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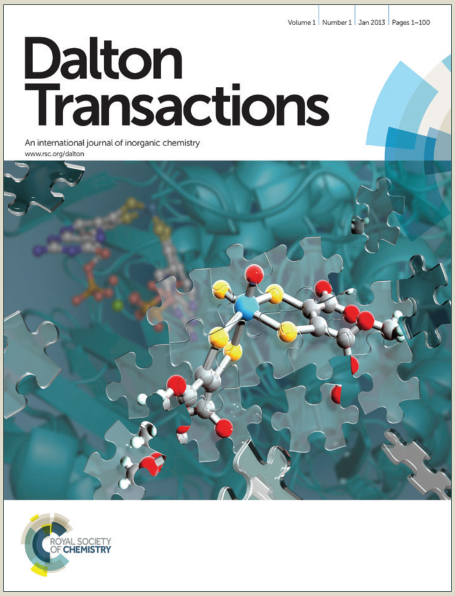

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Dinuclear Copper Complexes: Coordination of Group 14 Heteroborates

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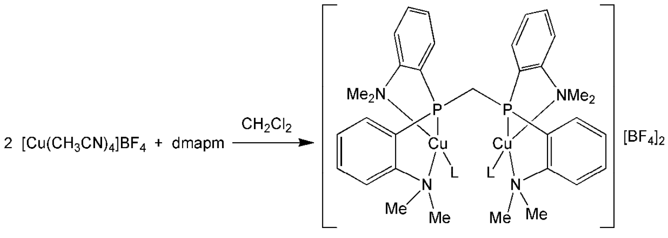
Dicopper(I) complexes with the chelating dmapm ligand [dmapm (1,1-bis{di(*o*-*N*,*N*-dimetylanilinyl)phosphino}methane)] have been synthesized and characterized structurally. A synthesis for the acetonitrile adduct [Cu_2(μ-dmapm)($CH_3CN)_2$][BF_4]$_2$ (**1**) has been presented and the dicopper electrophile has been used as the starting material in reaction with Group 14 heteroborates.
Coordination of the *closo*-borates at the dicopper moiety resulted to give different molecular structures with varying Cu···Cu distances. In the case of the side on coordinated stanna-*closo*-dodecaborate the tin vertex has been characterized by ^{119}Sn Mößbauer spectroscopy and the nucleophilicity at the tin was established in reaction with a molybdenum carbonyl complex.

Introduction

The coordination chemistry of tin and germanium ligands is already an attractive field of research for a long time: catalytic aspects of the [ECl_3]$^-$ (E = Ge, Sn) coordination play an important role together with the heavier carbene analogy of germylenes or stannylenes.[1-9] Besides these topics a large variety of heavier Group 14 ligands were synthesized and their coordination behaviour with transition metals was investigated.[1, 5, 7, 10-18] Especially in the tin case these investigations were carried out by means of ^{119}Sn NMR and ^{119}Sn Mößbauer spectroscopy.[10, 11, 16-22] We have developed the chemistry of Group 14 heteroborates [$EB_{11}H_{11}$]$^{2-}$ and [$E_2B_{10}H_{10}$]$^{2-}$ (E = Ge, Sn) with respect to transition metal coordination.[23-29] Besides hexacoordinated Ni, Pd and Pt in complexes like [$Ni(SnB_{11}H_{11})_6$]$^{8-}$ the flexible and ambidentate coordination of the heteroborates was reported.[25, 30] Furthermore we studied the reaction of the Ge and Sn ligands of type [$EB_{11}H_{11}$]$^{2-}$ with coinage metals.[31-36] In these reactions we found an interesting coinage metal–metal bond formation initiated by germanium or tin coordination, which resulted to give dimers and oligomers with bridging Ge or Sn ligands. In the case of the distanna-*closo*-dodecaborate a tripodal tin ligand was synthesized, which shows formation of a dinuclear tin bridged copper complex in reaction with a copper electrophile.[36] In this publication we present the synthesis of a dinuclear copper(I) complex and reactions of this dication with Group 14 heteroborates.

Results and Discussion

Dinuclear copper complexes are currently of major interest in particular in the field of bioinorganic chemistry and with respect to activation of small molecules.[37-53] A variety of polydentate ligands were synthesized in order to model the coordination sphere of copper in the enzyme tyrosinase.[42] Since we have found aggregation of coinage metals silver and gold caused by coordination of strong donor ligands like Group 14 heteroborates we were curious about the effect of the coordination of these ligands at two copper atoms. Therefore we aimed to synthesize a dinuclear copper complex with the copper atoms coordinated at a relatively flexible hexadentate ligand molecule. James *et al*. reported in 2002 the synthesis of the dmapm ligand, which is a bis-phosphine substituted with four *ortho*-dimethylanilin groups [dmapm (1,1-bis{di(*o*-*N*,*N*-dimetylanilinyl)phosphino}methane)].[54-57] The palladium, platinum, rhodium, iridium and ruthenium coordination chemistry of this hexadentate ligand was studied successfully.[55-61] Treatment of the dmapm ligand with two equivalents of the copper electrophile [$Cu(CH_3CN)_4$][BF_4] (Scheme 1) leads to the formation of the dinuclear copper complex **1**. The bisacetonitrile adduct **1** was isolated in high yield and was characterized by NMR spectroscopy, elemental analysis and single crystal structure analysis.



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Scheme 1 Synthesis of the dinuclear bis(acetonitril)adduct **1** (L = CH_3CN).

The best results of our structural investigations of the dinuclear copper complex were obtained with the carbastanna-*closo*-dodecaborate counteranion.[62] 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 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.[63-68] The acetonitrile coordination at copper is also known from complexes present in the literature.[38, 39, 41, 46, 69]

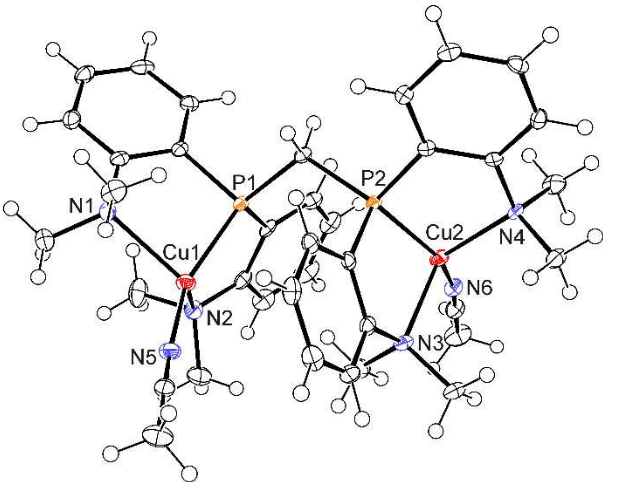
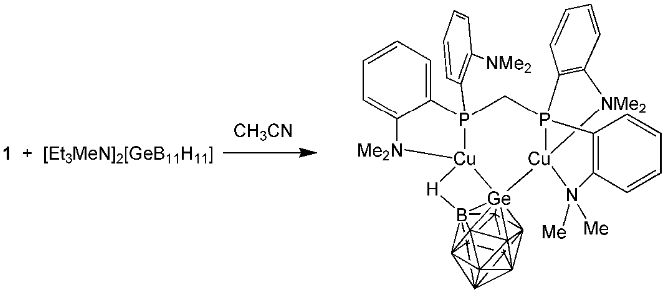


Fig. 1 ORTEP plot of the molecular structure of the dinuclear copper complex **1a**. Counteranions have been omitted; ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: Cu1–Cu2 5.524(1), Cu1–P1 2.169(1), Cu1–N1 2.258(3), Cu1–N2 2.229(4), Cu1–N5 1.891(4), Cu2–P2 2.179(1), 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.

We have investigated the aggregation reaction of coinage metals coordinated at germanium or tin donors $[EB_{11}H_{11}]^{2-}$ (E = Ge, Sn) and were interested to study the reaction between the dinuclear copper complex **1** and the nucleophilic ligands $[GeB_{11}H_{11}]^{2-}$, $[SnB_{11}H_{11}]^{2-}$, $[Ge_2B_{10}H_{10}]^{2-}$ and $[Sn_2B_{10}H_{10}]^{2-}$. 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 $SnB_{11}H_{11}$ reaction product **3** by ^{119}Sn Mößbauer and ^{119}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 $[GeB_{11}H_{11}]^{2-}$ and the chelating PN-ligand, are unsymmetrically coordinated at the 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] 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.[70-72] In these molecules the germanium atom is further coordinated by other germanium atoms,[70] a *β*-diketiminate ligand[71] or silyamides.[72] 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.[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{^{1}H} and ^{31}P{^{1}H} spectra indicate symmetrical coordination of the PN-ligand. The signals in the ^{11}B{^{1}H} NMR spectra of **2** (–1.8, –10.6, –13.8 ppm) are a good indicator for coordination of the cluster (^{11}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{^{1}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 ($\Delta\nu_{1/2}$ = 600 Hz) instead of the characteristic multiplet anticipated for spin-spin interactions with ^{63,65}Cu (vide infra) (VACP: variable amplitude crosspolarization).[75]



$[Cu_2(dmapm)(GeB_{11}H_{11})]$ (**2**)

Scheme 2 Reaction of the copper complex **1** with $[GeB_{11}H_{11}]^{2-}$.

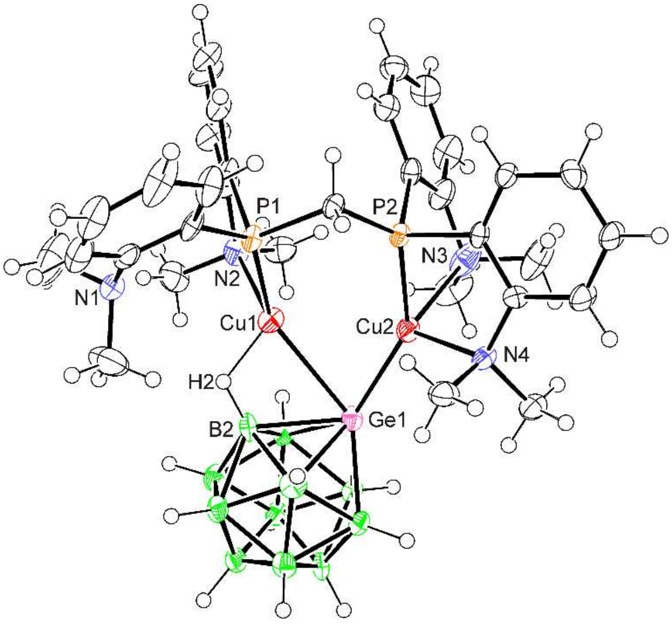
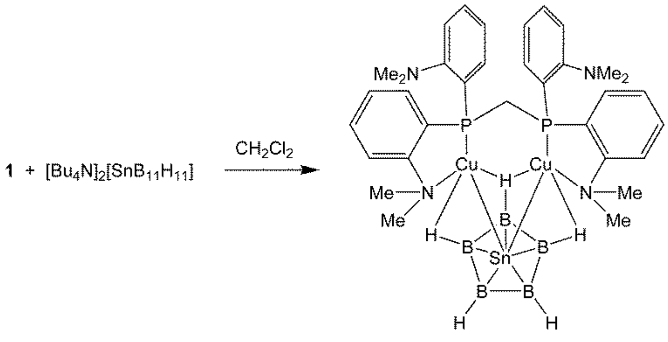


Fig. 2 ORTEP plot of the molecular structure of the dinuclear copper complex **2**. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: Ge1–Cu2 2.2838(7), Ge1–Cu1 2.7229(7), Cu1–N2 2.205(4), Cu1–P1 2.240(1), Cu1–Cu2 2.7910(8), Cu2–P2 2.172(1), Cu2–N4 2.198(4), Cu2–N3 2.387(5), Cu1–B2 2.334(6), Ge1–B2 2.141(5), Ge1–B6 2.145(5), Ge1–B5 2.154(5), Ge1–B3 2.163(5), Ge1–B4 2.170(5), P2–C1–P1 107.6(2).

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 Me_2N-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 BH-units of the upper boron belt with the copper atoms. The B–Cu interatomic distances can be compared with a variety of Cu-borane complexes.[76-82] Since the Cu_2-moiety is side on coordinated at the tin borate the Cu–Sn distances of 2.7687(2), 2.8363(2) Å are longer than the bond lengths in $[Cu-(SnB_{11}H_{11})_3(CH_3CN)]^{5-}$ [2.5928(5), 2.6037(8) Å] or $[\{Sn(Sn_2B_{10}H_{10})_3Cu\}_2]^{6-}$ [2.632(2), 2.547(2), 2.545(2) Å] exhibiting a direct interaction between copper and tin.[35, 36] Both copper atoms show coordination number five which can be explained as a tetrahedral coordination of the P, N donor and two BH-units plus a long interaction with the tin vertex of the borate. Due to this cluster copper interaction the Cu–Cu 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 BH-units of the upper and lower belt coordinating at ruthenium or iron transition metal fragments. These complexes show a reversible coordination mode rearrangement between η^3(BH) and η^1(Sn) coordination.[30, 83-85]

Table 1 Selected interatomic distances and angle

Bond length [Å], angle [°]	1	2	3	4	5	6
Cu–P	2.169(1)	2.250(1)	2.2287(4)	2.193(1)	2.1803(8)	2.1980(8)
	2.179(1)	2.172(1)	2.1932(4)	2.199(1)	2.1993(8)	2.1853(8)
$Cu-NMe_2$	2.258(3)	2.205(4),	2.272(1)	2.191(3)	2.208(3)	2.204(2)
	2.229(4)	2.198(4)	2.244(1)	2.188(4)	2.216(3)	2.287(2)
	2.189(4)	2.387(5)			2.221(3)	
	2.241(4)				2.227(3)	
Cu–Cu	5.524(1)	2.791(1)	3.012(1)	3.530(1)	4.499(1)	2.663(1)
Cu–E		2.2838(7)	2.7687(2)		2.3017(5)	
(E = Ge, Sn)		2.7229(7)	2.8363(2)		2.3049(5)	
Cu–B		2.145(5)	2.276(2)	2.284(4)		2.234(4)
		2.154(5)	2.196(2)	2.275(4)		2.542(3)
		2.163(5)	2.209(2)	2.273(4)		2.214(3)
			2.251(2)	2.256(4)		2.201(3)
P–C–P	111.2(2)	107.6(2)	115.6(1)	114.1(2)	114.4(2)	109.7(1)



$[Cu_2(dmapm)(SnB_{11}H_{11})]$ (**3**)

Scheme 3 Reaction of the copper complex **1** with $[SnB_{11}H_{11}]^{2-}$.

In the ^1H NMR spectrum of complex **3** for the coordinated and uncoordinated Me_2N-groups we detect at room temperature one signal at 2.48 ppm which is indicative for an exchange procedure and should be compared with the signal for the uncoordinated ligand at 2.76 ppm. At –80°C in the ^1H NMR spectrum three signals for the coordinated and uncoordinated Me_2N-groups were observed. In comparison to the uncoordinated tin borate [–5.3(1B), –10.5(5B), –12.2(5B) ppm], for complex **3** three signals in the room temperature ^{11}B NMR spectrum at –3.5 (1B, 132 Hz), –8.0 (5B, 128 Hz), –17.4 (5B, 97 Hz) ppm were found and are a good proof for coordination of the ligand.[86] However, the reduced number of signals in comparison to the low symmetry of the structure in the solid state and the reduced $^1J_{BH}$ coupling constant for the signal at –17.4 ppm (97 Hz) is a good indicator for a dynamic

B–H–Cu-interaction at the upper boron belt. Presumably a rotation of the borate in the Cu_2-sphere is responsible for the ^{11}B-NMR spectroscopic findings. In the $^{31}P\{^1H\}$ 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.[75] Detailed analysis (see Supporting Information) of the multiplets reveals spin-spin coupling constants, $^1J(^{63}Cu,^{31}P)$, 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 $[Fe(SnB_{11}H_{11})(triphos)]$ ($\delta = 2.71$, $\Delta E_Q = 1.54$ mm/s) and are therefore significant for the BH-coordinated cluster.[87] 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.[88] The latter signal was included as a simple Lorentzian in the fit.

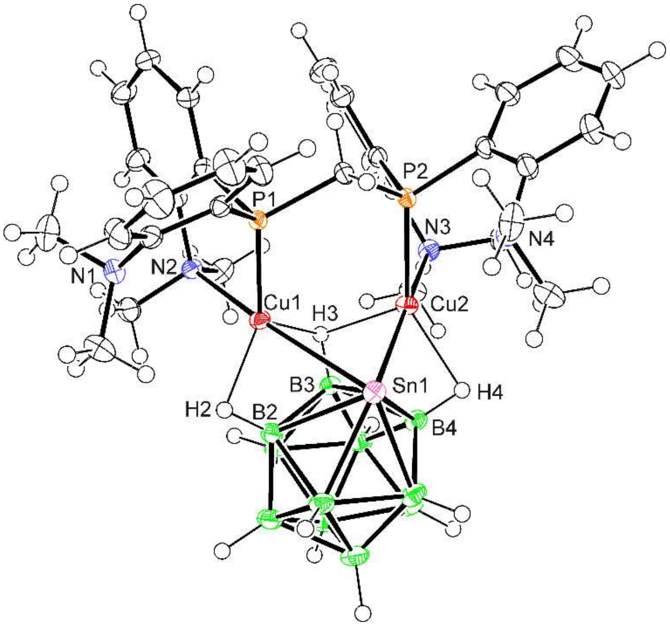


Fig. 3 ORTEP plot of the molecular structure of the dinuclear copper complex **3**. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: Cu1–Sn1 2.8363(2), Cu1–Cu2 3.0118(3), Cu2–Sn1 2.7687(2), P2–Cu2 2.2287(4), P1–Cu1 2.1932(4), N3–Cu2 2.272(1), N2–Cu1 2.244(1), B3–Cu2 2.276(2), B2–Cu1 2.196(2) B3–Cu2 2.209(2), B3–Cu1 2.251(2) B4–Sn1 2.491(2), B3–Sn1 2.587(2), B2–Sn1 2.490(2), B5–Sn1 2.372(2), B6–Sn1 2.374(2), P1–C1–P2 115.64(8).

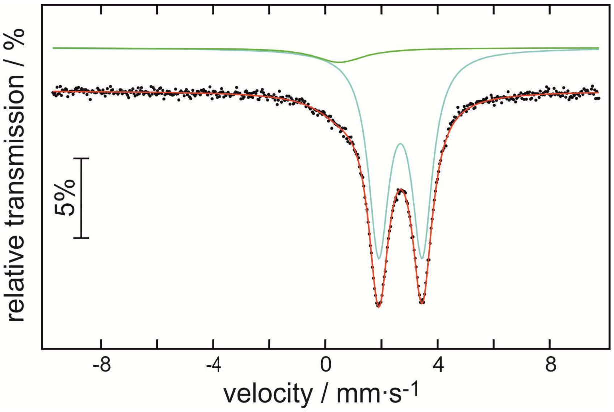
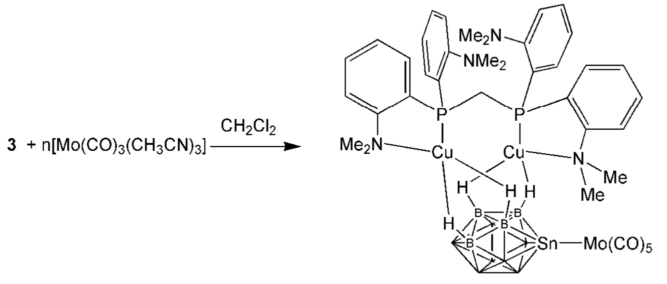


Fig. 4 Experimental (data points) and simulated (continuous lines) ^{119}Sn Mößbauer spectrum of $[Cu_2(dmapm)(SnB_{11}H_{11})]$ (**3**) at 78 K.

The nucleophilicity of the side on coordinated cluster was investigated by means of reaction with the electrophile $[Mo(CO)_3(CH_3CN)_3]$ (Scheme 4). This type of reaction is known for the side-on coordinated clusters in $[2,7,8\text{-}(\mu\text{-}H)_3\text{-}\{Fe(triphos)\}\text{-}EB_{11}H_{11}]$ (E = Ge, Sn).[30, 83-85, 89] In these cases the η^3-coordinated tin or germanium clusters show enough nucleophilicity to react with the transition metal electrophiles $[M(CO)_5(thf)]$ (M = Cr, Mo, W) under formation of a Mo–Ge or M–Sn (M = Cr, Mo, W) 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 $[Mo(CO)_3(CH_3CN)_3]$. Interestingly a carbonyl transfer has also taken place. Carbonyl transfer reactions with $[Mo(CO)(CH_3CN)_3]$ are known in the literature.[90-93] 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.



$[Cu_2(dmapm)\{(CO)_5Mo\text{-}SnB_{11}H_{11}\}]$ (**4**)

Scheme 4 Reaction of the stanna-*closo*-dodecaborate complex **3** with $[Mo(CO)_3(CH_3CN)_3]$ (n = 1.7).

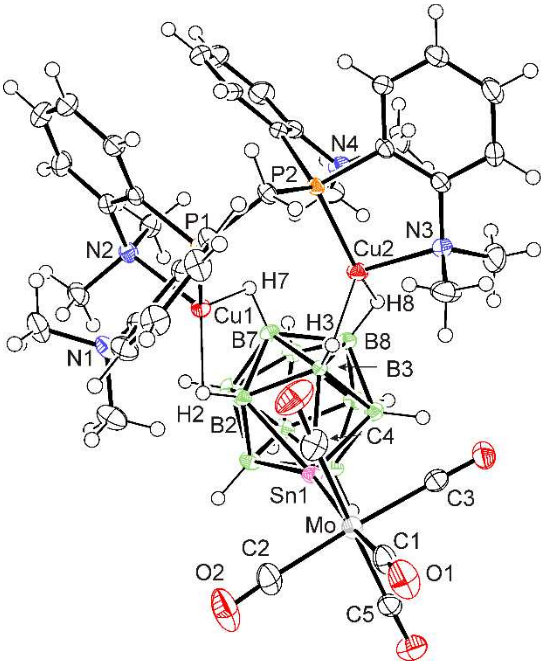
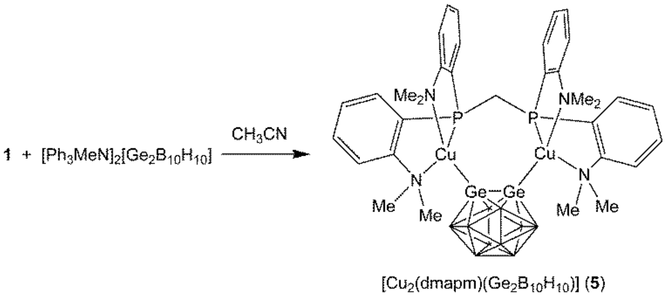


Fig. 5 ORTEP plot of the molecular structure of the dinuclear copper complex **4**. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: Sn1–B2 2.374(4), Sn1–B3 2.336(4), Sn1–B4 2.358(4), Sn1–B5 2.346(4), Sn1–B6 2.358(4), Cu1–B2 2.284(4), Cu1–B7 2.275(4), Cu2–B3 2.273(4), Cu2–B8 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 complex **3** the copper atoms are each coordinated at nitrogen, phosphorus and two BH-units. The respective interatomic distances are in the range of the other presented dinuclear copper complexes. However, the position of the BH-units coordinated at the copper atoms in complex **4** is different in comparison to **3**. In complex **3** only BH units from the upper boron belt (B2-B6) are coordinated while in **4** the coordinated BH units belong to the upper (B2-B6) and lower (B7-B11) boron belt. Furthermore the copper atoms in **4** exhibit no contact with the tin atom, which results to give a nearly tetrahedral arrangement at the Cu(I) atoms. The cluster has shown a rotation inside the di-copper pocket in comparison to complex **3**. The bond lengths of the $(OC)_5Mo–Sn$ coordination are comparable with the values found in $[1\text{-}\{Mo(CO)_5\}\text{-}2,7,8\text{-}(\mu\text{-}H)_3\text{-}\{Fe(triphos)\}\text{-}SnB_{11}H_{11}]$.[84] Due to the trans-influence of the tin ligand the CO-moiety in trans-position to the tin atom shows a slightly shorter Mo–C bond and a longer C–O bond in comparison to the other carbonyl groups.

Digerma-*closo*-dodecaborate forms with the dicationic electrophile **1** two Cu–Ge bonds (Scheme 5). The presented coordination compound **5** is the first transition metal complex of this heteroborate and the type of coordination can be compared with the complexation of the higher homologue $[Sn_2B_{10}H_{10}]^{2-}$.[36, 94] This dinucleophile was shown to react with electrophiles as a bridging ligand under formation of two Sn–M bonds. In the ^{31}P NMR spectrum of the reaction mixture between **1** and $[Ge_2B_{10}H_{10}]^{2-}$ a change in the chemical shift from –56.7 for **1** to –44.1 ppm is a good indicator for a successful reaction between electrophile and nucleophile. The quality of the ^{11}B NMR spectrum does not allow for interpretation of the cluster skeleton since the signals are very broad. A small amount of crystals suitable for single crystal structure analysis were obtained after slow diffusion of diethyl ether into the acetonitrile reaction mixture.



Scheme 5 Reaction of the copper complex **1** with $[Ge_2B_{10}H_{10}]^{2-}$.

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).[71, 72, 95-97]

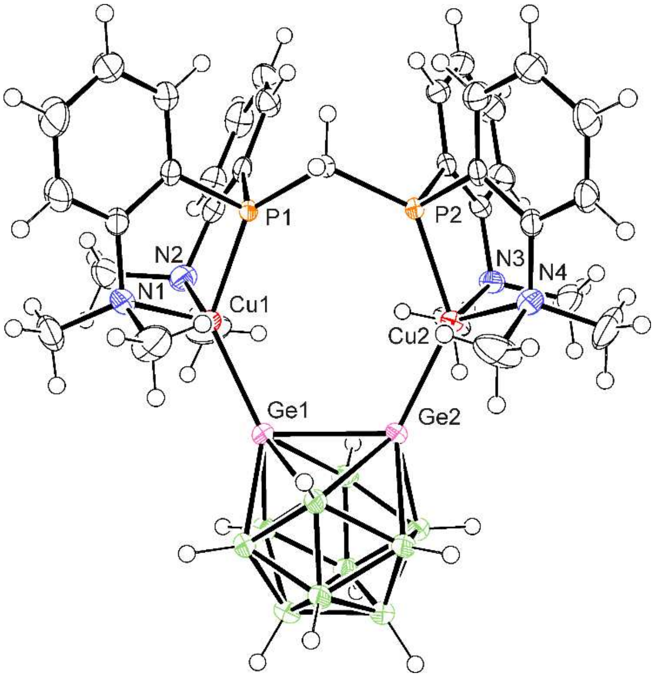
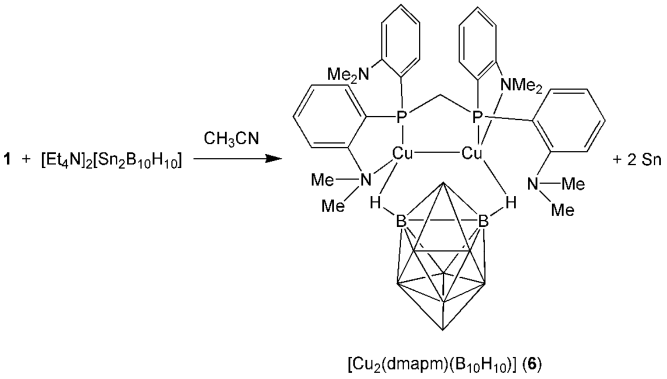


Fig. 6 ORTEP plot of the molecular structure of the dinuclear copper complex **5**. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: N1–Cu1 2.208(3), N2–Cu1

2.216(3), N3–Cu2 2.221(3), N4–Cu2 2.227(3), P1–Cu1 2.1803(8), P2–Cu2 2.1993(8), Cu1–Ge1 2.3017(5), Cu2–Ge2 2.3049(5), Ge1–Ge2 2.4915(4), P1–C1–P2 114.4(2).

Since we were interested about the effect of the change to the higher homologue of $[Ge_2B_{10}H_{10}]^{2-}$ 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 $[B_{10}H_{10}]^{2-}$ 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.[98-103]



Scheme 6 Reaction of the copper complex **1** with $[Sn_2B_{10}H_{10}]^{2-}$.

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-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.

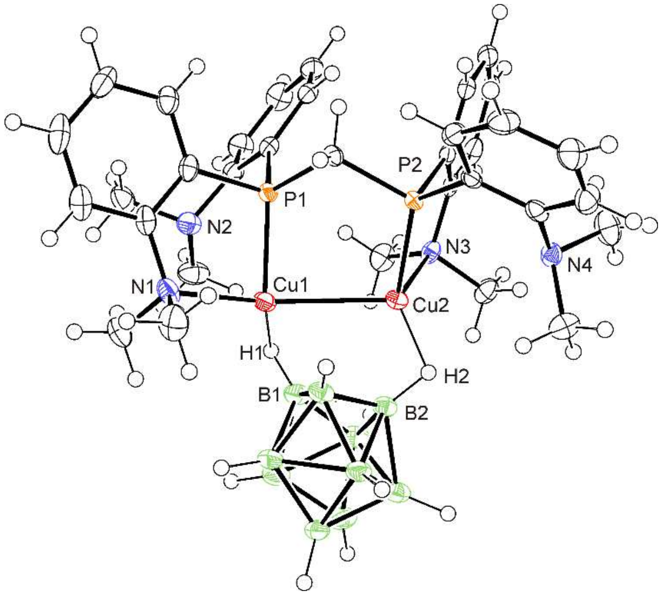


Fig. 7 ORTEP plot of the molecular structure of the dinuclear copper complex **6**. Ellipsoids at 50% probability. Interatomic distances [Å] and bond angles [deg]: N1–Cu1 2.204(2), N3–Cu2 2.287(2), B1–Cu1 2.214(3), B2–Cu2 2.201(3), P1–Cu1 2.1853(8), P2–Cu2 2.1980(8), Cu1–Cu2 2.6631(5), P2–C1–P1 109.65(13).

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.[54] 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 (^{1}H), 80.25 (^{11}B), 62.90 (^{13}C), 101.25 (^{31}P) 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 (^{1}H), 100.13

(^{13}C) and 161.97 MHz (^{31}P), a Bruker AvanceII+500 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 500.13 (^{1}H), 160.5 (^{11}B), 125.76 (^{13}C), 202.46 (^{31}P), and 186.5 MHz (^{119}Sn). Chemical shifts are reported in δ values in ppm relative to external TMS (^{1}H, ^{13}C), $BF_3{\cdot}Et_2O$ (^{11}B), 85 % aqueous H_3PO_4 (^{31}P) or $SnMe_4$ (^{119}Sn) using the chemical shift of the solvent ^{2}H resonance frequency. NMR Spectra of solid samples were obtained on a Bruker DSX-200 NMR spectrometer operating at 200.13 (^{1}H), 81.015 (^{31}P) and 74.60 MHz (^{119}Sn). The powdered samples were spinning about the magic angle at 10 kHz in 4 mm o.d. zirconia rotors. ^{119}Sn and ^{31}P NMR spectra were obtained after VACP, and under high-power ^{1}H decoupling or after single-pulse excitation. Chemical shifts are referenced with respect to external $SnMe_4$ (^{119}Sn) using the chemical shift of $SnCy_4$, –97.35 ppm, as secondary chemical shift reference, or to external 85% H3PO4 (^{31}P) using external $NH_4H_2PO_4$ as secondary reference. MAS spectra were analyzed using the program HBA.[104] Errors in chemical shifts are estimated to be 2 ppm, because of the greater line widths in the ^{119}Sn MAS spectra (2.5 kHz) attributed to ^{119}Sn–^{11}B spin-spin interactions. Principal components of the chemical shift tensors are accurate to about 2 % of Ω. The simulation of the MAS ^{119}Sn spectrum has been performed using the program WSolids1.[105]

Crystallography. X-ray data were collected with 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.[106, 107] Results of the crystal structure determination are presented in Table 1SI. Hydrogen atoms were placed in calculated positions and refined using the riding model. The following restraints were used during the refinement procedure: compound **2** EADP; **3** SIMU, DELU, ISOR, EADP for the severe disorder of a NMe_2 group of the ligand (N4 in Fig. 3); **5** DANG, DFIX, DELU, SIMU, ISOR, EADP for the severe disorder of the cocrystallized Et_2O molecule. For compounds **1**, **4**, **6** no additional restraints were used.

^{119}Sn Mössbauer spectroscopy. A $Ca^{119m}SnO_3$ source was used for the ^{119}Sn Mössbauer spectroscopic investigation. The $[Cu_2(dmapm)(SnB_{11}H_{11})]$ 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 conducted in the usual transmission geometry at 78 K.

Syntheses

$[Cu_2(\mu\text{-dmapm})(CH_3CN)_2][BF_4]_2$ (1). 565 mg (1.8 mmol) $[Cu(CH_3CN)_4][BF_4]$ and 500 mg (0.9 mmol) dmapm 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 $[C_{33}H_{42}Cu_2N_4P_2][BF_4]_2 \cdot CH_3CN \cdot C_3H_6O$ (956.50 g/mol): C, 47.72; H, 5.37; N, 7.32. **^{1}H NMR** (400.13 MHz, CD_2Cl_2): δ 2.40 (s, 6H, C*H$_3$*CN), 2.70 (s, 24H, NC*H$_3$*), 3.33 (t, ^{2}J(^{31}P-^{1}H) = 5.8 Hz, 2H, C*H$_2$*), 7.35–7.41 (m, 4H, Ar-*H*), 7.48–7.54 (m, 4H, Ar-*H*), 7.55–7.61 (m, 4H, Ar-*H*), 7.71–7.77 (m, 4H, Ar-*H*). **^{13}C{^{1}H} NMR** (100.13 MHz, CD_2Cl_2): δ 2.5 (s, *C*H$_3$CN), 19.2 (t, ^{1}J(^{31}P-^{13}C) = 8.0 Hz, *C*H$_2$), 49.9 (s, N*C*H$_3$), 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*). **^{31}P{^{1}H} NMR** (161.98 MHz, CD_2Cl_2): δ –56.7 (br s). Crystals suitable for single crystal structure analysis were obtained with the $[SnCB_{10}H_{11}]^-$ counteranion: **$[Cu_2(\mu\text{-dmapm})(CH_3CN)_2][SnCB_{10}H_{11}]_2$ (1a).** 50 mg (0.05 mmol) $[Cu_2(\mu\text{-dmapm})(CH_3CN)_2][BF_4]_2$ **(1)** and 31 mg (0.05 mmol) $[PPh_4][SnCB_{10}H_{11}]$ 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**.

$[Cu_2(\mu\text{-dmapm})(\mu\text{-}GeB_{11}H_{11})]$ (2). 50 mg (0.05 mmol) $[Cu_2(\mu\text{-dmapm})(CH_3CN)_2][BF_4]_2$ **(1)** and 23 mg (0.05 mmol) $[Et_3MeN]_2[GeB_{11}H_{11}]$, were stirred for 3 hours in 20 mL acetonitrile at room temperature. The yellow suspension was filtered and layered with diethyl ether to yield colourless crystals of **2**. Yield: 35 mg, 74 %. **Found:** C, 44.60; H, 5.63; N, 6.57; Calc. for $[C_{33}H_{42}Cu_2N_4P_2(GeB_{11}H_{11})]$ (886.38 g/mol): C, 44.71; H, 6.03; N, 6.32. **^{1}H NMR** (400.13 MHz, CD_2Cl_2): δ 2.57 (s, 24H, NC*H$_3$*), 2.98 (t, ^{2}J(^{31}P-^{1}H) = 9.7 Hz, 2H, C*H$_2$*), 7.13–7.19 (m, 4H, Ar-*H*), 7.20–7.26 (m, 4H, Ar-*H*), 7.34–7.40 (m, 4H, Ar-*H*), 7.43–7.50 (m, 4H, Ar-*H*). **^{11}B NMR** (80.25 MHz, CD_2Cl_2): δ –13.8 (br s, B2-6, 125 Hz), –10.6 (br s, B7-11, 140 Hz), –1.8 (br B12, BH-coupling constant not observed). **^{13}C{^{1}H} NMR** (100.13 MHz, CD_2Cl_2): δ 23.8–24.9 (m, *C*H$_2$), 49.1 (s, N*C*H$_3$), 123.3–123.5 (m, *Ar*), 127.3–127.5 (m, *Ar*), 132.0–132.2 (m, *Ar*), 132.9–133.0 (m, *Ar*), 149.8–151.8 (m, *Ar*), 157.2–157.4 (m, *Ar*). **^{31}P{^{1}H} NMR** (161.98 MHz, CD_2Cl_2): δ –28.2 (br s). Low temperature measurement: **^{31}P{^{1}H} NMR** (161.98 MHz, CD_2Cl_2, –80°C): δ –28.2 (br s). **^{31}P VACP/MAS NMR:** δ_{iso} –29.1.

$[Cu_2(\mu\text{-dmapm})(\mu\text{-}SnB_{11}H_{11})]$ (3). 100 mg (0.11 mmol) $[Cu_2(\mu\text{-dmapm})(CH_3CN)_2][BF_4]_2$ **(1)** and 78 mg (0.11 mmol) $[Bu_4N]_2[SnB_{11}H_{11}]$, were stirred for 3 hours at room temperature in 20 mL dichloromethane. The suspension was filtered and layered with *n*-hexane to obtain yellow crystals. Yield: 72 mg, 73 %. Found: C, 41.93; H, 5.39; N, 5.75; Calc. for $[C_{33}H_{42}Cu_2N_4P_2(SnB_{11}H_{11})]$ (932.48 g/mol): C, 42.51; H, 5.73; N, 6.01. **^{1}H NMR** (400.13 MHz, CD_2Cl_2): δ 2.48 (s, 24H, NC*H$_3$*), 3.27 (t, ^{2}J(^{31}P-^{1}H) = 11.0 Hz, 2H, C*H$_2$*), 7.04–7.10 (m, 4H, Ar-*H*), 7.10–7.16 (m, 4H, Ar-*H*), 7.35–7.40 (m, 4H, Ar-*H*), 7.43–7.48 (m, 4H, Ar-*H*). **^{11}B NMR** (80.25 MHz, CD_2Cl_2): δ –17.4 (br s, B2-6, 94 Hz), –8.0 (br s, B7-11, 128 Hz), –3.5 (br s, B12, 132 Hz). **^{13}C{^{1}H} NMR** (100.13 MHz, CD_2Cl_2): δ 22.1–23.5 (m, *C*H$_2$), 48.5 (s, N*C*H$_3$), 123.5 (s, *Ar*), 126.8 (s, *Ar*), 129.8–130.3 (m, *Ar*), 132.6 (s, *Ar*), 132.7 (s, *Ar*), 158.0–158.2 (m, *Ar*). **^{31}P{^{1}H} NMR** (161.98 MHz, CD_2Cl_2): δ –40.6 (br s). **^{119}Sn{^{1}H} NMR** (93.25 MHz): δ –601 (br). **^{31}P VACP/MAS NMR:** δ_{iso} –34.8 (^{1}J(^{63}Cu-^{31}P) = 1650 Hz), δ_{iso} –42.5 (^{1}J(^{63}Cu-^{31}P) = 1650 Hz). **^{119}Sn VACP/MAS NMR:** δ_{iso} –623, δ_{11} –243(3), δ_{22} –493(2), δ_{33} –1134(2), $\Omega = \delta_{11} - \delta_{33} = 891(2)$, $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega = 0.44(1)$.

$[Cu_2(\mu\text{-dmapm})(\mu\text{-}SnB_{11}H_{11})(Mo(CO)_5)]$ (4). 26 mg (0.03 mmol) $[Cu_2(\mu\text{-dmapm})(\mu\text{-}SnB_{11}H_{11})]$ **(2)** and 14 mg (0.05 mmol) $[Mo(CO)_3(CH_3CN)_3]$, 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 $[C_{33}H_{42}Cu_2N_4P_2(SnB_{11}H_{11})(Mo(CO)_5)] \cdot 0.5\ C_6H_6$ (1207.53 g/mol): C, 40.78; H, 4.67; N, 4.64. **^{1}H NMR** (400.13 MHz, CD_2Cl_2): δ 2.49 (s, 24H, NC*H₃*), 2.92 (t, $^2J(^{31}P\text{-}^1H)$ = 9.6 Hz, 2H, C*H₂*), 7.07–7.13 (m, 4H, Ar-*H*), 7.16–7.21 (m, 4H, Ar-*H*), 7.37–7.43 (m, 4H, Ar-*H*), 7.43–7.49 (m, 4H, Ar-*H*). **$^{11}B\{^1H\}$ NMR** (80.25 MHz, CD_2Cl_2): δ –16.5 (br s, half line width 300 Hz, 6B), –14.4 (br s, half line width 300 Hz, 5B). **$^{13}C\{^1H\}$ NMR** (100.13 MHz, CD_2Cl_2): δ 25.5–25.7 (m, *C*H₂), 48.8 (s, N*C*H₃), 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 C*O), 213.3 (s, *trans C*O). **$^{31}P\{^1H\}$ NMR** (161.98 MHz, CD_2Cl_2): δ –41.0 (br s). **$^{119}Sn\{^1H\}$ NMR** (93.25 MHz): δ –218 (br). **IR (ATR):** 2494 (b, BH), 2064 (m, CO), 1982 (w, CO), 1934 (s, CO), 1913 (vs, CO).

$[Cu_2(\mu\text{-dmapm})(\mu\text{-}Ge_2B_{10}H_{10})]$ (5). 50 mg (0.05 mmol) $[Cu_2(\mu\text{-dmapm})(CH_3CN)_2][BF_4]_2$ **(1)** and 42 mg (0.05 mmol) $[Ph_3MeN]_2[Ge_2B_{10}H_{10}]$ 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 $[C_{33}H_{42}Cu_2N_4P_2(Ge_2B_{10}H_{10})] \cdot 2$ Toluene (1131.45 g/mol): C, 49.89; H, 6.06; N, 4.95. **^{1}H NMR** (400.13 MHz, CD_2Cl_2): δ 2.59 (s, 24H, NC*H₃*), 3.21 (t, $^2J(^{31}P\text{-}^1H)$ = 6.3 Hz, 2H, C*H₂*), 7.20–7.29 (m, 4H, Ar-*H*), 7.39–7.54 (m, 12H, Ar-*H*). **$^{11}B\{^1H\}$ NMR** (80.25 MHz, CD_2Cl_2): δ –28.8 (br s, 2B, $\tau_{1/2}$ = 338Hz), –1.7 - –14.8 (br, 8B). **$^{13}C\{^1H\}$ NMR** (100.13 MHz, CD_2Cl_2): δ 23.1–24.3 (m, *C*H₂), 48.2 (s, N*C*H₃), 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*). **$^{31}P\{^1H\}$ NMR** (161.98 MHz, CD_2Cl_2): 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.

$[Cu_2(\mu\text{-dmapm})(B_{10}H_{10})]$ (6). 100 mg (0.11 mmol) $[Cu_2(\mu\text{-dmapm})(CH_3CN)_2][BF_4]_2$ **(1)** and 66 mg (0.11 mmol) $[Et_4N]_2[Sn_2B_{10}H_{10}]$, 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 $[C_{33}H_{42}Cu_2N_4P_2(B_{10}H_{10})]$ (801.95 g/mol): C, 49.42; H, 6.54; N, 6.99. **^{1}H NMR** (400.13 MHz, CD_2Cl_2): δ 2.46 (s, 24H, NC*H₃*), 3.10 (br s, 2H, C*H₂*), 7.15–7.23 (m, 4H, Ar-*H*), 7.29–7.43 (m, 8H, Ar-*H*), 7.47–7.54 (m, 4H, Ar-*H*). **^{11}B NMR** (80.25 MHz, CD_2Cl_2): δ –29.0 (br, d, ^1JB-H = 100 Hz, 2B), –8.1 (br d, ^1J B-H = 120 Hz, 8B). **$^{13}C\{^1H\}$ NMR** (100.13 MHz, CD_2Cl_2): δ 27.4–27.7 (m, *C*H₂), 48.5 (s, N*C*H₃), 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*). **$^{31}P\{^1H\}$ NMR** (161.98 MHz, CD_2Cl_2): δ –31.1 (br s).

Notes and references

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† 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

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Table of contents entry

The hitherto unknown dinuclear copper(I) complex [Cu_2(μ-dmapm)(CH_3CN)$_2$][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.