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Structural diversity in the coordination of amidines and guanidines to monovalent metal halides

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A series of structurally characterised, monovalent metal-halide complexes incorporating neutral amidine and guanidine ligands is reported. *N*,*N*′-diphenylbenzamidine reacted with copper(I) chloride to afford the bis-ligand complex $[CuCl(PhC\{NPh\}\{NHPh\})_2]_2$ (**1**), that exists as a chlorine bridged dimer in the solid state, with a non-symmetrical distribution of NH ··· Cl interactions within the 'Cu_2Cl_2' metallacycle. In contrast, only one equivalent of the guanidine, $Me_2NC\{N^iPr\}\{NH^iPr\}$ (**2**), is coordinated in the copper(I) iodide complex $[CuI(Me_2NC\{N^iPr\}\{NH^iPr\})]_2$ (**3**), which was also isolated as the dimer with bridging halide atoms. The molecular structure of the bicyclic guanidine, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH), is reported, revealing a hydrogen bridged dimer with extensive delocalisation throughout the ligand framework. Coordination of hppH to lithium chloride afforded the dimeric bis-ligand complex $[LiCl(hppH)_2]_2$ (**4**) in which each hppH molecule interacts with a different chlorine atom of the central 'Li_2Cl_2' core of the molecule *via* NH ··· Cl hydrogen bonding. In contrast the 2 : 1 ligand to metal complex is formed with silver(I) chloride to afford $AgCl(hppH)_2$ (**5**), a unique example of a monomeric, three-coordinate silver chloride supported by nitrogen-based ligands. The series of mixed ligand complexes $[CuX(hppH)(PPh_3)]_n$ (**6**, X = Cl, $n = 1$; **7**, X = Br, $n = 2$; **8** X = I, $n = 2$) have also been synthesised and structurally characterised, allowing comparisons of the relative coordinating behaviour of hppH and PPh_3 as neutral donors at copper(I) centres to be made.

Introduction

The application of neutral, N-based donor ligands in coordination chemistry is, perhaps, exemplified by the use of pyridine and pyridine-based compounds, where many different structural patterns are observed, depending upon the nature and extent of substitution of the C_5N-ring. During the 1990s, an extensive structural study was performed by White and coworkers on these, and other group 15 element donor compounds (*e.g.* phosphines, arsines, stibines), spanning many of the 'closed shell' metal ions of the periodic table.[1] Of particular relevance to the study presented in this work, research was conducted into the nature of the complexes formed with the group 1 and group 11 metals, employing a range of N-based ligands, typified by the examples illustrated in Fig. 1. In order to maximise the possibility and degree of adduct formation, a procedure that was often employed which took advantage of the liquid state of many of the nitrogen donor species, was the use of solvent-free conditions, where the metal salt was dissolved directly in the organic base and crystals were isolated from the resultant mixture. However, it was found that in certain cases, even these conditions were insufficient to promote formation of the desired adduct.

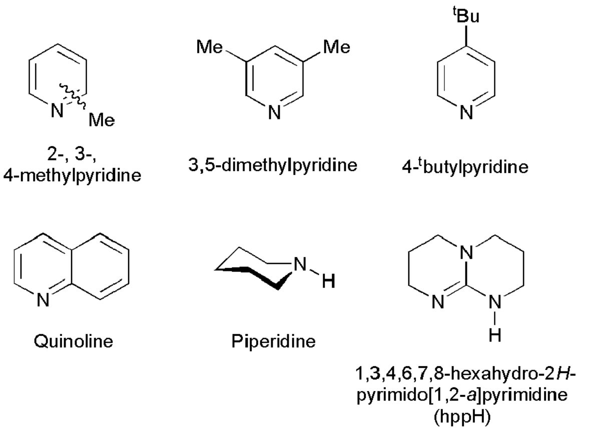

Fig. 1 Examples of nitrogen-based donor ligands typically used in coordination chemistry studies at monovalent metal halides.

Research in our laboratory has been concerned with the synthesis of a number of transition metal complexes incorporating neutral guanidines, $R_2NC\{NR'\}\{NHR'\}$, and their corresponding anions, $[R_2NC\{NR'\}_2]^-$, as N-based ligands.[2–5] Whilst application of the latter class of negatively charged guanidinates has become more widespread in coordination chemistry, the use of the former as neutral donors has not, to date, received similar attention.[6] We have previously found, however, that the combination of a donor-imine functionality and an NH group within the bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH, Fig. 1), permitted the facile coordination of this compound to copper(I) halides.[4] The solid-state structure of the resultant $CuX(hppH)_2$ compounds indicated a three-coordinate copper with intramolecular hydrogen bonds between the NH and halide atoms for the chloride and bromide species. We wish to present here our results from a further study into the coordinating potential of this versatile class of neutral ligand, and identify a number of different structural motifs with monovalent lithium, copper and silver halides, allowing detailed comparisons to be made with the solid-state structures of related Lewis-base adducts.

Experimental

General experimental procedures

All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. *N*,*N*′-di-

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phenylbenzamidine (Lancaster), hppH (Fluka), diisopropylcarbodiimide (Aldrich), lithium dimethylamide (Aldrich), copper(I) chloride (Aldrich), copper(I) bromide (Aldrich), copper(I) iodide (Fluka), silver(I) chloride (Aldrich) and lithium chloride, anhydrous (Acros) were purchased from commercial sources and used as received. PPh_3 (Aldrich) was recrystallised from Et_2O.

Elemental analyses were performed by S. Boyer at London Metropolitan University. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300 (^1H), 75 ($^{13}C\{^1H\}$) and 121 ($^{31}P\{^1H\}$) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances; phosphorus chemical shifts were referenced to an external 85% aqueous solution of H_3PO_4; lithium chemical shifts were referenced to an external aqueous solution of LiCl. Coupling constants (J) are quoted in Hz.

$[CuCl(PhC\{NPh\}\{NHPh\})_2]_2$ (1). A solution of PhC{NPh}{NHPh} (1.00 g, 3.67 mmol) in THF (25 mL) was added dropwise to a slurry of CuCl (0.18 g, 1.86 mmol) in THF (20 mL), resulting in immediate colour change to red–brown. On complete addition, most of the CuCl had dissolved, affording a slightly cloudy orange–yellow solution, which was stirred at room temperature for 18 h. The solution was filtered and the volatiles removed *in vacuo* to afford a dark yellow foam. Crystallisation from Et_2O at −30 °C resulted in formation of **1** as yellow crystals. Yield 0.73 g (60%).

Anal. Calc. for $C_{38}H_{32}N_4ClCu$: C, 70.9; H, 5.0; N, 8.7%. Found: C, 71.0; H, 5.0; N, 8.8%. ^1H NMR (C_6D_6, 298 K): δ 6.90 (br, C_6H_5), 6.70 (br, C_6H_5), NH not observed. ^{13}C NMR (C_6D_6, 298 K): δ 130.1 (CH), 129.5 (br, CH), 128.6 (br, CH), 128.3 (CH), 123.8 (br, CH). Mass spectrum (EI$^+$, m/z): 180 [PhC{NPh}]$^+$, 272 [PhC{NPh}{NHPh}]$^+$. IR (Nujol mull, cm^{-1}): 3191 (N–H), 1609s (C=N), 1582 (C–N), 1491m, 1239w, 1212m, 1170w, 1155w, 1123m, 1025w, 975w, 922m, 898w, 888w, 791m, 769m, 754m, 731m, 706m, 692s, 643w, 621m, 530m, 501m, 460w, 405w, 388w.

$Me_2NC\{N^iPr\}\{NH^iPr\}$ (2). A slurry of lithium dimethylamide (5.00 g, 98.0 mmol) in Et_2O (100 mL) was cooled to 0 °C and a solution of diisopropylcarbodiimide (12.40 g, 98.0 mmol) in Et_2O (50 mL) was added dropwise *via* cannula. The mixture was allowed to warm to room temperature to afford a cloudy yellow solution that was stirred for a further 14 h under ambient conditions. Degassed water (1.8 mL, 100 mmol) was subsequently added dropwise *via* syringe causing the formation of a clear yellow solution and a white precipitate. The mixture was filtered through Celite and the volatiles were removed to afford a pale yellow liquid that was used without further purification. Yield 11.75 g, 70%.

^1H NMR ($CDCl_3$, 298 K): δ 3.37 (sept, $^3J_{HH}$ = 6.4, 1H, CHMe$_2$), 3.25 (sept, $^3J_{HH}$ = 6.3, 1H, CHMe$_2$), 2.67 (s, 6H, NMe$_2$), 1.03 (d, $^3J_{HH}$ = 6.3, 6H, CHMe_2), 1.02 (d, $^3J_{HH}$ = 6.3, 6H, CHMe_2), NH not observed. ^{13}C NMR ($CDCl_3$, 298 K): δ 155.8 (CN$_3$), 47.3 (CHMe$_2$), 45.9 (CHMe$_2$), 39.0 (NMe$_2$), 25.1 (CHMe_2), 23.6 (CHMe_2).

$[CuI(Me_2NC\{N^iPr\}\{NH^iPr\})]_2$ (3). A solution of **2** (0.45 g, 2.63 mmol) in MeCN (20 mL) was added dropwise *via* cannula to a slurry of CuI (0.25 g, 1.31 mmol) in MeCN (20 mL). The CuI gradually dissolved during the course of the addition. The mixture was allowed to stir under ambient conditions for 24 h, after which time the solution was gently heated (*ca.* 40 °C) to redissolve precipitated product and filtered to remove any insoluble material. Slow cooling to room temperature afforded pale brown crystals of analytically pure **3**. Yield 0.52 g, 62%.

Anal. Calc. for $C_{18}H_{42}N_6Cu_2I_2$: C, 29.88; H, 5.85; N, 11.62%. Found C, 30.14; H, 5.68; N, 11.72%. ^1H NMR (C_6D_6, 298 K): δ 3.34 (br, sept, 2H, CHMe$_2$), 2.65 (s, 6H, NMe$_2$), 1.41 (br, d, 6H, CHMe_2), 0.72 (br, d, 6H, CHMe_2), NH not observed. ^1H NMR ($CDCl_3$, 298 K): δ 3.54 (br, sept, 2H, CHMe$_2$), 3.01 (s, 6H, NMe$_2$), 1.22 (br, d, 12H, CHMe_2), NH not observed. ^{13}C NMR ($CDCl_3$, 298 K): δ 161.3 (CN$_3$), 50.5 (CHMe$_2$), 47.1 (CHMe$_2$), 40.3 (NMe$_2$), 26.8 (CHMe_2), 24.1 (CHMe_2). IR (Nujol mull, cm^{-1}): 3374s (N–H), 1592s (C=N), 1260m, 1125m, 1094m, 1037m, 936m, 800s, 591m.

$[LiCl(hppH)_2]_2$ (4). A solution of hppH (1.00 g, 7.18 mmol) in THF (25 mL) was added dropwise to a slurry of LiCl (0.15 g, 3.59 mmol) in THF (20 mL) and the mixture was stirred under ambient conditions for 18 h. The solution was warmed (*ca.* 50 °C) and filtered before cooling to −30 °C, affording **4** as colourless crystals. Yield 0.73 g (63%).

Anal. Calc. for $C_{14}H_{26}N_6ClLi$: C, 52.4; H, 8.2; N, 26.2%. Found: C, 50.0; H, 8.5; N, 24.0%. ^1H NMR (C_6D_6, 298 K): δ 7.21 (s, 1H, NH), 3.21 (m, 4H, CH$_2$), 2.47 (m, 4H, CH$_2$), 1.44 (M, 4H, CH$_2$). ^{13}C NMR (C_6D_6, 298 K): δ 152.7 (CN$_3$), 47.9 (CH$_2$), 41.2 (CH$_2$), 43.2 (CH$_2$). ^7Li NMR (C_6D_6, 298 K): δ 2.01. Mass spectrum (EI$^+$, m/z): 138 [hpp − H]$^+$. IR (Nujol mull, cm^{-1}) 3299s (N–H), 1636s (C=N), 1520s (C–N), 1316m, 1249m, 1187m, 1110m, 1020m, 932w, 626m, 514w, 455m, 406m, 376m.

$AgCl(hppH)_2$ (5). A solution of hppH (1.60 g, 11.50 mmol) in THF (30 mL) was added to a slurry of silver chloride (0.85 g, 5.93 mmol) also in THF (30 mL) at room temperature with the exclusion of light. The solution was stirred in the dark for 48 h, after which time a small quantity of a pale pink precipitate was observed. The reaction was filtered and the volatiles were removed to afford crude AgCl(hppH)$_2$ as a pale pink solid. Analytically pure samples of **5** were obtained as colourless crystals by recrystallisation from toluene at 0 °C. Yield 1.50 g, 60%.

Anal. Calc. for $C_{14}H_{26}N_6AgCl$: C, 39.8; H, 6.2; N, 19.1%. Found: C, 39.9; H, 6.3; N, 19.4%. ^1H NMR (C_6D_6, 298 K): δ 7.77 (br, s, 1H, NH), 3.21 (t, $^3J_{HH}$ = 5.6, 4H, CH$_2$), 2.43 (t, $^3J_{HH}$ = 6.1, 4H, CH$_2$), 1.36 (m, 4H, CH$_2$). ^{13}C NMR (C_6D_6, 298 K): δ 153.9 (CN$_3$), 48.1 (CH$_2$), 44.0 (CH$_2$), 23.3 (CH$_2$). IR (Nujol mull, cm^{-1}): 3270w (N–H), 1599m (C=N), 1537m, 1315m, 1295m, 1261m, 1184m, 1102w, 1068m, 1018m, 802m, 569w, 515w, 450w.

$CuCl(hppH)(PPh_3)$ (6). A solution of PPh$_3$ (1.33 g, 5.05 mmol) and hppH (0.70 g, 5.05 mmol) in THF (25 mL) was added dropwise to a slurry of CuCl (0.50 g, 5.05 mmol). The CuCl gradually dissolved during the addition. The mixture was stirred for 24 h at room temperature then warmed gently (*ca.* 50 °C), filtered and cooled slowly to ambient temperature affording pale green crystals of analytically pure **6**. Yield 1.83 g, 72%.

Anal. Calc. for $C_{25}H_{28}N_3ClCuP$: C, 60.0; H, 5.6; N, 8.4%. Found C, 59.8; H, 5.6; N, 8.6%. ^1H NMR (C_6D_6, 298 K): δ 8.44 (br, s, 1H, NH), 7.74 (m, 6H, o-C$_6$H$_5$), 7.02 (m, 9H, m- and p-C$_6$H$_5$), 2.93 (br, s, 4H, CH$_2$), 2.28 (t, $^3J_{HH}$ = 6.1, 4H, CH$_2$), 1.17 (m, 4H, CH$_2$). ^{13}C NMR (C_6D_6, 298 K): δ 154.4 (CN$_3$), 134.6 (d, J_{PH} = 45.8, C$_6$H$_5$), 134.4 (d, J_{PH} = 15.4, C$_6$H$_5$), 129.7 (s, C$_6$H$_5$), 128.8 (d, J_{PH} = 9.2), 47.6 (2 coincident CH$_2$ peaks), 22.6 (CH$_2$). ^{31}P NMR (C_6D_6, 298 K) δ −6.4. Mass spectrum (EI$^+$, m/z): 499 [M]$^+$, 464 [M − Cl]$^+$. IR (Nujol mull, cm^{-1}): 3269s (N–H), 1593s (C=N), 1548m, 1434m, 1417m, 1313m, 1260m, 1092s, 1025m, 799m, 751m, 693m, 519m, 501m.

$[CuBr(hppH)(PPh_3)]_2$ (7). Compound **7** was prepared using the procedure described for **6**, using PPh$_3$ (0.91 g, 3.49 mmol), hppH (0.48 g, 3.49 mmol) and CuBr (0.50 g, 3.49 mmol). The compound was crystallised from THF, affording analytically pure, pale green crystals of **7**. Yield 1.26 g, 66%.

Anal. Calc. for $C_{50}H_{56}N_6Br_2Cu_2P$: C, 55.1; H, 5.2; N, 7.7%. Found C, 55.3; H, 5.1; N, 7.6%. ^1H NMR (C_6D_6, 298 K): δ 8.01 (br, s, 1H, NH), 7.74 (m, 6H, o-C$_6$H$_5$), 7.02 (m, 9H, m- and p-C$_6$H$_5$), 2.92 (br, s, 4H, CH$_2$), 2.26 (t, $^3J_{HH}$ = 6.1, 4H, CH$_2$),

Table 1 Crystal structure and refinement data for **1**, **3**, **4** and hppH

	1	**3**	**4**	hppH
Formula	$C_{76}H_{64}Cl_2Cu_2N_8$	$C_{18}H_{42}Cu_2I_2N_6$	$C_{28}H_{52}Cl_2Li_2N_{12}$	$C_7H_{13}N_3$
Formula weight	1287.33	723.46	641.60	139.20
T/K	173(2)	173(2)	173(2)	173(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal size/mm	0.2 × 0.2 × 0.1	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.1	0.4 × 0.3 × 0.3
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$Pbca$ (no. 61)
a/Å	10.7522(4)	8.2768(2)	8.8979(7)	8.5628(2)
b/Å	11.9924(6)	8.8985(2)	19.2720(19)	14.8659(3)
c/Å	13.9711(8)	10.8561(3)	10.7363(8)	11.6451(2)
α/°	112.261(2)	107.040(1)	90	90
β/°	107.954(3)	95.260(1)	113.465(5)	90
γ/°	92.424(3)	112.759(1)	90	90
V/Å^3	1559.9(1)	685.61(3)	1688.8(2)	1482.35(5)
Z	1	1	2	8
D_c/Mg m^{-3}	1.37	1.75	1.26	1.25
μ/mm^{-1}	0.82	3.82	0.23	0.08
θ Range for data collection/°	3.73–27.84	3.87–30.05	3.79–25.02	4.03–25.01
Reflections collected	12659	6652	8057	14208
Independent reflections	7363 [$R_{int} = 0.055$]	3871 [$R_{int} = 0.048$]	2934 [$R_{int} = 0.051$]	1298 [$R_{int} = 0.055$]
Reflections with $I > 2\sigma(I)$	5217	3643	2242	1148
Data/restraints/parameters	7363/0/405	3871/0/132	2934/0/277	1298/0/110
Goodness-of-fit on F^2	1.042	1.179	1.094	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.051$, $wR_2 = 0.110$	$R_1 = 0.033$, $wR_2 = 0.084$	$R_1 = 0.061$, $wR_2 = 0.136$	$R_1 = 0.049$, $wR_2 = 0.131$
R Indices (all data)	$R_1 = 0.084$, $wR_2 = 0.123$	$R_1 = 0.035$, $wR_2 = 0.085$	$R_1 = 0.084$, $wR_2 = 0.146$	$R_1 = 0.055$, $wR_2 = 0.136$
Largest diff. peak and hole/e Å^{-3}	0.60 and −0.567	1.27 and −0.98	0.76 and −0.29	0.30 and −0.27

1.15 (m, 4H, CH_2). ^{13}C NMR (C_6D_6, 298 K): δ 154.4 (CN_3), 134.5 (d, $J_{PH} = 25.9$, C_6H_5), 134.4 (d, $J_{PH} = 15.1$, C_6H_5), 129.7 (s, C_6H_5), 128.8 (d, J_{PH} = 9.2, C_6H_5), 47.6 (2 coincident CH_2 peaks), 22.6 (CH_2). ^{31}P NMR (C_6D_6, 298 K) δ −6.7. Mass spectrum (EI$^+$, m/z): 262 $[PPh_3]^+$. IR (Nujol mull, cm^{-1}): 3282s (N–H), 1615s (C=N), 1525m, 1315m, 1261m, 1180m, 1093m 1025m, 803m, 742m, 695m, 522m, 504m, 487w.

$[CuI(hppH)(PPh_3)]_2$ (8). Compound **8** was prepared using the procedure described for **6**, using PPh_3 (0.69 g, 2.63 mmol), hppH (0.37g, 2.63 mmol) and CuI (0.50 g, 2.63 mmol). The compound was crystallised from THF, affording analytically pure, pale brown crystals of **8**. Yield 1.10 g, 70%.

Anal. Calc. for $C_{50}H_{56}N_6Cu_2I_2P$: C, 50.7; H, 3.1; N, 7.1%. Found C, 50.7; H, 3.1; N, 7.0%. ^1H NMR (C_6D_6, 298 K): δ 7.74 (m, 6H, o-C_6H_5), 7.02 (m, 9H, m- and p-C_6H_5), 2.93 (br, s, 4H, CH_2), 2.25 (t, $^3J_{HH}$ = 6.1, 4H, CH_2), 1.16 (m, 4H, CH_2). ^{13}C NMR (C_6D_6, 298 K): δ 153.7 (CN_3), 134.7 (d, J_{PH} = 24.3, C_6H_5), 134.5 (d, J_{PH} = 14.9, C_6H_5), 129.6 (s, C_6H_5), 128.7 (d, J_{PH} = 9.0, C_6H_5), 47.6 (2 coincident CH_2 peaks), 22.6 (CH_2). ^{31}P NMR (C_6D_6, 298 K) δ −7.2. Mass spectrum (EI$^+$, m/z): 329 $[1/2\,M - PPh_3]^+$. IR (Nujol mull, cm^{-1}): 3290s (N–H), 1610s (C=N), 1526m, 1315m, 261m, 1183m, 1093m 1025m, 799m, 755m, 695m, 522m, 504m, 486w.

Crystallography

Details of the crystal data, intensity collection and refinement for complexes **1**, **3**, **4** and hppH are listed in Table 1, and for complexes **5**–**8** in Table 2. Crystals were covered in an inert oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[7] Compounds **1**, **3**, **4**, **7** and **8** all have crystallographically imposed inversion symmetry; additional features of note are described below.

CCDC reference numbers 224306–224313.

See http://www.rsc.org/suppdata/dt/b3/b314707j/ for crystallographic data in CIF or other electronic format.

$[CuCl(PhC\{NPh\}\{NHPh\})_2]_2$ (**1**): H(N) atoms freely refined; all others in riding mode.

$[CuI(Me_2NC\{N^iPr\}\{NH^iPr\})]_2$ (**3**): H atom on N(3) refined; all others in riding mode.

hppH: The C(6) atom is disordered over two positions, with occupancies 0.71 and 0.29. The H(N) atom is disordered over the two nitrogens, both with occupancy 0.5.

$[LiCl(hppH)_2]_2$ (**4**): H atoms on N(1) and N(4) refined; all others in riding mode.

$AgCl(hppH)_2$ (**5**): The data were collected at 253 K as upon cooling to 173 K, the crystal undergoes a phase change, seriously affecting the quality of the data (the crystal is observed to go opaque). The C(3) atom is disordered over two positions, with occupancies 0.74 and 0.26. H atoms on nitrogen were refined; all others in riding mode.

$CuCl(hppH)(PPh_3)$ (**6**): H atom on N(2) refined; all others in riding mode.

$[CuBr(hppH)(PPh_3)]_2$ (**7**): H atom on N(3) refined; all others in riding mode.

$[CuI(hppH)(PPh_3)]_2$ (**8**): Isomorphous with the bromide. H atom on N(3) refined; all others in riding mode.

Results and discussion

Our initial investigation of the coordinating behaviour of amidines and guanidines at monovalent metal centres concerned the addition of two molar equivalents of N,N'-diphenylbenzamidine to a slurry of copper(I) chloride in THF, following a protocol that had previously proved successful in our laboratory for the synthesis of $[CuX(hppH)_2]$.[4] On addition, the immediate formation of red colour was observed, and during the course of the addition, it was noted that the CuCl gradually dissolved to afford a clear, orange–yellow solution. Attempted recrystallisation from the reaction solvent or toluene failed due to the high solubility of the compound, which was subsequently found to be insoluble in pentane. Addition of diethylether to the dark yellow foam formed upon removal of the volatiles, however, formed a brown oil which slowly dissolved (*ca.* 1 h) and, on stirring for a further 4 h, precipitated a yellow crystalline solid **1**. ^1H and ^{13}C NMR spectra are non-informative in this instance, showing a number of broad resonances in the aromatic region of the spectrum, and no resonance corresponding to the NH atom was observed in the proton NMR spectrum. The IR spectrum shows absorptions at 3191 and 1609 cm^{-1}, attributed to ν(N–H) and ν(C=N) respectively, and

Table 2 Crystal structure and refinement data for **5**, **6**, **7** and **8**

	5	**6**	**7**	**8**
Formula	$C_{14}H_{26}AgClN_6$	$C_{25}H_{28}ClCuN_3P$	$C_{50}H_{56}Br_2Cu_2N_6P_2$	$C_{50}H_{56}Cu_2I_2N_6P_2$
Formula weight	421.73	500.46	1089.85	1183.83
T/K	253(2)	173(2)	223(2)	223(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal size/mm	0.30 × 0.30 × 0.20	0.30 × 0.30 × 0.30	0.30 × 0.20 × 0.20	0.20 × 0.10 × 0.10
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	7.4791(1)	9.3552(1)	9.6014(2)	9.6964(2)
b/Å	14.4246(2)	16.3599(3)	11.2158(2)	11.2108(2)
c/Å	16.1899(3)	15.2723(2)	12.0457(2)	12.2893(2)
α/°	90	90	74.402(1)	74.032(1)
β/°	97.165(1)	90.656(1)	73.373(1)	72.476(1)
γ/°	90	90	89.615(1)	89.277(1)
V/Å^3	1732.98(5)	2337.27(6)	1193.69(4)	1221.15(4)
Z	4	4	1	1
D_c/Mg m^{-3}	1.62	1.42	1.52	1.61
μ/mm^{-1}	1.32	1.14	2.67	2.24
θ Range for data collection/°	3.77–25.02	3.97–27.88	3.72–27.88	3.71–27.89
Reflections collected	17656	21620	15808	12510
Independent reflections	3020 [$R_{int} = 0.041$]	5515 [$R_{int} = 0.044$]	5659 [$R_{int} = 0.039$]	5758 [$R_{int} = 0.035$]
Reflections with $I > 2\sigma(I)$	2702	4591	4793	5282
Data/restraints/parameters	3020/0/217	5515/0/284	5659/0/284	5758/0/284
Goodness-of-fit on F^2	1.004	1.015	1.045	1.063
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.033$, $wR_2 = 0.084$	$R_1 = 0.032$, $wR_2 = 0.069$	$R_1 = 0.032$, $wR_2 = 0.067$	$R_1 = 0.025$, $wR_2 = 0.058$
R Indices (all data)	$R_1 = 0.038$, $wR_2 = 0.088$	$R_1 = 0.044$, $wR_2 = 0.074$	$R_1 = 0.043$, $wR_2 = 0.072$	$R_1 = 0.028$, $wR_2 = 0.060$
Largest diff. peak and hole/e Å^{-3}	0.68 and −0.91	0.29 and −0.37	0.58 and −0.43	0.42 and −0.73

combustion analysis is consistent with the bis-ligand complex [CuCl(PhC{NPh}{NHPh})$_2$]$_n$.

To determine the nuclearity of **1**, in addition to the bonding mode adopted by this ligand at the copper centre, X-ray diffraction analysis was performed. The molecular structure is illustrated in Fig. 2(a), crystal data are summarised in Table 1 and selected bond lengths and angles in Table 3.

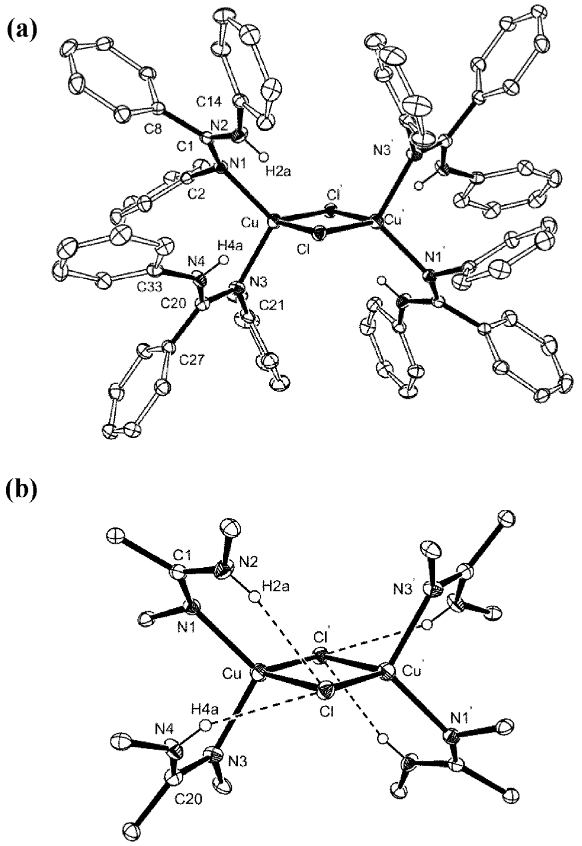


Fig. 2 (a) Molecular structure of [CuCl(PhC{NPh}{NHPh})$_2$]$_2$ (**1**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except NH atoms omitted. (b) Core of **1** showing two H-bonding interactions to secondary chlorine atoms.

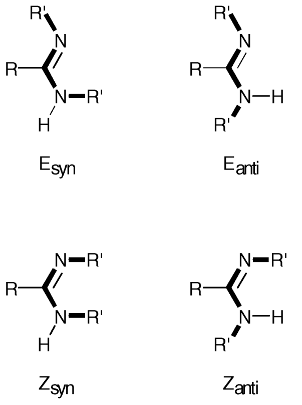
Table 3 Selected bond lengths (Å) and angles (°) for **1**

Cu–N(1)	2.050(2)	Cu–N(3)	2.063(2)
Cu–Cl	2.4900(8)	Cu–Cl′	2.3217(7)
C(1)–N(1)	1.302(3)	C(1)–N(2)	1.348(4)
C(20)–N(3)	1.302(3)	C(20)–N(4)	1.372(3)
H(2a)···Cl	2.42	H(4a)···Cl	2.56
N(1)–Cu–N(3)	105.88(9)	N(1)–Cu–Cl′	115.06(6)
N(3)–Cu–Cl′	113.04(6)	N(1)–Cu–Cl	111.38(6)
N(3)–Cu–Cl	100.34(7)	Cl–Cu–Cl′	110.12(2)
Cu–Cl–Cu′	69.88(2)		

Symmetry operation: ′ $-x$, $-y$, $-z$.

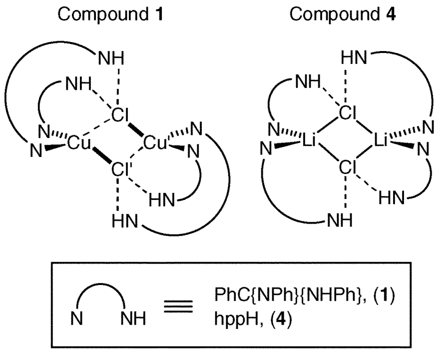
Compound **1** forms a μ,μ-dichlorobridged dimer, with two N$_{imine}$-bound amidine ligands, generating a distorted tetrahedral geometry at copper with angles in the range 115.06(6)–100.34(7)°. Similar halide-bridged dimeric structures have been reported for bis-pyridine adducts of copper(I) chloride.[8] The copper–nitrogen distances [2.050(2) and 2.063(2) Å] are longer than in the related guanidine adduct CuCl(hppH)$_2$ [1.962(2) and 1.966(2) Å],[4] which may be a simple consequence of the increased coordination number at the copper(I) centre in **1**.

Investigation of the carbon–nitrogen bond distances within the framework of amidine and guanidine ligands has been used as a diagnostic tool when considering the distribution of π-electron density throughout the core of the ligand.[9] A particularly informative parameter that has been used when discussing the extent of delocalisation across the amidine unit is the Δ_{CN} value,[10] defined as $d(\text{C–N}_{single}) - d(\text{C=N}_{double})$. Predicted values fall in the range 0 Å for a fully delocalised system to ~ 0.14 Å for localised single and double bonds at an sp^2-hybridised carbon.[11] Care should be exercised when discussing this parameter however as research in our laboratory has shown that this value can vary from as much as 0.008 to 0.108 Å in closely related linked-bis(*N*,*N*′-dialkylamidines).[12] The Δ_{CN} values for each of the amidine ligands within compound **1** are significantly different from each other [0.070 and 0.046 Å], with similar differences observed in the related cobalt adduct, CoCl$_2$(PhC{NPh}{NHPh})$_2$ [0.054 and 0.033 Å].[13] The former value is approximately midway between the values predicted for isolated C–N single and C=N double bonds, while the latter is closer to the Δ_{CN} values for the free ligand, which exists as a hydrogen bonded dimer with one N–H ··· N interaction [0.056 and 0.058 Å].[14] The nitrogen-phenyl substituents are distributed in an E_{anti} configuration about the amidine unit (Scheme 1),[15] shifting from the E_{syn} arrangement in the neutral ligand. This minimises steric interactions and allows stabilisation from intramolecular hydrogen bonding to occur (*vide infra*).



Scheme 1 Isomeric and tautomeric forms of the amidine unit.

The amidine ligands within **1** are orientated such that each amine-hydrogen atom is in close contact with one of the chlorine atoms, with NH ··· Cl distances of 2.42 and 2.56 Å (Fig. 2(b)). Considering the significant asymmetry present within the 'Cu_2Cl_2' core of the dimer [Cu–Cl 2.4900(8) Å; Cu–Cl′ 2.3217(7) Å], it is reasonable to consider the shorter copper–chlorine distance to Cl′ as being a primary interaction, and the other metal–halide bond to Cl as representing a secondary weaker interaction (Scheme 2). Using this model, both of the hydrogen bonding interactions are with the secondary chloride and therefore may represent a significant contribution to the stabilisation of the observed dimeric structure in the solid-state.



Scheme 2 Schematic representation of the hydrogen bonding within the metallacyclic cores of dimeric **1** and **4**.

Whilst a number of adducts of amidines at metal centres have been reported,[16] extension to neutral guanidines has to date not been investigated to a comparable degree.[6] Notable exceptions include adducts of the neutral palladium(II) and cobalt(II) dichlorides, and the cationic silver(I) triflate.[17,18] We have investigated the neutral bicyclic guanidine, hppH, as a ligand at copper(I) centres, demonstrating that different co-ordination modes are possible in the solid state.[3,4] As part of our interest in the application of such species as catalysts in the polymerisation of olefins,[4] we have investigated the co-ordination of the acyclic guanidine, Me$_2$NC{N^{i}Pr}{NH^{i}Pr} (**2**), at copper(I) halide centres. The guanidine is synthesised by quenching the intermediate lithium salt '[Me$_2$NC{N^{i}Pr}$_2$]Li′, generated from the reaction of lithium dimethylamide with diisopropylcarbodiimide, with a stoichiometric amount of water. For the purposes of this study, no further purification was necessary.

Table 4 Selected bond lengths (Å) and angles (°) for **3**

Cu–N(1)	1.993(2)	Cu–I	2.5469(4)
Cu–I′	2.6434(4)	C(1)–N(1)	1.304(3)
C(1)–N(2)	1.383(3)	C(1)–N(3)	1.375(3)
I–Cu–I′	121.378(12)	N(1)–Cu–I	127.82(7)
N(1)–Cu–I′	110.78(7)	Cu–I–Cu′	58.622(12)

Symmetry operation: ′ −*x*, −*y*, −*z*.

Initial attempts at coordinating **2** to copper(I) chloride were frustrated by the oily nature of the products, greatly complicating attempted purification. However, a crystalline solid (**3**) was isolated from the 2 : 1 reaction between **2** and CuI, allowing further characterisation to be performed. The ^{1}H NMR in C_6D_6 indicated broad resonances corresponding to the expected ligand signals, with separation of the isopropyl –CH_3 signals into two distinct doublets. In $CDCl_3$, these doublets resonances are coincident, suggesting the presence of fluxionality within the molecule. In contrast to the expected bis-ligand complex analogous to **1**, combustion analysis indicated that only one ligand was present per 'CuI' unit, giving the formula [CuI(Me$_2$NC{N^{i}Pr}{NH^{i}Pr})]$_n$. To establish the nature of the ligand bonding in **3**, X-ray structural analysis was performed. The molecular structure of **3** is illustrated in Fig. 3, crystal data are summarised in Table 1 and selected bond lengths and angles in Table 4.

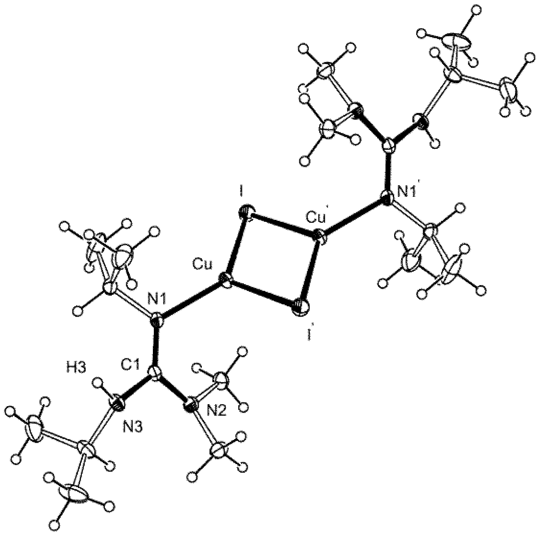


Fig. 3 Molecular structure of [CuI(Me$_2$NC{N^{i}Pr}{NH^{i}Pr})]$_2$ (**3**) with thermal ellipsoids drawn at the 30% probability level.

Compound **3** also crystallises as the μ,μ-dihalobridged dimer, with a single ligand coordinated to each copper (*cf.* compound **1**), giving an overall molecular formula of [CuI(Me$_2$NC{N^{i}Pr}{NH^{i}Pr})]$_2$. As expected, the ligand is coordinated through the N$_{imine}$ atom, to afford a distorted trigonal planar metal (Σ_{angles} = 359.97°) with angles in the range 110.78(7) to 127.82(7)°. Similar mono-ligand complexes with a central 'Cu_2I_2' core have been reported for the bulky N-based donors tetramethylpiperidine,[19] lutidine,[20] and 1,2,3,4,5,6,7,8-octahydroacridine.[21] The internal angles in the metallacycle of **3** are 121.378(12) and 58.622(12)° at copper and iodine, respectively, with unsymmetrical copper–iodine bond lengths of 2.5469(4) and 2.6434(4) Å. The resultant I ··· I distance [4.526 Å] is relatively long in comparison with the aforementioned dimers, being significantly greater than sum of the van der Waals radii [4.30 Å]. The Cu ··· Cu separation of 2.542 Å may be considered as a close non-bonded interaction, although the distance is slightly longer than in the previously reported [hpp]$^-$ bridged dimer [2.4527(10) Å].[22]

Table 5 Selected bond lengths (Å) and angles (°) for hppH

C(1)–N(1)	1.328(2)	C(1)–N(2)	1.367(3)
C(1)–N(3)	1.331(2)	H(3′) · · · N(1)	2.09
H(1) · · · N(3′)	2.08		
N(1)–C(1)–N(2)	121.19(15)	N(1)–C(1)–N(3)	117.90(14)
N(2)–C(1)–N(3)	120.89(14)	C(1)–N(2)–C(4)	122.15(13)
C(1)–N(2)–C(5)	122.29(14)	C(4)–N(2)–C(5)	115.47(13)

The C(6) atom is disordered over two positions (occupancies 0.71 and 0.29); the N(H) atom is disordered over the two nitrogens occupancies 0.5 : 0.5).

The ligand substituents are located in a Z_{anti} arrangement about the amidine unit (Scheme 1), precluding any hydrogen bonding interactions with the halogen atom. The Δ_{CN} value [0.071 Å] is typical for segregated single and double bonds within an amidine unit, with virtually no delocalisation of the amide lone-pair into the core reflected by the relatively large angle between the '–NMe$_2$' group and the 'CN$_2$' moiety [40.0°] and long carbon–nitrogen bond [1.383(3) Å].

Despite the application of the bicyclic guanidine hppH as a source of both anionic[2,9,23] and neutral[3,4] ligand, and subsequent interest in the distribution of π-electron density throughout the framework, the crystal structure of the neutral compound has not been reported.[24] A sample of commercial hppH was therefore recrystallised from THF and the crystals examined by X-ray diffraction. The molecular structure is illustrated in Fig. 4(a), crystal data are summarised in Table 1 and selected bond lengths and angles in Table 5.

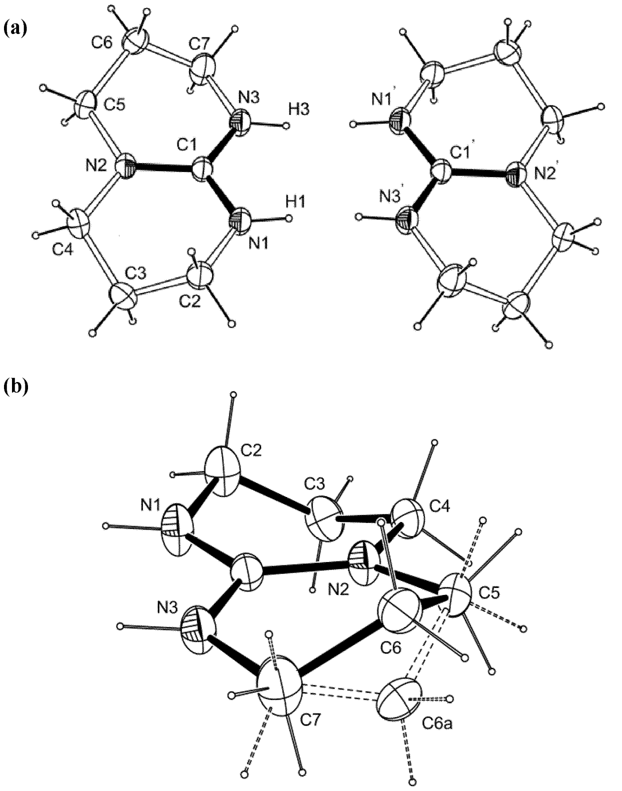


Fig. 4 (a) Dimeric structure of hppH. Thermal ellipsoids drawn at the 30% probability level. (b) Disorder present in the C(6) β-methylene group of hppH, with the major 'up–down' isomer illustrated by filled bonds.

Table 6 Selected bond lengths (Å) and angles (°) **4**

Li–Cl	2.398(5)	Li–Cl′	2.416(5)
Li–N(2)	2.028(5)	Li–N(5)	2.037(6)
C(1)–N(1)	1.377(3)	C(1)–N(2)	1.293(3)
C(1)–N(3)	1.369(3)	C(8)–N(4)	1.366(4)
C(8)–N(5)	1.295(4)	C(8)–N(6)	1.377(4)
H(1)· · ·Cl	2.45	H(4)· · ·Cl′	2.47
N(2)–Li–N(5)	102.9(2)	N(2)–Li–Cl	109.7(2)
N(2)–Li–Cl′	114.9(2)	N(5)–Li–Cl	119.3(2)
N(5)–Li–Cl′	110.0(2)	Cl–Li–Cl′	100.7(2)
N(1)–C(1)–N(2)	117.0(2)	N(1)–C(1)–N(3)	116.7(2)
N(2)–C(1)–N(3)	126.2(2)	N(4)–C(8)–N(5)	117.8(3)
N(4)–C(8)–N(6)	116.5(2)	N(5)–C(8)–N(6)	125.7(2)

Symmetry operation: ′ $-x, -y + 1, -z$

hppH crystallises as the hydrogen bridged dimer with two NH · · · N interactions [2.08 and 2.09 Å], similar to the reported structures of the neutral amidine MeC{NAr}{NHAr} (Ar = $2,6\text{-}^{i}Pr_2C_6H_3$).[15] Such an interaction is attainable due to the enforced E_{anti} configuration of the nitrogen substituents arising from their incorporation within the bicyclic framework of the molecule. The NH atom is disordered over two positions (occupancy 0.5 : 0.5) and, as a consequence, the carbon–nitrogen distances within the amidine moiety [1.328(2) and 1.331(2) Å] are commensurate with a delocalised bonding situation with an insignificant Δ_{CN} value. As is often the case with this bicyclic framework, disorder is observed in one of the β-methylene units (labeling with respect to CN$_2$) where the C(6) carbon atom is located above and below the plane defined by the 'CN$_3$' core of the molecule (Fig. 4(b)). The relative occupancies in this case are 0.71 and 0.29 with the predominant structure consisting of an 'up-down' arrangement of the C(6) and C(3) β-methylene units, respectively.

Having previously demonstrated that hppH is an effective ligand at copper(I) centres,[2,4] we were interested in investigating its potential to function as a neutral ligand at alternative metals. It was noted as part of White's previously mentioned study on adduct formation that substituted pyridine complexes of the lithium halides LiX (X = Cl, Br or I) often formed analogous structures to those observed in the copper(I) complexes. For example, when L = 3,5-Me$_2$-py or 4-^{t}Bu-py, the halides of both copper(I) and lithium form tris-ligand complexes [MXL$_3$], whilst the *ortho*-methyl substituted base L = 2-Me-py adopts the dihalobridged dimer structures, [L$_2$MX$_2$ML$_2$], in the solid state.[25,26] We therefore decided to investigate the solid state structure of the hppH adduct of lithium chloride, and compare it with the copper(I) complex, CuCl(hppH)$_2$.

The bis-ligand complex, [LiCl(hppH)$_2$]$_n$ (**4**) was generated from the reaction of two equivalents of the guanidine with LiCl in THF at room temperature. The ν(C=N) stretch in the IR spectrum (1636 cm^{-1}) is virtually unchanged when compared with the non-coordinated hppH value (1641 cm^{-1}), and the mass spectrum was similarly uninformative, with the highest molecular weight fragment (m/z = 138) only indicating the presence of the ligand. Combustion analysis was consistently inaccurate for the predicted bis-ligand complex [LiCl(hppH)$_2$]$_n$ which we attribute to the presence of a small amount of hydroxide contamination of the 'anhydrous' LiCl starting material, where it has previously been noted that absolute dryness of the starting material is not easily attained.[26] To unambiguously determine the molecular structure of **4**, an X-ray diffraction study was performed on representative crystals. The structure is illustrated in Fig. 5(a), crystal data are summarised in Table 1 and selected bond lengths and angles in Table 6.

In contrast to the molecular structure of the copper(I) chloride adduct of hppH, which is monomeric with a trigonal-planar metal centre, compound **4** exists as the μ,μ-dichlorobridged dimer, with each lithium atom coordinated by two N$_{imine}$ bound hppH ligands in a distorted tetrahedral geometry [angles in the range 100.7(2)–119.3(2)°]. The carbon–nitrogen distances within the ligand framework indicate a tendency towards localised single and double bonds, with Δ_{CN} values of 0.085 Å and 0.068, considerably larger than in the corresponding Cu(I) monomer [0.029 and 0.043 Å]. The C–N$_{amide}$ bond lengths [1.369(3) and 1.377(4) Å] are also shorter than predicted for

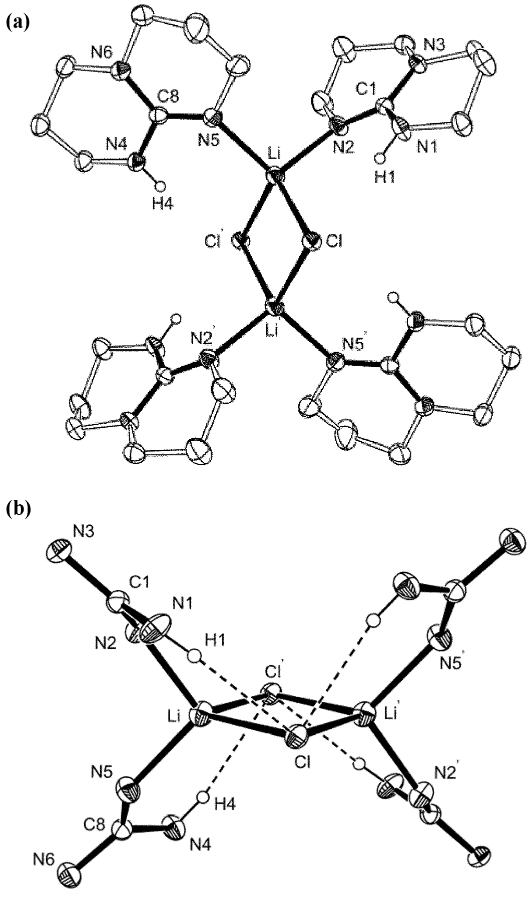


Fig. 5 (a) Molecular structure of $[LiCl(hppH)_2]_2$ (**4**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms excluding NH omitted. (b) Core of **4** illustrating H-bonding interactions to both primary and secondary chlorine atoms.

single $C(sp^2)$–N distance *ca.* 1.42 Å,[11] indicating some delocalisation of the nitrogen lone pair into the ligand π-system.

In contrast to the central metallacycle within compound **1**, the 'Li_2Cl_2' core of **4** forms a much more symmetrical structure with Li–Cl and Li–Cl′ distances of 2.398(5) and 2.416(5) Å, respectively. A plausible explanation for the observed similarity in bond length becomes apparent upon consideration of the NH ··· Cl hydrogen bonding interactions, where it is found that in contrast to **1**, each ligand of the metal centre is hydrogen-bonded to a different chloride ion with distances of 2.45 and 2.47 Å (Fig. 5(b) and Scheme 2). Thus we can consider any stabilisation from NH ··· Cl interactions as being approximately equal to the 'primary' and "secondary' chlorides, with the resultant structure of **4** containing an effectively symmetrical metallacyclic core.

Despite a wealth of information concerning the diversity of solid-state structures adopted by copper(I) halides incorporating unidentate N-donor ligands, extension to the heavier silver(I) congeners is somewhat restricted. It is reported that, even upon recrystallisation from the neat base, only well formed crystals of non-complexed AgCl are isolated when 2- or 4-methylpyridine is employed,[27] and, whilst under similar experimental conditions evidence exists for adduct formation with piperidine, morpholine and triethylamine, only quinoline afforded crystals suitable for an X-ray diffraction study, revealing the 1 : 1 complex.[28] The only structurally characterised example of a 2 : 1 ligand to silver chloride complex, to date, is the bis-piperidine adduct which forms an infinite one-dimensional –Cl–Ag–Cl–Ag– polymer chain with four-coordinate silver centres.[29] The related cationic silver triflate complex, $[Ag(PhHC\{NPh\}\{NHPh\})_2]^+[SO_3CF_3]^-$, should also be noted, consisting of a well separated ion pair with a linear coordination geometry at silver.[18] In light of the stabilising intramolecular NH ··· Cl interactions that favour formation of monomeric copper(I) halides[4] we decided to investigate the formation of hppH adducts at silver(I) chloride.

Table 7 Selected bond lengths (Å) and angles (°) **5**

Ag–Cl	2.550(1)	Ag–N(1)	2.197(3)
Ag–N(4)	2.191(3)	C(1)–N(1)	1.303(4)
C(1)–N(2)	1.348(4)	C(1)–N(3)	1.356(4)
C(8)–N(4)	1.306(4)	C(8)–N(5)	1.353(4)
C(8)–N(6)	1.360(4)	H(2n) ··· Cl	2.71
H(5n) ··· Cl	2.80		
N(1)–Ag–N(4)	128.25(9)	N(1)–Ag–Cl	115.55(7)
N(4)–Ag–Cl	115.81(7)	N(1)–C(1)–N(2)	118.6(3)
N(1)–C(1)–N(3)	124.4(3)	N(2)–C(1)–N(3)	117.0(3)
N(4)–C(8)–N(5)	118.1(3)	N(4)–C(8)–N(6)	124.4(3)
N(5)–C(8)–N(6)	117.5(3)		

Addition of two equivalents of a THF solution of hppH to a slurry of AgCl also in THF resulted in gradual dissolution of the solid over a 48 h period, during which time light was excluded from the reaction. A pale pink solid was isolated from the reaction upon removal of the volatiles and crystallisation from toluene afforded colourless crystals. Combustion analysis was consistent with formation of the bis-ligand complex $[AgCl(hppH)_2]_n$ (**5**), although mass spectrometry was once again uninformative. ^1H NMR data indicated a symmetrical environment for the bicyclic guanidine with a low field resonance at δ 7.77 assigned to the ligand NH proton. To determine the degree (if any) of oligomerisation within **5** the X-ray diffraction study was performed on representative crystals. The molecular structure is illustrated in Fig. 6, crystal data are summarised in Table 2 and selected bond lengths and angles in Table 7.

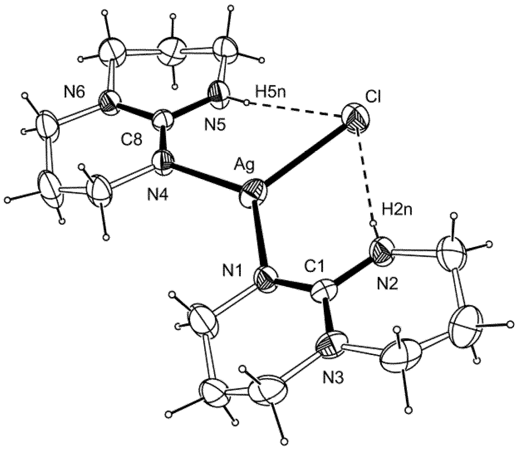


Fig. 6 Molecular structure of $AgCl(hppH)_2$ (**5**) with thermal ellipsoids drawn at the 30% probability level.

Compound **5** is isostructural to the copper(I) complex, and exists as a monomeric, trigonal-planar [$\Sigma_{angles} = 359.61°$] silver(I) chloride unit supported by two N_{imine} bound hppH ligands. This structure represents the first example of a three-coordinate silver(I) centre supported by nitrogen-based ligands, and is a likely consequence of the intramolecular NH ··· Cl stabilisation [H(2n) ··· Cl 2.71 Å; H(5n) ··· Cl 2.80 Å] resulting in a 'pseudo-chelating' bonding mode for the ligand with interactions at both the metal and the halide atoms. The carbon–nitrogen bond lengths within the guanidine core are similar to related complexes in which the ligand is acting as an N_{imine} donor with Δ_{CN} values of 0.045 and 0.047 Å indicating partial retention of the single and double bonds. The Ag–N distances [2.197(3) and 2.191(3) Å] in **5** are significantly shorter than in the aforementioned bis(piperidine) complex [2.385(8) and 2.347(11) Å],[29] a likely consequence of the reduced coordination geometry at the metal in **5**.

The Ag–Cl distance in **5** [2.550(1) Å] is comparable to that in the recently reported bis(triphenylphosphine) complex [2.539 Å],[30] but significantly longer than in the corresponding bis(tricyclohexylphosphine) complex [2.489(1) Å].[31] This suggests similar electronic donor properties from both the hppH and PPh_3 ligands, although it is difficult to make direct comparisons due to differences in the steric demands of the two ligand classes (*vide infra*). For example, the greater the Ag–X bond length, the closer this may be considered to an ionic bonding situation, where the extreme case corresponds to the ion-pair, $[AgL_2]^+[Cl]^-$, consisting of a linear L–Ag–L unit. However, comparison of this angle (θ) in the three-coordinate silver complexes above shows by far the largest P–Ag–P angle in the triphenylphosphine complex [137.17°] with indistinguishable values for the tricyclohexylphosphine [128.29(3)°] and **5** [128.25(9)°]. It is also likely that intramolecular H-bonding in **5** will influence both the Ag–Cl distance and the L–Ag–L angle.

Our initial interest in hppH bound copper(I) complexes focused on the application of such species as catalysts for the atom transfer radical polymerisation (ATRP) of methacrylates.[4] We demonstrated (by variable temperature NMR studies) that, for the precursor bis-ligand halide complexes, a fluxional process existed in solution likely involving decoordination of the guanidine from the 'CuX' fragment, and that this was a lower energy process than in Cu(I) bipy and pyridine imine systems.[32] We reasoned that by substituting one of the hppH ligands with a second ligand providing a greater electron-withdrawing effect or binding through an element with π-acceptor properties, a more electron deficient metal would result leading to an increased interaction of the N_{imine} lone pair and hence a stronger N–Cu interaction. As phosphines have been extensively used as neutral donors at copper(I) centres, we decided to focus initially on targeting the mixed ligand complexes $[CuX(hppH)(PPh_3)]_n$. In addition, the synthesis of a coherent series of complexes will allow a more meaningful delineation of the relative influences of the steric and electronic factors contributing to the bonding of hppH compared with PPh_3.

The mixed ligand complexes $[CuX(hppH)(PPh_3)]_n$ (**6**, X = Cl, n =1; **7**, X = Br, n = 2; **8** X = I, n = 2) were synthesised directly by the addition of a 1 : 1 mixture of hppH and PPh_3 in THF, to a slurry of CuX also in THF. The resultant complexes **6**–**8** are soluble in this solvent so that on complete addition, a clear solution is obtained. Crystallisation by slow cooling of a warmed, saturated solution to room temperature afforded the desired complex as off-white crystals in good (66–72%) yields. Spectroscopic (^{1}H, ^{13}C, ^{31}P NMR; IR) data were consistent with the incorporation of one guanidine and one phosphine per 'CuX' unit, and mass spectral analysis of **6** indicated a molecular ion peak corresponding to the monomeric unit [m/z 499].

In each of the compounds **6**–**8**, three resonances attributable to the guanidine methylene groups are observed in the room temperature ^{1}H NMR spectra, suggesting a similar fluxional process to that observed in the bis(hppH) adducts.[4] This was examined by variable temperature NMR experiments, the results of which are presented in Table 8. It is clear from these data that a higher energy barrier to the observed fluxional process is evident in the mixed ligand complexes compared with the $CuX(hppH)_2$ species, with values an average of 4.4 kJ mol^{-1} greater. This is in agreement with the supposition that ligand decoordination must occur in order to render the methylene units equivalent on each ring of the bicyclic guanidine, with a stronger $N_{imine} \longrightarrow Cu$ interaction observed upon replacement of the second hppH with a less basic PPh_3. Comparison of the different values within the two series of compounds reveals a similar trend in each, with a significantly higher value observed for the bromide. Presumably in this case the correct balance of steric and electronic factors are present to favour coordination of the guanidine and enhance intramolecular stabilisation. In order to further understand these observations, X-ray crystallographic studies were undertaken on compounds **6**–**8**; the molecular structures of **6** and **8** are illustrated in Figs. 7 and 8, crystal data are summarised in Table 2 and selected bond lengths and angles in Tables 9–11.

Table 8 Activation parameters for the fluxional process involving the hppH ligand

Compound	$\Delta G^{\ddagger a}$/kJ mol^{-1}
$CuCl(hppH)_2$	45.8 ± 0.2
$CuBr(hppH)_2$	47.2 ± 0.4
$CuI(hppH)_2$	44.9 ± 0.4
$CuCl(hppH)(PPh_3)$	50.2 ± 0.5
$[CuBr(hppH)(PPh_3)]_2$	51.6 ± 0.4
$[CuI(hppH)(PPh_3)]_2$	49.4 ± 0.2

[a] Values calculated from variable temperature ^{1}H NMR spectroscopy at 500 MHz in d_8-toluene.

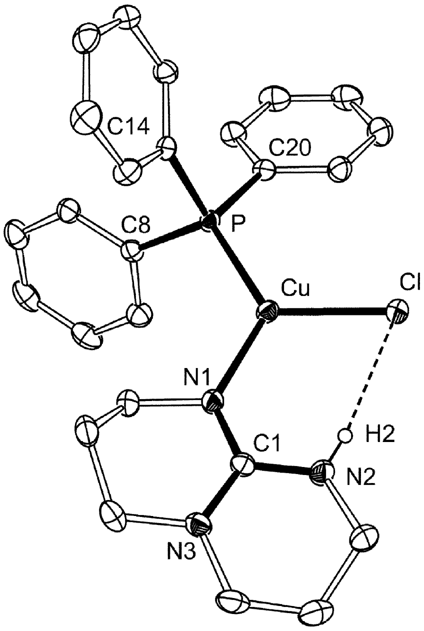


Fig. 7 Molecular structure of $CuCl(hppH)(PPh_3)$ (**6**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except NH omitted.

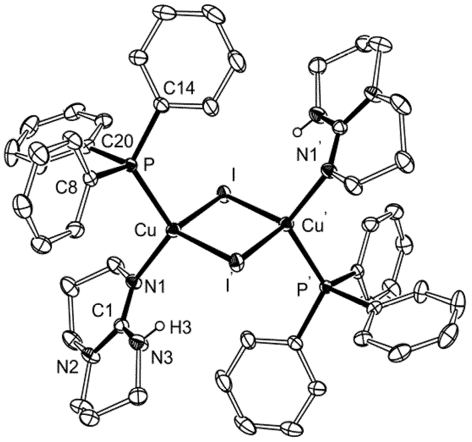


Fig. 8 Molecular structure of $[CuI(hppH)(PPh_3)]_2$ (**8**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except NH omitted.

In agreement with spectroscopic data, compounds **6**–**8** each exist as the mixed ligand compounds $[CuX(hppH)(PPh_3)]_n$. The chloride forms a monomeric, distorted trigonal planar copper centre (n = 1) while the bromide and iodide are isomorphous and consist of a dimeric structure (n = 2) with distorted tetrahedral metal atoms. Compound **6** is therefore most closely related to the bis(hppH) analogue, with the Σ_{angles} at Cu = 360° and an intramolecular NH ··· Cl interaction [2.47 Å]. The carbon–nitrogen distances within **6** again reveal a relatively low Δ_{CN} value [0.028 Å] suggesting a degree of delocalisation. Compounds **7** and **8** each contain distorted tetrahedral coppers with angles in the range 115.42(6)–101.70(5)° and 116.96(5)–102.20(5)°, respectively, with NH ··· X distances of 2.67 Å (**7**) and 2.83 Å (**8**). Using the same argument presented above, the hydrogen bonds in **7** and **8** may be considered as being to the primary halide in each case. Slightly larger Δ_{CN} values [**7**, 0.058 Å; **8**, 0.048 Å] imply a greater degree of localisation within the guanidine compared with the monomeric chloride, **6**.

Table 9 Selected bond lengths (Å) and angles (°) for **6**

Cu–N(1)	1.9722(15)	Cu–P	2.2018(5)
Cu–Cl	2.2718(5)	C(1)–N(1)	1.323(2)
C(1)–N(2)	1.351(3)	C(1)–N(3)	1.355(2)
H(2) ··· Cl	2.47		
P–Cu–N(1)	122.85(5)	P–Cu–Cl	121.115(19)
N(1)–Cu–Cl	116.02(5)	N(1)–C(1)–N(2)	118.52(16)
N(1)–C(1)–N(3)	123.55(17)	N(2)–C(1)–N(3)	117.87(17)
C(8)–P–Cu	115.30(6)	C(14)–P–Cu	113.25(6)
C(20)–P–Cu	117.29(6)	C(8)–P–C(14)	101.99(8)
C(8)–P–C(20)	102.52(8)	C(14)–P–C(20)	104.68(8)

Table 10 Selected bond lengths (Å) and angles (°) **7**

Cu–N(1)	2.0179(19)	Cu–P	2.2111(6)
Cu–Br	2.5807(4)	Cu–Br′	2.5272(3)
C(1)–N(1)	1.305(3)	C(1)–N(2)	1.359(3)
C(1)–N(3)	1.363(3)	H(3) ··· Br′	2.67
P–Cu–N(1)	115.42(6)	P–Cu–Br	106.136(18)
P–Cu–Br′	113.367(19)	N(1)–Cu–Br	101.70(5)
N(1)–Cu–Br′	113.69(5)	Br–Cu–Br′	104.868(11)
N(1)–C(1)–N(2)	125.1(2)	N(1)–C(1)–N(3)	118.0(2)
N(2)–C(1)–N(3)	116.8(2)	C(8)–P–Cu	115.39(7)
C(14)–P–Cu	118.44(8)	C(20)–P–Cu	110.82(7)
C(8)–P–C(14)	105.74(10)	C(8)–P–C(20)	102.11(10)
C(14)–P–C(20)	102.38(10)		

Symmetry operation: ′ $-x$, $-y$, $-z$.

Table 11 Selected bond lengths (Å) and angles (°) for **8**

Cu–N(1)	2.0282(17)	Cu–P	2.2377(5)
Cu–I	2.7248(3)	Cu–I′	2.6791(3)
C(1)–N(1)	1.310(3)	C(1)–N(2)	1.364(3)
C(1)–N(3)	1.358(3)	H(3) ··· I′	2.83
P–Cu–N(1)	113.85(5)	P–Cu–I	105.548(15)
P–Cu–I′	109.021(16)	N(1)–Cu–I	102.20(5)
N(1)–Cu–I′	116.96(5)	I–Cu–I′	108.285(9)
N(1)–C(1)–N(2)	124.81(19)	N(1)–C(1)–N(3)	118.47(18)
N(2)–C(1)–N(3)	116.64(19)	C(8)–P–Cu	114.51(7)
C(14)–P–Cu	119.60(7)	C(20)–P–Cu	110.55(6)
C(8)–P–C(14)	105.16(9)	C(8)–P–C(20)	102.25(9)
C(14)–P–C(20)	102.81(10)		

Symmetry operation: ′ $-x$, $-y$, $-z$.

Synthesis of **6**–**8** allows us to assess the different properties of hppH as a ligand compared to PPh_3, through comparison of bond lengths and angles with the previously reported CuX(PPh_3)$_2$ and CuX(hppH)$_2$ compounds (Table 12). The most valid series is comprised of the chlorides as each of the compounds crystallises as the monomeric species in the solid state. The bis(triphenylphosphine) adduct has been reported as both the hemi-THF solvate (entry 3),[33] and the hemi-benzene solvate (entry 4);[34] the structures are essentially identical and will be discussed together. It is also noted that the compound also crystallises as the μ,μ′-dichlorobridged dimer, with one molecule of acetone.[35]

On sequential replacement of an hppH ligand by PPh_3 we can see a notable shortening of the Cu–Cl bond distance from approximately 2.40 to 2.21 Å, consistent with an increased withdrawal of electron density from the metal by the phosphine (in agreement with the solution state behaviour, *vide supra*). However we do not observe a similar reduction of the Cu–N distances (entries 1 and 2) which may reflect steric interactions between the donor ligands in the solid-state, substantiated by comparison of the mixed ligand compound with the bis(phosphine) adducts, where introduction of a second PPh_3 group greatly increases both of the Cu–P distances. Steric interactions are also presumed to be the cause of the variation in L_1–Cu–L_2 angles (θ) which is largest for the bis(guanidine) derivative.

Further comparisons are complicated by the dimeric nature of compounds **7** and **8** and the accompanying change from trigonal to tetrahedral geometry; however both of the end members of the series for the bromides are monomeric (entries 6 and 8).[36] A similar shortening of the Cu–Br distance is evident on replacing the guanidines with phosphines, and comparable θ-values to the chlorides are noted. Comparing analogous compounds **7** and **8** we observe an increase in both the Cu–N and Cu–P distances when replacing the bromide with an iodide, reflecting the increased electron density at the metal.

In summary, X-ray diffraction studies of a number of monovalent halides of copper, lithium and silver incorporating neutral amidines and guanidines are presented, demonstrating a wide diversity in the types of structure adopted in the solid-state. Examples of monomeric (trigonal planar) and dimeric (tetrahedral) metal centres are reported, incorporating one or two donor ligands. The presence of different patterns of intramolecular NH ··· X (X = halogen) stabilisation are noted, and synthesis of the series of compounds [CuX(hppH)(PPh_3)]$_n$ has permitted a brief discussion of the relative donor properties of the two ligands to be carried out.

Table 12 Metrical parameters for the series of compounds $[CuX\{L_1\}\{L_2\}]_n$ (X = Cl, Br, I; L_1 and L_2 = hppH or PPh_3; n = 1 or 2; $\theta = L_1$–Cu–L_2 angle)

Entry	L_1	L_2	X	n	Cu–L_1/Å	Cu–L_2/Å	Cu–X/Å	Cu–X′/Å	θ/°	Ref.
1	hppH	hppH	Cl	1	1.962(2)	1.966(2)	2.3977(8)	–	130.37(9)	4
2	PPh_3	hppH	Cl	1	2.2018(5)	1.9722(15)	2.2718(5)	–	122.85(5)	This work
3	PPh_3	PPh_3	Cl	1[a]	2.2564(9)	2.2676(9)	2.214(1)	–	125.55(4)	33
4	PPh_3	PPh_3	Cl	1[b]	2.272(2)	2.260(2)	2.208(2)	–	125.48(7)	34
5	PPh_3	PPh_3	Cl	2[c]	2.279	2.295	2.401	2.403	116.49	35
6	hppH	hppH	Br	1	1.962(3)	1.962(3)	2.5611(5)	–	130.49(10)	4
7	PPh_3	hppH	Br	2	2.2111(6)	2.0179(19)	2.5807(4)	2.5272(3)	115.42(6)	This work
8	PPh_3	PPh_3	Br	1[d]	2.282(3)	2.263(3)	2.346(2)	–	126.0(1)	36
9	hppH	hppH	I	1	–	–	–	–	–	4
10	PPh_3	hppH	I	2	2.2377(5)	2.282(17)	2.7248(3)	2.6791(3)	113.85(5)	This work
11	PPh_3	PPh_3	I	1	2.273(2)	2.273(2)	2.524(2)	–	126.9(1)	34

[a] $(THF)_{0.5}$ solvate. [b] $(C_6H_6)_{0.5}$ solvate. [c] (acetone) solvate. [d] $(C_6H_6)_{0.5}$ solvate.

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