Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 7008

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**PAPER**

# Tri- and tetracoordinate copper(I) complexes bearing bidentate soft/hard SN and SeN ligands based on 2-aminopyridine†

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***Received 4th March 2011, Accepted 20th April 2011***
**DOI: 10.1039/c1dt10377f**



The coordination properties of the EN ligands *N*-(2-pyridinyl)amino-diphenylphosphine sulfide, *N*-(2-pyridinyl)amino-diisopropylphosphine sulfide, *N*-(2-pyridinyl)amino-diphenylphosphine selenide, *N*-(2-pyridinyl)amino-diisopropylphosphine selenide towards copper(I) precursors CuX (X = Br, I), [Cu(IPr)Cl] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), and $[Cu(CH_3CN)_4]PF_6$ were studied. Treatment of CuX with EN ligands resulted in the formation of tricoordinate complexes of the type [Cu(κ²(*E*,*N*)-EN)X]. The reaction of [Cu(IPr)Cl] with EN ligands, followed by halide abstraction with $AgSbF_6$, afforded cationic tricoordinate complexes [Cu(κ²(*S*,*N*)-EN)(IPr)]⁺, while the reaction of $[Cu(CH_3CN)_4]^+$ with two equivalents of EN ligands yielded tetrahedral complexes [Cu(κ²(*E*,*N*)-EN)₂]⁺. Halide removal from [Cu(κ²(*S*,*N*)-SN)I] with silver salts in the presence of L = $CH_3CN$ and CN*t*Bu afforded dinuclear complexes of the type $[Cu(\kappa^2(S,N),\mu(S)\text{-SN})(L)]_2^{2+}$ containing bridging SN ligands. With the terminal alkynes HC≡C$C_6H_4$Me and HC≡C$C_6H_4$OMe, complexes of the formula [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-HC≡C$C_6H_4$Me)]⁺ and [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-HC≡C$C_6H_4$OMe)]⁺ were obtained. The mononuclear nature of these compounds was supported by DFT calculations. Most complexes were also characterized by X-ray crystallography.

## Introduction

Heterodifunctional ligands are intensively studied and applied in coordination and organometallic chemistry owing to the often unique properties of their metal complexes and their ability to generate hemilabile systems which often display enhanced reactivity.[1] In particular, soft/hard, *e.g.*, P/N and P/O assemblies, are able to coordinate reversibly to a metal center providing or protecting temporarily a vacant coordination site, a feature very desirable for catalysts.

In this context, we have become interested in heterodifunctional PN ligands based on 2-aminopyridine in which the donor atoms are separated by an amino group.[2,3] These types of ligands are easily constructed by reacting 2-aminopyridine with $R_2PCl$ in the presence of a base (Scheme 1). $R_2PCl$ may contain both bulky and/or electron-rich dialkyl phosphines as well as P–O and P–N bond containing achiral and chiral phosphite units derived from diols, aminoalcohols, and diamines.[4] Due the comparative ease of phosphorus-nitrogen bond forming reactions, compared to those in which phosphorus-carbon bonds are formed, it is not surprising that many examples of transition metal complexes featuring this type of PN ligands have emerged over the last few decades.[5–14] The most prominent member of this ligand family, with a few exceptions,[15] is *N*-diphenylphosphino-2-aminopyridine (PN-Ph). Another very useful and interesting aspect of PN ligands is the fact that they can also be readily functionalized at the phosphorus site by oxidation with $H_2O_2$, sulfur, and gray selenium, respectively, to give chalcogen O, S, and Se derivatives (EN ligands), as shown in Scheme 1. Despite the fact that the synthesis of these heterodifunctional EN ligands has been known for some time,[11] it is surprising that transition metal complexes containing these ligands are relatively scarce.[7,10,16,17]

As part of our ongoing interest in transition metal complexes containing heterodifunctional ligands,[2,3] we herein report on the synthesis, structure, and reactivity of tri- and tetracoordinate Cu(I) complexes featuring soft/hard SN and SeN ligands with R = Ph and *i*Pr, as shown in Scheme 1. These ligands are expected to form stable and perhaps unusual complexes due the favorable soft acid–soft base interaction with this closed-shell $d^{10}$ metal ion.[18]

## Results and discussion

The coordination properties of the EN ligands **1** and **2** towards the copper(I) precursors CuX (X = Br, I), [Cu(IPr)Cl] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), and $[Cu(CH_3CN)_4]PF_6$ were investigated. Treatment of CuX with

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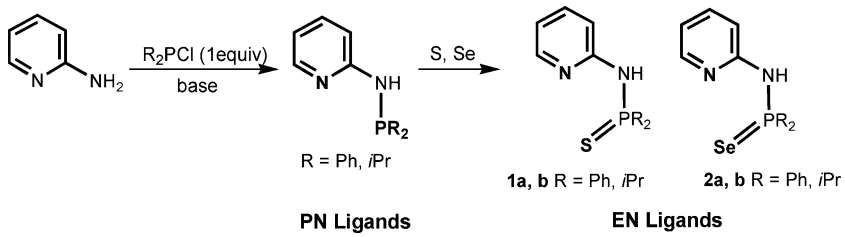
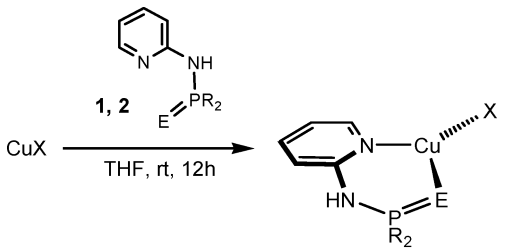
† Electronic supplementary information (ESI) available: $^1H$–$^{15}N$ HSQC spectra of **2b** and **5b**. CCDC reference numbers 810363–810377. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10377f




**Scheme 1**

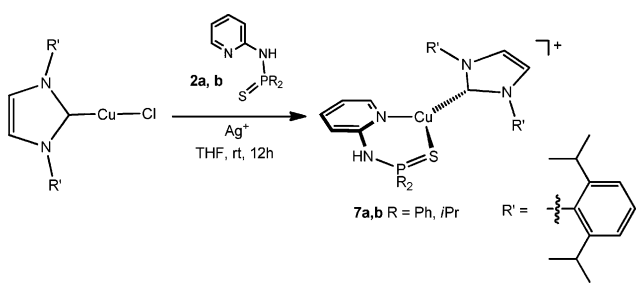


1 equiv. of **1** and **2** in THF at room temperature resulted in the formation of tricoordinate complexes of the type [Cu(κ²(*E*,*N*)-EN)X] (**3–6**) in 68 to 85% isolated yields (Scheme 2). The reaction of [Cu(IPr)Cl] with one equiv. of **1** in THF, followed by halide abstraction with $AgSbF_6$, afforded cationic tricoordinate complexes [Cu(κ²(*S*,*N*)-SN-Ph)(IPr)]$SbF_6$ (**7a**) and [Cu(κ²(*S*,*N*)-SN-*i*Pr)(IPr)]$SbF_6$ (**7b**) in good isolated yields (Scheme 3). When $[Cu(CH_3CN)_4]^+$ was treated with one equiv. of **1** and **2**, respectively, tetrahedral complexes of the type $[Cu(\kappa^2(E,N)\text{-EN})_2]^+$ (**8**, **9**) were obtained in low yields. There was no evidence for the formation of the expected bis-acetonitrile complex $[Cu(\kappa^2(E,N)\text{-EN})(CH_3CN)_2]^+$. In addition, substantial amounts of the starting material were recovered. When the same reaction was performed with two equiv. of EN ligands, complexes **8** and **9** were obtained in high isolated yields (Scheme 4).



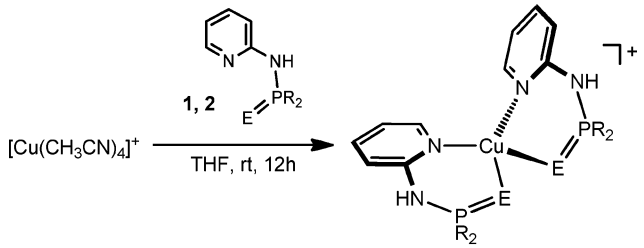

**3a,b** E = S, X = Br, R = Ph, *i*Pr
**4a,b** E = Se, X = Br, R = Ph, *i*Pr
**5a,b** E = S, X = I, R = Ph, *i*Pr
**6a,b** E = Se, X = I, R = Ph, *i*Pr

**Scheme 2**




**Scheme 3**

All the above complexes are thermally robust, white to pale yellow solids that are air stable both in the solid state and in solution for several days. Their identity was unequivocally established by $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR, and elemental analysis. In the case of the ligand **2b** and complex **5b**, the $^{15}N$ shifts




**8a,b** E = S, R = Ph, *i*Pr
**9a,b** E = Se, R = Ph, *i*Pr

**Scheme 4**

were determined by $^1H$–$^{15}N$ HMBC and $^1H$–$^{15}N$ HSQC NMR experiments (performed with $^{15}N$ natural abundance, referenced to $NH_4Cl$). In the $^1H$–$^{15}N$ HMBC spectra of both **2b** and **5b**, depicted in Fig. 1, cross peaks were observed between the pyridine nitrogen atom and the pyridine protons $H^3$, $H^5$, and $H^6$ that provided the $^{15}N$ chemical shifts at 252 and 222 ppm, respectively. In the $^1H$–$^{15}N$ HSQC spectra (see ESI†), cross peaks between the amine nitrogen and the NH protons were observed giving rise to $^{15}N$ chemical shifts at 66 and 58 ppm, respectively. Accordingly, coordination of SN-*i*Pr to copper(I) leads to an up-field shift of the $^{15}N$ resonances. In the $^{31}P\{^1H\}$ NMR spectra, all compounds exhibit singlets for the κ²(*E*,*N*)-coordinated EN ligands which are all slightly high-field shifted relative to the free uncoordinated ligands. Moreover, the phosphorus signals of the SeN ligands exhibit a singlet with a pair of Se satellites with $^{31}P$–$^{77}Se$ coupling constants in the range of 787 to 673 Hz.

The molecular structures of the ligands **1a**, **1b**, **2a**, **2b** and of the complexes **3a**, **3b**, **5b**, **6b**, **7a**, **7b**, and **8b** were determined by X-ray crystallography. Structural diagrams for **1a**, **1b**, **3a**, **5b**, **7a**, and **8b** are depicted in Fig. 2–7 with selected bond distances and angles reported in the captions. Structural views of **2a**, **2b**, **3b**, **6b**, and **7b** are given in the ESI.†

The free EN ligands **1a**, **1b**, **2a**, and **2b** exhibit in solid state bond lengths which do not differ significantly from those of their Cu-complexes (see below), except that P–S bonds are shorter than those in the Cu-complexes by about 0.03 Å. However, the conformation of the free ligands differs from that of the Cu-complexes (see below) because the S and Se atoms are turned away from the pyridine N-atoms, as shown for instance in Fig. 2, whereas in all Cu-complexes the EN ligands are chelating and S and Se atoms are turned to the pyridine N-atoms. It is a characteristic feature of all free ligands that their N–H groups form intermolecular hydrogen bonds to either the pyridine N-atoms or the E-atoms (S, Se) as acceptors and that they build up hydrogen bonded dimers. Whereas the phenyl-bearing ligands

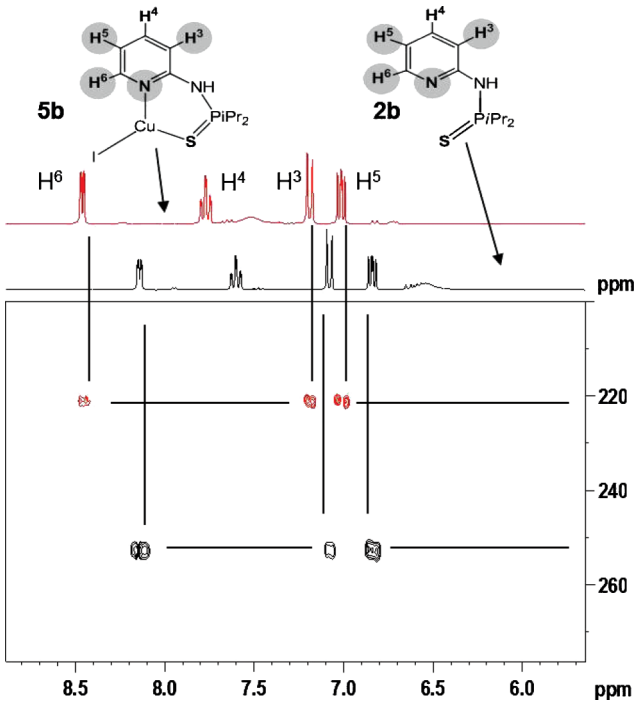



**Fig. 1** 300 MHz $^{1}H$–$^{15}N$ HMBC spectra of SN-*i*Pr (**2b**) and [Cu(SN-*i*Pr)I] (**5b**) in acetone-$d_6$ at 25 °C.

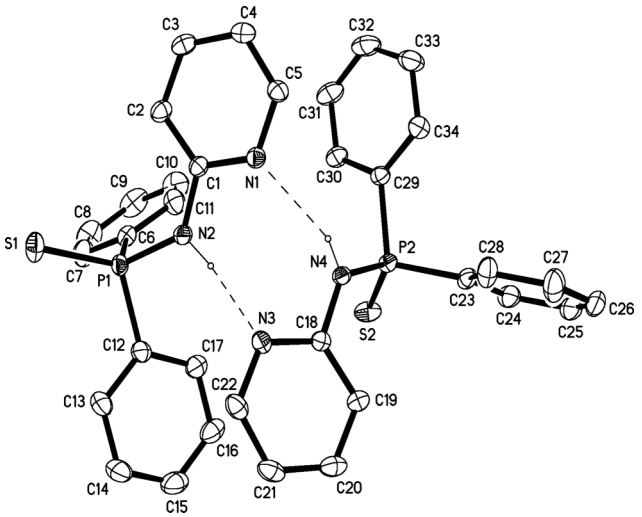


**Fig. 2** ORTEP diagram of **1a** showing the two independent molecules of the structure with 50% displacement ellipsoids. The Se-analogue **2a** is isostructural. Carbon-bonded H atoms omitted for clarity. Selected distances and angles (Å, °): P1–S1 1.9470(4), P2–S2 1.9497(4), P1–N2 1.6689(9), P2–N4 1.6706(9), N2–P1–S1 117.02(4), N4–P2–S2 115.89(3), N1–C1–N2–P1 179.8(1), N3–C18–N4–P2 −151.5(1), C1–N2–P1–S1 −61.2(1), C18–N4–P2–S2 45.3(1), N2···N3 2.935(1), N4···N1 2.926(1).

**1a** and **2a** are isostructural and form N–H···N bonded dimers, the isopropyl-bearing ligands **1b** and **2b** are not isostructural and form N–H···S (**1b**; Fig. 3) or N–H···Se bonded dimers (**2b**; see ESI†).

Complexes **3a** through **7b** contain Cu in triangular and approximately planar coordination geometry. As representative example [Cu(κ²(*S*,*N*)-SN-Ph)Br] (**3a**) is shown in Fig. 4. The coordination triangle formed by the three ligands N1, S1 and

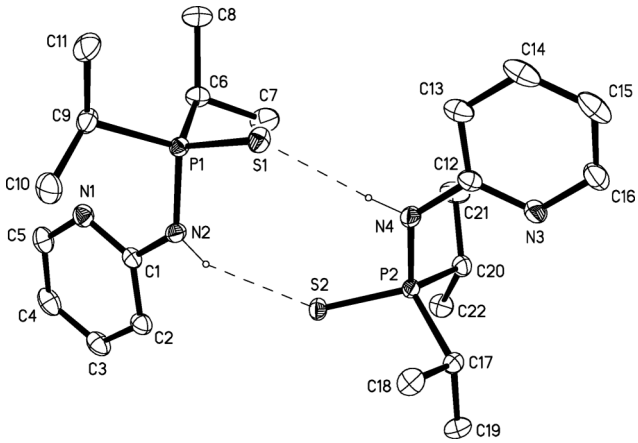


**Fig. 3** ORTEP diagram of **1b** showing the two independent molecules of the structure with 50% displacement ellipsoids. Se-analogue **2b** is not isostructural. Carbon-bonded H atoms omitted for clarity. Selected distances and angles (Å, °): P1–S1 1.9627(3), P2–S2 1.9596(3), P1–N2 1.6826(8), P2–N4 1.6830(8), N2–P1–S1 107.18(3), N4–P2–S2 108.60(3), N1–C1–N2–P1 −8.9(1), N3–C12–N4–P2 −5.7(1), C1–N2–P1–S1 −179.8(1), C12–N4–P2–S2 179.4(1), N2···S2 3.375(1), N4···S1 3.470(1).

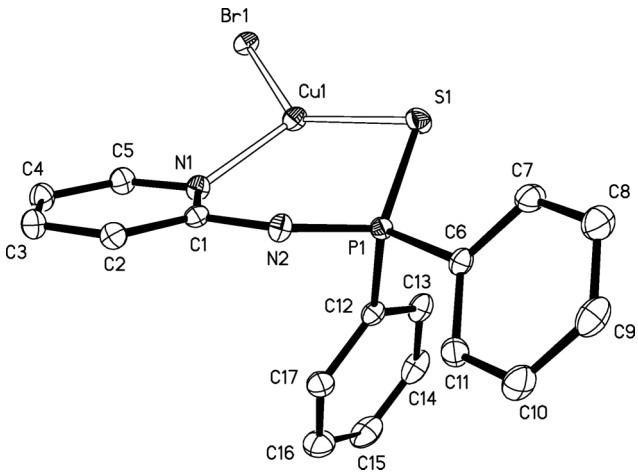


**Fig. 4** Molecular structure of **3a** showing 50% displacement ellipsoids. H atoms omitted for clarity. Selected distances and angles (Å, °): Cu1–N1 2.0597(12), Cu1–S1 2.2092(4), Cu1–Br1 2.3410(3), P1–S1 1.9791(5), P1–N2 1.6746(12), N2–C1 1.391(2), N1–Cu1–S1 113.51(3), N1–Cu1–Br1 111.67(3), S1–Cu1–Br1 133.73(1), P1–S1–Cu1 89.10(2), N2–P1–S1 117.18(4), C1–N2–P1 127.7(1), N1–C1–N2 118.6(1), Cu1–N1–C1 122.6(1).

Br1 is strongly distorted with bond lengths of Cu1–N1 2.0597(12), Cu1–S1 2.2092(4), Cu1–Br1 2.3410(3) Å and bond angles between 111.67(3) and 133.73(1)°. Copper deviates by 0.131 Å from the N1–S1–Br1 plane being displaced to the pyridine plane. The six-membered chelate ring formed by the EN ligand has a ring bond angle sum of 688.7° – the planar hexagon has 720° – and is therefore distinctly puckered. Most responsible for this puckering is the P–S–Cu bond angle, which is near 90° in all these Cu complexes, for electronic reasons originating from S and Se. Using the pyridine ring as the reference plane, the following deviations from this plane are observed in compound **3a**: N2 −0.03, P1 −0.34, S1 0.97, Cu1 0.78, and Br1 1.59 Å. A further consequence of

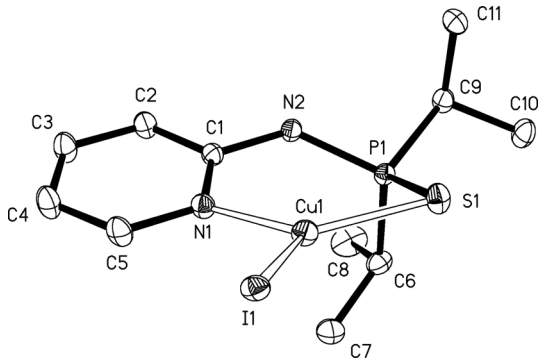



**Fig. 5** Molecular structure of **5b** showing 50% displacement ellipsoids (isostructural with **3b** and **6b**). H atoms omitted for clarity. Selected distances and angles (Å, °): Cu1–N1 2.0209(13), Cu1–S1 2.2174(5), Cu1–I1 2.4961(3), P1–S1 1.9900(5), P1–N2 1.6822(13), N1–Cu1–S1 116.00(4), N1–Cu1–I1 114.41(4), S1–Cu1–I1 128.95(1), P1–S1–Cu1 92.73(2).

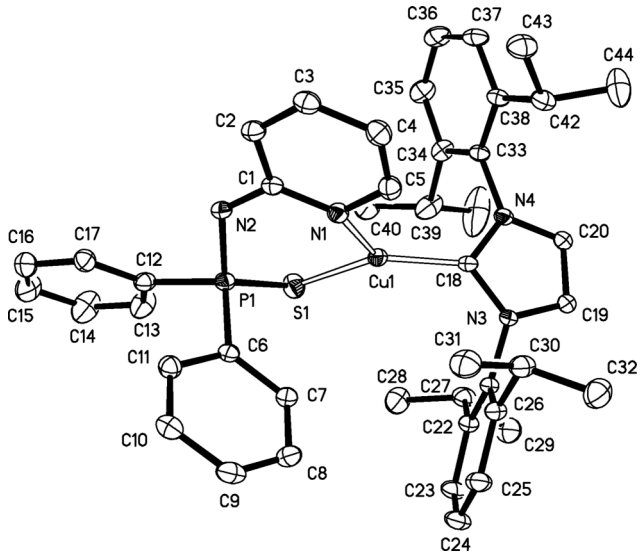



**Fig. 6** Molecular structure of **7a** showing 50% displacement ellipsoids. $SbF_6^-$ anion, $(CH_3)_2CO$ solvent molecule, and H atoms omitted for clarity. Selected distances and angles (Å, °): Cu1–C18 1.913(2), Cu1–N1 2.048(2), Cu1–S1 2.2674(8), P1–S1 1.9732(9), P1–N2 1.668(2), C18–Cu1–N1 129.15(9), C18–Cu1–S1 121.60(8), N1–Cu1–S1 108.84(6), P1–S1–Cu1 92.60(3).

the chelate ring puckering is that one of the two P–C bonds is approximately parallel to the pyridine ring, whereas the second is steeply inclined to it. The N2–H group of the complex forms an intermolecular hydrogen bond to Br1 of a neighboring molecule, N2 ··· Br1 = 3.475(1) Å, linking the complexes into infinite straight chains.

The isopropyl-substituted complexes **3b** (S, Br), **5b** (S, I), and **6b** (Se, I) form an isostructural series with monoclinic symmetry and space group $P2_1/c$, of which **5b** is shown as a representative example in Fig. 5. These complexes follow essentially the geometric characteristics outlined already for complex **3a**. A comparison of important geometric data of these complexes is given in Table 1. In their crystal lattice the complexes are linked by intermolecular N–H ··· Br, I hydrogen bonds into infinite zig-zag chains (N ··· Br, I 3.447, 3.676 and 3.721 Å for **3b**, **5b**, and **6b**, respectively).

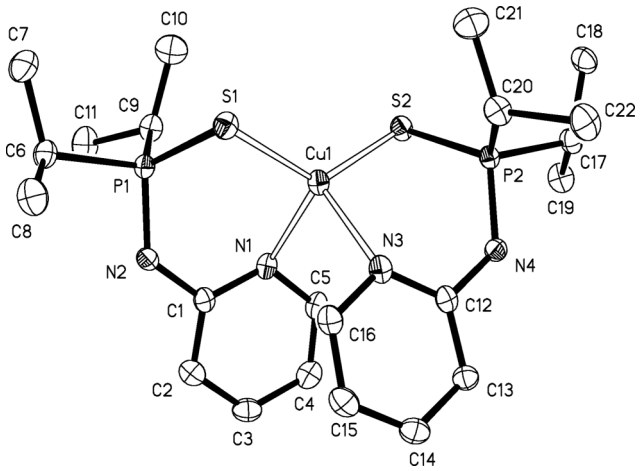



**Fig. 7** Molecular structure of **8b** showing 50% displacement ellipsoids. $PF_6^-$ anion and H atoms omitted for clarity. Selected distances and angles (Å, °): Cu1–N1 2.140(2), Cu1–N3 2.163(2), Cu1–S1 2.2602(8), Cu1–S2 2.2706(7), P1–S1 1.9860(7), P1–N2 1.676(2), P2–S2 1.9863(7), P2–N4 1.678(2), N1–Cu1–N3 89.84(9), S1–Cu1–S2 128.22(4), N1–Cu1–S1 107.21(5), N3–Cu1–S2 106.29(5), N1–Cu1–S2 109.90(5), N3–Cu1–S1 108.63(5).

Complexes **7a** and **7b**, which contain a Cu–C bonded neutral N-heterocyclic ligand (NHC) and an uncoordinated $SbF_6$ anion instead of a Cu-bonded halide anion maintain the triangular coordination of Cu and the chelate ring puckering of the previous complexes. They show very short Cu–C bonds of *ca.* 1.92 Å and compensate this by having slightly longer Cu–N and Cu–S bonds, along with some changes in the bond angles around Cu (Table 3). For example, the cationic complex **7a** is shown in Fig. 6, which reveals that the NHC ligand is oriented approximately perpendicular to the Cu coordination triangle, a feature that also holds true for **7b**.

In complex **8b** (Fig. 6) the copper atom adopts a distorted tetrahedral coordination by two N and two S atoms from two chelating SN-ligands. Here the Cu–N bonds are longer by about 0.10 Å and the Cu–S bonds by about 0.06 Å than in the previous triangular Cu-complexes. Crystallographically the Cu-complex of **8b** is $C_1$-symmetric, but geometrically it is close to a $C_2$ symmetry. This $C_2$-pseudosymmetry is also valid for the monoclinic crystal lattice of the compound in the lattice direction [$\bar{1}$01] perpendicular to which the complex cations and the $SbF_6^-$ counter anions are linked into N–H ··· F hydrogen bonded chains.

Complexes [Cu(κ²(*S*,*N*)-SN)I] (**5a**, **5b**) were reacted with silver salts in the presence of ligands such as $CH_3CN$, CN*t*Bu, $PPh_3$, terminal alkynes, olefins, and CO. Abstraction of the metal bound halide from complexes **5a** and **5b** with $AgSbF_6$ (1 equiv.) in neat $CH_3CN$ led to the formation of the cationic complexes [Cu(κ²(*S*,*N*)-SN-Ph)$(NCCH_3)_2$]$^+$ (**10a**) and [Cu(κ²(*S*,*N*)-SN-*i*Pr)$(NCCH_3)_2$]$^+$ (**10b**), respectively (Scheme 5). It has to be noted that these complexes were not accessible by treating [Cu$(CH_3CN)_4$]$^+$ with stoichiometric amounts of the corresponding SN ligands. They are stable in the solid state and in acetonitrile solution. In other solvents, *e.g.*, acetone or nitromethane, both complexes dimerize slowly to afford complexes of the type [Cu(κ²(*S*,*N*),μ(*S*)-SN-Ph)$(CH_3CN)]_2^{2+}$ (**11a**) and [Cu(κ²(*S*,*N*),μ(*S*)-SN-*i*Pr)$(CH_3CN)]_2^{2+}$ (**11b**), respectively, which feature bridging SN ligands. In the course of this dimerization,

**Table 1** Comparison of selected geometric parameters (Å, °) of the complexes **3a**, **3b**, **5b**, **6b**, **7a**, and **7b**, with triangular coordination of Cu

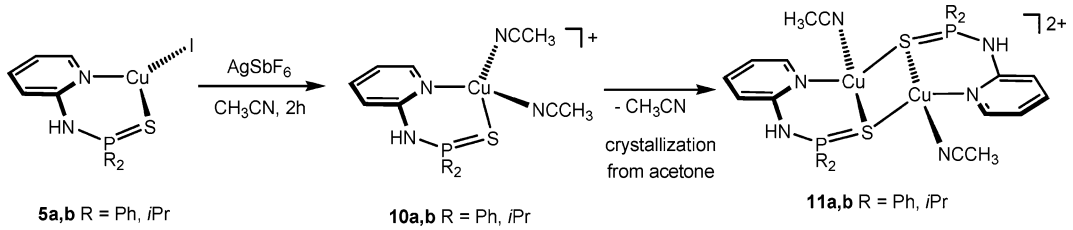
| | E = | X = | Cu–N | Cu–E | Cu–X | N–Cu–E | N–Cu–X | E–Cu–X | *CuPD* |
|---|---|---|---|---|---|---|---|---|---|
| **3a** | S | Br | 2.060 | 2.209 | 2.341 | 113.5 | 111.7 | 133.7 | 0.131 |
| **3b** | S | Br | 2.026 | 2.205 | 2.327 | 115.2 | 113.4 | 130.3 | 0.100 |
| **5b** | S | I | 2.021 | 2.217 | 2.496 | 116.0 | 114.4 | 128.9 | 0.104 |
| **6b** | Se | I | 2.017 | 2.323 | 2.495 | 117.1 | 115.5 | 127.0 | 0.088 |
| **7a** | S | C | 2.048 | 2.267 | 1.913 | 108.8 | 129.2 | 121.6 | 0.075 |
| **7b** | S | C | 2.044 | 2.306 | 1.935 | 106.9 | 135.2 | 117.7 | 0.047 |

For convenience, bond lengths and angles were rounded to three and one decimal place, respectively. E = S or Se, X = Br, I, or C of the NHC-ligand. "*CuPD*" is the distance of Cu from the N–E–X plane.

**Table 2** Comparison of selected geometric parameters (Å, °) of the dinuclear complexes **11a**, **11b**, and **12**, with tetrahedral coordination about Cu

| | L = | Cu1–L | Cu1–N1 | Cu1–S1 | Cu1–S1a | Cu1 ··· Cu1a | S1–Cu1–S1a | S1 ··· S1a |
|---|---|---|---|---|---|---|---|---|
| **11a** | N3 | 1.964 | 2.069 | 2.326 | 2.435 | 2.671 | 111.8 | 3.943 |
| **11b** | N3 | 1.966 | 2.096 | 2.298 | 2.411 | 2.871 | 107.7 | 3.802 |
| **12** | C12 | 1.877 | 2.092 | 2.360 | 2.428 | 3.126 | 98.5 | 3.628 |

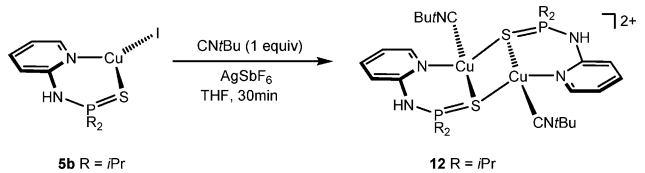
For convenience, bond lengths and angles were rounded to three and one decimal place, respectively. L = N3 of an acetonitrile or C12 of a CN*t*Bu ligand. S1a and Cu1a are the centrosymmetric equivalents of S1 and Cu1.




**5a,b** R = Ph, *i*Pr **10a,b** R = Ph, *i*Pr **11a,b** R = Ph, *i*Pr

**Scheme 5**

one $CH_3CN$ ligand was liberated. A similar reaction took place when iodide abstraction from **10b** was performed in the presence of CN*t*Bu (1 equiv.) as depicted in Scheme 6. NMR monitoring of this reaction did not provide any evidence for the formation of a monomeric intermediate such as $[Cu(\kappa^2(S,N)\text{-SN-}i\text{Pr})(CNt\text{Bu})_2]^+$. Even if two or three equiv. of CN*t*Bu were used, only the formation of the dimeric complex $[Cu(\kappa^2(S,N),\mu(S)\text{-SN-}i\text{Pr})(CNt\text{Bu})]_2^{2+}$ (**12**) was observed (Scheme 6).




**5b** R = *i*Pr **12** R = *i*Pr

**Scheme 6**

Compounds **10**, **11**, and **12** were again characterized by a combination of $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectroscopy and elemental analysis. In addition, **11a**, **11b**, and **12** were characterized by X-ray crystallography. Structural views are depicted in Fig. 8–10 with important bond distances and angles reported in the caption. All three compounds contain crystallographically centrosymmetric dinuclear complexes with the copper atoms in modestly distorted tetrahedral coordination by one pyridine N, two sulfur atoms and a N or C atom of the ancillary ligand. The two Cu and S atoms form a perfectly planar rhombus-like parallelogram with two shorter and two longer Cu–S bonds. The shorter Cu–S bond subtends with the S–P bond angle close to 90°, whereas for the longer Cu–S bond this angle is between 111 and 119°. Table 2 gives a comparison of geometric

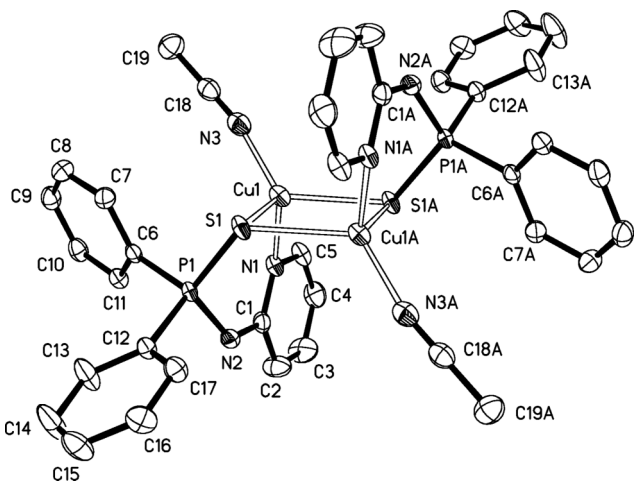



**Fig. 8** Molecular structure of **11a** showing 50% displacement ellipsoids. $SbF_6^-$ anion, diethyl ether solvent molecule, and H atoms omitted for clarity. The molecule is centrosymmetric. Selected distances and angles (Å, °): Cu1–N3 1.964(2), Cu1–N1 2.069(2), Cu1–S1 2.3264(5), Cu1–S1A 2.4349(5), Cu1 ··· Cu1A 2.6711(4), P1–S1 1.9943(5), P1–N2 1.6621(14), N3–Cu1–N1 111.59(6), N3–Cu1–S1 113.12(5), N3–Cu1–S1A 118.98(5), N1–Cu1–S1 110.14(4), N1–Cu1–S1A 88.58(4), S1–Cu1–S1A 111.792(14), P1–S1–Cu1 87.49(2), P1–S1–Cu1A 118.96(2).

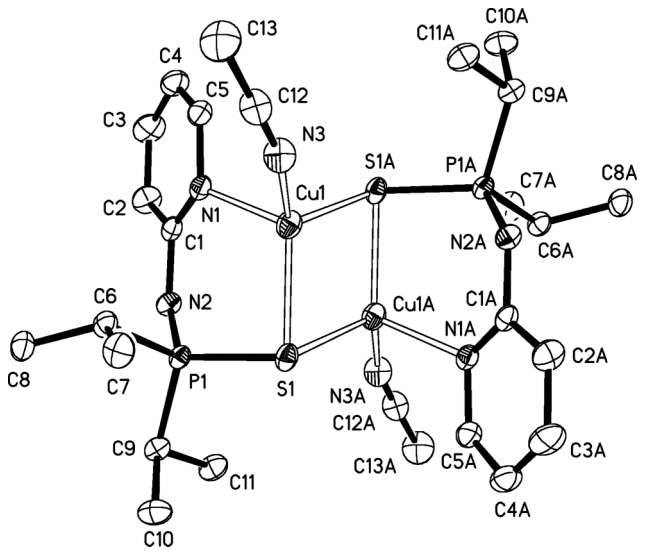



**Fig. 9** Molecular structure of **11b** showing 50% displacement ellipsoids. $SbF_6^-$ anion and H atoms omitted for clarity. The molecule is centrosymmetric. Selected distances and angles (Å, °): Cu1–N3 1.9661(14), Cu1–N1 2.0957(11), Cu1–S1 2.2984(5), Cu1–S1A 2.4110(4), Cu1 ··· Cu1A 2.7810(5), P1–S1 2.0032(5), P1–N2 1.6735(12), N3–Cu1–N1 103.08(5), N3–Cu1–S1 122.28(4), N3–Cu1–S1A 118.77(4), N1–Cu1–S1 109.16(4), N1–Cu1–S1A 90.42(3), S1–Cu1–S1A 107.655(14), P1–S1–Cu1 91.37(2), P1–S1–Cu1A 112.04(2).

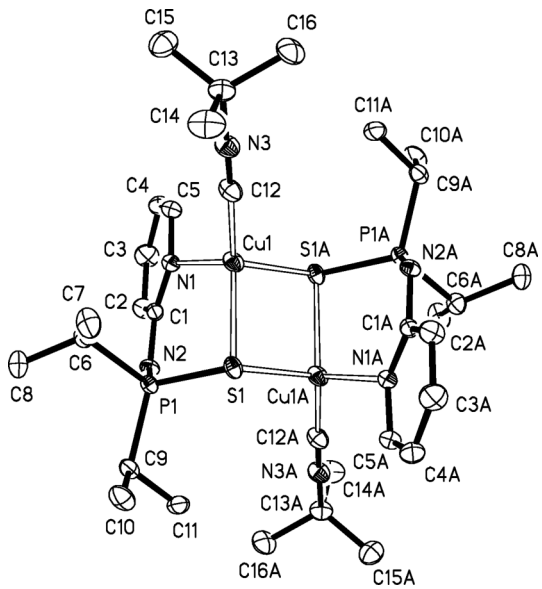
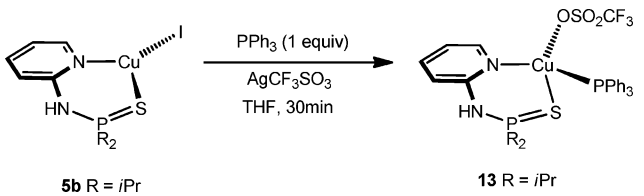



**Fig. 10** Molecular structure of **12** showing 50% displacement ellipsoids. $SbF_6^-$ anion, diethyl ether solvent molecule, and H atoms omitted for clarity. The molecule is centrosymmetric. Selected distances and angles (Å, °): Cu1–C12 1.8873(12), Cu1–N1 2.0924(10), Cu1–S1 2.3598(3), Cu1–S1A 2.4280(3), Cu1 ··· Cu1A 3.1255(3), P1–S1 1.9971(4), P1–N2 1.6736(9), C12–Cu1–N1 117.98(5), C12–Cu1–S1 117.99(4), C12–Cu1–S1A 121.66(4), N1–Cu1–S1 106.17(3), N1–Cu1–S1A 89.63(3), S1–Cu1–S1A 98.51(1), P1–S1–Cu1 91.46(1), P1–S1–Cu1A 111.25(1).

data revealing that these complexes, despite their general geometric uniformity, exhibit a large variation in the intramolecular Cu–Cu distance, ranging from 2.671 Å in **11a** to 2.781 Å in **11b** and 3.126 Å in **12**.

In this context it has to be noted that Cu–Cu $d^{10}$–$d^{10}$ interactions have been the subject of many experimental and theoretical studies due to their biological relevance, *e.g.*, cytochrome oxidase and hemocyanins contain a Cu(I)–Cu(I) active site.[19] However, copper–copper separations in the range of 2.7–3.6 Å are observed for many complexes of the formula $L_nCu(\mu\text{-}X)_2CuL_m$ ($m$ = 1, 2; $n$ = 1, 2) which contain X bridges such as halides, alkoxides, and sulfides. In all these cases, a direct Cu–Cu bond can be excluded as the separation exceeds by at least 0.3 Å the sum of the copper covalent radii (1.17 Å).[20]

Halide abstraction from **5b** with $AgCF_3SO_3$ in THF, followed by the addition of one equiv. of $PPh_3$, afforded the tetracoordinate complex [Cu(κ²(*S*,*N*)-SN-*i*Pr)($PPh_3$)(κ¹(O)-$CF_3SO_3$)] (**13**) in 51% isolated yield (Scheme 7). This complex contains a coordinated $CF_3SO_3^-$ anion. In the $^{31}P\{^1H\}$ NMR spectrum, the SN-*i*Pr and $PPh_3$ ligands give rise to singlets at 91.1 and 11.8 ppm, respectively (for comparison, the free ligands exhibit resonances at 103.5 and –6.5 ppm).




**Scheme 7**

A structural view of **13** is shown in Fig. 11 with selected bond distances and angles reported in the caption. Copper has a distorted tetrahedral coordination by each one N, P, S, and O atom with bond angles between 90 and 133°. As the Cu1–O1 bond is clearly the longest and weakest of the four bonds, the coordination of this Cu is not far off a flat triangular one with the metal atom only 0.340 Å above the plane of the N–P–S triangle

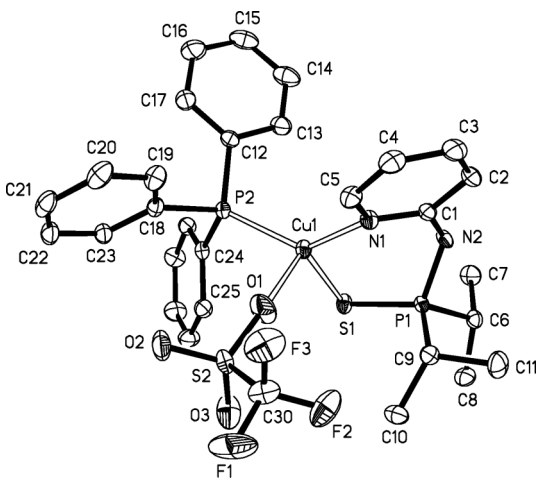
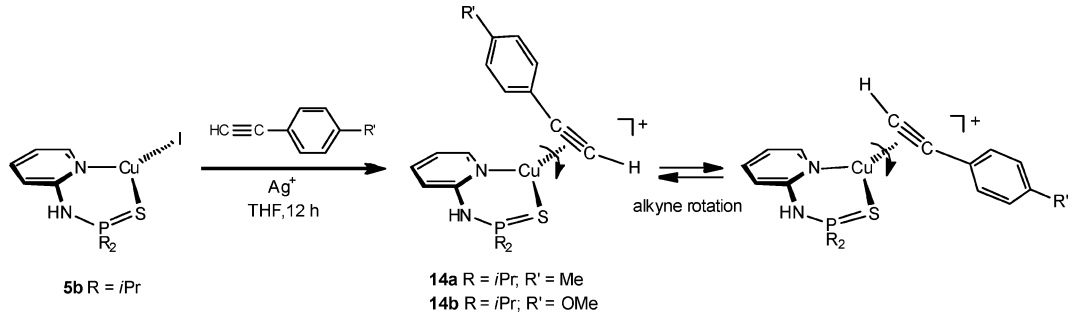



**Fig. 11** Molecular structure of **13** showing 50% displacement ellipsoids. H atoms omitted for clarity. Selected distances and angles (Å, °): Cu1–N1 2.0261(13), Cu1–P2 2.2099(4), Cu1–O1 2.2395(14), Cu1–S1 2.3101(4), P1–S1 1.9756(5), P1–N2 1.6870(14), N1–Cu1–P2 132.86(4), N1–Cu1–O1 90.06(6), N1–Cu1–S1 109.84(4), P2–Cu1–O1 99.03(4), P2–Cu1–S1 109.71(2), O1–Cu1–S1 110.71(5), P1–S1–Cu1 92.25(2).

**Table 3** Details for the crystal structure determinations of compounds **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **5b**, **6b**, **7a**·$(CH_3)_2CO$, **7b**, **8b**, **11a**·2($Et_2O$), **11b**, **12**·2($Et_2O$), and **13**

| Compound | **1a** | **1b** | **2a** | **2b** | **3a** | **3b** | **5b** | **6b** | **7a**·$(CH_3)_2CO$ | **7b** | **8b** | **11a**·2($Et_2O$) | **11b** | **12**·2($Et_2O$) | **13** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Formula | $C_{17}H_{15}N_2PS$ | $C_{11}H_{19}N_2PS$ | $C_{17}H_{15}N_2PSe$ | $C_{11}H_{19}N_2PSe$ | $C_{17}H_{15}$-$BrCuN_2PS$ | $C_{11}H_{19}$-$BrCuN_2PS$ | $C_{11}H_{19}$-$CuIN_2PS$ | $C_{11}H_{19}$-$CuIN_2PSe$ | $C_{47}H_{57}CuF_6$-$N_4OPSSb$ | $C_{38}H_{55}CuF_6$-$N_4PSSb$ | $C_{22}H_{38}CuF_6$-$N_4P_3S_2$ | $C_{46}H_{56}Cu_2$-$F_{12}N_6O_2P_2$-$S_2Sb_2$ | $C_{26}H_{44}Cu_2$-$F_{12}N_6P_2$-$S_2Sb_2$ | $C_{40}H_{76}Cu_2$-$F_{12}N_6O_2P_2$-$S_2Sb_2$ | $C_{30}H_{34}CuF_3$-$N_2O_3P_2S_2$ |
| *Fw* | 310.34 | 242.31 | 357.24 | 289.21 | 453.79 | 385.76 | 432.75 | 479.65 | 1056.29 | 930.18 | 693.13 | 1449.61 | 1165.31 | 1397.71 | 717.19 |
| Crystal size [mm] | 0.42 × 0.28 × 0.25 | 0.59 × 0.25 × 0.23 | 0.50 × 0.40 × 0.25 | 0.42 × 0.28 × 0.25 | 0.48 × 0.29 × 0.22 | 0.58 × 0.04 × 0.03 | 0.45 × 0.22 × 0.12 | 0.40 × 0.06 × 0.05 | 0.50 × 0.40 × 0.15 | 0.44 × 0.32 × 0.30 | 0.58 × 0.34 × 0.28 | 0.42 × 0.37 × 0.35 | 0.53 × 0.40 × 0.30 | 0.48 × 0.35 × 0.28 | 0.38 × 0.28 × 0.12 |
| Color, shape | colourless prism | colourless prism | colourless plate | colourless block | pale yellow prism | colourless prism | colourless prism | colourless prism | colourless plate | colourless column | colourless block | colourless block | colourless block | colourless block | colourless plate |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic |
| Space group | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/n$ (no. 14) | $C2/c$ (no. 15) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) | $P2_1/n$ (no. 14) | $P2_1/c$ (no. 14) | $Pn$ (no. 7) | $P2_1/n$ (no. 14) | $C2/c$ (no. 15) | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) |
| $a$ [Å] | 12.4734(10) | 16.0217(4) | 12.5485(10) | 10.3823(4) | 12.6449(15) | 10.4358(3) | 10.3862(12) | 10.4116(6) | 12.8052(5) | 9.1074(2) | 7.8770(6) | 9.2387(5) | 24.901(3) | 13.3328(5) | 9.2999(1) |
| $b$ [Å] | 13.0561(11) | 10.5230(2) | 13.0789(11) | 10.6502(5) | 11.8148(14) | 12.6065(4) | 13.2474(16) | 13.4179(7) | 28.0150(12) | 12.8043(2) | 13.3222(10) | 14.4373(7) | 12.6741(17) | 14.0819(6) | 9.8907(1) |
| $c$ [Å] | 19.8602(16) | 16.4570(4) | 20.0218(16) | 12.1081(5) | 23.312(3) | 11.7714(3) | 11.5122(14) | 11.6623(6) | 13.2949(6) | 35.3387(6) | 14.8577(11) | 21.7631(11) | 16.782(2) | 16.0780(7) | 19.5996(2) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 96.154(1) |
| $\beta$ (°) | 97.388(1) | 108.842(1) | 97.078(1) | 91.147(1) | 102.80(1) | 92.938(1) | 98.430(1) | 97.501(2) | 92.056(2) | 95.920(1) | 101.953(1) | 102.035(2) | 126.310(1) | 101.539(2) | 100.620(1) |
| $\gamma$ (°) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 112.400(1) |
| $V$ [Å$^3$] | 3207.5(5) | 2625.91(10) | 3260.9(5) | 1338.57(10) | 3409.5(7) | 1546.60(8) | 1566.9(3) | 1615.30(15) | 4766.3(4) | 4099.0(2) | 1525.3(2) | 2839.0(3) | 4267.9(10) | 2957.7(2) | 1606.71(3) |
| $T$ [K] | 100 | 100 | 100 | 100 | 100 | 296 | 100 | 296 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| $Z$ | 8 | 8 | 8 | 4 | 8 | 4 | 4 | 4 | 4 | 4 | 2 | 4 | 4 | 2 | 2 |
| $\rho_c$ [g cm$^{-3}$] | 1.285 | 1.226 | 1.455 | 1.435 | 1.768 | 1.657 | 1.835 | 1.972 | 1.472 | 1.507 | 1.509 | 1.696 | 1.814 | 1.569 | 1.482 |
| $\mu$ [mm$^{-1}$] (Mo-K$\alpha$) | 0.296 | 0.341 | 2.395 | 2.898 | 3.840 | 4.216 | 3.582 | 5.598 | 1.153 | 1.327 | 1.067 | 1.891 | 2.488 | 1.812 | 0.961 |
| $F$(000) | 1296 | 1040 | 1440 | 592 | 1808 | 776 | 848 | 920 | 2160 | 1904 | 716 | 1440 | 2288 | 1408 | 740 |
| $\theta_{max}$ (°) | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 27.55 | 30.0 | 25.96 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 | 30.0 |
| Number of rflns measd | 47 406 | 28 789 | 36 143 | 15 945 | 24 172 | 21 214 | 25 638 | 11 943 | 57 145 | 55 780 | 13 666 | 60 222 | 38 535 | 70 429 | 30 738 |
| $R_{int}$ | 0.019 | 0.017 | 0.028 | 0.017 | 0.0245 | 0.0340 | 0.0261 | 0.0494 | 0.0522 | 0.0251 | 0.0251 | 0.0244 | 0.0266 | 0.0238 | 0.0244 |
| Number of rflns unique | 9339 | 7633 | 9478 | 3894 | 4952 | 3559 | 4544 | 3142 | 13 615 | 11 931 | 6486 | 8250 | 6224 | 8606 | 9308 |
| Number of rflns [$I > 2\sigma(I)$] | 8341 | 6948 | 7638 | 3687 | 4619 | 2702 | 4297 | 2459 | 11492 | 11075 | 6136 | 7816 | 5816 | 8040 | 8348 |
| Number of parameters | 379 | 279 | 379 | 140 | 208 | 158 | 158 | 158 | 569 | 495 | 351 | 337 | 270 | 316 | 395 |
| $R_1$ [$I > 2\sigma(I)$][a] | 0.0344 | 0.0267 | 0.0331 | 0.0191 | 0.0199 | 0.0246 | 0.0165 | 0.0360 | 0.0427 | 0.0313 | 0.0396 | 0.0237 | 0.0207 | 0.0164 | 0.0343 |
| $R_1$ [all data] | 0.0390 | 0.0299 | 0.0470 | 0.0206 | 0.0226 | 0.0446 | 0.0178 | 0.0517 | 0.0535 | 0.0346 | 0.0421 | 0.0253 | 0.0227 | 0.0187 | 0.0390 |
| w$R_2$ [all data] | 0.0954 | 0.0768 | 0.0884 | 0.0515 | 0.0486 | 0.0543 | 0.0437 | 0.1050 | 0.1034 | 0.0690 | 0.1049 | 0.0602 | 0.0538 | 0.0420 | 0.0897 |
| Min./max. resid. Electron dens./e Å$^{-3}$ | −0.49/0.55 | −0.46/0.50 | −0.39/0.98 | −0.33/0.58 | −0.39/0.51 | −0.24/0.33 | −0.47/1.00 | −0.86/1.39 | −1.22/0.99 | −0.91/0.81 | −0.98/1.82 | −1.00/2.07 | −0.69/0.79 | −0.437/0.52 | −0.40/2.27 |




**Scheme 8**



(expected elevation in a regular tetrahedron is about 0.7 Å). The NH group of this complex forms a hydrogen bond to O2 of a neighboring complex (N2 ··· O2 = 2.877(2) Å) linking them into linear chains.

Halide abstraction from **5b** with $AgSbF_6$ (1 equiv.) in THF was also performed in the presence of the terminal alkynes HC≡$CC_6H_4$Me and HC≡$CC_6H_4$OMe yielding copper(I) alkyne complexes of the tentative formula [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-HC≡$CC_6H_4$Me)]⁺ (**14a**) and [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-HC≡$CC_6H_4$OMe)]⁺ (**14b**), respectively, as shown in Scheme 8. It has to be noted that complex **5b** did not undergo a reaction with olefins and carbon monoxide under the same reaction conditions. The exact structure of **14a** and **14b** could not be fully established, since we were unable to obtain single crystals suitable for an X-ray analysis. Thus, merely based on NMR spectroscopic data we cannot exclude that these complexes are dimeric (*vide infra*).

The $^1$H NMR spectra of **14a** and **14b** in $CD_2Cl_2$ exhibits a singlet corresponding to the *H*C≡C– moiety of the alkynes at 4.68 ppm, which is a downfield shift compared to the corresponding signals of the free HC≡$CC_6H_4$Me and HC≡$CC_6H_4$OMe alkynes (3.56 and 3.49 ppm). The resonances of the acetylenic carbon atoms are barely shifted upon η²-coordination of the C≡C triple bond to the copper(I) center, which is a common observation in alkyne–copper(I) chemistry.[21,22] In the case of **14a**, the $^{13}$C{$^1$H} NMR signals of the terminal and internal acetylenic carbons H*C*≡C– and HC≡*C*–in acetone-$d_6$ appear at 79.2 and 87.9 ppm, respectively, which is slightly downfield shifted relative to the free ligand which gave rise to signals at 77.6 and 83.5 ppm (DFT calculated shift values for the free ligand: 75.5 and 80.8 ppm; for complex **14a**: 80.8 and 108.9 ppm). Concurrent $^{13}$C{$^1$H} NMR spectra were observed for **14b** giving signals at 78.5 and 88.5 ppm, respectively, for the terminal and internal acetylenic carbons atoms (calculated shift values: 80.4 and 111.3 ppm). Accordingly, the room temperature NMR spectra are consistent with rapid spinning of the alkyne around the axis connecting the Cu to the C≡C centroid on the NMR time scale (*vided infra*).

In order to obtain further information of the structure of complexes **14**, DFT calculations were carried out with the monomeric and dimeric model complexes [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-HC≡$CC_6H_5$)]⁺ and [Cu(κ²(*S*,*N*),μ(*S*)-SN-*i*Pr)(η²-HC≡$CC_6H_5$)]$_2^{2+}$, respectively. Interestingly, the dimeric complex featuring bridging SN-*i*Pr ligands turned out to be unstable at this level of theory and spontaneous monomerization took place. Accordingly, these results suggest that complexes **14** are most likely monomeric. This may be attributed to the higher steric demand of η²-coordinated terminal alkynes as compared to the terminally coordinated ligands $CH_3CN$ and CN*t*Bu, respectively, where dimeric structures were formed. Moreover, it has to be noted that, in principle, the alkyne ligands can be coordinated in two conformations where the internal alkyne carbon atom is either in a *trans* or *cis* position with respect to the S atom of the SN-*i*Pr ligand. The free energy of the two rotamers of **14a** and **14b** (shown for **14b** in Fig. 12) is nearly the same, differing only by 0.6 kcal mol$^{-1}$ in both cases. The free activation energies ($\Delta G^{\ddagger}$) for alkyne rotation were calculated to be 15.1 and 17.9 kcal mol$^{-1}$, respectively, which is consistent with free rotation of the C–C bonds of the η²-bound alkyne ligand at room temperature. For comparison, the energy barrier ($\Delta G^{\ddagger}$) for alkyne rotation in the tetrameric Cu(I) alkyne complexes [$Cu_4$-μ⁴-*O*-μ²-$X_2$(η²-tmtch)$_4$] (tmtch = 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne, X = Cl, Br) was experimentally determined to be 13.4 and 12.9 kcal mol$^{-1}$, respectively. Similarly, the energy barrier for alkyne rotation in the β-diketiminato complex [Cu($Me_3$NN)(η²-HC≡CPh)] was determined to be 13.4 kcal mol$^{-1}$. These data correspond to fast rotation at room temperature.[23,24] In the transition state, $TS_{rot}$, the alkyne has rotated roughly by about 90° around the axis, connecting the Cu to the C≡C centroid. The Cu–C bond to the internal alkyne carbon atom is significantly elongated from 2.12 Å in **14a** to 2.55 Å in $TS_{rot}$, while the Cu–C bond to the terminal alkyne carbon atom has changed only from 1.96 to 1.99 Å.

## Conclusion

In this work we have synthesized a series of tri- and tetra-coordinated copper(I) complexes with the EN ligands *N*-(2-pyridinyl)amino-diphenylphosphine sulfide, *N*-(2-pyridinyl)-amino-diisopropylphosphine sulfide, *N*-(2-pyridinyl)amino-diphenylphosphine selenide, *N*-(2-pyridinyl)amino-diisopropylphosphine selenide by using the copper(I) precursors CuX (X = Br, I), [Cu(IPr)Cl] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), and [Cu($CH_3CN$)$_4$]$PF_6$. Several mononuclear tri- and tetracoordinate complexes could be obtained. In some cases, it was found that SN ligands are capable of acting as bridging ligands, thereby forming dinuclear complexes. Terminal alkynes were found to react with the [Cu(κ²(*S*,*N*)-SN-*i*Pr)]⁺ fragment to form complexes of the type [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-alkyne)]⁺. The mononuclear nature of these compounds was supported by DFT calculations.

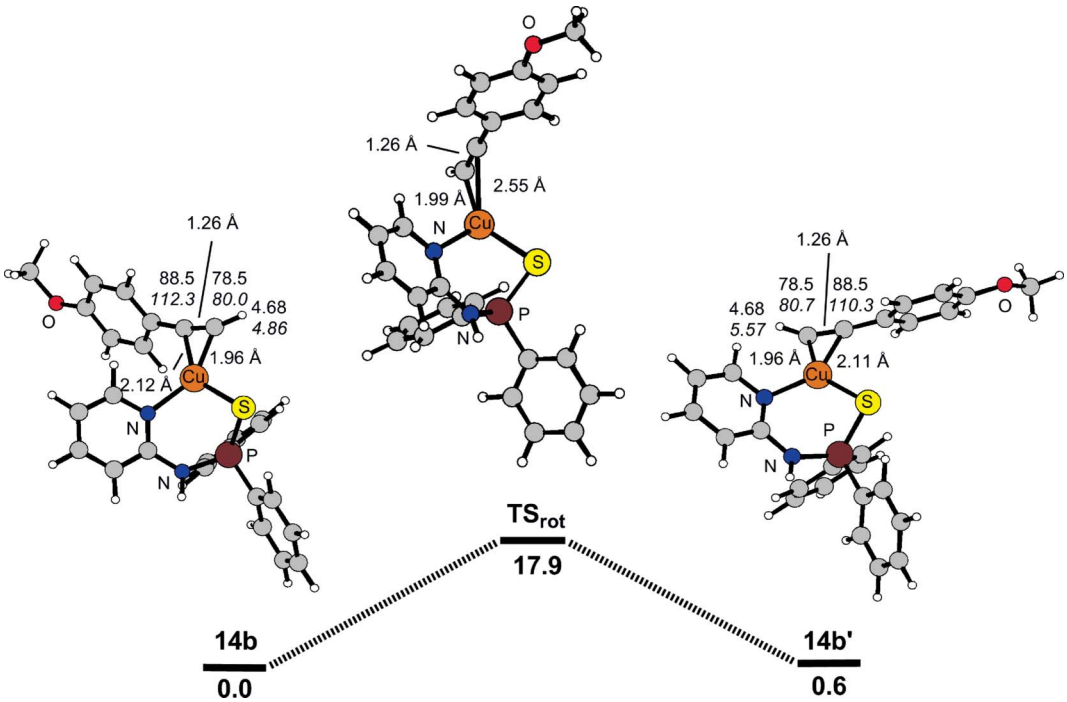



**Fig. 12** Free energy profile for the rotation of the HC≡CC$_6$H$_4$OMe ligand in [Cu(κ$^2$(*S*,*N*)-SN-*i*Pr)(η$^2$-HC≡CC$_6$H$_4$OMe)]$^+$ (**14b**) (experimental and calculated (*italic*) $^1$H and $^{13}$C NMR chemical shifts $\delta$ in ppm relative to TMS).

## Experimental Section

### General

All manipulations were performed under an inert atmosphere of argon by using Schlenk techniques. The solvents were purified according to standard procedures.[25] The ligands *N*-diphenylphosphino-2-aminopyridine (PN-Ph) and *N*-diisopropylphosphino-2-aminopyridine (PN-*i*Pr),[2] and the copper(I) precursors [Cu(CH$_3$CN)$_4$]PF$_6$,[26] and Cu(IPr)Cl (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene)[27] were prepared according to the literature. The deuterated solvents were purchased from Aldrich and dried over 4 Å molecular sieves. $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR spectra were recorded on Bruker AVANCE-250 and AVANCE-300 DPX spectrometers and were referenced to SiMe$_4$ and H$_3$PO$_4$ (85%), respectively. The $^{15}$N NMR parameters were obtained through $^1$H–$^{15}$N HMBC (heteronuclear multiple bond correlation) and $^1$H–$^{15}$N HMQC (heteronuclear single quantum coherence) experiments and are referenced to NH$_4$Cl. $^1$H and $^{13}$C NMR signal assignments were confirmed by $^1$H-COSY, 135-DEPT, $^1$H-$^{13}$C HMQC and $^1$H-$^{13}$C HMBC experiments.

### *N*-(2-pyridinyl)amino-diphenylphosphine sulfide (SN-Ph) (1a)

This ligand has been prepared according to literature[11a] with PN-Ph (1.0 g, 3.5 mmol) and elemental sulphur (115 mg, 3.5 mmol) as starting materials. The crude product was purified by recrystallization from a 1 : 1 mixture of Et$_2$O–THF. Yield: 556 mg (86%). $^1$H NMR ($\delta$, CD$_2$Cl$_2$, 20 °C): 8.18–7.95 (m, 4H, Ph), 7.81 (d, $J$ = 4.5 Hz, py$^6$), 7.61–7.33 (m, 7H, Ph, py$^4$), 7.28 (s, NH), 6.91 (d, $J$ = 8.3 Hz, py$^3$), 6.73 (dd, $J$ = 5.2 Hz, $J$ = 7.1 Hz, py$^5$). $^{13}$C{$^1$H} NMR ($\delta$, CDCl$_3$, 20 °C): 153.7 (s, py$^2$), 147.9 (s, py$^6$), 137.4 (s, py$^4$), 133.5 (d, $J_{CP}$ = 115.2 Hz, Ph$^1$), 132.0 (s, Ph$^4$), 131.6 (d, $J_{CP}$ = 11.4 Hz, Ph$^{2,6}$), 128.6 (d, $J_{CP}$ = 13.4 Hz, Ph$^{3,5}$), 117.0 (s, py$^5$), 112.1 (d, $J_{CP}$ = 3.4 Hz, py$^3$). $^{31}$P{$^1$H} NMR ($\delta$, CD$_2$Cl$_2$, 20 °C): 64.4.

### *N*-(2-pyridinyl)amino-diisopropylphosphine sulfide (SN-*i*Pr) (1b)

This ligand has been prepared analogously to **1a** with PN-*i*Pr (1.68 g, 8.0 mmol) and elemental sulphur (256 mg, 8.0 mmol) as starting materials. Yield: 1.56 g (80%). $^1$H NMR ($\delta$, CDCl$_3$, 20 °C): 8.08 (d, $J$ = 4.3 Hz, py$^6$), 7.48 (t, $J$ = 7.6 Hz, py$^4$), 6.76 (m, 2H, py$^{3,5}$), 5.33 (s, NH), 3.11–2.91 (dh, $J$ = 2.0 Hz, $J$ = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.32–1.09 (m, 12H, CH(C*H*$_3$)$_2$). $^{13}$C{$^1$H} NMR ($\delta$, CDCl$_3$, 20 °C): 154.5 (s, py$^2$), 147.6 (s, py$^6$), 138.0 (s, py$^4$), 116.2 (s, py$^5$), 110.9 (d, $J_{CP}$ = 5.7 Hz, py$^3$), 29.22 (d, $J_{CP}$ = 58.6 Hz, *C*H(CH$_3$)$_2$), 17.1 (s, CH(*C*H$_3$)$_2$), 16.6 (d, $J_{CP}$ = 2.7 Hz, CH(*C*H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($\delta$, CDCl$_3$, 20 °C): 104.6.

### *N*-(2-pyridinyl)amino-diphenylphosphine selenide (SeN-Ph) (2a)

This ligand has been prepared according to literature[11a] with PN-Ph (100 mg, 0.36 mmol) and gray selenium (28.4 mg, 0.36 mmol) as starting materials. Yield: 70 mg (55%). $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.10–7.92 (m, 5H, Ph, py$^6$), 7.55–7.40 (m, 7H, Ph, py$^4$), 7.03 (d, $J$ = 8.21 Hz, 1H, py$^3$), 7.00 (t, $J$ = 5.84 Hz, 1H, py$^5$), 7.37 (bs, 1H, NH). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 154.6 (d, $J_{CP}$ = 3.0 Hz, py), 147.2 (s, py), 137.3 (s, py), 131.9 (d, $J_{CP}$ = 12.2 Hz, Ph), 131.7 (d, $J_{CP}$ = 12.3 Hz, Ph), 128.2 (d, $J_{CP}$ = 13.8 Hz, Ph), 116.4 (s, py), 112.4 (d, $J_{CP}$ = 6.1 Hz, py). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 58.3 (with satellites $J_{P-Se}$ = 787 Hz).

### *N*-(2-pyridinyl)amino-diisopropylphosphine selenide (SeN-*i*Pr) (2b)

This ligand has been prepared analogously to **2a** with PN-*i*Pr (1.0 g, 4.50 mmol) and gray selenium (375.5 mg, 4.50 mmol) as

starting materials. Yield: 1.16 g (89%). $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.13 (d, $J$ = 4.11 Hz, 1H, py$^6$), 7.70 (t, $J$ = 7.42 Hz, 1H, py$^4$), 7.05 (d, $J$ = 8.21 Hz, 1H, py$^3$), 6.84 (t, $J$ = 6.00 Hz, 1H, py$^5$), 6.75 (bs, 1H, NH), 7.19 (m, 2H, C$H$(CH$_3$)$_2$), 1.24–0.99 (m, 12H, CH(C$H_3$)$_2$). $^{13}$C{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 155.5 (d, $J$ = 6.1 Hz, py), 147.2 (s, py), 138.0 (s, py), 115.9 (s, py), 111.4 (d, $J_{CP}$ = 7.3 Hz, py), 28.6 (d, $J_{CP}$ = 49.0 Hz, $C$H(CH$_3$)$_2$), 17.5 (s, CH($C$H$_3$)$_2$), 16.6 (d, $J$ = 3.0 Hz, CH($C$H$_3$)$_2$. $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 102.0 (with satellites $J_{P\text{-}Se}$ = 752 Hz).

### [Cu(κ$^2$(*S*,*N*)-SN-Ph)Br] (3a)

A solution of CuBr (183 mg, 1.28 mmol) and SN-Ph (396 mg, 1.28 mmol) in THF (15 mL) was stirred for 12 h at room temperature. After that, the insoluble materials were removed by filtration and the solvent was removed under reduced pressure. The remaining product was washed twice with diethyl ether (10 mL) and dried under vacuum. Yield: 462 mg (80%). Anal. Calcd. for C$_{17}$H$_{15}$BrCuN$_2$PS: C, 44.99; H, 3.33; N, 6.83%. Found: C, 45.14; H, 3.40; N, 6.70%. $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.19 (bs, 1H, NH), 8.02 (s,1H, py$^6$), 7.99–7.80 (m, 4H, Ph), 7.84 (t, $J$ = 7.57 Hz, 1H, py$^4$), 7.67–7.58 (m, 6H, Ph), 7.29 (d, $J$ = 8.15 Hz, 1H, py$^3$), 6.96 (t, $J$ = 6.53 Hz, 1H, py$^5$). $^{13}$C{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 154.4 (d, $J_{CP}$ = 4.6 Hz, py), 149.0 (s, py), 140.1 (s, py), 133.1 (s, Ph), 131.5 (d, $J_{CP}$ = 12.4 Hz, Ph), 130.1 (d, $J_{CP}$ = 38.2 Hz, Ph), d, $J_{CP}$ = 13.8 Hz, Ph), 117.6 (s, py), 115.3 (d, $J_{CP}$ = 7.67 Hz, py). $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 49.8.

### [Cu(κ$^2$(*S*,*N*)-SN-*i*Pr)Br] (3b)

This complex has been prepared analogously to **3a** with CuBr (296 mg, 2.06 mmol) and SN-*i*Pr (500 mg, 2.06 mmol) as starting materials. Yield: 540 mg (68%). Anal. Calcd. for C$_{11}$H$_{19}$BrCuN$_2$PS: C, 34.25; H, 4.96; N, 7.26%. Found: C, 34.30; H, 4.80; N, 7.12%. $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.43 (s, 1H, py$^6$), 7.78 (t, $J$ = 7.01 Hz, 1H, py$^4$), 7.62 (bs, 1H, NH), 7.11–7.03 (m, 2H, py$^{3,5}$), 2.73 (m, 2H, C$H$(CH$_3$)$_2$), 1.41–1.25 (m, 12H, CH(C$H_3$)$_2$). $^{13}$C{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 155.5 (d, $J_{CP}$ = 4.4 Hz, py$^2$), 148.7 (s, py$^6$), 139.8 (s, py$^4$), 117.2 (s, py$^5$), 114.6 (d, $J_{CP}$ = 5.00 Hz, py$^3$), 29.5 (d, $J_{CP}$ = 54.3 Hz, $C$H(CH$_3$)$_2$), 16.3 (s, CH($C$H$_3$)$_2$), 15.6 (s, CH($C$H$_3$)$_2$). $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 86.7.

### [Cu(κ$^2$(*Se*,*N*)-SeN-Ph)Br] (4a)

This complex has been prepared analogously to **3a** with CuBr (40 mg, 0.280 mmol) and SeN-Ph (100 mg, 0.280 mmol) as starting materials. Yield: 120 mg (85%). Anal. Calcd. for C$_{17}$H$_{15}$CuBrN$_2$PSe: C, 40.78; H, 3.02; N, 5.59%. Found: C, 40.69; H, 3.12; N, 5.46%. $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.21 (s, 1H, py$^6$), 8.01–7.92 (m, 4H, Ph), 7.90 (t, $J$ = 7.42 Hz, 1H, py$^4$), 7.66–7.49 (m, 7H, NH, Ph), 7.28 (d, $J$ = 8.53 Hz, 1H, py$^3$), 6.96 (t, $J$ = 5.84 Hz, 1H, py$^5$). $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 53.3 (with satellites $J_{P\text{-}Se}$ = 693 Hz).

### [Cu(κ$^2$(*Se*,*N*)-SeN-*i*Pr)Br] (4b)

This complex has been prepared analogously to **3a** with CuBr (262 mg, 1.83 mmol) and SeN-*i*Pr (528 mg, 1.83 mmol) as starting materials. Yield: 670 mg (85%). Anal. Calcd. for C$_{11}$H$_{19}$BrCuN$_2$PSe: C, 30.54; H, 4.43; N, 6.74%. Found: C, 30.47; H, 4.41; N, 6.27%. $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.49 (d, $J$ = 4.11 Hz, 1H, py$^6$), 7.77 (t, $J$ = 7.11 Hz, 1H, py$^4$), 7.60 (bs,1H, NH), 7.10 (d, $J$ = 8.21 Hz, 1H, py$^3$), 7.01 (t, $J$ = 6.21 Hz, 1H, py$^5$), 2.82 (m, 2H, C$H$(CH$_3$)$_2$), 1.30 (m, 12H, CH(C$H_3$)$_2$). $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 82.2 (with satellites $J_{P\text{-}Se}$ = 688 Hz).

### [Cu(κ$^2$(*S*,*N*)-SN-Ph)I] (5a)

This complex has been prepared analogously to **3a** with CuI (123 mg, 0.65 mmol) and SN–Ph (200 mg, 0.65 mmol) as starting materials. Yield: 277 mg (85%). Anal. Calcd. for C$_{17}$H$_{15}$CuIN$_2$PS: C, 40.77; H, 3.02; N, 5.59%. Found: C, 40.63; H, 2.92; N, 5.46%. M.P.: 214 °C. $^{1}$HNMR ($\delta$, acetone-d$_6$, 20 °C): 8.30 (s, 1H, py$^6$), 8.00–7.94 (m, 4H, Ph), 7.84 (s, 1H, py$^4$), 7.59 (s, 6H, Ph), 7.55 (bs, 1H, NH), 7.29 (d, $J$ = 8.15 Hz, 1H, py$^3$), 7.00 (s, 1H, py$^5$). $^{13}$C{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 154.4 (d, $J_{CP}$ = 3.0 Hz, py), 149.8 (s, py), 140.1 (s, py), 133.0 (d, $J_{CP}$ = 3.0 Hz, Ph), 131.7 (d, $J_{CP}$ = 12.2 Hz, Ph), 130.5 (d, $J_{CP}$ = 32.2 Hz, Ph), 129.0 (d, $J_{CP}$ = 13.8 Hz, Ph), 117.61 (s, py), 115.4 (d, $J_{CP}$ = 6.1 Hz, py). $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 50.7.

### [Cu(κ$^2$(*S*,*N*)-SN-*i*Pr)I] (5b)

This complex has been prepared analogously to **3a** with CuI (1.37 g, 8.24 mmol) and SN-*i*Pr (2.0 g, 8.24 mmol) as starting materials. Yield: 3.15 g (89%). Anal. Calcd. for C$_{11}$H$_{19}$CuIN$_2$PS: C, 30.53; H, 3.80; N, 6.47%. Found: C, 30.61; H, 3.89; N, 6.56%. M.P.: 147 °C. $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.48 (d, $J$ = 5.17 Hz, 1H, py$^6$), 7.76 (t, $J$ = 7.90 Hz, 1H, py$^4$), 7.52 (bs, 1H, NH), 7.10 (d, $J$ = 8.50 Hz, 1H, py$^3$), 7.02 (t, $J$ = 6.32 Hz, 1H, py$^5$), 2.76 (m, 2H, C$H$(CH$_3$)$_2$), 1.39–1.23 (m, 12H, CH(C$H_3$)$_2$). $^{13}$C{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 155.5 (d, $J_{CP}$ = 4.4 Hz, py$^2$), 149.6 (s, py$^6$), 139.8 (s, py$^4$), 117.2 (s, py$^5$), 114.8 (d, $J_{CP}$ = 4.99 Hz, py$^3$), 29.5 (d, $J_{CP}$ = 54.3 Hz, $C$H(CH$_3$)$_2$), 16.3 (d, $J_{CP}$ = 2.49 Hz, CH($C$H$_3$)$_2$), 15.6 (s, CH($C$H$_3$)$_2$). $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 89.3.

### [Cu(κ$^2$(*Se*,*N*)-SeN-Ph)I] (6a)

This complex has been prepared analogously to **3a** with CuI (106 mg, 0.56 mmol) and SeN-Ph (200 mg, 0.56 mmol) as starting materials. Yield: 210 mg (69%). Anal. Calcd. for C$_{17}$H$_{15}$CuIN$_2$PSe: C, 37.25; H, 2.76; N, 5.11%. Found: C, 37.15; H, 2.80; N, 5.20%. $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.01 (d, $J$ = 5.34 Hz, 1H, py$^6$), 7.97–7.76 (m, 5H, Ph), 7.64 (t, $J$ = 7.28 Hz, 1H, py$^4$), 7.60–7.57 (m, 6H, Ph, NH), 7.27 (d, $J$ = 8.21 Hz, 1H, py$^3$), 6.98 (t, $J$ = 5.83 Hz, 1H, py$^5$). $^{13}$C{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 154.2 (s, py), 150.0 (s, py), 139.9 (s, py), 132.9 (d, $J_{CP}$ = 3.0 Hz, Ph), 131.8 (d, $J_{CP}$ = 12.2 Hz, Ph), 130.4 (d, $J_{CP}$ = 38.3 Hz, Ph), 129.0 (d, $J_{CP}$ = 13.8 Hz, Ph), 117.4 (s, py), 115.5 (d, $J_{CP}$ = 6.1 Hz, py). $^{31}$P{$^{1}$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 42.3 (with satellites $J_{P\text{-}Se}$ = 698 Hz).

### [Cu(κ$^2$(*Se*,*N*)-SeN-*i*Pr)I] (6b)

This complex has been prepared analogously to **3a** with CuI (198 mg, 1.04 mmol) and SeN-*i*Pr (301 mg, 1.04 mmol) as starting materials. Yield: 370 mg (75%). Anal. Calcd. for C$_{11}$H$_{19}$CuIN$_2$PSe: C, 27.54; H, 3.99; N, 5.84%. Found: C, 27.44; H, 4.12; N, 6.06%. $^{1}$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.49 (d, $J$ = 5.05 Hz, 1H, py$^6$), 7.78 (t, $J$ = 7.74 Hz, 1H, py$^4$), 7.52 (bs, 1H, NH), 7.17 (d, $J$ = 8.21 Hz, 1H, py$^3$), 7.02 (t, $J$ = 6.16 Hz, 1H, py$^5$), 2.90 (m, 2H, C$H$(CH$_3$)$_2$),

1.27 (m, 12H, CH($CH_3$)$_2$). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 149.5 (s, py), 139.6 (s, py), 117.0 (s, py), 114.4 (d, $J_{CP}$ = 4.4 Hz, py), 29.8 (d, $J_{CP}$ = 48.8 Hz, $C$H(CH$_3$)$_2$), 16.3 (s, CH($C$H$_3$)$_2$), 16.2 (s, CH($C$H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 84.6 (with satellites $J_{P\text{-}Se}$ = 684 Hz).

**[Cu(κ²(*S*,*N*)-SN-Ph)(IPr)]SbF$_6$ (7a)**

A solution of [Cu(IPr)Cl] (100 mg, 0.20 mmol) in THF (20 mL) was treated with SN–Ph (64 mg, 0.20 mmol) and AgSbF$_6$ (70 mg, 0.20 mmol) and the mixture was stirred for 12 h at room temperature. Insoluble materials were removed by filtration and the solvent was then removed under reduced pressure. The product was washed with diethyl ether (2 × 10 mL) and dried under vacuum. Yield: 155 mg (78%). Anal. Calcd. for $C_{44}H_{51}CuF_6N_4PSSb$: C, 52.94; H, 5.15; N, 5.61%. Found: C, 52.80; H, 5.31; N, 5.66%. $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.55 (bs, 1H, py$^6$), 7.74 (s, 2H, IPr), 7.71–7.50 (m, 3H, IPr, py$^4$), 7.45–7.42 (d, $J$ = 7.89 Hz, 4H, IPr), 7.19 (d, $J$ = 7.89 Hz, 1H, NH), 6.61 (bs, 1H, py$^3$), 6.39 (bs, 1H, py$^5$), 2.73–2.70 (m, 4H, C$H$(CH$_3$)$_2$), 1.26–0.9 (m, 24H, CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 183.1 (s, IPr), 156.0 (s, py), 149.9 (s, py),145.7 (s, IPr), 140.7 (s, py), 133.0 (d, $J_{CP}$ = 3.0 Hz, Ph), 131.7 (d, $J_{CP}$ = 12.2 Hz, Ph), 130.3 (s, Ph), 129.0 (d, $J_{CP}$ = 13.8 Hz, Ph), 124.7 (s, IPr), 124.3 (s, IPr), 124.1 (s, IPr), 117.7 (s, py), 116.5 (s, py), 28.5 (s, IPr), 23.6 (s, IPr), 23.4 (s, IPr), 22.8 (s, IPr). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 55.2.

**[Cu(κ²(*S*,*N*)-SN-*i*Pr)(IPr)]SbF$_6$ (7b)**

This complex has been prepared analogously to **7a** with [Cu(IPr)Cl] (100 mg, 0.17 mmol), SN-*i*Pr (42 mg, 0.17 mmol), and AgSbF$_6$ (60 mg, 0.17 mmol) as the starting materials. Yield: 100 mg (63%). Anal. Calcd. for $C_{38}H_{55}CuF_6N_4PSSb$: C, 49.07; H, 5.96; N, 6.02%. Found: C, 49.25; H, 5.65; N, 6.76%. $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.43 (s, 1H, Py$^6$), 7.74 (s, 2H, IPr), 7.71 (t, $J$ = 8.79 Hz, 1H, py$^4$), 7.58 (t, $J$ = 7.91 Hz, 2H, IPr), 7.51 (d, $J$ = 7.69 Hz, 4H, IPr), 7.24 (d, $J$ = 7.69 Hz, 1H, NH), 7.02 (d, $J$ = 8.35 Hz, 1H, py$^3$), 7.00 (t, $J$ = 6.15 Hz, 1H, py$^5$), 2,81–2.75 (m, 4H, C$H$(CH$_3$)$_2$), 2.53–2.50 (m, 2H, C$H$(CH$_3$)$_2$), 1.26–0.9 (m, 36H, CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 183.3 (IPr), 156.0 (s, py), 149.0 (s, py), 145.7 (IPr), 140.3 (IPr), 135.8 (s, py), 130.2 (IPr), 124.2 (IPr), 124.0 (IPr), 117.8 (s, py), 111.3 (s, py), 29.3 (d, $J_{CP}$ = 58.3 Hz, $C$H(CH$_3$)$_2$), 28.6 (IPr), 23.8 (IPr), 23.2 (IPr), 15.5 (IPr), 15.1 (CH($C$H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 88.9.

**[Cu(κ²(*S*,*N*)-SN-Ph)$_2$]PF$_6$ (8a)**

To a solution of [Cu(CH$_3$CN)$_4$]PF$_6$ (200 mg, 0.537 mmol) in THF (20 mL) SN-Ph (333 mg, 1.074 mmol) was added and the mixture was stirred for 12 h at room temperature. After that the solvent was removed under reduced pressure. The remaining product was washed twice with diethyl ether (10 mL) and dried under vacuum. Yield: 350 mg (78%). Anal. Calcd. for $C_{34}H_{30}CuF_6N_4P_3S_2$: C, 27.54; H, 3.99; N, 5.84%. Found: C, 27.45; H, 3.75; N, 5.71%. $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.53 (s, 2H, py), 7.98–7.92 (m, 8H, Ph, py), 7.64–7.63 (m, 16H, Ph, NH), 7.25 (d, $J$ = 8.21 Hz, 2H, py$^3$), 6.76 (t, $J$ = 5.37 Hz, 2H, py$^5$). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 154.0 (d, $J_{CP}$ = 3.0 Hz, py), 147.8 (s, py), 139.4 (s, py), 133.0 (d, $J_{CP}$ = 3.0 Hz, Ph), 131.7 (d, $J_{CP}$ = 12.0 Hz, Ph), 129.0 (d, $J_{CP}$ = 13.8 Hz, Ph), 131.0 (d, $J_{CP}$ = 113.4 Hz, Ph), 117.7 (s, py), 115.3 (d, $J_{CP}$ = 6.1 Hz, py). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 52.8.

**[Cu(κ²(*S*,*N*)-SN-*i*Pr)$_2$]PF$_6$ (8b)**

This complex has been prepared analogously to **8a** with [Cu(CH$_3$CN)$_4$]PF$_6$ (154 mg, 0.41 mmol) and SN-*i*Pr (200 mg, 0.82 mmol) as starting materials. Yield: 171 mg (60%). Anal. Calcd. for $C_{22}H_{38}CuF_6N_4P_3S_2$: C, 38.12; H, 5.53; N, 8.08%. Found: C, 38.21; H, 5.62; N, 8.12%. $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.09 (d, $J$ = 4.42 Hz, 2H, py$^6$), 7.66(t, $J$ = 7.13 Hz, 2H, py$^4$), 7.30 (bs, 2H, NH), 7.05 (d, $J$ = 8.15 Hz, 2H, py$^3$), 6.86 (t, $J$ = 5.84 Hz, 2H, py$^5$), 2.90 (m, 4H, C$H$(CH$_3$)$_2$), 1.29 (m, 24H, CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 155.8 (d, $J_{CP}$ = 6.13 Hz, py), 147.7 (s, py), 149.5 (s, py), 117.3 (s, py), 114.8 (d, $J_{PC}$ = 4.6 Hz, py), 29.5 (d, $J_{CP}$ = 33.7 Hz, $C$H(CH$_3$)$_2$), 16.2 (s, CH($C$H$_3$)$_2$), 15.40 (s, CH($C$H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 92.9.

**[Cu(κ²(*Se*,*N*)-SeN-Ph)$_2$]PF$_6$ (9a)**

This complex has been prepared analogously to **8a** with [Cu(CH$_3$CN)$_4$]PF$_6$ (104.3 mg, 0.28 mmol) and SeN-Ph (200 mg, 0.56 mmol) as starting materials. Yield: 200 mg (78%). Anal. Calcd. for $C_{34}H_{30}CuF_6N_4P_3Se_2$: C, 44.24; H, 3.28; N, 6.07%. Found: C, 44.18; H, 3.12; N, 6.16%. $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 7.99–7.73 (m, 10H, Ph, py), 7.67–7.58 (m, 16H, Ph, py), 7.26 (d, 2H, $J$ = 8.01 Hz, py), 6.73 (t, $J$ = 5.87 Hz, 2H, py). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 154.7 (d, $J_{CP}$ = 3.0 Hz, py), 148.0 (s, py), 139.7 (s, py), 132.9 (d, $J_{CP}$ = 12.2 Hz, Ph), 131.9 (d, $J_{CP}$ = 12.2 Hz, Ph), 130.6 (d, $J_{CP}$ = 35.6 Hz, Ph), 129.0 (d, $J_{CP}$ = 13.8 Hz, Ph), 117.4 (s, py), 115.6 (d, $J_{CP}$ = 6.1 Hz, py). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 44.8 (with satellites $J_{P\text{-}Se}$ = 694 Hz).

**[Cu(κ²(*Se*,*N*)-SeN-*i*Pr)$_2$]PF$_6$ (9b)**

This complex has been prepared analogously to **8a** with [Cu(CH$_3$CN)$_4$]PF$_6$ (200 mg, 0.70 mmol) and SeN-*i*Pr (129 mg, 0.35 mmol) as starting materials. Yield: 200 mg (72%). Anal. Calcd. for $C_{22}H_{38}CuF_6N_4P_3Se_2$: C, 33.58; H, 4.87; N, 7.12%. Found: C, 33.66; H, 4.65; N, 7.00%. $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.14 (d, $J$ = 5.37 Hz, 2H, py$^6$), 7.70 (t, $J$ = 7.90 Hz, 2H, py$^4$), 7.50 (bs, 2H, NH), 7.07 (d, $J$ = 8.21 Hz, 2H, py$^3$), 6.87 (t, $J$ = 6.48 Hz, 2H, py$^5$), 2.90 (m, 4H, C$H$(CH$_3$)$_2$), 1.34 (m, 24H, CH(C$H_3$)$_2$). $^{13}$C{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 155.5 (d, $J_{CP}$ = 4.6 Hz, py), 148.0 (s, py), 139.5 (s, py), 117.3 (s, py), 115.1(d, $J_{CP}$ = 6.1 Hz, py), 29.6 (d, $J_{cp}$ = 50.6 Hz, $C$H(CH$_3$)$_2$), 16.7 (s, CH($C$H$_3$)$_2$), 15.6 (s, CH($C$H$_3$)$_2$). $^{31}$P{$^1$H} NMR ($\delta$, acetone-d$_6$, 20 °C): 83.7 (with satellites $J_{P\text{-}Se}$ = 673 Hz).

**[Cu(κ²(*S*,*N*)-SN-Ph)(NCCH$_3$)$_2$]SbF$_6$ (10a)**

A solution of **4a** (649 mg, 1.43 mmol) and AgSbF$_6$ (491 mg (1.43 mmol) in CH$_3$CN (15 mL) was stirred for 2 h at room temperature. Insoluble materials (AgI) were removed by filtration and the solvent was then removed under reduced pressure and the product was washed with diethyl ether (2 × 10 mL) and dried under vacuum. Yield: 593 mg (60%). Anal. Calcd. for $C_{21}H_{21}CuF_6N_4PSSb$: C, 36.46; H, 3.06; N, 8.10%. Found: C, 36.55; H, 3.12; N, 8.01%. $^1$H NMR ($\delta$, acetone-d$_6$, 20 °C): 8.71 (s, 1H, py), 8.00–7.71 (m, 6H, Ph, py), 7.68–7.61 (m, 6H, Ph, NH), 7.36

(d, $J$ = 8.21 Hz, 1H, py$^3$), 7.07 (t, $J$ = 6.79 Hz, 1H, py$^5$), 2.18 (s, 6H, $CH_3$). $^{13}C\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 154.8 (d, $J_{CP}$ = 4.6 Hz, py), 148.3 (s, py), 140.9 (s, py), 133.4 (d, $J_{CP}$ = 3.1 Hz, Ph), 131.9 (d, $J_{CP}$ = 13.1 Hz, Ph), 131.7 (d, $J_{CP}$ = 12.2 Hz, Ph), 131.5 (s, N≡*C*-), 129.3 (d, $J_{CP}$ = 13.8 Hz, Ph), 118.3 (s, py), 116.1 (d, $J_{CP}$ = 7.67 Hz, py). $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 51.8. IR (ATR, cm$^{-1}$): 2280 ($\nu_{N\equiv C}$), 2213 ($\nu_{N\equiv C}$).

### [Cu(κ²(*S*,*N*),μ(*S*)-SN-Ph)(NCCH$_3$)]$_2$(SbF$_6$)$_2$ (11a)

Crystals of **11a** were grown by diethyl ether diffusion into a saturated acetone solution of **10a**. Anal. Calcd. for $C_{38}H_{36}Cu_2F_{12}N_6P_2SSb_2$: C, 35.07; H, 2.79; N, 6.46%. Found: C, 35.12; H, 3.50; N, 6.55%. $^1H$ NMR ($\delta$, acetone-$d_6$, 20 °C): 8.80 (s, 2H, py), 7.99–7.91 (m, 12H, Ph, py), 7.71 (d, $J$ = 6.63 Hz, 2H, NH), 7.62 (bs, 10H, Ph), 7.40 (d, $J$ = 7.90 Hz, 2H, py$^3$), 7.08 (t, $J$ = 6.32 Hz, 2H, py$^5$), 2.29 (s, 6H, $CH_3$). $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 51.6.

### [Cu(κ²(*S*,*N*)-SN-*i*Pr)(NCCH$_3$)$_2$]SbF$_6$ (10b)

This complex has been prepared analogously to **10a** with **4b** (1.0 g, 2.3 mmol) and $AgSbF_6$ (794 mg, 2.30 mmol) as starting materials. Yield: 750 mg (52%). Anal. Calcd. for $C_{15}H_{25}CuF_6N_4PSSb$: C, 28.89; H, 4.04; N, 8.98%. Found: C, 28.99; H, 3.91; N, 8.82%. $^1H$ NMR ($\delta$, acetone-$d_6$, 20 °C): 8.21 (d, $J$ = 5.37 Hz,1H, py$^6$), 8.10 (d, $J$ = 8.85 Hz, 1H, NH), 7.87 (t, $J$ = 7.74 Hz, 1H, py$^4$), 7.31 (d, $J$ = 8.53 Hz,1H, py$^3$),7.12(t, $J$ = 6.48 Hz, 1H, py$^5$), 2.81–2.74 (m, 2H, C*H*(CH$_3$)$_2$), 2.23 (s, 6H, NCC*H*$_3$), 1.40–1.21 (m, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 155.6 (s, py), 148.3 (s, py), 141.2 (s, py), 118.5 (s, py), 116.1 (s, py), 29.6 (d, $J_{CP}$ = 51.1 Hz, *C*H(CH$_3$)$_2$), 15.9 (s, CH(*C*H$_3$)$_2$), 15.3 (s, CH(*C*H$_3$)$_2$), 1.0 (s, *C*H$_3$). The nitrile carbon atom could not be detected. $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 88.6. IR (ATR, cm$^{-1}$): 2276 ($\nu_{N\equiv C}$).

### [Cu(κ²(*S*,*N*),μ(*S*)-SN-*i*Pr)(NCCH$_3$)]$_2$(SbF$_6$)$_2$ (11b)

Crystals of **11b** were grown by diethyl ether diffusion into a saturated acetone solution of **10b**. Anal. Calcd. for $C_{26}H_{44}Cu_2F_{12}N_6P_2S_2Sb_2$: C, 26.80; H, 3.81; N, 7.21%. Found: C, 26.70; H, 3.92; N, 7.14%. $^1H$ NMR ($\delta$, acetone-$d_6$, 20 °C): 8.23 (d, $J$ = 5.05 Hz,2H, py$^6$), 7.89 (t, $J$ = 7.74 Hz, 2H, py$^4$) 7.80 (d, $J$ = 9.16 Hz, 2H, NH), 7.16 (d, $J$ = 7.58 Hz, 2H, py$^3$), 7.14(t, $J$ = 5.21 Hz, 2H, py$^5$), 2.78–2.68 (m, 4H, C*H*(CH$_3$)$_2$), 2.21 (s, 6H, C*H*$_3$), 1.40–1.23 (m, 24H, CH(C*H*$_3$)$_2$). $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 88.4.

### [Cu(κ²(*S*,*N*),μ(*S*)-SN-*i*Pr)(CN*t*Bu)]$_2$(SbF$_6$)$_2$ (12)

A solution of **4b** (300 mg, 0.69 mmol) in THF (25 mL) and $AgSbF_6$ (237 mg, 0.69 mmol) was stirred for 5 min. After that CN*t*Bu (57 mg (0.69 mmol) was added and the mixture was stirred for 12 h. Insoluble materials (AgI) were removed by filtration and the solvent was then removed under reduced pressure and the product was washed twice with diethyl ether (10 mL) and dried under vacuum. Yield: 380 mg (78%). Anal. Calcd. for $C_{32}H_{56}Cu_2F_{12}N_6P_2S_2Sb_2$: C, 30.76; H, 4.52; N, 6.73%. Found: C, 30.80; H, 4.47; N, 6.72%. $^1H$ NMR ($\delta$, acetone-$d_6$, 20 °C): 8.34 (s, 2H, py$^6$), 7.94–7.91 (m, *4*H, NH, py$^4$), 7.22–7.17 (m, 4H, py$^{3,5}$), 2.70 (m, 4H, C*H*(CH$_3$)$_2$), 1.59 (s, 18H, C(C*H*$_3$)$_3$, 1.53–1.20 (m, 24H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 156.0 (s, py), 149.8 (s, py), 141.5 (s, py), 133.8 (s, *C*≡N-), 118.4 (s, py), 116.4 (d, $J_{CP}$ = 4.6 Hz, py), 57.6 (s, *C*(CH$_3$)$_3$), 29.4 (d, $J_{CP}$ = 55.1 Hz, *C*H(CH$_3$)$_2$), 29.1 (s, C(*C*H$_3$)$_3$, 15.7 (s, CH(*C*H$_3$)$_2$), 15.2 (s, CH(*C*H$_3$)$_2$), 0.6 (*C*H$_3$). $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 91.3. IR (ATR, cm$^{-1}$): 2177 ($\nu_{C\equiv N}$), 2160 ($\nu_{C\equiv N}$).

### [Cu(κ²(*S*,*N*)-SN-*i*Pr)(PPh$_3$)(κ¹(O)-CF$_3$SO$_3$)] (13)

A solution of **4b** (300 mg, 0.69 mmol) in THF (15 mL) and $AgCF_3SO_3$ (179 mg, 0.69 mmol) was stirred for 5 min. After that $PPh_3$ (364 mg (1.38 mmol) was added and the mixture was stirred for 12 h. Insoluble materials (AgI) were removed by filtration and the solvent was then removed under reduced pressure and the product was washed twice with diethyl ether (10 mL) and dried under vacuum. Yield: 250 mg (51%). Anal. Calcd. for $C_{30}H_{34}CuF_3N_2O_3P_2S_2$: C, 50.24; H, 4.78; N, 3.91%. Found: C, 49.95; H, 4.59; N, 3.79%. Mp: 120.4 °C. $^1H$ NMR ($\delta$, acetone-$d_6$, 20 °C): 8.08 (d, $J$ = 5.05 Hz, 1H, py$^6$), 7.99 (bs, 1H, NH), 7.92 (t, $J$ = 7.11 Hz, 1H, py$^4$), 7.52 (d, $J$ = 6.63 Hz,15H, Ph), 7.24 (d, $J$ = 8.21 Hz, 1H, py$^3$), 7.00 (t, $J$ = 6.48 Hz, 1H, py$^5$), 2.73 (m, 2H, C*H*(CH$_3$)$_2$), 1.38–1.22 (m,12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 156.0 (d, $J_{CP}$ = 4.6 Hz, py), 149.5 (s, py), 141.2 (s, py), 133.5 (d, $J_{CP}$ = 13.8 Hz, Ph), 131.4 (s, Ph), 129.2 (d, $J_{CP}$ = 10.7 Hz, Ph), 118.2 (s, py), 116.7 (d, py, $J_{CP}$ = 4.6 Hz), 29.5 (d, $J_{CP}$ = 58.2 Hz, *C*H(CH$_3$)$_2$), 15.8 (s, CH(*C*H$_3$)$_2$), 15.2 (s, CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 91.1 (P*i*Pr$_2$), 11.8 (PPh$_3$).

### [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-HC≡CC$_6$H$_4$Me)]SbF$_6$ (14a)

A solution of **4b** (300 mg, 0.69 mmol) in THF (10 mL) was treated with $AgSbF_6$ (238 mg, 0.69 mmol) and stirred for 5 min. After that, 1-ethynyl-4-metylbenzene (HC≡CC$_6$H$_4$Me) (483 mg, 4.16 mmol) was added and the mixture was stirred for 12 h. Insoluble materials (AgI) were then removed by filtration and the solvent was then removed under reduced pressure and the product was washed twice with diethyl ether (10 mL) and dried under vacuum. Yield: 350 mg (77%). Anal. Calcd. for $C_{20}H_{27}CuF_6N_2PSSb$: C, 36.52; H, 4.14; N, 4.26%. Found: C, 36.45; H, 4.00; N, 4.36%. $^1H$ NMR ($\delta$, $CD_2Cl_2$, 20 °C): 7.98 (d, $J$ = 4.65 Hz,1H, py$^6$), 7.87 (t, $J$ = 8.09 Hz, 1H, py$^4$), 7.45 (d, $J$ = 8.08 Hz, 2H, Ph), 7.30 (d, $J$ = 7.78 Hz, 1H, py$^3$), 7.22 (d, $J$ = 7.78 Hz, 2H, Ph), 7.09 (t, $J$ = 6.88 Hz, 1H, py$^5$), 6.56 (d, $J$ = 8.53 Hz, 1H, NH), 4.68 (s, 1H, *H*C≡C–), 2.62 (m, 2H, C*H*(CH$_3$)$_2$), 2.39(s, 3H, C(C*H*$_3$)) 1.41-1.21(m, 12H, CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$NMR ($\delta$, acetone-$d_6$, 20 °C): 155.6 (d, $J_{CP}$ = 6.1 Hz, py), 148.8 (s, py), 141.3 (s, py), 131.7 (s, Ph), 129.3 (s, Ph), 118.9 (s, py), 117.1 (d, $J_{CP}$ = 4.8 Hz, py), 87.9 (s, HC≡*C*-), 79.2 (s, H*C*≡C–), 30.1 (d, $J_{CP}$ = 54.8 Hz, *C*H(CH$_3$)$_2$), 20.5 (s, Me), 15.9 (d, $J_{CP}$ = 3.0 Hz, CH(*C*H$_3$)$_2$), 15.2 (s, CH(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 96.0.

### [Cu(κ²(*S*,*N*)-SN-*i*Pr)(η²-HC≡CC$_6$H$_4$OMe)]SbF$_6$ (14b)

This complex has been prepared analogously to **14a** with **4b** (300 mg, 0.69 mmol), $AgSbF_6$ (238 mg, 0.69 mmol), and 1-ethynyl-4-methoxybenzene (HC≡C–C$_6$H$_4$OMe) (183 mg, 1.38 mmol) as starting materials. Yield: 390 mg (84%). Anal. Calcd. for $C_{20}H_{27}CuF_6N_2OPSSb$: C, 35.65; H, 4.04; N, 4.16%. Found: C, 35.55; H, 3.98; N, 4.24%. $^1H$ NMR ($\delta$, acetone-$d_6$, 20 °C): 8.32

(d, $J$ = 4.87 Hz,1H, py[6]), 8.31 (d, $J$ = 8.53 Hz, 1H, NH), 7.95 (t, $J$ = 7.01 Hz, 1H, py[4]), 7.50 (d, $J$ = 8.53 Hz, 2H, Ph), 7.26 (d, $J$ = 8.53 Hz, 1H, py[3]), 7.18 (t, $J$ = 6.40 Hz, 1H, py[5]), 6.97 (d, $J$ = 8.53 Hz, 2H, Ph), 4.68 (s, 1H, $HC{\equiv}C$-), 3.83 (s, 3H, $OCH_3$), 2.96 (m, 2H, $CH(CH_3)_2$), 1.42–1.21(m, 12H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 155.7 (d, $J_{CP}$ = 4.6 Hz, py), 148.9 (s, py), 141.5 (s, py), 133.3 (s, Ph), 118.8 (s, py), 116.9 (d, $J_{CP}$ = 4.6 Hz, py), 114.2 (s, Ph), 88.5 (s, $HC{\equiv}C$–), 78.5 (s, $HC{\equiv}C$–), 54.8 (s, $OCH_3$), 30.1 (d, $J_{CP}$ = 55.2 Hz, $CH(CH_3)_2$), 15.9 (d, $J_{CP}$ = 3.0 Hz, $CH(CH_3)_2$), 15.2 (s, $CH(CH_3)_2$). $^{31}P\{^1H\}$ NMR ($\delta$, acetone-$d_6$, 20 °C): 91.5.

### X-ray structure determinations

X-ray single crystal data for **1a**, **1b**, **2a**, **2b**, **3a**, **3b**, **5b**, **6b**, **7a**·$(CH_3)_2CO$, **7b**, **8b**, **11a**·2($Et_2O$), **11b**, **12**·2($Et_2O$), and **13** were collected on two Bruker CCD diffractometers (Kappa APEX-2 and Smart APEX) using graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å) and fine-sliced $\omega$- and $\varphi$-scan frames mostly covering complete spheres of the reciprocal space with $\theta_{max}$ = 30° (27.55° and 25.96° for **3b** and **6b**, respectively). After data integration with program SAINT corrections for absorption and $\lambda/2$ effects were applied with the program SADABS.[28] The structures were solved by direct methods (SHELXS97) and refined on $F^2$ with program SHELXL97.[29] All non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. The compounds **1a**, **1b** and **3b**, **5b**, **6b**, respectively, form two isostructural solid series. Complexes **7a**, **11a**, and **12** form stoichiometric solvates with well-ordered solvent molecules (one $(CH_3)_2CO$ for **7a**, two $Et_2O$ for **11a** and **12**). Orientation disorder of one *iso*-propyl group and one $SbF_6^-$ octahedron was encountered in **7b** and **11b**, respectively, and was taken into account. Crystal data and experimental details are given in Table 3.

CCDC 810363 (for **1a**), 810364 (for **1b**), 810365 (for **2b**), 810366 (for **2b**), 810367 (for **3a**), 810368 (for **3b**), 810369 (for **5b**), 810370 (for **6b**), 810371 (for **7a**·$(CH_3)_2CO$)), 810372 (for **7b**), 810373 (for **8b**), 810374 (for **11a**·2 $Et_2O$), 810375 (for **11b**), 810376 (for **12**·2($Et_2O$)), and 810377 (for **13**) contain the supplementary crystallographic data for this paper and are available in the ESI.†

### Computational details

Calculations were performed using the GAUSSIAN 03 software package,[30] and the PBE functional[31] without symmetry constraints. The optimized geometries were obtained with the Stuttgart/Dresden ECP (SDD) basis set[32] to describe the electrons of the copper atom. For all other atoms the 6–31g** basis set was employed.[33] Frequency calculations were performed to confirm the nature of the stationary points. NMR chemical shift calculations were obtained from single point calculations using the optimized structures of **14a** and **14b** (BPE functional) with the GIAO method at the B3LYP/6-31++G** level. $SiMe_4$, calculated at the same level of theory, was used as reference to scale the absolute shielding value.

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