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Contrasting Connectivity of Amidine and Phosphaamidine (1,3-P,N) Cu(I) complexes

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A B S T R A C T

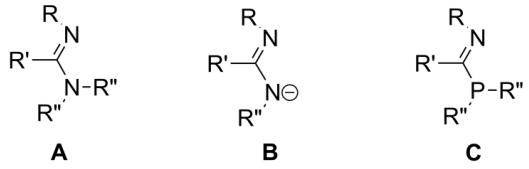
Aprotic acetamidine $\{Me_2N–C(Me)=N(R)(CuBr)\}_2$ {R = ^{i}Pr (**2a**), Cy (**2b**), Ph (**2c**)} and neutral 1,3-P,N phosphaamidine copper bromide complexes $\{(CuBr)(Ph_2PC(Ph)=NPh)\}_4$ (**6a**), $\{(CuBr)_4(Ph_2PC(Ph)=N^iPr)_2\}\cdot\{2CH_2Cl_2\}$ (**6b**), $(CuBr)_4$ ($^iPr_2PC(Ph)=NPh)_2$} (**7a**) and $\{(CuBr)_4(^iPr_2PC(Ph)=N^iPr)_2\}$(**7b**) are prepared by direct combination of corresponding amidine and phosphaamidine with CuBr(DMS). X–ray crystallographic analysis of the acetamidine complexes reveal monodentate N_{imine} coordination to copper with significant degree of delocalization about the N–C=N framework and a relatively short Cu–Cu interaction of 2.5758(8) Å in **2c** compared to (2.9801)(10) Å **2a**. The phosphaamidine ligands are never η^1–N_{imine} bound; instead they are η^1–P bound in the cubane complex **6a** or η^2–bound in the step cluster complexes **6b**, **7a** and **7b**.

Keywords: Amidines, Phosphaamidines, Hemilabile ligands, Copper(I) complexes

1. Introduction

Nitrogen-based ligands have played an integral role in the development of coordination chemistry, with a historical focus on pyridine-derived ligands [1]. Pyridine-based ligands are attractive for coordination chemistry as a result of their structural diversity and substituent tenability [2]. Amidines (**A** in Scheme 1) are another class of nitrogen–based ligands, with a similar degree of electronic and steric tunability, but they have received far less attention [3]. The most widespread application of amidine-derived ligands in transition metal [4] and main group chemistry [5] are the anionic amidinates (**B**) rather than the neutral amidines themselves.

Research in our laboratory has exploited the basicity of amidines in reactions with CO_2, in aqueous or alcoholic media, for the generation of amidinium bicarbonate/carbonate salts [6] for applications as ionic liquids [7] and surfactants [8]. We have also explored the use of amidines as promoters of CO_2 fixation to other products [9] and thus a natural extension of our research program leads to the preparation of amidine-metal complexes.



Scheme 1. Amidines, amidinate anion and phosphaamidine

A modest number of examples of cyclic amidine-metal complexes, such as η^1–N_{imine} complexes of imidazole [10], DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) [11], and DBN (1,5-diazabicyclo[4.3.0]non-5-ene) [12], exist in the literature. In addition, examples involving bidentate chelating amidines as ligands, either as a bisamidine [13], or pyridyl substituted amidine [14] have been reported. However, acyclic amidine-metal complexes are comparatively scarce. Complexes of formamidine [15,16], benzamidine [15c,17], and protic acetamidines [18] with η^1–N_{imine} have been observed but no examples of aprotic acetamidines complexes (aprotic in the sense of lacking an N–H bond) have been reported so far to the best of our knowledge.

Because there might be significant advantages to having the N_{imine} atom available for ligand–based reactivity, one might prefer that atom to be either weakly bound to the metal (e.g. in an η^2–binding geometry) or unbound (e.g. in an η^1–N_{amine}), we chose to also explore the chemistry of acyclic phosphaamidines, in which a phosphorus atom replaces the N_{amine} (**C**, Scheme 1). Phosphaamidines have been made by the reaction of acid chloride (N-phenyl imide chloride of benzoic acid) with $MePR'_2$ (R' = C_6H_5) to give $RC(NR)\text{-}PR'_2$ [19]. A few examples of such 1,3-P,N ligands have been prepared by reaction of imidoyl chloride or *N*–aryl formimidates with alkali metal phosphide [20] or silylphosphanes [21]. Recently, Lammertsma and his groups prepared phosphaamidines using nitrilium ions as an imine synthon [22], while different routes for preparation of phosphaamidines are being explored, the coordination chemistry of such ligands with transition metals have received little attention [22a,22c,23].

The substitution of N_{amine} of amidine with phosphorus should encourage transition metal binding to the P atom, leaving the N_{imine} atom either unbound or weakly coordinated. The anticipated advantages of a free or hemilabile N_{imine} atom include its Brønsted basicity for proton transfer and its nucleophilicity for CO_2 binding. While those aspects are currently being explored, the subject of this paper is a comparison of the binding geometries of aprotic acyclic amidines and phosphaamidines, to determine whether a soft metal such as Cu(I) would bind exclusively to the phosphorus atom, leaving the basic N_{imine} atom free, or whether the N_{imine} would also be bound. In this study, we restrict the discussion to acyclic and aprotic amidines and phosphaamidines and their copper(I) complexes.

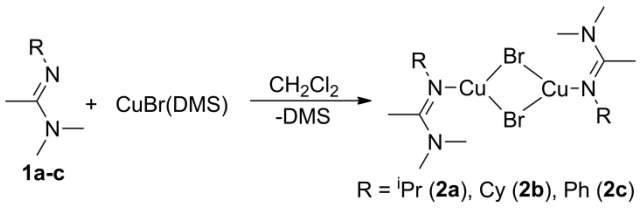
2. Results and discussion

2.1. Synthesis of amidine Cu(I) Complexes

The coordination chemistry of a protic acyclic amidine with Cu(I) has been studied before. Coles and co-workers reported the preparation of a *N*,*N*'–diphenylbenzamidine copper complex $[CuCl(PhC\{NPh\}\{NHPh\})_2]_2$ via direct combination of the benzamidine ligand with CuCl in THF solution [17]. Each Cu(I) is coordinated with the N_{imine} atoms of two benzamidine ligands with the ligand coordination supported by the intermo-

lecular hydrogen bonding of the N_{amine}–H proton to bridging chloride atoms.

We studied amidine Cu(I) complexes but using amidines that contain no N–H bonds. The binding geometry is affected by this change because intermolecular hydrogen bonding is prevented. The direct combination of a CH_2Cl_2 solution of acetamidine **1a**–**b** with an equimolar suspension of CuBr·dimethylsulfide (DMS) in CH_2Cl_2 at ambient temperature (Scheme 2) results in the gradual formation of a clear orange solution within 30 min. Removal of all volatiles from the reaction solution yields an orange oil (an orange foam (R = ^{i}Pr (**2a**), Cy (**2b)**). ^{1}H NMR spectroscopic characterization, in $CDCl_3$, of the crude material reveals downfield shifts for the diagnostic $N(CH_3)_2$ and N–C(CH_3)=N protons, in addition to downfield shifts for the R substituent protons compared to the free ligand.[Supporting information (SI)] Crystals of **2a** were grown via Et_2O vapour diffusion into a saturated CH_2Cl_2 solution at –15 °C and its molecular structure was determined by a single–crystal X–ray diffraction study (Figure 1, crystallographic data in the SI).



Scheme 2. Synthesis of acetamidine Cu(I) Complexes

Direct combination of acetamidine **1c** with CuBr(DMS) in CH_2Cl_2 did not result in an observable reaction as was observed for **1a-b**, even at elevated temperatures (40 °C) because of the low basicity of **1c** (pK_{aH} 8.3) compared to **1a**–**b** (pK_{aH} 12.3–12.5) [24]. Product **2c** was prepared under neat conditions at an elevated temperature with addition of twelve equivalents of **1c** to CuBr(DMS), which gradually formed a yellow solution after 2 h at 55 °C. ^{1}H NMR spectroscopy of the crude material suggested coordination of **1c** to copper from the diagnostic downfield shifts compared to the free ligand, although the magnitude of the shifts were smaller than those observed for **2a**–**b**. **2c** crystals were grown and subjected to a single-crystal X–ray diffraction study (Figure 1, crystallographic information in SI).

The molecular structure of **2a** (Figure 1) exists as a μ,μ-dibromobridged dimer with a N_{imine}–Cu bond length of 1.968(3) Å. No close contact is present between the amine nitrogen and Cu. The Cu–Cu distance is 2.9801(10) Å, which is greater than the sum of the covalent radii of two Cu atoms (2.34 Å) [25], indicating the absence of a Cu–Cu bond. The extent of delocalization within the N–C=N framework can approximately be described by Δ_{CN}, where Δ_{CN} equals the bond length difference between a C–N single bond of an

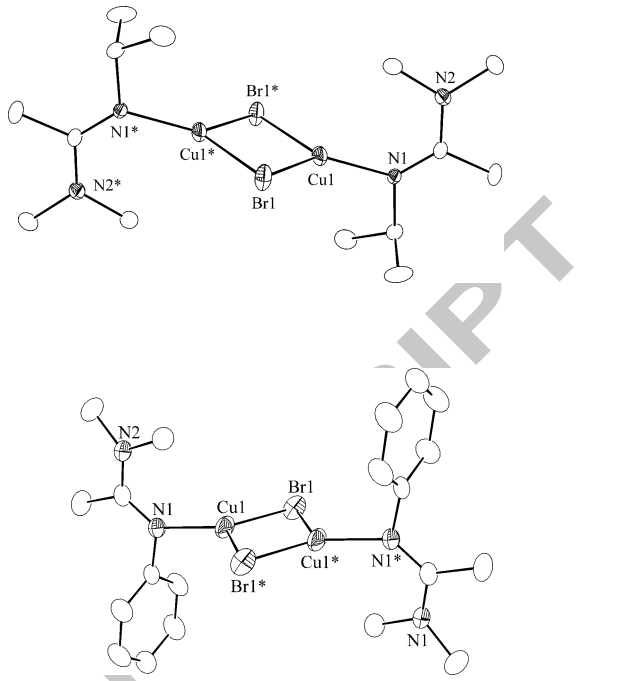


Figure 1. Molecular structure of **2a** (top) and **2c** (below) showing displacement ellipsoids at the 50% probability level. The hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms for **2a**: *: 1 - x, -y, -z and **2c**: *: 1 - x, 1 - y, 1 - z.

amine (~1.46 Å) and a C=N double bond of an imine (~1.28 Å). A value of Δ_{CN} = 0 Å indicates a fully delocalized system whereas a value of ~0.18 Å indicates a fully localized system [21]. For **2a** the N_{imine}– C(4) and N_{amine}–C(4) bond lengths are similar at 1.296(4) Å and 1.352(5) Å respectively with a Δ_{CN} of only 0.056 Å, which indicates a significant degree of delocalization. The sum of bond angles around the amine nitrogen is 360°, i.e. a planar nitrogen, and thus further supports the description of a delocalized system in the N–C=N framework. The sum of bond angles around the imine N (N1) is also 360°, showing that the Cu is coplanar with the amidine, consistent with a sigma coordination.

The molecular structure of **2c** is analogous to that of **2a**. The Cu–Cu distance is shorter at 2.5758(8) Å, with a N_{imine}–Cu bond length of 1.971(3) Å. The N_{imine}– C(7) and N_{amine}–C(7) bond lengths are again similar at 1.301(4) Å and 1.353(4) Å respectively with a Δ_{CN} of only 0.052 Å. With a sum of bond angles of 359°, the amine nitrogen again adopts a planar geometry, thus indicating a significant degree of delocalization. Again, the Cu is coplanar with the amidine. While the molecular structures of **2a** and **2c** are similar, it is interesting to note that they are appreciably different from the analo-

gous benzamidine copper chloride [17], where binding appears to be supported by intramolecular hydrogen bonding between the amidine proton and the bridging halide atoms; an interaction which is not possible with our aprotic amidines.

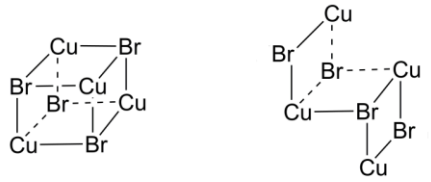
2.2. Synthesis of phosphaamidines

The phosphaamidines were prepared from imidoyl chloride (**3a**, **3b**) which was itself prepared from benzoyl chloride [26]. A lithiated secondary phosphine (Ph_2PLi or $^iPr_2PLi$) [27], was reacted with imidoyl chloride [PhC(Cl)NR'] (R' = ^{i}Pr or Ph) in situ or separately to give phosphaamidines (Scheme 3). All the phosphaamidines were obtained in pure form with little purification required, in 35 to 88% yield. Phosphaamidine, *N*–[(diphenylphosphino)phenylmethylene] benzenamine ($Ph_2PC(Ph)=NPh$) **4a** which has been reported before [19], was prepared by using lithiated diphenyl phosphine instead of the published reagent methyl diphenyl phosphine. **4a,** *N*–[(diphenylphosphino)phenylmethylene] isopropylamine ($Ph_2PC(Ph)=N^iPr$) (**4b**), and *N*–[(diisopropylphosphino)phenylmethylene]benzenamine ($^iPr_2PC(Ph)=NPh$) (**5a**) were obtained in solid form while *N*–[(diisopropylphosphino)phenylmethylene]isopropylamine ($^iPr_2PC(Ph)=N^iPr$) (**5b**) was obtained as a viscous liquid. Compound **4b** has been reported recently by the reaction of diphenylphosphane with either pyridine or dimethylaminopyridine (DMAP) adduct and is obtained in the form/mixture of *E* and *Z*-conformers [22b]. $^{31}P\{^1H\}$ NMR spec trum at 6.95 ppm and –8.68 ppm shows two types of conformer. The identity of each product was confirmed by ^1H, ^{13}C, $^{31}P\{^1H\}$ NMR, EI–MS and EI–HRMS (SI)

Scheme 3. Synthesis of phosphaamidine ligands

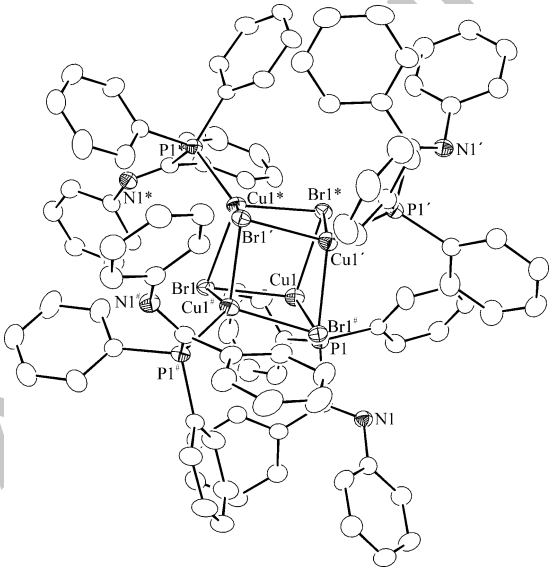
2.3. Phosphaamidine Cu(I) complexes

CuBr(DMS) was reacted with phosphaamidines to compare the coordination modes of the phosphaamidines to those of the amidines. Compound **6a** was prepared by the reaction of a suspension of CuBr(DMS) in CH_2Cl_2 with a yellow solution of **4a** in CH_2Cl_2. A yellow crystalline compound was obtained at –15 °C by slow evaporation of ether into CH_2Cl_2/toluene. The crystal is tetragonal with space group $I4_1/a$. The molecular structure consists of a Cu_4Br_4 cubane core (Scheme 4) with only the phosphaamidine phosphorus coordinated to the Cu(I) leaving the N_{imine} uncoordinated (Fig. 2). Crystallographic information is given in the SI.



Scheme 4. Cubane (left) and step (right)

Figure 2. Molecular structure of **6a** showing displacement

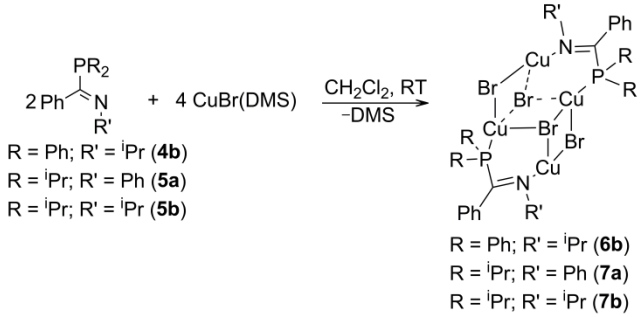


ellipsoids at the 30% probability level. The hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: *: ¼ - y, ¼ + x, ¼ -z; ‘: -x, ½ -y, -z; #: -1/4 + y, ¼ - x, ¼ -z.

The coordination geometry of complex **6a** is significantly different from that of acetamidine complexes **2a** and **2c**; the amidine complexes bind η^1 by the basic N_{imine} atom, while the phosphaamidine in **6a** binds η^1 by the P–phosphine, leaving the basic N_{imine} atom dangling free. A Au(I) phosphanyl trimer with core has been reported with a phosphaamidine coordinated leaving the N_{imine} free [22], the core of **6a** is a Cu_4Br_4 cubane. Other phosphorus ligands like PPh_3 when reacted with copper halide are known to form cubane like [28] or step like [29] cores (Scheme 4), with the type of core depending on the conditions, the metal to phosphine ratio, or the steric properties of the ligand used [30]. The obtained Cu_4Br_4 core is distorted with Br–Cu–Br angles of 100.981(14)° and 101.24(1)° and Cu–Br–Cu angles of 77.81(1)° and 77.98(1)°. The bond lengths and angles are shown in the SI. The failure of the N_{imine} atom to bind to the metal may be due either to steric factors (which would not be surprising considering the large number of phenyl groups around the core) or to the poor basicity of the phenyl-substituted N_{imine} atom. To explore this

further, we made related complexes with other phosphaamidines.

On reaction of **4b**, **5a** and **5b** with CuBr(DMS) in CH_2Cl_2 (Scheme 5), isostructural crystals were obtained with Cu_4Br_4 step core structures, rather than cubane cores. Compound **6b** cocrystallized with two molecules of CH_2Cl_2 in the unit cell.



Scheme 5. Synthesis of copper(I) complexes with **4b**, **5a** and **5b**

The molecular structures of **6b**, **7a** and **7b** are shown in Fig. 3 and the crystallographic information is given in SI. Such step type structures are common for CuCl or CuBr complexes with bidentate ligands [31] but have not previously been reported for phosphaamidine complexes. The core can be denoted as $Cu_4(\mu\text{–}Br)_2(\mu_3\text{–}Br)_2$, where P and three Br atoms coordinate the inner Cu atoms in a distorted tetrahedral geometry and N and two Br atoms coordinate to the outer Cu atoms in a distorted trigonal structure. The four Cu atoms lie in a plane while Br atoms above and below the plane. The Cu–N bond lengths range from 1.954 to 1.970 Å, similar to amidine complexes **2a** (1.968 Å) and **2c** (1.971 Å). However, the C=N bond is slightly longer in η^1–amidines complexes (1.296 Å in **2a** and 1.301 Å in **2c**) than in the η^2–bound phosphaamidine complexes (1.281–1.293 Å) and especially the η^1-phosphamidine complex **6a** (1.268(3) Å), where N_{imine} is free and sp^2 hybridized.

The basicity of the N_{imine} atom in acetamidines played a significant role in the binding of N_{imine} with Cu(I) with **1c**. However, the failure of the basic N_{imine} to bind to the metal in the η^1–P phosphaamidine complex **6a** appears to be the result of the steric bulk of the phenyl rings in **4a** rather than or in addition to the weak basicity of the N_{imine}. If weak basicity alone were the cause then η^2–coordination would not have occurred with the similarly weak basic N_{imine} in complex **7a.**

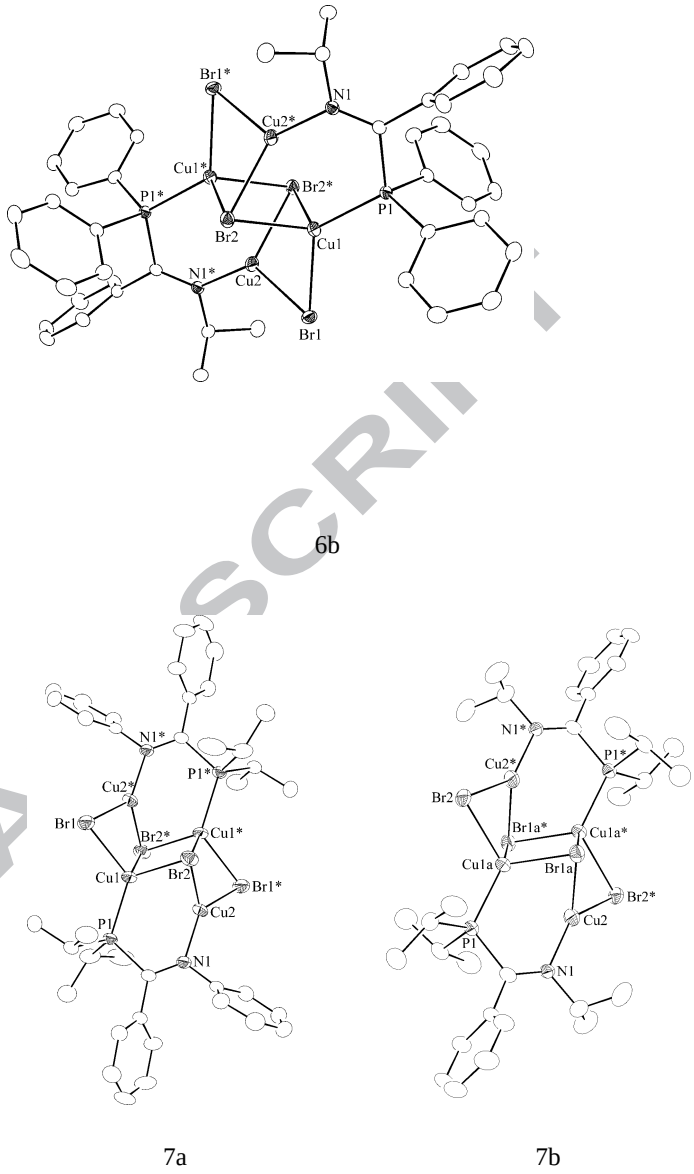


Figure 3. Molecular structure of **6b**,**7a** and **7b** showing displacement ellipsoids at the 50% probability level. Solvent molecules in **6b** are removed for clarity. The hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms **6b**: *: 1 - x, -y, 1 – z, **7a**: *: 1 - x, 1 - y, 1 – z, and **7b**: *: 2 - x, 1 - y, 1 - z.

3. Conclusions

A series of aprotic and acyclic amidine and phosphaamidine Cu(I) bromide complexes have been prepared. Acetamidine ligands **1a** and **1c** coordinate to Cu through solely the N_{imine}. The ease of complex formation is dependent on the basicity of the acetamidine ligand under consideration. X–ray diffraction studies reveal a significant degree of delocalization about the N–C=N framework. The lack of an N–H proton in these aprotic ligands prevents them from coordinating to copper with the same binding geometry

as a protic amidine ligand in an analogous copper complex reported previously [17]. Structurally similar, neutral phosphaamidine ligands coordinate η^1–P with Cu(I)Br to form cubane Cu_4Br_4 complex or η^2–P,N to form step Cu_4Br_4 complexes. Phosphaamidine **4a** coordinated by the P atom alone, leaving N_{imine} free, because of the bulky phenyl group. This steric effect is reduced in other phosphaamidines so that they coordinate through both sites to form step structures. The coordinating ability of these ligands to other metals ions and catalytic properties of such complexes are currently under exploration.

4. Experimental

All reactions were carried out with the exclusion of air and moisture under an atmosphere of pre-purified nitrogen or argon (Praxair), unless otherwise noted, using standard Schlenk techniques or an inert atmosphere glovebox (Vacuum Atmospheres Company). Acetamidines were prepared according to the literature method [24,25]. N-phenylbenzimidoyl chloride and N-isopropylbenzimidoyl chloride were prepared according to the literature method [26]. CuBr(DMS) was purchased from Sigma-Aldrich and used as received. CH_2Cl_2 and $CDCl_3$ were dried by refluxing over CaH_2 for 4 h, followed by distillation prior to use. Et_2O and hexanes were dried by refluxing over sodium ketyl radical for 4 h followed by distillation prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 and 75 MHz respectively) and referenced to protic impurities ($CHCl_3$) in the solvent (^1H) or externally to $Si(CH_3)_4$ ($^{13}C\{^1H\}$). The amidine complexes and phosphaamidine complexes are unstable if exposed to air.

4.1 X-ray diffraction Studies: A crystal of each compound suitable for single–crystal X-ray diffraction was mounted on a glass fiber with grease and cooled to –93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 3.68 ~ 52.00º. No significant decay was observed during the data collection. Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package [32]. Data collection: *APEX2* [32a]; cell refinement: SAINT [32b]; data reduction: SAINT [32b]; absorption correction: SADABS [32c]; structure solution: XPREP [32d]; and SHELXTL [32e]; structure refinement: SHELXTL; molecular graphics: SHELXTL; publication materials: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber [33]. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\sum w (F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically. All H atoms bound to carbon atoms were placed in geometrically idealized position using the appropriate HFIX instructions in SHELXL. The isotropic thermal parameters of these hydrogen atoms were fixed at 1.2 (phenyl-CH, ipso-CH) and 1.5 (CH_3 groups) that of the preceding carbon.

4.2. Preparation of **2a and 2b**. To a suspension of copper bromide dimethyl sulfide in CH_2Cl_2 was added an equimolar amount of acetamidine (**1a** and **2b**) dissolved in CH_2Cl_2. Typical reaction scale was approximately 10 mmol with an overall concentration of approximately 0.01 M. After the mixture was stirred for 2 h, all volatiles were removed from the resulting orange solution. The residue was isolated and purified by precipitation induced by addition of a 5 mL CH_2Cl_2 solution into rapidly stirred hexanes to obtain compounds **2a** and **2b**.

$Me_2NC(Me)=N^iPr\cdot CuBr$ **(2a).** Yellow powder. Yield = 1.84 g, 68%. ^1H NMR ($CDCl_3$): δ = 1.35 (6H, *d*, $^3J_{HH}$ = 6.3 Hz, $C(CH_3)_2$), 2.11 (3H, *s*, CCH_3), 3.31 (6H, *s*, $N(CH_3)_2$), and 3.66 ppm (1H, *sept*, $^3J_{HH}$ = 6.3 Hz, NC*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.4, 26.4, 40.6, 51.6, and 163.3 ppm. IR (nujol): 1640 cm^{-1} ($\nu_{C=N}$). EI-MS (70 eV, m/z, %): 267.27 ([M^+]-$C_7H_{16}BrCuN_2$, 10%), 128.13 ($C_7H_{16}N_2$, 100%).

$Me_2NC(Me)=NCy\cdot CuBr$ **(2b).** Yellow powder. Yield = 1.90 g, 61%. ^1H NMR ($CDCl_3$): δ = 1.28 (4H, *m*, CH_2CH_2CH), 1.65 (4H, *m*, $CH_2CH_2CH_2$), 1.81 (2H, *m*, $CH_2(CH_2)_2$), 2.20 (3H, *s*, CCH_3); 3.20 (1H, *m*, $CH(CH_2)_2$), and 3.31 ppm (6H, *s*, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.6, 25.0, 25.4, 37.4, 40.7, and 60.4 ppm. IR (nujol): 1638 cm^{-1} ($\nu_{C=N}$). EI-MS (70 eV, m/z, %): 551.67 ([M^+]-C_6H_{11}, 5%), 169.16 ($C_{10}H_{20}N_2$, 100%).

4.3. $Me_2NC(Me)=NPh\cdot CuBr$ **(2c).** Copper bromide dimethyl sulfide (0.50 g, 2.43 mmol) and N-phenyl-N',N'-dimethylacetamidine **1c** (5.0 g, 0.031 mol) were combined in a glass pressure tube and heated for 2 h at 55 °C. The resulting yellow solution was added dropwise to hexanes yielding a beige precipitate, which was then subsequently filtered. The crude material was washed with 3 x 10 mL of hexanes and then dried *in vacuo*. Yield = 0.50 g (67.3%). Crystals of **2c** were grown by vapour diffusion of Et_2O into a saturated CH_2Cl_2 solution. ^1H NMR ($CDCl_3$): δ = 1.90 (3H, *s*, CCH_3), 3.23 (6H, *s*, $N(CH_3)_2$), 6.84 (2H, *d*, Ar*H*), 7.05 (1H, *t*, Ar*H*), and 7.28 ppm (2H, *t*, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 16.1, 39.3, 123.3, 123.6, 129.2, 153.0, and 163.7 ppm. IR (nujol): 1576 cm^{-1} ($\nu_{C=N}$). EI-MS (70 eV, m/z, %): 304.58 ([M^+]-$C_{10}H_{14}BrCuN_2$, 5%), 162.11 ($C_{10}H_{14}N_2$, 75%).

4.4. Preparation of phosphaamidines **4a** and **4b:** A Et_2O solution of Ph_2PLi was prepared by the addition of a 1.6 M hexanes solution of ^{n}BuLi (4.3 mL, 6.88 mmol) to a clear and colourless Et_2O (80 mL) solution of Ph_2PH (1.26 g, 6.77 mmol) at 0 °C. The resulting yellow solution was stirred for 1 h at 0 °C, then warmed to ambient temperature and stirred for an additional 1 h. To this yellow solution was slowly added an Et_2O (20 mL) solution of *N*-phenylbenzimidoyl chloride (1.46 g, 6.77 mmol) or *N*-isopropylbenzimidoyl chloride (1.23 g, 6.77 mmol) at –78 °C separately to obtain compound **4a** or **4b** respectively. The yellow mixture was allowed to slowly warm to ambient temperature then stirred for an additional 18 h. The resulting pale yellow suspension was reduced to dryness *in vacuo* and the residue was extracted with refluxing hexanes (200 mL) for 2 h. After slowly cooling to ambient temperature, the mixture was filtered and the yellow filtrate was concentrated to incipient crystallization. Pale yellow crystalline

compounds of **4a** (44%) and **4b** (35%) were grown from the concentrated hexanes solution at -30 °C.

$Ph_2PC(Ph)=NPh$ **(4a).** Yellow solid. Yield = 1.09 g, 44%. ^{31}P NMR ($CDCl_3$): δ = 9.0 ppm. ^{1}H NMR ($CDCl_3$): δ = 6.72 (m, 2H), 6.80 (m, 1H), 6.93 (m, 1H), 7.11-7.14 (m, 6H), 7.24 (m, 1H), 7.34 (m, 6H), and 7.60 ppm (m, 3H). ^{13}C NMR ($CDCl_3$): δ = 119.3, 120.7, 123.3, 123.6, 127.7, 128.4, 128.8, 129.1, 134.2, 135.0 (d, *J* = 19.2 Hz), 151.6, and 178.9 ppm. EI-MS (70 eV, m/z, %): 365.14 ([M^+], 100%). EI-HRMS ($C_{25}H_{20}NP$): 365.1333 (calcd.), 365.1325 (found).

$Ph_2PC(Ph)=N^iPr$ **(4b).** Yellow solid. Yield = 0.78 g, 35%. ^{31}P NMR ($CDCl_3$): δ = 6.95, –8.68 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.22 (d, *J* = 6.1 Hz, 6H), 3.61 (sept, *J* = 6.1 Hz, 1H), 6.81 (m, 2H), 7.03 (m, 2H), 7.14 (m, 3H), 7.30 (m, 9H), and 7.34 ppm (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 23.0, 23.7, 55.6, 126.3, 127.4, 127.7 (d, *J* = 7.1 Hz), 128.0 (d, *J* = 6.9 Hz), 128.4 (d, *J* = 6.8 Hz), 128.6 (d, *J* = 4.5 Hz), 133.5 (d, *J* = 19.2 Hz), 134.4 (d, *J* = 18.9 Hz), and 174.7 ppm. EI-MS (70 eV, m/z, %): 331.15 ([M^+], 1%), 146.09 ([M^+]-PPh_2, 100%). EI-HRMS ($C_{22}H_{22}NP$): 331.1490 (calcd.), 331.1502 (found).

4.5. Preparation of phosphaamidines **5a** and **5b:** A Et_2O solution of $^iPr_2PLi$ was prepared from the addition of a 1.6 M hexanes solution of ^{n}BuLi (4.3 mL, 6.88 mmol) to a clear and colourless Et_2O (80 mL) solution of $^iPr_2PH$ (10 mL, 6.77 mmol) (10 wt% in hexane) at 0 °C. The resulting yellow solution was stirred for 1 h at 0 °C, then warmed to ambient temperature and stirred for an additional 1 h. To this yellow solution was slowly added an Et_2O (20 mL) solution of *N*-phenylbenzimidoyl chloride (1.46 g, 6.77 mmol) or *N*-isopropylbenzimidoyl chloride (1.23 g, 6.77 mmol) at –78 °C. The yellow mixture was allowed to slowly warm to ambient temperature then stirred for an additional 18 h. The resulting solution was reduced to dryness *in vacuo* and the residue was dissolved in minimum CH_2Cl_2 and then filtered. The filtrate was dried to obtain white solid compound **5a** and red oily compound **5b** in good yield.

$^iPr_2PC(Ph)=NPh$ **(5a).** White solid. Yield = 1.44 g, 72%. ^{31}P NMR ($CDCl_3$): δ = 27.7 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.04 (m, 6H), 1.23 (m, 6H), 2.22 (d of sept, *J* = 3.0 and 7.1 Hz, 2H), 6.66 (d, *J* = 7.5 Hz, 2H), 6.92 (t, *J* = 7.1 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.22 (br, 5H), and 7.49 ppm (m, 1H). ^{13}C NMR ($CDCl_3$): δ = 19.0 (d, *J* = 10.8 Hz), 20.3 (d, *J* = 11.9 Hz), 22.7 (d, *J* = 12.6 Hz), 120.4, 122.8, 127.9, 128.4, 128.7, 128.8, 129.4, 139.3, 139.7, 152.2 (d, *J* = 3.8 Hz), and 178.8 ppm (d, *J* = 21.3 Hz). EI-MS (70 eV, m/z, %): 297.17 ([M^+], 6%), 180.11 ([M^+]-P^iPr_2, 100%). EI-HRMS ($C_{19}H_{24}NP$): 297.1646 (calcd.), 297.39 (found).

$^iPr_2PC(Ph)=N^iPr$ **(5b).** Red oil. Yield = 1.56 g, 88%. ^{31}P NMR ($CDCl_3$): δ = 26.0 ppm. ^{1}H NMR ($CDCl_3$): δ = 0.95 (m, 6H), 1.10 (m, 12H), 2.04 (d of sept, *J* = 3.4 and 7.1 Hz, 2H), 3.65 (sept, *J* = 6.2 Hz, 1H), 7.18 (m, 2H), and 7.33 ppm (m, 3H). ^{13}C NMR ($CDCl_3$): δ = 18.8 (d, *J* = 9.9 Hz), 18.9 (d, *J* = 11.4 Hz), 22.2 (d, *J* = 14.0 Hz), 23.3, 24.0, 53.4, 127.0, 128.1, 129.8, 140.0, and 172.6 ppm (d, *J* = 17.8 Hz). EI-MS (70 eV, m/z, %): 263.18 ([M^+], 4%), 104.09 (C_7H_6N, 100%). EI-HRMS ($C_{16}H_{26}NP$): 263.1803 (calcd.), 263.1795 (found).

4.6. General preparation of **6a** and **6b.** To a suspension of CuBr(DMS) (0.256 g, 1.24 mmol) in CH_2Cl_2 (5 mL) was added dropwise a CH_2Cl_2 (5 mL) solution of either **4a** (0.455 g, 1.25 mmol) or **4b** (0.209 g, 0.63 mmol). The solids in the initially beige suspension slowly dissolved into solution after 1 h yielding a burnt orange solution. All volatiles from the reaction solution were removed *in vacuo* to afford orange foam. The remaining solids were washed with toluene (2 x 2 mL) and dried under vacuum to obtain **6a** or **6b** in 72% or 83% yield, respectively. Yellow crystals were grown from Et_2O vapour diffusion into a saturated 1:1 (vol.) CH_2Cl_2/toluene solution at –15 °C.

$[Ph_2PC(Ph)=NPh{\cdot}CuBr]_4$ **(6a).** Orange foam. Yield = 0.45 g, 72%. ^{31}P NMR ($CDCl_3$): δ = 10.8 ppm. ^{1}H NMR ($CDCl_3$): δ = 6.70 (m, 2H), 6.91-6.96 (m, 5H), 7.07-7.09 (m, 2H), 7.28-7.41 (m, 6H), and 7.61-7.72 ppm (m, 5H). ^{13}C NMR ($CDCl_3$): δ = 122.2, 125.8, 123.3, 127.6, 128.1, 128.5, 128.8, 128.9, 129.9, 130.9, 134.4 (d, *J* = 14.8 Hz), 149.1, and 180.9 ppm.

$[(Ph_2PC(Ph)=N^iPr{\cdot}(CuBr)_2]_2$ **(6b).** Orange foam. Yield = 0.36 g, 83%. ^{31}P NMR ($CDCl_3$): δ = 8.7 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.39 (d, *J* = 5.6 Hz, 6H), 3.85 (sept, *J* = 6.1 Hz, 1 H), 6.76 (br, 2H), 7.09 (m, 2H), 7.16 (m, 4H), 7.30 (m, 2H), and 7.47 ppm (m, 5H). ^{13}C NMR ($CDCl_3$): δ = 23.9, 57.4, 126.2, 128.1, 128.4, 129.2, 130.1, 132.1, 134.4 (d, *J* = 49.6 Hz), and 172.7 ppm. ESI-HRMS ($C_{44}H_{44}Br_3Cu_4N_2P_2$): 1156.7665 (calcd.), 1156.7542 (found).

4.7. General preparation of **7a** and **7b.** To a suspension of CuBr(DMS) (0.655 g, 3.18 mmol) in CH_2Cl_2 (40 mL) was added a solution of either **5a** (0.472 g, 1.58 mmol) or **5b** (0.415 g, 1.58 mmol) separately. The resulting orange mixture was stirred for 1 h then filtered through Celite, and the filtrate was then reduced to dryness to yield an orange residue. The residue was taken up in CH_2Cl_2 (10 mL) then precipitated into hexanes (50 mL). Orange solid was obtained following filtration to obtain **7a** or **7b** at 63% or 43%, respectively. Single crystals of **7a** were grown from Et_2O vapour diffusion into a saturated CH_2Cl_2 solution of **7a** at –18 °C, while crystals of **7b** were obtained by slow evaporation of a CH_2Cl_2 solution at room temperature

$[(^iPr_2PC(Ph)=NPh{\cdot}(CuBr)_2]_2$ **(7a).** Orange solid. Yield = 0.58 g, 63%. ^{31}P NMR ($CDCl_3$): δ = 35.5 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.34 (d, *J* = 7.0 Hz, 6H), 1.39 (d, *J* = 6.9 Hz, 6H), 2.38 (m, 2H), 6.84 (d, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 7.13 (m, 4H), and 7.15 ppm (m, 3H). ^{13}C NMR ($CDCl_3$): δ = 19.4 (d, *J* = 8.3 Hz), 20.1 (d, *J* = 5.1 Hz), 25.1 (d, *J* = 13.9 Hz), 121.8, 125.2, 127.6, 128.6, 128.8, 129.2, 136.5 (d, *J* = 11.3 Hz), 149.5 (d, *J* = 16.2 Hz), and 179.1 ppm. ESI-HRMS ($C_{38}H_{48}Br_3Cu_4N_2P_2$): 1088.7975 (calcd.), 1088.7880 (found).

[($^{i}Pr_2PC(Ph)=N^{i}Pr\cdot(CuBr)_2]_2$ **(7b).** Orange solid. Yield = 0.37 g, 43%. ^{31}P NMR ($CDCl_3$): δ = 35.2 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.32 (d, *J* = 6.9 Hz, 3H), 1.34 (d, *J* = 6.9 Hz, 3H), 1.37 (d, *J* = 6.9 Hz, 3H), 1.40 (d, *J* = 6.9 Hz, 3H), 1.44 (d, *J* = 6.2 Hz, 6H), 2.17 (m, 2H), 3.89 (sept, *J* = 6.2 Hz, 1H), 7.13 (m, 2H), and 7.50 ppm (m, 3H). ^{13}C NMR ($CDCl_3$): δ = 19.9 (d, *J* = 8.7 Hz), 20.0 (d, *J* = 5.3 Hz), 24.8 (d, *J* = 11.8 Hz), 58.4 (d, *J* = 13.4 Hz), 124.8, 125.2, 128.8, 129.4, 136.2 (d, *J* = 7.4 Hz), and 178.0 ppm (d, *J* = 27.3 Hz). ESI-HRMS ($C_{32}H_{52}Br_3Cu_4N_2P_2$): 1020.8287 (calcd.), 1020.7412 (found).

Supporting Information

Text, figures, tables, and CIF and xyz files giving spectroscopic and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC .. also contain supplementary crystallographic data for this paper. 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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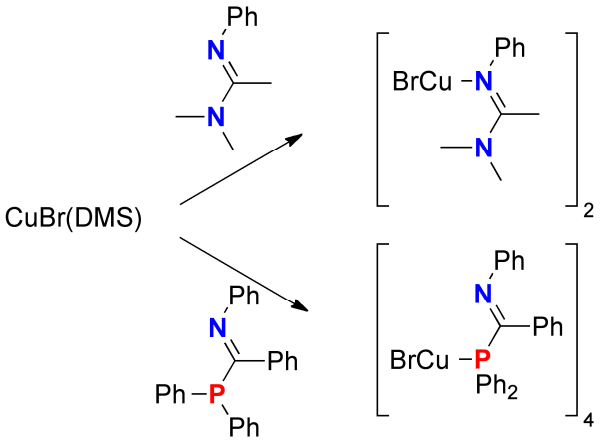
Graphical abstract synopsis

Coordination geometries of uncharged and aprotic amidines and 1,3-(P,N) phosphaamidines on Cu(I) centres.



Highlights

• Aprotic acetamidine ligands coordinate to Cu through solely the N_{imine}.

• A bulky aprotic phosphaamidine ligand coordinates ^{1}•**P** with Cu(I)Br to form cubane Cu_4Br_4 complex, leaving the N_{imine} basic site dangling.

• Less bulky aprotic phosphaamidine ligands coordinate ^{2}•**P,N** to form step Cu_4Br_4 complexes.