Reactivity of Cu(I) Compounds towards Ethylenediamine and Dimethylformamide: Crystal Structure of $CuCl(P^iPr_3)_n$ ($n = 1, 2$), $CuX(PPh_3)(en)_2$ (X = Cl, Br) and $CuX(PPh_3)(dmf)$

Sandra Scharfe and Thomas F. Fässler
Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

Reprint requests to Prof. Dr. Th. F. Fässler. Fax: (+49) 89 289 13186.
E-mail: Thomas.Faessler@lrz.tum.de

Z. Naturforsch. **2012**, *67b*, 564 – 572 / DOI: 10.5560/ZNB.2012-0101
Received April 6, 2012

Dedicated to Professor Wolfgang Beck on the occasion of his 80th birthday

The synthesis of several phosphine Cu(I) complexes is reported, and their reactivity towards the solvents ethylenediamine (en) and dimethylformamide (dmf) has been investigated. $CuX(PPh_3)$ [X = Cl (**1**), Br (**2**)], $CuCl(PCy_3)$ (**3**) and $CuCl(P^iPr_3)_n$ [n = 1 (**4**), 2 (**5**)] were prepared according to adapted literature procedures. The complexes $CuCl(P^iPr_3)_n$ were obtained in crystalline form from a hexane solution at −70 °C and structurally characterized for n = 1 and 2. Copper halide complexes of PCy_3 (**3**) and P^iPr_3 [n = 1 (**4**)] gave colorless solutions in both en and dmf indicating the absence of Cu(II) ions. $CuCl(P^iPr_3)_2$ is stable in dmf solutions. By contrast, the complexes $CuX(PPh_3)$ (X = Cl, Br) dissolve with blue color in en and with greenish-yellow color in dmf at higher temperatures under inert gas indicating a redox process affording Cu(II). At room temperature colorless crystals of $CuX(PPh_3)(en)_2$ [X = Cl (**6**), Br (**7**)] and $CuX(PPh_3)(dmf)$ [X = Cl (**8**), Br (**9**)] were isolated from the solutions and analyzed by single-crystal X-ray diffraction.

Key words: Copper, Phosphine, Structure, Reactivity

Introduction

The emerging field of metalloid and intermetalloid clusters [1, 2] demands an improvement of synthetic routes. One approach is the reaction of transition metal complexes with soluble polyhedral nine-atom cluster anions of tetrel elements $[E_9]^{4-}$ (E = Si, Ge, Sn, Pb) known as Zintl anions [3, 4] which hold an enormous synthetic potential and even allow a bottom-up synthesis of nano-structured materials [5, 6]. Polyanions are available by dissolving salt-like intermetallic phases of the general composition A_4E_9 (A = alkali metal) in polar, aprotic solvents such as ethylenediamine (en), dimethylformamide (dmf) and liquid ammonia [7]. A variety of products can be formed by the reaction of these solutions with compounds of transition metals in low oxidation states. Zintl ions can function as ligands in *d*-block element complexes, or by stripping off all ligands the *d*-block element can slip into the Zintl cluster to give endohedrally filled polyhedra [8]. Additionally, $[E_9]^{4-}$ polyhedra can be functionalized to *e. g.* $[Ge_9\text{-Mes}]^{3-}$ through the reaction of $[Ge_9]^{4-}$ with Mes-Ag [9]. The diversity of the crystallographically characterized compounds yielded from tetrel clusters was recently reviewed [5, 10].

In the course of our pertinent investigations of transition metals and their complexes we found that elemental mercury forms polyanionic $^1_\infty[\text{-}(Ge_9)\text{-Hg-}]$ chains, whereas reactions of $[Ge_9]^{4-}$clusters with $AuCl(PPh_3)$ afford $[Au_3Ge_{18}]^{5-}$ and $[Au_3Ge_{45}]^{9-}$ clusters [11 – 13]. Currently no complexes of Ag and homoatomic Ge_9 clusters are known, but Ag_4Mes_4 reacts with $[Sn_9]^{4-}$ solutions under formation of an Ag^+ complex of the dimeric $[Sn_9\text{-}Sn_9]^{6-}$ anion [14]. Finally, $CuCl(PCy_3)$ and $CuCl(P^iPr_3)$ were successfully used in reactions with Zintl anions, and several new copper complexes of tetrel atom clusters were obtained (Fig. 1) [15].

By contrast, the reaction of these Cu complexes with $[Sn_9]^{4-}$ and $[Pb_9]^{4-}$ clusters led to the incorporation of

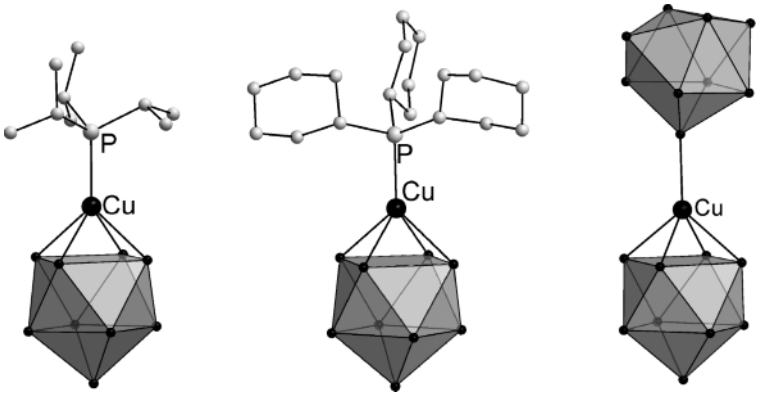

Fig. 1. Examples of copper complexes with $[Ge_9]^{4-}$ clusters as ligands. Zintl anions $[Ge_9]^{4-}$ are represented as polyhedra that coordinate to the Cu atom in η^4 and η^1 fashion as a σ-donor [15].

the Cu atom into the cluster to give endohedrally filled species $[Cu@Sn_9]^{3-}$ and $[Cu@Pb_9]^{3-}$ [16].

The preferred oxidation state of copper atoms strongly depends on the properties of the solvent and the provided ligands. Due to the completely filled *d* shell Cu(I) compounds are generally colorless, whereas Cu(II) complexes comprise nine *d* electrons and appear in different colors, which are controlled by the attached ligands. Autoxidation is frequently observed for solutions of Cu(I) compounds in solvents that are strong σ-donors such as water, en and dmf since Cu(II) is a harder Lewis acid and a better σ-acceptor than Cu(I) [17]. Thus, the dissolution of ligand-free copper(I) halides in these solvents immediately leads to intensively blue (en) and yellow (dmf) solutions of the corresponding Cu(II) solvate or halide complexes and to the precipitation of elemental copper. Electrochemical investigations of the copper redox system in en and dmf have revealed two close-lying potential steps indicating the instability of Cu(I) [18, 19]. In en the formation of the Cu(II) chelate complex $[Cu(en)_3]^{2+}$ with the structure of a tetragonally Jahn-Teller-distorted octahedron dominates the redox equilibrium [20]. Dmf is a weaker Lewis base, and the resulting Cu(II) ions are complexed by both halide anions and solvent molecules in varying ratios [21]. To the best of our knowledge solid-state structures of Cu(I) or Cu(II) dmf solvates have not been described in the literature. During the reaction of a copper(I) compound with the Zintl anions $[E_9]^{4-}$ the formation of Cu(II) ions must be prevented since they oxidize the tetrel cluster to the elemental state. For that reason we examined the redox behavior of several copper phosphine complexes in en and dmf. Phosphines are known to stabilize the d^{10} electron configuration of Cu(I) atoms against oxidation reactions.

Results and Discussion

Following up the experiments with analogous gold complexes, the investigations started from $CuX(PPh_3)$ [X = Cl (**1**), Br (**2**)]. Subsequently, $CuCl(PCy_3)$ (**3**) and $CuCl(P^iPr_3)_n$ [n = 1 (**4**), 2 (**5**)] were also studied. All copper compounds were synthesized according to adapted literature procedures [22–24]. The complexes $CuCl(P^iPr_3)_n$ were obtained in crystalline form from hexane solutions at −70 °C and structurally characterized for n = 1 and 2. Copper halide complexes of PCy_3 and P^iPr_3 (n = 1) led to colorless solutions in both en and dmf indicating the absence of Cu(II) ions. Indeed, for the preparation of $CuCl(PCy_3)$, CuCl was dissolved in dmf giving a yellow solution of Cu(II) ions and elemental copper, and the addition of PCy_3 induced the comproportionation reaction after heating the mixture [22]. $CuCl(P^iPr_3)_2$ proved to be stable in dmf, but gave a pale-blue solution in en.

By contrast, the complexes $CuX(PPh_3)$ (X = Cl, Br) dissolved with blue color in warm en and with greenish yellow color in warm dmf under inert gas conditions. Thus, the Cu(I) ions are oxidized to Cu(II) and are not sufficiently stabilized by the PPh_3 ligand. At room temperature colorless crystals were isolated from the solutions. They consisted of the compounds $CuX(PPh_3)(en)_2$ [X = Cl (**6**), Br (**7**)] and $CuX(PPh_3)(dmf)$ [X = Cl (**8**), Br (**9**)], respectively.

$CuCl(P^iPr_3)_n$ (n = 1, 2)

The compounds $CuCl(P^iPr_3)_n$ [n = 1 (**4**), 2 (**5**)] were synthesized from Cu(I)Cl and stoichiometric amounts

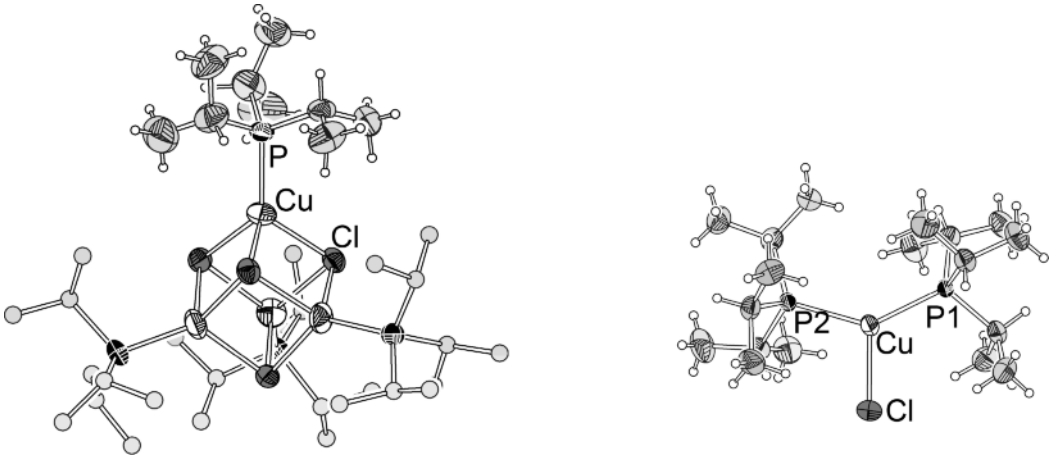

Fig. 2. Molecular structures of the $CuCl(P^iPr_3)_n$ complexes [$n = 1$ (**4**), 2 (**5**)]. The non-hydrogen atoms are shown with 70 % occupation probability. Cu, P, and Cl atoms are labeled, H atoms are shown as white balls. Left: tetrameric $[CuCl(P^iPr_3)]_4$ unit of **4**; right: monomeric $CuCl(P^iPr_3)_2$ **5**.

of P^iPr_3 in toluene [24].

$$CuCl + nP^iPr_3 \rightarrow CuCl(P^iPr_3)_n$$
$$[n = 1(\mathbf{4});\ \ n = 2(\mathbf{5})]$$

From a hexane solution of $CuCl(P^iPr_3)$ (**4**) large colorless crystals were obtained at a temperature of −70 °C. $CuCl(P^iPr_3)_2$ (**5**) showed an extremely high solubility in toluene as well as hexane at ambient temperature. At a temperature of −70 °C, **5** crystallized in the shape of large, colorless needles. The precipitate can be separated from the supernatant solution by filtration, but it still dissolves completely in the solvent remaining on the crystal surfaces after being warmed to room temperature, resulting in an oily solution. The solvent was removed under dynamic high vacuum within several hours, and the copper complex was obtained as a colorless powder.

$CuCl(P^iPr_3)$ (**4**) crystallizes in the orthorhombic space group *Ccca* with 16 formula units per unit cell. All atoms occupy general positions, and the asymmetric unit comprises one formula unit. No solvent molecules were found in the crystal structure. $CuCl(P^iPr_3)_2$ (**5**) crystallizes – also solvent-free – in the triclinic system with space group $P\bar{1}$.

For complex **4** a tetrameric heterocubane structure was observed (Fig. 2). Four symmetry- equivalent copper and chloride ions occupy the vertices of the cube. Each copper atom is coordinated by three chlorine atoms and one phosphine ligand in a distorted tetrahedral environment. This type of structure is frequently reported for complexes of the general composition $CuX(PR_3)$, *e. g.* for R = Ph, Me and ^{t}Bu [25 – 28]. In contrast to this result, Werner *et al.* suggested a dimeric molecule for $CuCl(P^iPr_3)$ as it was found for $CuCl(PCy_3)$ [24]. In $[CuCl(P^iPr_3)]_4$ the Cu–P distance amounts to 2.1926(5) Å, and the Cu–Cl distances along the cube edge range from 2.3981(5) to 2.5282(5) Å. All bond lengths are similar to those of analogous compounds [25 – 29].

The Cu–P bonds are directed towards the center of the cubane. The P–Cu–Cl angles are between 113.26(2) and 128.33(2)° and are larger than the tetrahedral angle. By contrast, the Cl atoms draw angles of up to 96.23° at the Cu atoms, and correspondingly the Cu–Cl–Cu angles (max. 87.07°) are smaller than 90°. The Cu–Cu distances (3.3017(4) – 3.3943(4) Å) are shorter than the Cl–Cl distances (3.5000(6) – 3.8641(6) Å).

The deviation of the copper chlorine structures in different complexes of the type $[CuCl(PR_3)]_4$ from a regular cube depends on the organic substituent R and increases in the series ^{t}Bu < ^{t}Pr < Ph < Me [25 – 28]. According to Tolman the steric repulsion of the phosphines PR_3 rises with the cone angle which is 182°, 160°, 145°, and 118° for P^tBu_3, P^iPr_3, PPh_3, and PMe_3, respectively [30]. Thus, the more flexible the ligands are, the more distorted is the heterocube.

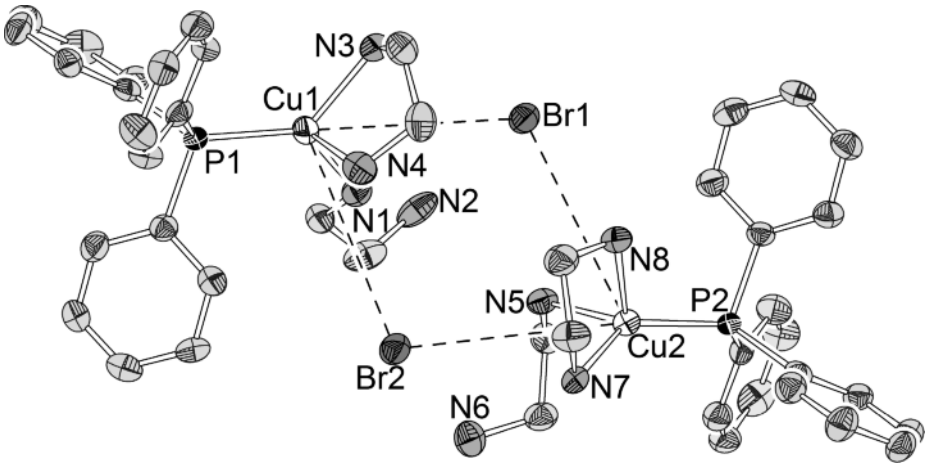

Fig. 3. Molecular structure of $CuBr(PPh_3)(en)_2$ (**7**). The non-hydrogen atoms are shown with 70 % occupation probability. H atoms are omitted for clarity.

Compound **5** is monomeric in the solid state (Fig. 2). The copper atom is coordinated by one Cl atom and two P atoms in an almost ideal trigonal-planar arrangement which was also found for numerous other complexes of the general formula $CuCl(PR_3)_2$ with large groups *R* [22, 31, 32]. The Cu–Cl distance is 2.2592(6) Å, and the Cu–P distances amount to 2.2419(6) and 2.2652(6) Å. The P–Cu–P angle (137.41(2)°) is wider than the P–Cu–Cl angles (105.73(2) and 116.52(2)°).

$CuX(PPh_3)(en)_2$

Compounds **6** and **7** were obtained from the $(Ph_3P)CuX$ precursors in excess ethylenediamine upon gentle heating.

$$CuX(PPh_3) + 2en \rightarrow CuX(PPh_3)(en)_2$$
$$[X = \text{Cl } (\mathbf{6});\ X = \text{Br } (\mathbf{7})]$$

At ambient temperature colorless crystals of $CuCl(PPh_3)(en)_2$ (**6**) or $CuBr(PPh_3)(en)_2$ (**7**) formed in moderate yield. They were suitable for structure determination only for *X* = Br. However, $CuCl(PPh_3)(en)_2$ gave the same unit cell parameters, and the composition was determined by elemental analysis and mass spectrometry.

Compound **7** crystallizes in the triclinic space group *P*1 with two formula units per unit cell. The Flack parameter of 0.380(5) indicated that a twin refinement was necessary. The program package PLATON [33] was used to verify the space group, and no additional symmetry was found. Both molecules of each unit cell are not related by an inversion center. A detailed structure examination reveals significant differences in the conformation of the atoms Cu1 and Cu2. Each copper atom is coordinated by one PPh_3 ligand and two ethylenediamine molecules (Fig. 3). One diamine acts as a chelating and the other as a monodentate ligand. The Br atom is eliminated from the coordination sphere of the Cu atom and interacts with the amino groups of the complex molecules *via* hydrogen bonds.

A similar coordination pattern was found for the complex cation of $[Cu_2(CO)_2(en)_3][CuCl_2]$ [34]. Therein, the less bulky CO ligand takes the place of the phosphine ligand, and one ethylenediamine molecule with an antiperiplanar conformation bridges two copper atoms. By contrast, in $CuBr(PPh_3)(en)_2$ the second donor function of the singly bonded ethylenediamine molecule is not connected to a copper atom, and the two amino groups are orientated synclinally to each other. The copper coordination modes deviate significantly from a tetrahedral configuration which can be ascribed to the small bite angle of the chelating ligand.

The Cu1 and Cu2 atoms in compound **7** are in an almost ideal trigonal-planar environment of the atoms P1, N1, N3 and P2, N5, N7, respectively. Within these planes the angles are 123.28(8)° (P1–Cu1–N1), 131.93(8)° (P1–Cu1–N3) and 100.52(11)° (N1–Cu1–N3) at Cu1 and 116.68(8)° (P2–Cu2–N5), 135.52(8)° (P2–Cu2–N7) and 99.92(10)° (N5–Cu2–N7) at Cu2. The bonds Cu1–N4 and Cu2–N8 are directed approximately perpendicular to theses planes. The resulting five-membered rings hold angles of 83.36(10)° (N3–Cu1–N4) and 84.17(10)°

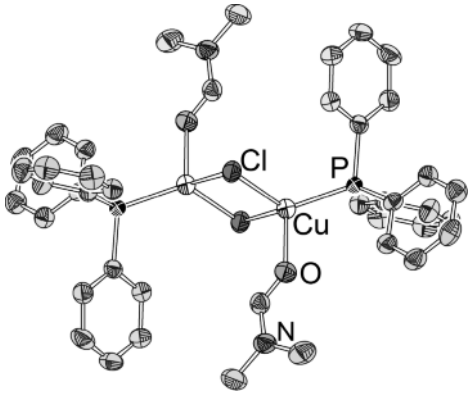

Fig. 4. Structure of the dimeric structure of $CuCl(PPh_3)(dmf)$ (**8**). $CuBr(PPh_3)(dmf)$ (**9**) is isostructural. Atoms are shown with 70 % occupation probability. H atoms are omitted for clarity.

(N7–Cu2–N8) at the copper atoms. The atoms N4 and N8 are shifted towards N1 and N5, respectively, since the angles N1–Cu1–N4 (97.36(10)°) and N5–Cu2–N8 (100.55(10)°) are smaller than N4–Cu1–P1 (107.23(8)°) and N8–Cu2–P2 (111.06(8)°). The structure of the reported complex cation $[Cu_2(CO)_2(en)_3]^+$ is closer to a tetrahedral configuration, and the bond angles range from 105.7(1)° to 123.3(1)° except for the chelate angle which amounts to 83.8(1)° [34]. The Cu–N distances in compound **7** range from 2.071(3) to 2.186(2) Å, and the Cu–P distances are 2.164(2) (Cu1–P1) and 2.166(2) Å (Cu2–P2). Thus, the Cu–N bond lengths as well as the bond angles at Cu1 and Cu2 mirror the steric stress in the complexes.

$CuX(PPh_3)(dmf)$

Compounds **1** and **2** dissolve with greenish-yellow color in dimethylformamide when the solution is slightly heated.

$$\underset{\mathbf{1},\mathbf{2}}{CuX(PPh_3)} + dmf \rightarrow \underset{\mathbf{8},\mathbf{9}}{CuX(PPh_3)(dmf)}$$

[X = Cl: **1**, **8**; X = Br: **2**, **9**]

After several days at ambient temperature large, colorless crystals of $CuCl(PPh_3)(dmf)$ (**8**) or $CuBr(PPh_3)(dmf)$ (**9**) were found and characterized by X-ray diffraction.

The isotypic compounds crystallize in the triclinic space group $P\bar{1}$ with two formula units per unit cell. The complexes dimerize in the solid state with formation of a planar four-membered ring frequently found also for other copper halide phosphine complexes (Fig. 4). Each Cu atom is coordinated by two X atoms. The coordination sphere of the transition metal is completed by one phosphine ligand and one O donor atom of a dmf molecule. Coordination compounds of Cu(I) and dmf have previously not been mentioned in the literature which might be due to the instability of the +I oxidation state in this solvent. In the cases of **8** and **9** the phosphine ligand prevents the disproportionation through π back donation. The Cu–P bond lengths are typical for copper phosphine complexes (**8**: 2.1887(7) Å, **9**: 2.1975(5) Å).

The mean Cu–X distances along the edges of the central quadrangle amount to 2.3780(9) Å for X = Cl and to 2.4975 Å for X = Br. They are shorter than the Cu–X bonds in the tetrameric $[CuX(PPh_3)]_4$ units [29, 35] which have a heterocubane structure similar to $[CuCl(P^iPr_3)]_4$. Because Cu(I) prefers a tetrahedral coordination, the central quadrangle has a rhombus shape, and the X–Cu–X angles (**8**: 96.47(3)°, **9**: 98.99(1)°) are wider than the Cu–X–Cu angles (**8**: 83.53°, **9**: 81.02(1)°). Consequently, the Cu–Cu diagonals (**8**: 3.1676(5) Å, **9**: 3.2444(4) Å) are shorter than the X–X diagonals (**8**: 3.547(1) Å, **9**: 3.7977(4) Å). The phosphine ligands cause a strong steric repulsion which leads to P–Cu–X angles of 121.95(3)° and 122.64(3)° for X = Cl and of 119.85(2)° and 121.62(2)° for X = Br. The dimethylformamide molecules coordinate with Cu–O distances of 2.131(2) Å (**8**) and 2.115(2) Å (**9**).

Experimental Section

Materials and methods

Green CuX_2 impurities were removed from CuX by standard methods [36]. Methylene chloride was distilled from molecular sieve, ethylenediamine and dimethylformamide from CaH_2 under inert gas conditions. All solvents were used immediately after collection. Educts were stored in an argon-filled glove box. All syntheses were carried out in an argon atmosphere using standard Schlenk techniques.

Characterization

NMR solvents were stored over molecular sieves. NMR spectra were recorded on a Bruker AMX400 instrument and locked on the signal of the deuterated solvent. ^1H and ^{13}C NMR shifts were referred to solvent signals or Me_4Si as external standard, ^{31}P NMR shifts with respect to phosphoric

Table 1. Crystallographic data for $CuCl(P^iPr_3)$ (**4**) and $CuCl(P^iPr_3)_2$ (**5**).

	4	**5**
Empirical formula	$C_9H_{21}ClCuP$	$C_{18}H_{42}ClCuP_2$
Formula weight	259.22	419.45
Crystal size, mm^3	$0.6 \times 0.2 \times 0.2$	$0.30 \times 0.10 \times 0.05$
T, K	150(2)	150(2)
Crystal system	orthorhombic	triclinic
Space group	*Ccca*	$P\bar{1}$
a, Å	15.7533(5)	8.6620(3)
b, Å	23.6504(6)	9.9213(4)
c, Å	13.1617(3)	14.1937(6)
α, deg	90	77.776(3)
β, deg	90	85.239(3)
γ, deg	90	71.181(3)
V, $Å^3$	4903.7(2)	1128.26(8)
Z	16	2
$D_{calcd.}$, $g\,cm^{-3}$	1.40	1.24
Absorption coefficient, mm^{-1}	2.1	1.21
$F(000)$, e	2176	452
θ range for data collection, deg	3.10 to 30.09	3.31 to 27.57
Index ranges	$0 \le h \le 22$	$-11 \le h \le 11$
	$0 \le k \le 33$	$-12 \le k \le 12$
	$0 \le l \le 18$	$0 \le l \le 18$
Reflections collected	42 779	16 535
Independent reflections/R_{int}	3606/0.0396	5173/0.0465
Completeness, %	99.8	99.2
Max./min. transmission	0.84524/0.73752	1.00000/0.79160
Data/restraints/parameters	3606/0/182	5173/0/367
Goodness-of-fit on F^2	0.926	0.868
R_1 $[I > 2\sigma(I)]$	0.0317	0.0308
wR_2 $[I > 2\sigma(I)]$	0.0801	0.0554
R_1 (all data)	0.0518	0.0569
wR_2 (all data)	0.0841	0.0588
Largest diff. peak/hole, e $Å^{-3}$	0.90/ − 0.47	0.36/ − 0.41

acid (85 %, 0 ppm) sealed in a glass capillary. Fast atom bombardment mass spectrometry (FAB MS) was preformed on a Finnigan MAT 90 instrument. The solids were dispersed in 4-nitrobenzyl alcohol and ionized with xenon gas.

*Syntheses of **1** and **2***

The complexes $CuX(PPh_3)$ were obtained according to the literature [25] in 86 and 90 % yield, respectively. – FAB MS (%) for **1**: m/z = 185 (27.1, $[PPh_2]^+$), 262 (100.0, $[PPh_3]^+$), 325 (82.0, $[CuPPh_3]^+$), 587 (80.9, $[Cu(PPh_3)_2]^+$). – FAB MS (%) for **2**: m/z = 185 (12.1, $[PPh_2]^+$), 262 (100.0, $[PPh_3]^+$), 325 (60.0, $[CuPPh_3]^+$), 587 (30.6, $[Cu(PPh_3)_2]^+$).

*Synthesis of **3***

$CuCl(PCy_3)$ was obtained according to the literature [22] in 80 % yield. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.89–1.77 (m, 4H, C^3H_2), 1.68 (b, 1H, C^1HP), 1.38 (m, 2H, C^4H_2), 1.23 (m, 4H, C^2H_2). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.54 (d, 1C, C^1HP, $^1J(^{13}C\text{-}^{31}P)$ = 20.22 Hz), 30.76 (d, 2C, C^2H_2, $^3J(^{13}C\text{-}^{31}P)$ = 2.76 Hz), 27.25 (d, 2C, C^3H_2, $^2J(^{13}C\text{-}^{31}P)$ = 11.03 Hz), 25.97 (s, 1C, C^4H_2). – ^{31}P NMR (162 MHz, $CDCl_3$): δ = 26.04 (b). – Analysis: calcd. C 57.0, H 8.7, P 8.2, Cu 16.8, Cl 9.4; found C 56.1, H 9.0, P 7.6, Cu 14.1, Cl 10.9. – FAB MS (%): m/z = 198 (23.1, $[PCy_3]^+$), 261 (27.1, $[CuPCy_2]^+$), 281 (16.2, $[PCy_3]^+$), 343 (34.8, $[Cu(PCy_3)]^+$), 623 (100.0, $[Cu(PCy_3)_2]^+$), 722 (6.8, $[(Cu\{PCy_3\})_2Cl]^+$).

*Syntheses of **4** and **5***

$CuCl(P^iPr_3)_n$ [n = 1 (**4**), 2 (**5**)] were prepared according to the literature [24] with 80 % yield. – ^{1}H NMR of **4** (400 MHz, C_6D_6): δ = 1.17 (dd, 6H, CH_3, $^3J(^1H\text{-}^{31}P)$ = 13.4 Hz, $^3J(^1H\text{-}^1H)$ = 7.3 Hz), 1.85 (oct., 1H C*H*P, $^3J(^1H\text{-}^1H)$ = 7.3 Hz). – ^{13}C NMR of **4** (100 MHz, C_6D_6): δ = 20.18 (d, 2C, CH_3, $^2J(^{13}C\text{-}^{31}P)$ = 4.9 Hz), 22.40 (d, 1C, *C*HP, $^1J(^{13}C\text{-}^{31}P)$ = 17.3 Hz). – ^{31}P NMR of **4** (162 MHz, C_6D_6): δ = 23.60 (s). – FAB MS for **4** (%): m/z =159 (22.0, $[P^iPr_3]^+$), 223 (25.9, $[Cu(P^iPr_3)]^+$), 383 (19.9, $[Cu(P^iPr_3)_2]^+$), 483 (100.0, $[(Cu\{P^iPr_3\})_2Cl]^+$), 580 (24.8, $[(Cu\{P^iPr_3\})_2CuCl_2]^+$). – ^{1}H NMR of **5** (400 MHz, $CDCl_3$): δ =1.14 (dd, 12H, CH_3, $^3J(^1H\text{-}^{31}P)$ = 12.2 Hz, $^3J(^1H\text{-}^1H)$ = 7.4 Hz), 1.95 (m, 2H C*H*P,$^2J(^1H\text{-}^{31}P)$ =

Table 2. Crystallographic data for $CuBr(PPh_3)(en)_2$ (**7**), $CuCl(PPh_3)(dmf)$ (**8**) and $CuBr(PPh_3)(dmf)$ (**9**).

	7	**8**	**9**
Empirical formula	$C_{22}H_{31}BrCuN_4P$	$C_{21}H_{22}ClCuNOP$	$C_{21}H_{22}BrCuNOP$
Formula weight	525.93	434.36	478.82
Crystal size, mm^3	$0.4 \times 0.4 \times 0.3$	$0.5 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.1$
T, K	150(2)	150(2)	150(2)
Crystal system	triclinic	triclinic	triclinic
Space group	$P1$	$P\bar{1}$	$P\bar{1}$
a, Å	8.3788(5)	8.6891(7)	8.6270(5)
b, Å	9.2655(6)	9.0503(7)	9.1832(4)
c, Å	16.765(1)	14.2616(13)	14.3124(7)
α, deg	84.554(5)	83.373(7)	83.350(4)
β, deg	81.489(6)	74.899(7)	74.481(5)
γ, deg	65.177(7)	64.443(8)	64.946(5)
V, $Å^3$	1167.5(1)	976.84(14)	989.74(9)
Z	2	2	2
$D_{calcd.}$, $g\,cm^{-3}$	1.50	1.48	1.61
Absorption coefficient, mm^{-1}	2.7	1.3	3.2
$F(000)$, e	540	448	484
θ range for data collection, deg	2.87 to 30.51	2.67 to 26.37	2.80 to 32.62
Index ranges	$-11 \le h \le 6$	$-10 \le h \le 10$	$-12 \le h \le 13$
	$-13 \le k \le 13$	$-11 \le k \le 11$	$-13 \le k \le 13$
	$-23 \le l \le 23$	$0 \le l \le 17$	$0 \le l \le 21$
Reflections collected	20 595	30 156	30 342
Independent reflections (R_{int})	11802 (0.0303)	3991 (0.0722)	6529 (0.0353)
Completeness, %	99.6	99.9	99.4
Max./min. transmission	1.00000/0.60485	1.00000/0.81854	1.00000/0.48570
Data/restraints/parameters	11802/3/524	3991/0/300	6529/0/301
Goodness-of-fit on F^2	0.888	0.945	1.027
R_1 [$I > 2\sigma(I)$]	0.0304	0.0433	0.0294
wR_2 [$I > 2\sigma(I)$]	0.0571	0.1043	0.0705
R_1 (all data)	0.0475	0.0642	0.0487
wR_2 (all data)	0.0604	0.1101	0.0739
Largest diff. peak/hole, e $Å^{-3}$	0.52/−0.87	0.94/−0.42	0.77/−0.63

6.1 Hz, $^3J(^1H\text{-}^1H) = 7.3$ Hz). – ^{13}C NMR of **5** (100 MHz, $CDCl_3$): δ = 20.16 (s, 4C, CH_3), 22.88 (d, 2C, CHP, $^1J(^{13}C\text{-}^{31}P) = 11.0$ Hz). – ^{31}P NMR of **5** (162 MHz, $CDCl_3$): δ = 22.18 (b). – FAB MS for **5** (%): m/z = 159 (5.4, $[P^iPr_3]^+$), 223 (20.9, $[Cu(P^iPr_3)]^+$), 383 (100.0, $[Cu(P^iPr_3)_2]^+$), 483 (14.7, $[(Cu\{P^iPr_3\})_2Cl]^+$), 580 (2.1, $[(Cu\{P^iPr_3\})_2CuCl_2]^+$).

*Syntheses of **6** and **7***

2.8 mmol $CuCl(PPh_3)$ (1.0 g) or 2.5 mmol $CuBr(PPh_3)$ (1.0 g) was dissolved in 5 mL of ethylenediamine by gentle heating of the reaction mixture. While the blue solution was cooled slowly to ambient temperature colorless, needle-shaped crystals of $CuCl(PPh_3)(en)_2$ and $CuBr(PPh_3)(en)_2$, respectively, began to form. The mixture was filtered, and the precipitate was dried in a vacuum. 0.85 g (72 %) of compound **6** and 0.81 g of compound **7** (70 %) were obtained. – Analysis for **6** (481.48): calcd. C 55.3, H 5.7, N 11.7, P 6.5, Cu 13.3, Cl 7.4; found C 54.7, H 6.4, N 11.8, P 6.5, Cu 13.7, Cl 7.4. – FAB MS for **6** (%): m/z = 183 (32.2, $[Cu(en)_2]^+$), 262 (28.4, $[PPh_3]^+$), 325 (100.0, $[Cu(PPh_3)]^+$), 385 (98.3, $[Cu(PPh_3)(en)]^+$), 587 (63.2, $[Cu(PPh_3)]^+$), 687 (10.7, $[(Cu\{PPh_3\})_2Cl]^+$). – Analysis for **7** (525.93): calcd. C 50.6, H 5.2, N 10.7, P 5.9, Cu 12.2, Br 15.3; found C 50.3, H 5.9, N 10.8, P 5.9, Cu 12.6, Br 18.9. – FAB MS for **7** (%): m/z = 183 (26.4, $[Cu(en)_2]^+$), 262 (24.6, $[PPh_3]^+$), 325 (80.6, $[Cu(PPh_3)]^+$), 385 (100.0, $[Cu(PPh_3)(en)]^+$), 587 (55.2, $[Cu(PPh_3)]^+$), 731 (4.1, $[(Cu\{PPh_3\})_2Br]^+$).

*Syntheses of **8** and **9***

2.8 mmol $CuCl(PPh_3)$ (1.0 g) or 2.5 mmol $CuBr(PPh_3)$ (1.0 g) was dissolved in 5 mL of dimethylformamide by gentle heating of the reaction mixture. When the greenish yellow solutions were cooled slowly to ambient temperature, colorless needle-shaped crystals of $CuCl(PPh_3)(dmf)$ and $CuBr(PPh_3)(dmf)$, respectively, began to form. The mixture was filtered, and the precipitate was dried in a vacuum. 0.75 g (75 %) of compound **8** and 0.86 g (72 %) of compound **9** were obtained. – Analysis for **8** (434.36): calcd. C 58.1, H 5.1, N 3.2, P 7.1, Cu 14.6, Cl 8.2; found C 58.3, H 5.1, N 3.2, P 7.7, Cu 15.5, Cl 8.8. – Analysis for **9** (478.82): calcd. C 52.7, H

4.6, N 2.9, P 6.4, Cu 13.3, Br 16.7; found C 52.1, H 4.8, N 2.9, P 6.5, Cu 13.1, Br 16.8.

Structure determination

Suitable crystals of the compounds were selected under perfluoropolyalkylether inside an argon-filled glove box. The crystals of compound **5** were transferred out of the mother liquor into perfluoropolyalkylether oil at −60 °C under a cold stream of N_2 gas. The single crystals were fixed on glass capillaries and positioned in a cold N_2 stream to carry out the diffraction experiment. For compound **5** the crystal cap system was used. The data sets were collected on an Oxford Diffraction Xcalibur3 diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å) at 150(2) K. The structures were solved by Direct Methods and refined by full-matrix least-squares calculations against F^2 using the SHELXTL V6.1 package [37]. The positions of hydrogen atoms were either found and refined from difference Fourier maps, or geometrically determined and refined using a riding model. All crystals of **6** gained so far were heavily disordered. Therefore the crystal structure refinement could not be successfully finished (unit cell parameters: triclinic, $P\bar{1}$, $a = 8.376(2)$, $b = 9.205(2)$, $c = 16.521(3)$ Å, $\alpha = 84.64(1)°$, $\beta = 81.64(1)°$, $\gamma = 64.82(2)°$, $V = 1139.7(3)$ Å^3. Parameters of the data collection, structure solution and refinement of the parameters for compound **4**, **5**, **7**, **8**, and **9** are given in Tables 1 and 2, respectively.

CCDC 873066, 873067, 873068, 873069, and 873070 contain the supplementary crystallographic data for compounds **4**, **5**, **7**, **8** and **9**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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