination abilities of the dicopper complex were investigated in reaction with Group 14 heteroborates. We have isolated four different motives for the coordination of the dicopper complex with four different dianionic closo-clusters. Obviously the dmapm ligand offers flexibility with respect to the used number of donor sites and geometry. The characterized structures exhibit a large range for the intermolecular Cu–Cu distance [5.524(1)–2.663(1) Å]. With this electrophilic dinuclear copper complex in hand we foresee interesting opportunities in the field of cooperative catalysis.

Experimental Section

Experimental Details. Unless otherwise stated, all manipulations were carried out under exclusion of air and moisture in an argon atmosphere using standard Schlenk techniques. Solvents were purified by standard methods. All starting materials were purchased commercially from Aldrich Chemical Co. and used without further purification. Dmapm was synthesized according to literature methods.$^{24}$ Elemental analyses were performed by the Institut für Anorganische Chemie Universität Tübingen using a Vario EL analyzer and a Vario MICRO EL analyzer.

NMR Spectroscopy. NMR spectra were recorded with a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 (1H), 80.25 (13B), 62.90 (13C), 101.25 (31P) and 93.25 MHz ($^{119}$Sn), a Bruker AvanceII+400 NMR spectrometer equipped with a 5 mm QNP (quad nucleus probe) head and operating at 400.13 (1H), 100.13...
A Cu$_{119}$Sn$_{42}$ source was used for the $^{119}$Sn Mössbauer spectroscopic investigation. The [Cu$_{2}$m(m-dmapm)]$_{2}$[Sn$_{3}$H$_{11}$]$_{2}$ sample was placed within a thin-walled glass container at a thickness of about 10 mg Sn/cm$^2$. A palladium foil of 0.05 mm thickness was used to reduce the tin 92%. Spectra were analyzed using the program HBA. Hydrogen atoms were placed in calculated positions and refined using the structure determination are presented in Table 1SI. Hydrogen in vacuo geometry at 78 K.

Crystallography. A Bruker Smart APEX II diffractometer with graphite-monochromated MoKα radiation. The programs used in this work are Bruker’s APEX2 v2011.8-0 including SADABS for multiscan absorption correction and SAINT for structure solution in combination with WinGX suite of programs v1.70.01 including SHELXL for structure refinement. Results of the crystal structure determination are presented in Table SI. Hydrogen atoms were placed in calculated positions and refined using the riding model. The following restraints were used during the refinement procedure: 2 EADP, 3 SIMU, DELU, ISOR, EADP for the severe disorder of the cocrystallized Et$_{2}$O molecule. For compounds 1, 4, 6 no additional restraints were used.

Mössbauer spectroscopy. A Cu$_{119}$Sn$_{42}$ source was used for the $^{119}$Sn Mössbauer spectroscopic investigation. The [Cu$_{2}$m(m-dmapm)]$_{2}$[Sn$_{3}$H$_{11}$]$_{2}$ sample was placed within a thin-walled glass container at a thickness of about 10 mg Sn/cm$^2$. A palladium foil of 0.05 mm thickness was used to reduce the tin K X-rays concurrently emitted by this source. The measurement was performed in the usual transmission geometry at 78 K.

Syntheses

[Cu$_{2}$m(m-dmapm)]$_{2}$[Sn$_{3}$H$_{11}$]$_{2}$ (1). 565 mg (1.8 mmol) [Cu(CH$_{2}$CN)$_{4}$][BF$_{4}$] and 500 mg (0.9 mmol) dmnapm were stirred in 50 mL dichloromethane for 3 hours at room temperature. The suspension was filtered through a plug and the solvent was removed in vacuo yielding a yellow solid. Crystals of 1 were obtained by layering an acetone solution of 1 with n-hexane. Yield: 776 mg, 92%. Found: C, 47.27; H, 4.98; N, 7.60. Calc. for [Cu$_{2}$H$_{2}$C$_{4}$N$_{2}$P$_{2}$][BF$_{4}$]·CH$_{2}$CN·CH$_{3}$O (95.60 g/mol): C, 47.72; H, 5.37; N, 7.32.

$^{11}$B NMR (400.13 MHz, CD$_{2}$Cl$_{2}$): $\delta$ 2.40 (s, 6H, CH$_{3}$CN), 7.35–7.41 (m, 4H, Ar-H), 7.48–7.54 (m, 4H, Ar-H), 7.55–7.61 (m, 4H, Ar-H).

$^{119}$Sn NMR (100.13 MHz, CD$_{2}$Cl$_{2}$): $\delta$ 2.5 (s, CH$_{3}$CN), 19.2 (t, $\delta^{(119)}$P$^{(119)}$Sn = 8.0 Hz, CH$_{3}$CN) 49.9 (s, NCH$_{3}$), 122.4 (s, Ar), 128.1 (s, Ar), 129.3–129.8 (m, Ar), 132.2 (s, Ar), 133.1 (s, Ar), 156.9–157.1 (m, Ar).

$^{13}$C NMR (161.98 MHz, CD$_{2}$Cl$_{2}$): $\delta$ –56.7 (br s). Crystals suitable for single crystal structure analysis were obtained with the [Sn$_{3}$Bu$_{3}$H$_{11}$]$_{2}$ counterion: [Cu$_{2}$m(m-dmapm)][Sn$_{3}$H$_{11}$]$_{2}$ (1a). 50 mg (0.05 mmol) [Cu$_{2}$m(m-dmapm)]$_{2}$[CN$_{4}$]$_{2}$[BF$_{4}$]$_{2}$ (1) and 31 mg (0.05 mmol) [PPh$_{4}$][Sn$_{3}$Bu$_{3}$H$_{11}$]$_{2}$ were stirred in 20 mL acetonitrile for 3 hours at room temperature. After filtration slow diffusion of diethyl ether into the acetonitrile solution gave very small amounts of colourless crystals of 1a.

$^{51}$V PACP/MAS NMR: $\delta_{00} = 29.1$.
[Cu₂(µ-dmapm)(µ-SnB₄H₁₀)](Mo(CO)₃) (4). 26 mg (0.03 mmol) [Cu₂(µ-dmapm)(µ-SnB₄H₁₀)] (2) and 14 mg (0.05 mmol) [Mo(CO)₃(CH₂CN)] were stirred for 4 hours at room temperature in 10 mL dichloromethane. The suspension was filtered, 5 mL benzene were added and the solution was layered with n-hexane to give yellow crystals. Yield: 13 mg, 41 %. Found: C, 39.98; H, 4.62; N, 4.77. Calc. for [Cu₂H₂Cu₂N₃P₃(SnB₄H₁₀)(Mo(CO)₃)] - 0.5 CuH₂ (120.75 g/mol): C, 40.78; H, 4.67; N, 4.64. ¹H NMR (400.13 MHz, CDCl₃): δ 2.49 (s, 24H, NCH₃), 2.92 (t, 2J = 338Hz) = 1) = 300 Hz, 6B), –16.5 and 14.3 (br s, 2H, Ar-H). ¹³C[¹H] NMR (100.13 MHz, CDCl₃): δ 26.5–25.7 (m, CH₃), 48.8 (s, NCH₃), 123.8 (s, Ar), 127.0 (s, Ar), 130.7–131.2 (m, Ar), 132.5 (s, Ar), 132.6 (s, Ar), 157.6–157.9 (m, Ar), 207.7 (s, cis CO), 213.3 (s, trans CO). ¹⁹⁷Au NMR (80.25 MHz, CDCl₃): δ –16.5 (br s, half line width 300 Hz, 6B), –16.5 and 14.3 (br s, 2H, Ar-H). ¹¹⁷Sn[¹H] NMR (93.25 MHz): δ –218 (br). ¹³P[¹H] NMR (161.98 MHz, CDCl₃): δ –40.1 (br s).

[Cu₂(µ-dmapm)(µ-Ge₂B₁₀H₁₀)] (5). 50 mg (0.05 mmol) [Cu₂(µ-dmapm)(CH₂CN)]²⁺ (1) and 42 mg (0.05 mmol) [Ph₂Me₂N]₂[Ge₂B₁₀H₁₀] were stirred at room temperature for 3 hours in 20 mL acetonitrile. The suspension was filtered and diethyl ether or toluene was slowly diffused into the solution to obtain yellow crystals. Yield: 13 mg, 26 %. Found: C, 49.82; H, 6.01; N, 5.68. Calc. for [Cu₂H₂Cu₂N₃P₃(µ-Ge₂B₁₀H₁₀)] – 2 Toluene (1131.45 g/mol): C, 49.89; H, 6.06; N, 4.95. ¹H NMR (400.13 MHz, CDCl₃): δ 2.59 (s, 24H, NCH₃), 3.21 (t, 2J = 338Hz) = 6.3 Hz, 2H, CH₂), 7.20–7.29 (m, 4H, Ar-H), 7.39–7.54 (m, 12H, Ar-H, Ar-CH). ¹³C[¹H] NMR (100.13 MHz, CDCl₃): δ –28.8 (br s, 2B, τ₁₂ = 338Hz), 1.7 –1.4 (8B, 8B). ¹³C[¹H] NMR (100.13 MHz, CDCl₃): δ 23.1–24.3 (m, CH₃), 48.2 (s, NCH₃), 123.3–123.5 (m, Ar), 126.8–127.0 (m, Ar), 132.4–132.5 (m, Ar), 132.5–132.6 (m, Ar), 150.0–151.9 (m, Ar), 158.1–158.4 (m, Ar). ³¹P[¹H] NMR (161.98 MHz, CDCl₃): δ –44.1 (br s). Due the high sensitivity of ⁵, we never observed an elemental analysis of a pure compound. Instead solvent inclusion is always present.

[Cu₂(µ-dmapm)(B₁₀H₁₀)] (6). 100 mg (0.11 mmol) [Cu₂(µ-dmapm)(CH₂CN)]²⁺ (1) and 66 mg (0.11 mmol) [Et₄N]₂[SnB₁₀H₁₀], were stirred at room temperature for 3 hours 20 mL acetonitrile. The suspension was filtered and diethyl ether was slowly diffused into the solution to obtain colourless crystals. Yield: 14 mg, 17 %. Found: C, 49.57; H, 6.95; N, 7.27. Calc. for [Cu₂H₂Cu₂N₃P₃(B₁₀H₁₀)] (801.95 g/mol): C, 49.42; H, 6.54; N, 6.99. ¹H NMR (400.13 MHz, CDCl₃): δ 2.46 (s, 24H, NCH₃), 3.10 (br s, 2H, CH₂), 7.15–7.23 (m, 4H, Ar-H), 7.29–7.43 (m, 8H, Ar-H), 7.47–7.54 (m, 4H, Ar-H). ¹³B NMR (80.25 MHz, CDCl₃): δ –29.0 (br, d, ¹J/B-H = 100 Hz, 2B), –8.1 (br, d, ¹J/B-H = 120 Hz, 8B). ¹³C[¹H] NMR (100.13 MHz, CDCl₃): δ 27.4–27.7 (m, CH₃), 48.5 (s, NCH₃), 123.5–123.7 (m, Ar), 127.3–127.6 (m, Ar), 132.6 (s, Ar), 133.1 (s, Ar), 157.2–157.5 (m, Ar). ³¹P[¹H] NMR (161.98 MHz, CDCl₃): δ –31.1 (br s).

Notes and references

a Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: lars.wesemann@uni-tuebingen.de

b Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, D-48149 Münster, Germany

t Electronic Supplementary Information (ESI) available: details of crystallographic data and solid state NMR data. See DOI: 10.1039/b000000x/
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Dinuclear Copper Complexes: Coordination of Group 14 Heteroborates

Holger Scheel, Jessica Wiederkehr, Klaus Eichele, Hermann A. Mayer, Florian Winter, Rainer Pöttgen, and Lars Wesemann

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The hitherto unknown dinuclear copper(I) complex \([\text{Cu}_2(\mu_4\text{dmap})(\text{CH}_3\text{CN})_2][\text{BF}_4]_2\) was reacted with Group 14 heteroborates. Four different coordination motives have been characterized structurally and in the case of the side on coordinated SnB\(_{11}\)H\(_{11}\) cluster the nucleophilicity at the tin vertex has been established in reaction with a molybdenum carbonyl complex.