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Synthesis and structures of copper and gold complexes of the P,N ligands RN=C(Bu^t)C(H)RPPh$_2$ (R = SiMe$_3$, H)

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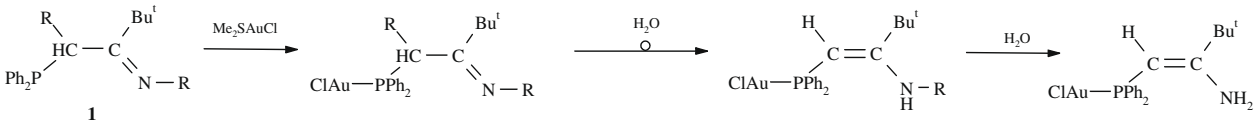
ABSTRACT

The reaction of the chelating P,N ligand RN=C(Bu^t)CH(R)PPh$_2$ (R = SiMe$_3$) (**1**) with CuCl and CuCl$_2$ (probably by way of reduction to Cu(I) by the phosphine ligand) or Cu(NCCH$_3$)$_4$ClO$_4$ yielded the dimeric 1:1 complex [Cu{PPh$_2$CH(R)C(Bu^t)=NR}Cl]$_2$ (**2**) or the monomeric 2:1 complex [Cu{PPh$_2$CH(R)C(Bu^t)=NR}$_2$]-ClO$_4$ (**3**), respectively. The presence of trace amounts of water during the reaction resulted in the successive cleavage of the two trimethylsilyl groups of the ligand and the formation of the monomeric chelate complexes [Cu{PPh$_2$CH(R)C(Bu^t)=NH}$_2$]ClO$_4$ (**4**) and [Cu{PPh$_2$CH$_2$C(Bu^t)=NH}$_2$]ClO$_4$ (**5**). Oxidation of **5** by atmospheric oxygen led to small quantities of the blue Cu(II) complex [Cu{(O)PPh$_2$CH$_2$C(Bu^t)=NH}$_2$](ClO$_4$)$_2$ (**6**). The dimeric gold complexes [Au{PPh$_2$CH$_2$C(Bu^t)=NH}]$_2$X$_2$ (X = BF$_4$, ClO$_4$) (**7**) were similarly obtained from the previously described Au{PPh$_2$CH(R)C(Bu^t)=NR}Cl by replacing the covalently bound chlorine with the weakly coordinating anions ClO$_4^-$ and BF$_4^-$ in the presence of small quantities of water. The solution and solid state structures (except **5**) of all complexes were determined by NMR spectroscopy and X-ray crystallography.

1. Introduction

Bidentate P,N ligands are of considerable interest as chelating ligands due to the different σ-donor and π-acceptor properties of their P and N donor atoms and there have been numerous reports on the synthesis and applications of their metal complexes – mostly from Groups 9 and 10 – in the context of catalytic alkene and alkene/CO-copolymerisations as well as stereospecific and non-stereo-specific hydrogenation-, allylic alkylation- and homo- and cross-coupling-reactions [1], the oxidative coupling reaction between diphenylphosphine and various imines [2] and a paper on Cu-catalysed conjugate addition to enones [3].

During our investigations into the role of the 1-azaallyl ligand [Li{N(R)C(Bu^t)CHR}]$_2$ (R = SiMe$_3$) in phosphorus chemistry a series of cyclic phosphonium salts [P^a(R′)N(R)C(Bu^t)=CHP^{b}Ph$_2$](*P^a*–*P^b*)X (R = SiMe$_3$, H; R′ = Cl, NEt$_2$, Ph, Et; X = Cl, BPh$_4$, CF$_3$SO$_3$) and the imino phosphine RN=C(Bu^t)CH(R)PPh$_2$ (R = SiMe$_3$) (**1**) were synthesised [4]. Following a more recent study into the potential of these phosphonium salts as anti-tumour agents and the synthesis of a 1:1 adduct of AuCl and **1** and its subsequent interconversion to ClAuP(Ph$_2$)C(H)=C(Bu^t)NHR and ClAuP(Ph$_2$)C(H)=C(Bu^t)NH$_2$ (Eq. (1)) [5] we have now turned our attention to Cu as the lighter congener of Au and have expanded our investigations to the weakly coordinating counterions ClO$_4^-$ and BF$_4^-$ with the aim to better understand the coordination properties of the new ligand.



R = SiMe$_3$

(1)

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2. Experimental

2.1. Preparations

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents were distilled from drying agents and degassed. Anhydrous CuCl was purchased from Sigma–Adrich, $Cu(NCCH_3)_4ClO_4$ [6], Me_2SAuCl [7] and $Me_3SiN{=}C(Bu^t)CH(SiMe_3)PPh_2$ (**1**) [4] were synthesised according to literature procedures. NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, CD_3CN or DMSO-d_6 at ambient probe temperature using the following Bruker instruments: DRX 400 (^{1}H 400.13, ^{31}P 161.9, ^{13}C 100.6 MHz), Avance 300 (^{1}H 300.13, ^{13}C 75.48), Avance I (^{1}H 400.13, ^{31}P 161.98 MHz), Avance III (^{1}H, 400.03, ^{31}P 161.94, ^{13}C 100.59, ^{29}Si 79.47 MHz) or AC200 (^{1}H 200.13, ^{31}P 81.01, ^{13}C 50.32 MHz) and referenced internally to residual solvent resonances (chemical shift data in δ). ^{13}C and ^{31}P NMR spectra were all proton-decoupled. Elemental analyses were determined by the microanalytic laboratory of the Westfälische Wilhelmsuniversität Münster. The following abbreviations are used throughout the experimental section: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, m = multiplet; t = triplet, vt = virtual triplet. Coupling constants (J) are given in Hz.

2.1.1. Synthesis of $[Cu\{(Me_3Si)NC(Bu^t)CH(SiMe_3)PPh_2\}Cl]_2$ (**2**)

Solid CuCl (0.182 g, 1.84 mmol) was added to a solution of **1** (0.785 g, 1.84 mmol) in CH_2Cl_2 (20 mL) at room temperature and the mixture was stirred overnight. The slightly turbid reaction mixture was then filtered by means of a cannula. The filtrate was concentrated and layered with hexane to give **2** as a colourless solid (0.7 g, 72.2%). *Anal.* Calc. for $C_{24}H_{38}ClCuNPSi_2$ (526.71): C, 54.73; H, 7.27; N, 2.66. Found: C, 54.77; H, 7.26; N, 2.67; ^{1}H NMR (CD_2Cl_2) δ: 0.09 (9H, d, $^4J_{HP}$ = 0.8 Hz, $CSiMe_3$), 0.36 (9H, s, $NSiMe_3$), 0.85 (9H, *s*, Bu^t), 4.18 (1H, d, $^2J_{HP}$ = 15.4, PC*H*), 7.36 (3H, m, *m*/*p*-Ph), 7.48 (3H, m, *m*/*p*-Ph), 7.72 (2H, m, *o*-Ph), 7.95 (2H, m, *o*-Ph). ^{31}P NMR (CD_2Cl_2) δ: 14.9 (s, *P*Ph_2). ^{13}C NMR (CD_2Cl_2) δ: 1.1 (d, $^3J_{CP}$ = 4.8 Hz, $CSiMe_3$), 3.6 ($NSiMe_3$), 29.5 (CMe_3), 40.0 (d, $^1J_{CP}$ = 20.1 Hz, CHP), 43.6 (s, *C*Me_3), 129.2 (d, $^3J_{CP}$ = 10.5 Hz, *m*-C), 129.7 (d, $^3J_{CP}$ = 10.5 Hz, *m*-C), 131.5 (d, $^4J_{CP}$ = 2.1 Hz, *p*-C), 131.9 (d, $^4J_{CP}$ = 1.9 Hz, *p*-C), 132.0 (d, $^1J_{CP}$ = 39.8 Hz, *ipso*-C), 133.9 (d, $^1J_{CP}$ = 34.4 Hz, *ipso*-C), 134.6 (d, $^2J_{CP}$ = 15.7 Hz, *o*-C), 135.0 (d, $^2J_{CP}$ = 16.7 Hz, *o*-C), 183.8 (d, $^2J_{CP}$ = 3.7 Hz, CN); MS (EI) *m*/*z*: 525–530(expected isotopic pattern) (0.3%, $[M(monomer)]^+$), 486 (1.2%, $[M-Bu^t]^+$). IR (cm^{-1}): ν_{CN} 1686.

^{1}H NMR ($CDCl_3$) δ: 0.09 (9H, d, $^4J_{HP}$ = 0.5 Hz, $CSiMe_3$), 0.38 (9H, s, $NSiMe_3$), 0.83 (9H, *s*, Bu^t), 4.13 (1H, d, $^2J_{HP}$ = 15.4, PC*H*), 7.37 (3H, m, *m*/*p*-Ph), 7.47 (3H, m, *m*/*p*-Ph), 7.70 (4H, m, *o*-Ph), 7.93 (4H, m, *o*-Ph). ^{31}P NMR ($CDCl_3$) δ: 12.8 (s, *P*Ph_2). ^{29}Si ($CDCl_3$) δ: −9.3 (bs, N*Si*Me_3), 3.3 (d, $^2J_{SiP}$ = 4.7 Hz, CH*Si*Me_3). ^{13}C NMR ($CDCl_3$) δ: 0.6 (d, $^3J_{CP}$ = 4.7 Hz, $CSiMe_3$), 3.2 ($NSiMe_3$), 28.9 (CMe_3), 39.4 (d, $^1J_{CP}$ = 17.7 Hz, CHP), 42.9 (s, *C*Me_3), 128.2 (d, $^3J_{CP}$ = 10.4 Hz, *m*-C), 128.7 (d, $^3J_{CP}$ = 10.4 Hz, *m*-C), 130.4 (d, $^4J_{CP}$ = 1.8 Hz, *p*-C), 130.9 (d, $^4J_{CP}$ = 1.4 Hz, *p*-C), 131.7 (d, $^1J_{CP}$ = 36.2 Hz, *ipso*-C), 133.4 (d, $^1J_{CP}$ = 32.2 Hz, *ipso*-C), 133.9 (d, $^2J_{CP}$ = 15.7 Hz, *o*-C), 134.2 (d, $^2J_{CP}$ = 16.8 Hz, *o*-C), 182.7 (d, $^2J_{CP}$ = 3.7 Hz, CN).

2.1.2. Reaction of $CuCl_2$ with **1**

Solid $CuCl_2$ (0.070 g, 0.052 mmol) was added to a solution of **1** (0.437 g, 1.02 mmol) in CH_2Cl_2 (20 mL). The initial dark green solution turned yellow after 1 h. The solution was stirred overnight and concentrated to approximately 3 mL and layered with hexane (approx. 10 mL) to give a few colourless crystals at −45 °C. The reaction mixture was then concentrated *in vacuo* until a colourless solid started to crystallise at the glass wall. After standing overnight at room temperature compound **2** was obtained as a colourless solid (0.260 g, 95%).

2.1.3. Synthesis of $[Cu\{(Me_3Si)NC(Bu^t)CH(SiMe_3)PPh_2\}_2]ClO_4$ (**3**)

A solution of 0.357 g (0.83 mmol) **1** in CH_2Cl_2 (20 mL) was added dropwise to a suspension of $Cu(NCCH_3)_4ClO_4$ (0.130 g, 0.040 mmol) in CH_2Cl_2 (5 mL). The resulting pale yellow solution was stirred overnight, then concentrated and layered with Et_2O (approx. 15 mL) to give on standing colourless crystals of **3** (0.35 g, 84%). *Anal.* Calc. for $C_{50}H_{81}ClCuN_2O_{4.5}P_2Si_4$ [**3**·$(Et_2O)_{0.5}$; 1055.46]: C, 56.90; H, 7.74; N, 2.65. Found: C, 56.59; H, 7.67; N, 2.61%; ^{1}H NMR (CD_3CN) δ: 0.01 (9H, s, br, $CSiMe_3$), 0.27 (9H, *s*, $NSiMe_3$), 0.78 (9H, *s*, Bu^t), 4.16 (1H, d, $^2J_{HP}$ = 10.1 Hz, PC*H*), 7.36 (3H, m, *m*/*p*-Ph), 7.45 (3H, m, *m*/*p*-Ph), 7.58 (2H, m, *o*-Ph), 7.79 (2H, m, *o*-Ph). ^{31}P NMR (CD_3CN) δ: 1.3 (s, PPh_2). ^{13}C NMR (CD_3CN) δ: 1.2 (s, $CSiMe_3$), 3.8 ($NSiMe_3$), 29.6 (CMe_3), 41.1 (d, $^1J_{CP}$ = 6.2 Hz, CHP), 44.7 (s, *C*Me_3), 129.5 (d, $^3J_{CP}$ = 8.5 Hz, *m*-C), 130.0 (d, $^3J_{CP}$ = 8.9 Hz, *m*-C), 131.0 (s, *p*-C), 131.3 (s, *p*-C), 135.4 (d, $^2J_{CP}$ = 6.4 Hz, *o*-C), 135.8 (d, $^2J_{CP}$ = 4.5 Hz, *o*-C), 137.2 (d, not resolved, *ipso*-C), 138.8 (d, $^1J_{CP}$ = 6 Hz, *ipso*-C), 186.1 (bs, CN). IR (cm^{-1}): ν_{CN} 1672.

2.1.4. Synthesis of $[Cu\{HNC(Bu^t)CH(SiMe_3)PPh_2\}_2]ClO_4$ (**4**)

Dry $Cu(NCCH_3)_4ClO_4$ was exposed for 3 days in an open container to humid air until the colourless solid had turned pale blue-green. 0.130 g (0.41 mmol) of this solid were then suspended in CH_2Cl_2 and the reaction mixture was treated with a solution of **1** (0.400 g, 0.94 mmol). There was a colour change from blue to yellow. The reaction mixture was stirred at room temperature overnight, then filtered by means of a cannula, and the filtrate was concentrated and layered with Et_2O to give colourless crystals. Concentration of the mother liquid and layering gave a second and a third fraction resulting in a total yield of 0.24 g (67%) of compound **4**. *Anal.* Calc. for $C_{42}H_{60}ClCuN_2O_4P_2Si_2$ (874.07): C, 57.71; H, 6.92; N, 3.20. Found: C, 57.24; H, 6.91; N, 3.08%. The NMR spectra indicate the presence of two isomers in solution (the given δ values represent the minor/major isomer). ^{1}H NMR (CD_2Cl_2; ratio 1:1.5) δ: 0.19 (9H, bs, $CSiMe_3$), 0.92/0.94 (5.5/3.5H, s, Bu^t), 3.66 (1H, m, PCH), 7.40 (3H, m, *m*/*p*-Ph), 7.56 (3H, m, *m*/*p*-Ph), 7.79 (4H, m, *o*-Ph), 9.20/9.54 (0.6/0.4H, bs, NH). ^{31}P NMR (CD_2Cl_2) δ: 13.4 (bs, PPh_2). ^{1}H NMR ($CDCl_3$; ratio 1:3) δ: 0.175/0.185 (9H, s, $CSiMe_3$), 0.95/0.96 (9H, s, Bu^t), 3.63/3.48 (1H, m, PCH), 7.34–7.80 (10H, m, Ph), 9.31/10.30 (1H, bs, NH). ^{31}P NMR ($CDCl_3$) δ: 13.3/14.8 (s, br, PPh_2). ^{1}H NMR (CD_3CN 300 K; ratio 1:1.9) δ: 0.170/0.175 (9H, s, $CSiMe_3$), 0.90/0.95 (9H, s, Bu^t), 3.83/3.93 (1H, bs, PCH), 7.39 (3H, bs, *m*/*p*-Ph), 7.53 (3H, bs, *m*/*p*-Ph), 7.83 (2H, bs, *o*-Ph), 7.92 (2H, bs, *o*-Ph), 9.36/9.62 (1H, bs, NH). ^{31}P NMR (CD_3CN 300 K) δ: 13.5/18.1 (bs, PPh_2). ^{29}Si (CD_3CN, 300 K) δ: 4.62/4.66 (overlapping vt, $J_{SiP} \approx 7$ Hz; $SiMe_3$). ^{13}C NMR (CD_3CN 300 K) δ: 1.7/1.9 (vt, J_{CP} = 4.2/4.6 Hz, $SiMe_3$), 27.5/27.9 (s, CMe_3), 39.2/39.3 (vt, J_{CP} = 7.0/7.0 Hz, CHP), 42.3 (s, *C*Me_3, only 1 signal observed), 130.0 (vt, J_{CP} = 9.6 Hz, Ph), 130.4 (vt, J_{CP} = 9.6 Hz, Ph), 132.0 (s, Ph), 132.4(s, Ph), 134.4 (vt, J_{CP} = 21.2, *ipso*-C), 135.0 (overlapping m, Ph), 136.6 (vt, J_{CP} = 20.0 Hz, *ipso*-C), 198.7 (vt, J_{CP} = 3.6 Hz, CN). IR (cm^{-1}): ν_{NH} 3294, $\nu_{CN/C=C}$ 1587/1572.

2.1.5. Synthesis of $[Cu\{HNC(Bu^t)CH_2PPh_2\}_2]ClO_4$ (**5**) from **3**

A solution of 0.5 mL CH_3OH (0.040 g, 1.25 mmol) was added dropwise to a solution of 0.650 g (0.65 mmol) of **3** in CH_2Cl_2 (20 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed *in vacuo*, the remaining solid was redissolved in CH_2Cl_2 and layered with Et_2O to give colourless crystals of **5** (0.45 g, 95%). *Anal.* Calc. for $C_{36}H_{44}ClCuN_2O_4P_2$ (729.70): C, 59.24; H, 6.08; N, 3.84. Found: C, 59.22; H, 6.12; N, 3.71%. ^{1}H NMR (CD_2Cl_2) δ: 1.22 (9H, s, Bu^t), 3.47 (2H, bs, PCH), 7.38 (10H, bs, Ph); 9.62 (1H, bs, NH). ^{31}P NMR

Table 1
Crystal data and structure refinement for **2**, **3** · $(Et_2O)_{0.5}$, **4**, **6**, **6** · CH_2Cl_2 and **7a** · $(CDCl_3)_2$.

Compound	**2**	**3** · $(Et_2O)_{0.5}$	**4**	**6**	**6** · CH_2Cl_2	**7a** · $(CDCl_3)_2$
Empirical formula	$C_{24}H_{38}ClCuNPSi_2$	$C_{50}H_{81}ClCuN_2O_{4.5}P_2Si_4$	$C_{42}H_{60}ClCuN_2O_4P_2Si_2$	$C_{36}H_{44}Cl_2CuN_2O_{10}P_2$	$C_{37}H_{46}Cl_4CuN_2O_{10}P_2$	$C_{38}H_{46}Au_2B_2Cl_6F_8N_2P_2$
Formula weight	526.96	1055.46	874.03	861.11	946.04	1372.96
T (K)	153(2)	153(2)	173(2)	153(2)	173(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	*Pbca*	$P2_1/c$	$P2_1/c$
Unit cell dimensions						
a (Å)	9.713(5)	11.9268(3)	12.5652(19)	13.3041(5)	14.759(2)	13.8696(8)
b (Å)	10.290(5)	14. 9073(4)	19.719(3)	15.8696(5)	16.486(3)	13.3486(8)
c (Å)	14.088(5)	17.7672(5)	18.345(3)	18.7464(6)	18.090(3)	27.1597(16)
α (°)	78.019(5)	72.3380(10)				
β (°)	88.506(5)	70.9800(10)	102.113(3)		101.683(3)	92.2990(10)
γ (°)	83.840(5)	86.1520(10)				
V (Å^3)	1369.4(11)	2843.94(13)	4444.3(12)	3957.9(2)	4310.2(11)	5024.3(5)
Z	1	2	4	4	4	4
D_{calc} (Mg/m^3)	1.277	1.233	1.306	1.445	1.458	1.815
Absorption coefficient (mm^{-1})	1.053	0.614	0.719	0.825	0.884	6.275
F(000)	556	1126	1848	1788	1956	2640
Crystal size (mm^3)	0.08 × 0.06 × 0.05	0.16 × 0.14 × 0.10	0.44 × 0.21 × 0.17	0.21 × 0.14 × 0.08	0.24 × 0.21 × 0.14	0.17 × 0.16 × 0.14
Theta range (°) for data collection	1.48–27.50	1.27–29	1.53–27.00	2.17–30.34	1.41–26.00	2.56–25.00
Index ranges	$-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-18 \leqslant l \leqslant 18$	$-16 \leqslant h \leqslant 16$, $-20 \leqslant k \leqslant 20$, $-24 \leqslant l \leqslant 24$	$-15 \leqslant h \leqslant 16$, $-19 \leqslant k \leqslant 25$, $-21 \leqslant l \leqslant 23$	$-18 \leqslant h \leqslant 18$, $-22 \leqslant k \leqslant 22$, $-26 \leqslant l \leqslant 26$	$-16 \leqslant h \leqslant 18$,$-10 \leqslant k \leqslant 20$,$-22 \leqslant l \leqslant 22$	$-16 \leqslant h \leqslant 5$, $-15 \leqslant k \leqslant 15$, $-32 \leqslant l \leqslant 32$
Reflections collected	13734	31601	27840	45379	24718	25947
Independent reflections [$R_{(int)}$]	6307 [0.0206]	15086 [0.0270]	9666 [0.0378]	5953 [0.0463]	8459 [0.0512]	8779 [0.0358]
Absorption correction	empirical	empirical	integration	empirical	integration	empirical
Maximum and minimum transmission	0.9493 and 0.9205	0.9412 and 0.9082	0.8857 and 0.7362	0.9369 and 0.8458	0.8862 and 0.8158	0.4737 and 0.4151
Data/restraints/parameters	6307/0/280	15086/38/596	9666/404/547	5953/0/244	8459/297/643	8779/422/529
Goodness-of-fit (GOF) on F^2	1.027	1.069	1.031	1.019	1.069	1.047
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0321$, $wR_2 = 0.0799$	$R_1 = 0.0406$, $wR_2 = 0.1005$	$R_1 = 0.0431$, $wR_2 = 0.1050$	$R_1 = 0.0337$, $wR_2 = 0.0825$	$R_1 = 0.0532$, $wR_2 = 0.1362$	$R_1 = 0.0398$, $wR_2 = 0.1019$
R indices (all data)	$R_1 = 0.0393$, $wR_2 = 0.0848$	$R_1 = 0.0565$, $wR_2 = 0.1067$	$R_1 = 0.0646$, $wR_2 = 0.1133$	$R_1 = 0.0494$, $wR_2 = 0.0905$	$R_1 = 0.0952$, $wR_2 = 0.1540$	$R_1 = 0.0563$, $wR_2 = 0.1148$
Largest difference in peak and hole (e Å^{-3})	0.746 and −0.490	0.514 and −0.406	0.589 and −0.653	0.450 and −0.392	0.887 and −0.455	1.282 and −1.049

(CD_2Cl_2) δ: −7.2 (bs, PPh_2). ^{13}C NMR (CD_2Cl_2) δ: 27.4 (s, CMe_3), 38.1 (vt, J_{CP} = 23.8 Hz, CHP), 41.5 (s, CMe_3), 129.6 (s, *m*-C), 130.9 (s, *p*-C), 133.0 (vt, J_{CP} = 14.2 Hz, *o*-C), 133.6 (vt, J_{CP} = 27.8 Hz, *ipso*-C), 192.4 (bs, CN). IR (cm^{-1}): ν_{NH} 3317/3298, $\nu_{CN/C=C}$ 1616.

*2.1.6. Synthesis of $[Cu\{HNC(Bu^t)CH_2PPh_2\}_2]ClO_4$ (**5**) from **4***

Complex **4** (0.070 g, 0.08 mmol) was dissolved in CH_2Cl_2 (5 mL) and treated with CH_3OH (0.5 mL) at room temperature. The reaction mixture was stirred overnight. The solvent was removed *in vacuo* and the residue treated with pentane (2 mL). Removal of the pentane *in vacuo* gave **5** as a NMR-spectroscopically pure colourless solid (0.059 g, 100%).

*2.1.7. Synthesis of $[Cu\{HNC(Bu^t)CH_2P(O)Ph_2\}_2](ClO_4)_2$ (**6**)*

Complex **5** (0.25 g, 0.34 mmol) was dissolved in a mixture (15 mL) of CH_2Cl_2 and CH_3OH and allowed to stir in an open flask at room temperature for several days. The initial colourless solution turned blue and a precipitate formed. From the supernatant liquid blue crystals of complex **6** suitable for X-ray analysis were obtained (0.03 g, 10%). *Anal.* Calc. for $C_{36}H_{44}Cl_2CuN_2O_{10}P_2$ (861.11): C, 50.21; H, 5.15; N, 3.25. Found: C, 49.94; H, 5.17; N, 3.01%. IR (cm^{-1}): ν_{NH} 3318, $\nu_{CN/C=C}$ 1641/1589. ε_{max}(627 nm) 2400 L mol^{-1} cm^{-1}.

*2.1.8. Synthesis of $[Au\{HNC(Bu^t)CH_2PPh_2\}]_2(BF_4)_2$ (**7a**)*

Solid $Au(SMe_2)Cl$ (0.083 g, 0.28 mmol) was added to a solution of **1** (0.120 g, 0.28 mmol) in THF (10 mL^3) at 0 °C. The mixture was stirred for 15 min at 0 °C and then allowed to warm to room temperature. The solvent was removed *in vacuo* and the remaining solid residue was dissolved in CH_2Cl_2. Solid $AgBF_4$ (0.055 g, 0.29 mmol) was added and the mixture was stirred overnight. The reaction mixture was filtered into a Schlenk tube by means of a cannula, the solvent was removed *in vacuo* and the solid residue recrystallised from CH_2Cl_2/Et_2O (0.13 g, 68%). Colourless crystals suitable for X-ray analysis were obtained from a NMR sample ($CDCl_3$). ^1H NMR ($CDCl_3$) δ: 0.98 (9H, bs, Bu^t), 3.95 (2H, d, $^2J_{HP}$ = 14.6, PCH_2), 7.54–7.59 (6H, m, *m*/*p*-Ph), 7.80–7.85 (4H, m, *o*-Ph), 10.34 (1H, bs, NH). ^{31}P NMR ($CDCl_3$) δ: 34.2 (s, PPh_2). MS-FAB, *m*/*z*: 1047 (30%, $[Au_2L_2BF_4]^+$), 959 (32%, $[(AuL_2-1)]^+$), 763 (10%, $[AuL_2]^+$), 480 (33%, $[AuL]^+$).

2.1.9. Synthesis of $[Au\{HNC(Bu^t)CH_2PPh_2\}]_2(ClO4)_2$ (7b)

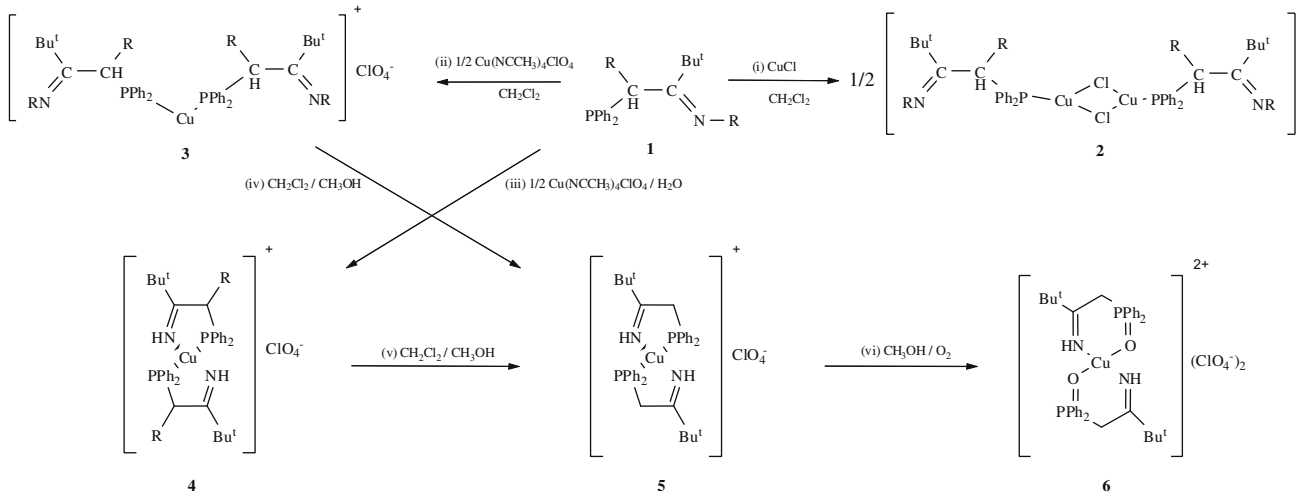
A solution of $Au(SMe_2)Cl$ (0.055 g, 0.19 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of **1** (0.080 g, 0.19 mmol) in CH_2Cl_2 (20 mL) and the reaction mixture was stirred for 4 h. The solvent was removed, the remaining residue was dried *in vacuo* and subsequently dissolved in a mixture of CH_2Cl_2/toluene (1:1; 20 mL) and added to a solution of $AgClO_4$ (0.037 g, 0.19 mmol) in the same mixture of solvents (10 mL). The reaction mixture was kept in the dark for 3 h. After filtration and concentration of the filtrate, a white solid was precipitated (0.60 g, 55%) by addition of Et_2O (20 mL). ^1H NMR (DMSO-d_6) δ: 0.91 (9H, s, Bu^t), 4.36 (2H, d, $^2J_{HP}$ = 15.1, PCH_2), 7.59–7.71 (6H, m, *m*,*p*-Ph), 7.92–7.97 (4H, m, *o*-Ph), 10.31 (1H, bs, NH). ^{31}P NMR (DMSO-d_6) δ: 33.8 (s, PPh_2). MS-FAB, *m*/*z*: 481 (11%) $[AuL+1]^+$. IR (cm^{-1}): 3453(ν_{NH}), 1634(ν_{CN}).

2.2. X-ray crystallography

Intensity data were collected on a Bruker SMART 1K CCD (**4**, **6** · **CH_2Cl_2**) area detector diffractometer, a Bruker APEX II diffractometer (**2**, **3** · **$(OEt_2)_{0.5}$**, **6**) or a Siemens P4 diffractometer equipped with a Bruker SMART 1K CCD detector (**7a** · **$(CDCl_3)_2$**) with graphite-monochromated Mo Kα radiation. The collection method involved ϕ- and ω-scans. Data reduction were carried out using the program SAINT+ [8], with absorption correction carried out as indicated in Table 1. The crystal structures were solved by direct methods using SHELXTL [9]. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on F^2 using SHELXTL. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms.

Compound **3** · **$(OEt_2)_{0.5}$** includes a disordered Et_2O molecule over a centre of inversion and one of the $NSiMe_3$ groups is disordered. A treatment of the ether molecule by PLATON SQUEEZE [10] accounted for 41 electrons (42 electrons required for Et_2O). The minority component of the $NSiMe_3$ group was refined isotropically. Compound **4** and **6** · **CH_2Cl_2** each have a disordered ClO_4^- anion and **6** · **CH_2Cl_2** additionally a disordered CH_2Cl_2 solvent molecule. Compound **7a** · **$(CDCl_3)_2$** crystallises with two molecules of $CDCl_3$ in the asymmetric unit. The disordered groups were refined over two/three positions such that their site occupancy summed up to unity. Appropriate restraints were used on bond lengths, angles and atomic displacement parameters on each disordered fragment of each species.

Further crystallographic data are summarised in Table 1. Diagrams and publication material were generated using SHELXTL [9], PLATON [10] and ORTEP3 [11].



Scheme 1. Synthesis and reactions of copper phosphine complexes (R = $SiMe_3$).

3. Results and discussion

3.1. Synthesis of compounds

The synthesis of the ligand RN=C(Bu^t)CH(R)PPh$_2$ (*R* = SiMe$_3$) (**1**) via salt elimination from [RN=C(Bu^t)CH(R)Li]$_2$ and Ph$_2$PCl has been described elsewhere [4a]. The obtained racemic mixture of **1** was, without attempts of separating the enantiomers, used directly for further reactions as summarised for Cu(I) salts in Scheme 1. The issue of isomerism has been addressed in the discussion of the solution and solid state structures of the products.

Treatment of CuCl with RN=C(Bu^t)CH(R)PPh$_2$ (**1**) in CH$_2$Cl$_2$ at room temperature [(i) in Scheme 1] led in high yield, independent of stoichiometry (CuCl: **1** = 1:1 or 1:2), to the crystalline adduct **2**. Stepwise addition of excess ligand **1** to complex **2** in an NMR experiment resulted in broadening of the ^{31}P NMR signal, but there was no evidence for the existence of an 1:2 adduct. The analogous reaction of CuCl$_2$ with two equivalents of ligand yielded also only the Cu(I) complex **2**, probably as a result of reduction of the Cu(II) salt by excess ligand and formation of phosphine oxide. The ability of phosphines to reduce Cu(II) compounds has been mentioned previously [12–14].

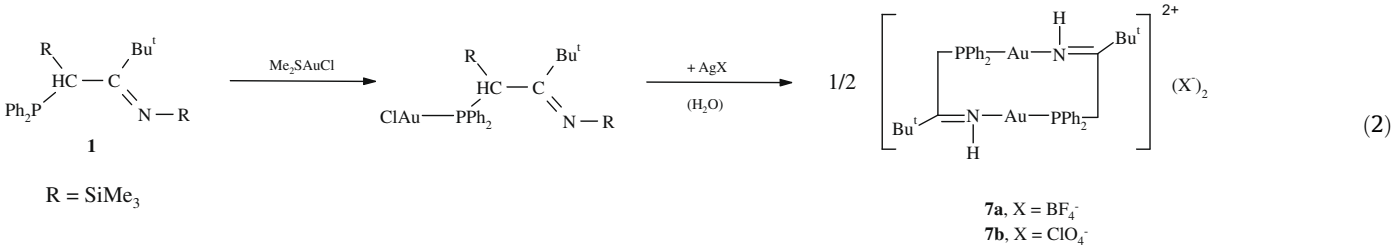
Reaction of **1** with Cu(NCCH$_3$)$_4$ClO$_4$ [(ii) in Scheme 1] yielded in contrast to reaction (i) the 1:2 complex **3**. When a sample of **3** in CD$_3$CN was heated at 70 °C for several weeks in a sealed NMR tube the signals of the complex were slowly replaced by those of the enamine z-Ph$_2$P(H)C=C(Bu^t)NR$_2$. The experiment was discontinued after 6 weeks when the ratio of **3** to enamine equalled approximately 1:5.5 as estimated from the integration in the ^{1}H and ^{31}P NMR spectra. Rearrangement of the free ligand by a 1,3-SiMe$_3$ shift from C to N to give the observed *z*-enamine has been noted previously during attempts to purify **1** by distillation [4a]. While the ^{31}P NMR signal of **3** had broadened significantly in the final mixture – the ^{1}H NMR parameters had remained essentially constant – and shifted towards the signal of the free ligand **1**, the signal of the enamine remained fairly sharp ($\upsilon_{1/2} \approx 10$ Hz) making the formation of a stable Cu(I)–enamine complex unlikely. The related Au(I)–enamine complexes ClAuPPh$_2$C(H)=C(Bu^t)NHR and ClAuPPh$_2$C(H)= C(Bu^t)NH$_2$ have in contrast been described previously (*c.f.* Eq. (1)) [5].

When **1** was treated with Cu(NCCH$_3$)$_4$ClO$_4$ [(iii) in Scheme 1], that had been exposed to humidity for several days, cleavage of the SiMe$_3$ group bound to the nitrogen atom was observed and complex **4** was isolated in moderate yield. This partial hydrolysis of the ligand is reproducible and believed to be the result of absorbed moisture in the Cu(I) starting material. Attempts to obtain **4** by controlled hydrolysis of **3** with stoichiometric amounts of CH$_3$OH or water were not successful.

Reaction of **3** with CH$_3$OH [(iv) in Scheme 1] led to the loss of both SiMe$_3$ groups and the isolation of complex **5**, which was also obtained by the hydrolysis of **4** in CH$_2$Cl$_2$/CH$_3$OH [(v) in Scheme 1]. Oxidation of a solution of **5** by atmospheric oxygen [(vi) in Scheme 1] led to the isolation of small, but reproducible, quantities of the blue Cu(II)-complex **6** and larger amounts of an unidentified colourless precipitate.

While all described copper complexes could be crystallised without too many difficulties, it was not possible to obtain crystals of **5** suitable for single crystal X-ray diffraction. Numerous attempts of recrystallisation in a variety of solvents at different temperatures resulted repeatedly only in a microcrystalline material.

In a previous publication [5] we have reported the reaction of **1** with Me$_2$SAuCl to give the monomeric complex ClAuPPh$_2$-CH(R)C(Bu^t)=NR. In continuation of these studies on the coordination behaviour of **1** with Au(I) halides, the latter complex was treated with AgBF$_4$ and AgClO$_4$ in an attempt to replace the covalently bound Cl$^-$ anion with a less strongly coordinating counter-ion. This resulted in the isolation of the dimeric complexes **7a** and **7b** (Eq. (2)). The observed facile loss of SiMe$_3$ groups in the products is likely to be the result of traces of moisture in the used silver salts and a characteristic feature of the ligand and its complexes as evident from Scheme 1 and our previous investigations [5].



1

R = SiMe$_3$

7a, X = BF$_4^-$
7b, X = ClO$_4^-$

(2)

Table 2
Selected NMR- and IR-spectroscopic data of compounds **1**–**5**, **7** and some related phosphines.

Complex	δ ^{31}P NMR($\upsilon_{1/2}$)	δ ^{1}H NMR		δ ^{13}C NMR		Solvent	υ_{CN}(cm^{-1})
		HN	CH($^2J_{HP}$, Hz)	CP($^1J_{CP}$, Hz)	NC($^2J_{CP}$, Hz)		
Iminoalkyl compounds							
RN=C(Bu^t)CH(R)PPh$_2$ (**1**) [4]	−1.5 (3 Hz)		3.95 (5.7)	40.7 (27.8)	183.0	C_6D_6	1711
RN=C(Bu^t)CH(R)PPh$_2$AuCl [5]	40.7		4.46 (15.8)	38.8 (30.4)	179.4 (6.0)	$CDCl_3$	
[Au{HN=C(Bu^t)CH$_2$PPh$_2$}]$_2$(BF$_4$)$_2$ (**7a**)	34.2	10.34	3.95 (14.6)			$CDCl_3$	
[Cu{RN=C(Bu^t)CH(R)PPh$_2$}Cl]$_2$ (**2**)	17.0 (60 Hz)		4.13 (15.4)	39.4 (17.7)	182.7 (3.7)	$CDCl_3$	1686
[Cu{RN=C(Bu^t)CH(R)PPh$_2$}$_2$]ClO$_4$ (**3**)	1.3 (160 Hz)		4.16 (10.1)	41.1 (6.2)	186.1 (s, br)	CD_3CN	1672
[Cu{HN=C(Bu^t)CH(R)PPh$_2$}$_2$]ClO$_4$ (**4**) (major isomer only)	18.1 (160 Hz)	9.62	3.93 (s, br)	39.3 (vt, 7.0)[a]	198.7 (vt, 3.6)[b]	CD_3CN	1587/1572
[Cu{HN=C(Bu^t)CH$_2$PPh$_2$}$_2$]ClO$_4$ (**5**)	−7.2 (240 Hz)	9.62	3.47 (s, br)	38.1 (vt, 23.8)[a]	192.4 (s, br)	CD_2Cl_2	1616
Aminoalkenyl compounds							
R$_2$NC(Bu^t)C=CH(R)PPh$_2$ (Z isomer) [4]	−31.8		6.33 (4.8)	120.0 (s)	171.9 (21.9)	C_6D_6	
RHNC(Bu^t)=CHPPh$_2$AuCl [5]	10.6	4.81	4.33 (5.6)	86.4 (72.3)	173.3	$CDCl_3$	
H$_2$NC(Bu^t)=CHPPh$_2$AuCl [5]	7.1	4.82	4.32 (8.8)	72.8 (71.9)	168.9	$CDCl_3$	

[a] $|^1J_{CP} + {}^3J_{CP}|$.
[b] $|^2J_{CP} + {}^{3/4}J_{CP}|$.

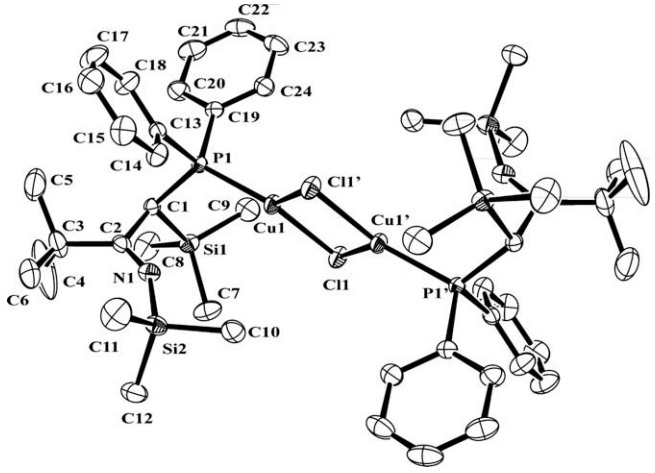


Fig. 1. Molecular structure of $[Cu\{RN{=}C(Bu^t)CH(R)PPh_2\}Cl]_2$ (**2**). Displacement ellipsoids are drawn at the 50% level. H atoms have been omitted for clarity. (Symmetry operation for symmetry related atoms: $-x+2$, $-y+1$, $-z+1$).

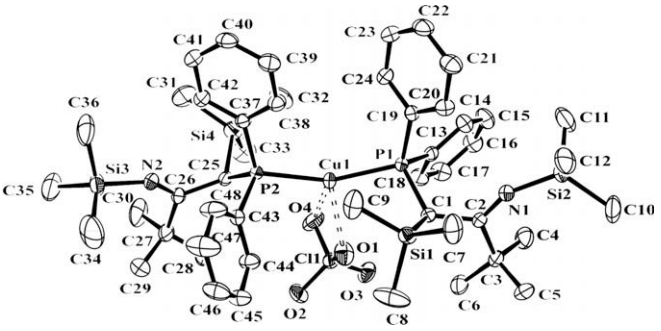


Fig. 2. Molecular structure of $[Cu\{RN{=}C(Bu^t)CH(R)PPh_2\}_2]ClO_4$ ($\mathbf{3}\cdot\mathbf{(OEt_2)_{0.5}}$). Displacement ellipsoids are drawn at the 50% level. H atoms and solvent molecules have been omitted for clarity.

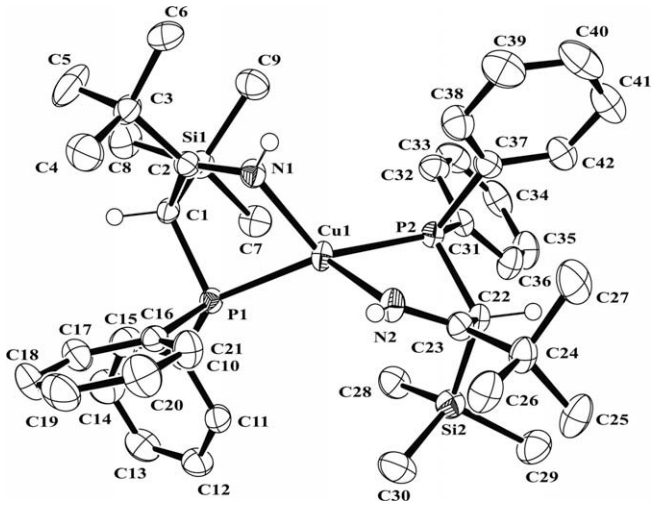


Fig. 3. Molecular structure of the cation of $[Cu\{HN{=}C(Bu^t)CH(R)PPh_2\}_2]ClO_4$ (**4**) (Λ(S,S) isomer). Displacement ellipsoids are drawn at the 50% level. H atoms (except in the backbone of the ligand; drawn with arbitrary radius) have been omitted for clarity.

The metal complexes are colourless (**2**–**5**, **7**) or dark blue [**6**, ε_{max}(627 nm)] solids, that are soluble in polar solvents such as CH_2Cl_2 or CH_3CN, but insoluble in hydrocarbons.

3.2. Spectroscopic studies

Selected spectroscopic parameters of **1**–**5**, **7** and some related compounds are summarised in Table 2.

It is evident, that in all complexes the iminoalkyl backbone (*N*=C–C) of the ligand has remained intact and no rearrangement to an aminoalkene (N–C=C) has taken place as was described previously as a consequence of the hydrolysis of the monomeric iminoalkyl complexes $ClAuPPh_2CH(R)C(R')$=NR (R = $SiMe_3$; R′ = Bu^t, Ad) (*c.f.* Eq. (1)) [5] or the heating of the free ligand $Ph_2PCH(R)C(Bu^t)$=NR (R = $SiMe_3$) [4]. The iminoalkyl complexes are characterised by a high field shift (^{1}H, $\delta \approx 4$ ppm; ^{13}C, $\delta \approx 40$ ppm), a large $^2J_{HP}$ (>10 Hz; not resolved in complexes **4**, **5** as a result of exchange processes) and a small $^1J_{CP}$ (<30 Hz) coupling constant compared to the corresponding values of the aminoalkene derivatives that show low-field shifts (^{1}H, $\delta \approx 4.3$ ppm; ^{13}C, $\delta \approx 70$–80 ppm) and small $^2J_{HP}$ (<10 Hz) and $^1J_{CP}$ (>70 Hz) coupling constants, respectively. There is also a small low-field shift (>10 ppm) of the CN signal of the iminoalkyl- as compared to the enamine complexes in the ^{13}C NMR spectrum.

In those iminoalkyl complexes, in which the $SiMe_3$ group on the N atom has been replaced by a hydrogen atom (**4**, **5**, **7**), that proton is found in the ^{1}H NMR spectrum in the low-field region at close to 10 ppm. In the case of **7a** a rigid dimer as observed in the solid state (*c.f.* Fig. 5) would make the two hydrogen atoms of the CH_2 group inequivalent, but only a singlet is observed. This indicates virtual C_{2h} symmetry for the molecule as a result of dynamic behaviour in solution and may be due to rapid ring inversion of the 10-membered heterocycle. The well resolved doublet for CHP and aromatic carbon atoms in the ^{13}C NMR spectrum of the free ligand and the metal complexes **2**, **3** and $ClAuPPh_2CH(R)C(Bu^t)$=NR is indicative of coupling to a single phosphorus atom and consistent with a solution structure with no metal–N bond and a low coordination number similar to the situation found for these compounds in the solid state (*c.f.* Figs. 1 and 2). Complex **5** shows in contrast virtual triplets (*c.f.* [15]) for CHP as well as *ipso*- and *o*-C atoms of the phenyl rings consistent with an AXX′ spin system [16] (A = ^{13}C, X, X′ = ^{31}P; significant J_{PP} coupling) in a tetrahedral complex with chelating ligands. While no attempts for a rigorous analysis have been made, the observed spectrum was simulated for coupling constants of $^{1+3}J_{PC}$ = 23.8 Hz (CHP), $^{1+3}J_{CP}$ = 27.8 Hz

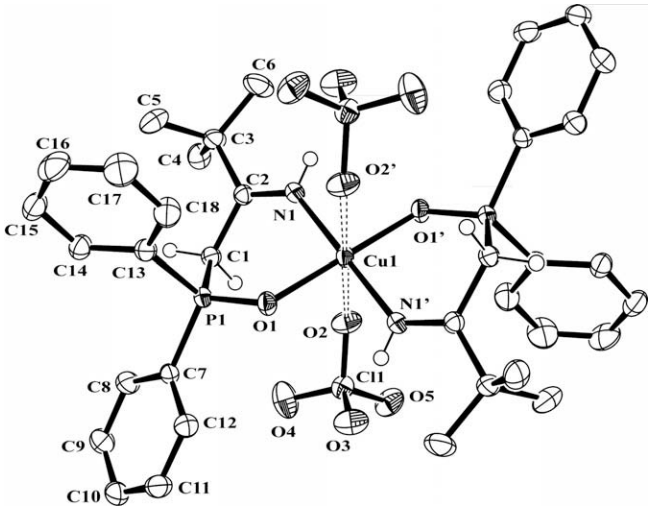


Fig. 4. Molecular structure of $[Cu\{HN{=}C(Bu^t)CH_2PPh_2\}_2](ClO_4)_2$ (**6**). Displacement ellipsoids are drawn at the 50% level. H atoms (except in the backbone of the ligand; drawn with arbitrary radius) have been omitted for clarity. (Symmetry operation for symmetry related atoms: $-x+1$, $-y$, $-z+1$.)

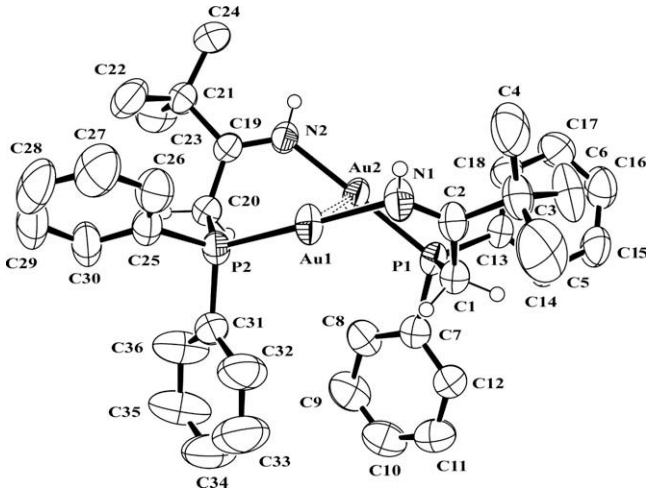


Fig. 5. Molecular structure of the cation of $[Au\{HN{=}C(Bu^t)CH_2PPh_2\}]_2(BF_4)_2$ (**7a** · **$(CDCl_3)_2$**). Displacement ellipsoids are drawn at the 50% level. H atoms (except in the backbone of the ligand; drawn with arbitary radius) and solvent molecules have been omitted for clarity.

(*ipso*-C), $^{2+4}J_{CP}$ = 14.2 Hz (*o*-C) and $^{2}J_{PP}$ = 60 Hz. A similar situation was found for complex **4**, that shows virtual triplets in the ^{13}C-(CHP, *ipso*-C, *o*-C, CN) and ^{29}Si NMR spectrum. Furthermore, there is evidence for the existence of two isomers of complex **4** in solution, whose relative stability appears to dependent on the solvent (CD_2Cl_2 1:1.5; CD_3CN 1:1.9; $CDCl_3$ 1:3) and temperature (CD_3CN: 240 K 1:2.5; 300 K 1:1.9; 335 K 1:1.5). Since the crystal structure of **4** (*c.f.* Fig. 3) reveals the presence of a mixture of enantiomers [Λ(S,S) and Δ(R,R)] in the solid state it seems plausible, that the major species in solution corresponds to these enantiomers. The minor species may then be one of the possible other isomers [Δ(R,S), Λ(S,R); Δ(S,S), Λ(RR)].

The absence of $^{63/65}$Cu–^{31}P spin–spin coupling and the large half widths observed in the ^{31}P NMR spectra of the copper complexes indicate the presence of chemical exchange processes on the NMR time scale. $^{63/65}$Cu–^{31}P spin–spin coupling has previously only been observed for highly symmetrical, typically tetrahedral, Cu(I) phosphine complexes such as $Cu(PMe_3)_4X$ (X = PF_6 [17], BF_4 [17], $F_3CC(O)CHC(O)CF_3$ [18], $CuCl_2$ [18a], $CuMe_2$ [18b]) or $[Cu(Me_2PCH_2CH_2PMe_2)]_2(BF_4)_2$ [19]. The exchange process could involve chelating of the N atom in complexes **2** and **3** or more likely rapid exchange between coordinated and uncoordinated ligand. Addition of excess ligand to $[Cu\{RN{=}C(Bu^t)CH(R)PPh_2\}Cl]_2$ (**2**) (CD_3CN, see above) led to only marginal changes in the ^{1}H spectrum (minor shift changes and a small decrease of $^2J_{HP}$) of the complex/ligand mixture and a broadening of the ^{31}P NMR signal accompanied by a shift in the direction of the free ligand.

IR-spectroscopy also suggest a differentiation between a chelating (**4**, **5**, **6**) and non-chelating bonding (**2**, **3**) mode in the copper complexes as is evident from the wavenumber of ν_{CN}, that is very similar to that of the free ligand in **2** and **3**, but shifts to lower wavenumbers in the chelate complexes **4**, **5** and **6** (*c.f.* Table 2).

3.3. Solid state structures of compounds **2**, **3** · **$(OEt_2)_{0.5}$**, **4**, **6** and **7a** · **$(CDCl_3)_2$**

The molecular structures of **2**, **3** · **$(OEt_2)_{0.5}$**, **4**, **6** and **7a** · **$(CDCl_3)_2$** with the atom numbering are shown in Figs. 1–5. Selected bond distances and angles are summarised in Table 3.

Crystallographically characterised Cu(I)-complexes with neutral P,N ligands are comparatively rare. Simple Cu(I)-chlorides are frequently solvated by both P and N atoms resulting in dimeric complexes [PNCu(μ-X)$_2$CuPN] with a tetrahedral coordination of the Cu(I) atom and bridging Cl atoms. Typical examples are $[(Ph_2PCH_2CH_2NC_5H_{11})CuCl]_2$ [20], $[C_6H_4\text{-}(1,2\text{-}PPh_2)_2\{N^aC(Me)CHC(Me)N^b(N^a\text{–}N^b)\}CuCl]_2$ [21], $[Ph_3P(NC_5H_9)CuCl]_2$ [22] or derivatives of the latter compound with variations in the phosphine and/or the nitrogen base.

Complex $[Cu\{RN{=}C(Bu^t)CH(R)PPh_2\}Cl]_2$ (**2**) (Fig. 1) has a centre of inversion resulting in both the R- and the S-isomer of the ligand being present in the dimer. It deviates from the above discussed structural pattern in so far as the nitrogen atom of the imino ligand does not interact with the copper atom resulting in a trigonal planar (Σ∠Cu = 359.6°) coordination of the metal. The absence of Cu–N contacts may be the result of steric hindrance in the backbone of the ligand (even in the case of the weakly coordinating counterion ClO_4^- in complex **3** there is no interaction between Cu and N; see below) while removal of the $SiMe_3$ group bound to the nitrogen atom results in N–Cu coordination in compounds **4** and **5**. A similar

Table 3
Selected bond distances (Å) for compounds **2**, **3** · **$(OEt_2)_{0.5}$**, **4**, **6**, **6** · **CH_2Cl_2** and **7a** · **$(CDCl_3)_2$**.

Bond distances	Compound **2**	Compound **3** · **$(OEt_2)_{0.5}$**	Compound **4**	Compound **6**	Compound **6** · **CH_2Cl_2**	Compound **7a** · **$(CDCl_3)_2$**
M–P1(O1 in case of **6**)	2.1725(8)	2.2392(5)	2.2857(7)	1.966(1)	1.970(3)	2.242(2)
M–P2(O2 in case of **6**)		2.2409(5)	2.2810(7)		1.972(2)	2.243(2)
M-N1			2.062(2)	1.956(2)	1.970(3)	2.065(6)
M–N2			2.067(2)		1.959(3)	2.050(5)
M···O(ClO_4)		2.369(2)		2.527	2.466	
M···O(ClO_4)		2.915			2.511	
M–Cl1	2.265(1)					
M–Cl1′	2.3413(8)					
N1–C2	1.256(3)	1.260(2)	1.279(3)	1.276(2)	1.283(5)	1.262(9)
N2–C		1.260(3)[a]	1.283(3)		1.281(4)	1.287(8)
C1–C2	1.533(3)	1.532(2)	1.520(3)	1.515(2)	1.521(5)	1.51(1)
C(P2)–C(N2)		1.531(2)	1.515(3)		1.507(5)	1.50(1)
P1–C1	1.852(2)	1.846(2)	1.862(2)	1.812(2)	1.797(4)	1.844(7)
P2–C(alkyl)		1.842(2)	1.852(3)		1.804(4)	1.852(7)
P1–O1				1.512(1)	1.509(3)	
P2–O2					1.514(3)	

M = Au [**7a** · **$(CDCl_3)_2$**], Cu [**2**, **3** · **$(OEt_2)_{0.5}$**, **4**, **6**].
C(N2): carbon atom in second chelate ring bound to N2.
C(P2): carbon atom in second chelate ring bound to P2.
[a] Major part of disordered group only.

situation has only been observed for $[Ph_2PCH_2NPh_2CuCl]_2$ [23], where the lack of N–Cu interaction is probably more likely to be the result of ring strain in the hypothetical four-membered CuPCN heterocycle. Compound **2** has a planar $(CuCl)_2$ heterocycle with slightly differing Cu–Cl bond lengths [Cu1–Cl1 2.265(1); Cu1–Cl1′ 2.3413(8) Å] similar to related copper phosphine halides such as $[Cu\{P(Pr^i_2)C(Et)=CEt_2\}Cl]_2$ [24], $[Cu\{P(C_6H_4\text{-}2\text{-}Me)_3Cl]_2$ [25], $[Cu\{P(CH_2Ph)_3\}Cl]_2$ [26] and $[Cu\{P(C_6H_{11})_3Cl\}Cl]_2$ [27]. Other bond distances and angles are also in good agreement with reported values.

Replacement of the Cl^-- against ClO_4^--anion leads to the monomeric 1:2 complex **3** · **$(OEt_2)_{0.5}$**, that crystallises as a racemic mixture of S,S (Fig. 2) and R,R isomer. There are two short Cu–P bonds [Cu1–P1 2.2392(5), Cu1–P2 2.2409(5) Å] with a P–Cu–P angle of 152.85(2)°. There is an additional contact to one oxygen atom of the ClO_4^--counterion [Cu1···O1 2.369(2) Å] resulting in a nearly planar environment at the copper atom ($\Sigma\angle$Cu1 = 356.2°) with a slight pyramidalisation towards O4 [Cu1···O4 2.915 Å]. Bond distances and angles may be compared to $[Cu\{P(CH_2Ph)_3\}_2]PF_6$ [28], $[Cu\{P(CH_2Ph)_3\}_2]CuBr_2$ [29], $[Cu(PPh_3)_2]BH_4$ [30], $[Cu\{P(C_7H_7)_3\}_2]PF_6$ [31], $[Cu\{P(C_6H_2(Bu^t)_3)C(NMe_2)_2\}_2]BF_4$ [32] or $[Cu\{P(c\text{-}C_6H_{12})_3\}_2]X$ (X = ClO_4, PF_6) [33].

The cation of compound **4** shows a distorted tetrahedral coordination at the copper atom with the endocyclic P–Cu–N angles being acute (approx. 80°) compared to the exocyclic angles (112–139°). The approximate C_2-symmetry of the cation requires the presence of two ligands of the same chirality in the complex. As a consequence of the crystallographic centre of inversion there are both the Λ(S,S) (Fig. 3) and the Δ(R,R) isomer present in the unit cell. The two five-membered $CuPC_2N$ heterocycles of the cation adopt a half-chair conformation, as evident from the sequence of torsions angles (−44.9/−44.6, 37.6/36.6, −7.1/−5.8, −20.7/−21.4, 32.5/32.5°) around the rings [34], with the bulky substituents being orientated approximately opposite to each other. The ClO_4^- anion is bound to the cation via two weak NHO contacts (N1H1···O1 2.389; ∠N1–H1–O1 145.9°; N2H2···O2 2.458; ∠N2–H2–O2 148.2°). The Cu–P and Cu–N bond distances of Cu1–P1 2.2857(7) and Cu1–P2 2.2810(7) Å as well as Cu1–N1 2.062(2) and Cu1–N2 2.067(2) Å are comparable to those in $[Cu\{C_6H_4\text{-}1,2(NH_2)P(MePh)\}_2]PF_6$ [35], $[Cu\{P(Ph_2)(C_6H_4\text{-}2\text{-}NH_2)\}]ClO_4$ [36], $[Cu\{(CH_2)_3(\text{-}(2\text{-}NH)(1\text{-}PPh_2)C_6H_4)_2\}]BF_4$ [37], $[Cu\{(CH_2)_3(\text{-}2\text{-}N=CH)(1\text{-}PPh_2)C_6H_4)_2\}]ClO_4$ [38], $[Cu\{c\text{-}C_6H_{10}(\text{-}2\text{-}NH_2)(1\text{-}PPh_2)C_6H_4)_2\}]ClO_4$ [39]} and $[Cu\{MeN(CH_2)_3PR_2)CH_2CH_2N(Me)(CH_2)_3PR_2\}]BF_4$ (R = Ph, C_6H_{11}) [40] although the observed Cu–N distances are on the shorter side of reported values.

The geometry of the Cu(II) ion in complex **6** may be described as distorted octahedral with short Cu–N [Cu1–N1 1.956(2) Å] and Cu–O distances [Cu1–O1 1.966(1) Å] to the chelating phosphinoxide ligand and much longer contacts [Cu1–O2 2.527 Å] to one oxygen atom of each of the two ClO_4^- counterions in axial position. The two six-membered heterocycles that are formed by coordination of the ligand to the metal ion adopt a chair conformation and are related to each other by an inversion centre at the Cu atom. The solvent polymorph **6** · **CH_2Cl_2** shows essentially the same structure, but the symmetry of the molecule is broken by the presence of the solvent molecule. A very similar structure has been observed for $Cu[OP(iPr)_2CH_2\{C^aNCHCHN^bMe(C^a\text{–}N^b)\}]_2(BF_4)_2$ [12a], that also shows crystallographically imposed symmetry between the two chelate rings and close contacts between the Cu(II) ion and one F atom from each of the two BF_4^- counterions.

Compound **7a** · **$(CDCl_3)_2$** is a rare example for a dimeric Au-complex with a chelating P,N ligand. The molecular structure of the cation shows a 10-membered heterocycle, whose conformation is determined by the typical paddle-like arrangement [N1–Au1–Au2–N2 −125.1(3), P2–Au2–Au1–P1 −126.14(7)°] of the approximately linear N–Au–P [N1–Au1–P2 177.2(2), N2–Au2–P1 177.6(2)°] fragments as a consequence of a maximisation of aurophilic interactions [41] between the two Au ions [Au···Au 2.8691(4) Å]. The Au–P and Au–N distances are unexceptional and may be compared with the related chelate complexes $[Au\{C_6H_4(1\text{-}PPh_2)(2\text{-}N=CMe_2)\}]_2(ClO_4)_2$ [42] and $[Au\{NC_5H_4(2\text{-}PMe_2)\}]_2(BF_4)_2$ [43] or monomeric complexes such as $[Me_3PAuNH_2(tBu)]BF_4$ [43], $[Ph_2MePAuNH_2(tBu)](BF_4)$ [44] and $[Ph_3PAuNMe_3]ClO_4$ [45]. The closest contacts between the cation of **7a** · **$(CDCl_3)_2$** and the BF_4^- couterions are found between N1 and F6 (N1H1···F6 2.158 Å; N1–H1–F6 131.40°) and N2 and F8 (N2H2···F8 2.216 Å; N2–H2–F8 145.27°), respectively.

The NCC and CC bond distances in the backbone of the ligand of all presented complexes are in agreement with *N*=C double and C–C single bonds.

4. Supplementary material

CCDC 699810, 699811, 699812, 699813, 699814 and 699815 contain the supplementary crystallographic data for **2**, **3** · **$(OEt_2)_{0.5}$**, **4**, **6** · **CH_2Cl_2**, **6**, **7a** · **$(CDCl_3)_2$**. 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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