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Quaternization and oxidation reactions of cyclodiphosphazane derivatives and their copper(I) and gold(I) complexes

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Abstract. The reactions of cyclodiphosphazane derivatives, *cis*-{^{t}BuN(H)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu} (**1**), *cis*-{MeN(C_4H_8N)P(μ-N^{t}Bu)$_2$P(NC_4H_8Me)} (**2**) and {$Me_2NCH_2CH_2O$)P(μ-N^{t}Bu)$_2$P($OCH_2CH_2NMe_2$)} (**3**) with methyl iodide and methyl triflate and their subsequent reactions with elemental sulfur and selenium are reported. Interestingly the reactions of **1**-**3** with an excess of methyl iodide resulted in quaternising only one phosphorus atom in *cis*-[{^{t}BuNHP(μ-N^{t}Bu)$_2$P(CH_3)NH^{t}Bu}](I) (**4**), two exocyclic nitrogen atoms and one of the phosphorus atoms in *cis*-{($Me_2NC_4H_8$N)P(μ-N^{t}Bu)$_2$P(CH_3)($NC_4H_8NMe_2$)}](I)$_3$ (**7**) and only two exocyclic nitrogen atoms in *cis*-[{$Me_3NCH_2CH_2O$)P(μ-N^{t}Bu)$_2$P($OCH_2CH_2NMe_3$)}](I)$_2$ (**8**), respectively. The reaction of **1** with one equiv of methyl triflate produced *cis*-[{^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(CH_3)N(H)^{t}Bu}]OTf (**5**), whereas the same reaction in a 1:2 molar ratio afforded *cis*-{^{t}BuN(H)P(CH_3)(μ-N^{t}Bu)$_2$P(CH_3)N(H)^{t}Bu}(OTf)$_2$ (**6**). Compounds **4** and **5** showed poor solubility in water, whereas **7** and **8** were high melting crystalline solids with moderate to good water solubility. Treatment of **4** with either elemental sulfur or selenium gave both *cis*- and *trans*-chalcogenide derivatives. Similar reactions of **7** and **8** produced both mono- and bischalcogenides. Reactions between **4** or **7** and CuI yielded dinuclear complexes, *cis*-[{Cu_2(μ-

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$I)_3(^tBuN(H)P)(\mu\text{-}N^tBu)_2(P(CH_3)N(H)^tBu)]_2\}(I)]$ (**15**) and *cis*-$[\{Cu_2(\mu\text{-}I)_3[(Me_2NC_4H_8N)P(\mu\text{-}N^tBu)_2P(CH_3)(NC_4H_8NMe_2)]_2\}(I)_5]$ (**16**), while the reaction of **8** with CuI produced a coordination polymer $[\{Cu_2(\mu\text{-}I)_3(\mu\text{-}N^tBuP)_2(OCH_2CH_2NMe_3)_2\}I]_\infty$ (**17**), containing triiodo-bridged $[Cu_2(\mu\text{-}I)_3]$ linkers. The molecular structures of several of these compounds were confirmed by single crystal X-ray diffraction studies. The $Cu^I\cdots Cu^I$ distance of 2.55 Å in **15** is quite short and is the same as that found in copper metal and also in complexes containing $[Cu_2(\mu\text{-}I)_3]$ linkers. All the metal complexes exhibit strong intra-, inter- or both intra- and inter-molecular hydrogen bonding interactions.

Introduction

The successful employment of platinum metal complexes of phosphorus compounds in homogeneous catalysis prompted several research groups to develop water soluble phosphine systems to take homogeneous catalysis another step forward to make the separation of organic product from catalyst easier and also abet the facile recovery and reuse of the precious metals as well as the ligands.[1-4] The aqueous/organic biphasic systems require solubilizing the catalyst in water which can be achieved by incorporating highly polar functionalities such as SO_3^-,[5-9] COO^-,[10,11] NR_3^+,[12-17] PR_3^+[18-21] or OH[22-25] into the ligand framework. However, apart from the sulfonation of arylphosphines, the utility of other polar groups is less extensive. This may be due to the limitations in choosing the ligand framework and the availability of suitable sites for the incorporation of such functional groups. This problem can be addressed by choosing an appropriate phosphorus-based ligand framework containing nitrogen atoms which on simple addition of alkyl halide can produce a Zwitterion thus making them soluble in polar solvents.[12,13,26] The selective quaternization of nitrogen atoms in aminophosphines is not easy as phosphorus atoms can also form phosphonium salts. However, by choosing the proper ligand

framework with appropriate steric and electronic attributes it should be possible to control the quaternization sites thereby leaving the phosphorus atoms unaffected. In this context, we found that cyclodiphosphazanes or diazadiphosphatedines are ideal candidates as both nitrogen and phosphorus atoms can be readily tuned in terms of both steric and electronic aspects.[27] If the phosphorus substitutents are amines with direct phosphorus-nitrogen bonds, the lone pairs on nitrogen show different chemical behavior compared to that when they are separated with spacers. Of course the lone pairs on the endocyclic nitrogen atoms are always delocalized into appropriate molecular orbitals ($N_{p\pi} \rightarrow (PN)_{\sigma^*}$) through negative hyperconjugation. Recently, we have explored the coordination chemistry of a variety of cyclodiphosphazane derivatives[28-30] and also the antitumor activities of gold and copper complexes.[31,32] As an extension of our interest and the interest of others[33-40] in cyclodiphosphazanes, we report herein the interactions of three cyclodiphosphazanes with methyl iodide or methyl triflate and their subsequent reactions with chalcogens, copper(I) iodide and $AuCl(SMe_2)$ which led to the isolation of binuclear complexes with $[Cu(\mu\text{-}I)_3Cu]$ units. The crystal structures of several derivatives with extensive inter- and intramolecular hydrogen bonding are also described.

Results and discussion

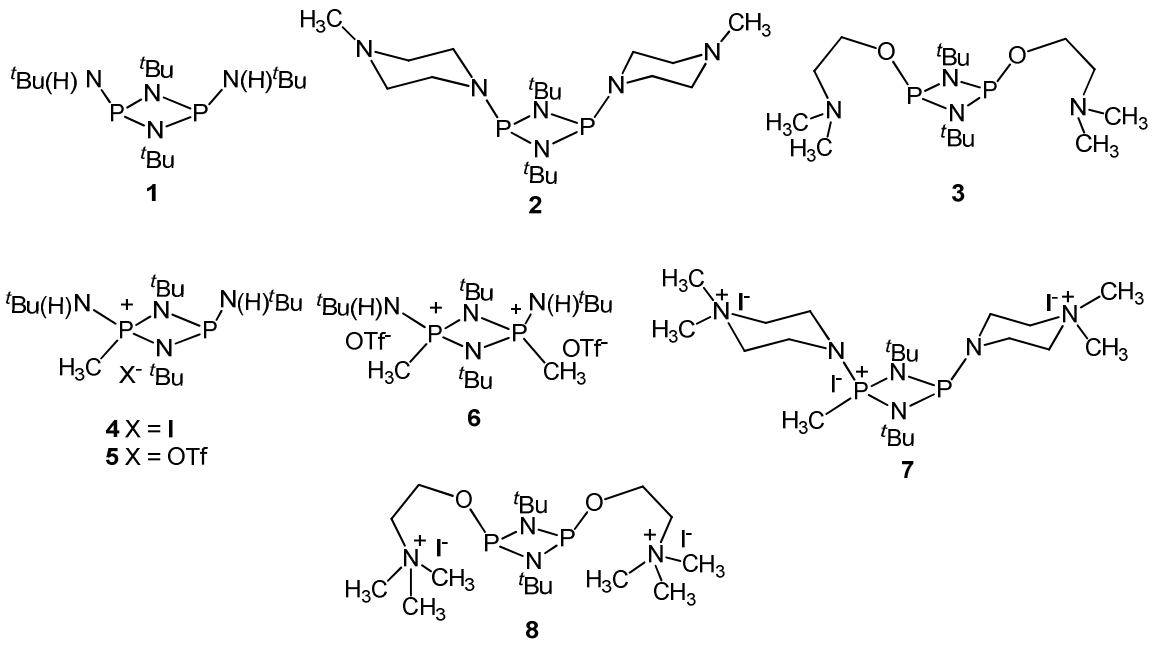
Syntheses of Ligands. The cyclodiphosphazane derivatives *cis*-{^{t}BuN(H)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu} (**1**), *cis*-{MeN(C_4H_8N)P(μ-N^{t}Bu)$_2$P(NC_4H_8Me)} (**2**) and {$Me_2NCH_2CH_2O$)P(μ-N^{t}Bu)$_2$P($OCH_2CH_2NMe_2$)} (**3**) were prepared by the reported procedure[30,41] and characterized by multinuclear NMR techniques. The reaction of *cis*-{^{t}BuN(H)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu} (**1**) with an excess of methyl iodide under refluxing conditions or with one equiv of methyl triflate at room temperature afforded the mono P-methylated compounds, *cis*-[{^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(CH_3)N(H)^{t}Bu}]X (**4** X = I and **5** X = OTf) (Chart 1).[32] The reaction of **1** with two equiv

of methyl triflate gave a dicationc product *cis*-{^{t}BuN(H)P(CH$_3$)(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu}(OTf)$_2$ (**6**). Only one of the two ring phosphorus atoms is methylated by excess methyl iodide even under reflux conditions while the more electrophilic methyl triflate quaternizes both the phosphorus centers. The reaction between *cis*-{MeN(C$_4$H$_8$N)P(μ-N^{t}Bu)$_2$P(NC$_4$H$_8$Me)} (**2**) and an excess of methyl iodide at ambient temperature gave *cis*-{(Me$_2$NC$_4$H$_8$N)P(μ-N^{t}Bu)$_2$P(CH$_3$)(NC$_4$H$_8$NMe$_2$)}](I)$_3$ (**7**) in which methylation occurred at one of the phosphorus atoms and the two *exo*-cyclic N-methyl nitrogen atoms. The slow addition of an excess of methyl iodide to *cis*-{Me$_2$NCH$_2$CH$_2$O)P(μ-N^{t}Bu)$_2$P(OCH$_2$CH$_2$NMe$_2$)} (**3**) yielded exclusively *cis*-[{Me$_3$NCH$_2$CH$_2$O)P(μ-N^{t}Bu)$_2$P(OCH$_2$CH$_2$NMe$_3$)}](I)$_2$ (**8**) where the methylation occurred only at the *exo*-cyclic nitrogen atoms and the phosphorus atoms remain unaffected. Compounds **7** and **8** are high melting crystalline solids with moderate to good solubility in water, methanol and dimethyl sulfoxide, whereas compounds **4** and **5** are sparingly soluble in water.

Interestingly, the quaternization reactions gave some insight into the electronic situation that arises at the phosphorus atoms depending on the nature of the substituents and their steric and electronic attributes. In the case of cyclodiphosphazane **1**, similar to endocylic nitrogen atoms, the exocyclic nitrogens are also assumed to be involved in negative hyperconjugation ($N_{p\pi}\rightarrow(PN)_{\sigma*}$) with the phosphorus atoms making it difficult to quaternize them and for the same reason the P_2N_2 ring nitrogens can not be quaternized.[42-45] No such interactions are anticipated between the phosphorus atoms and the exocyclic nitrogens of either N-methylmorpholine in **2** or the NMe_2 groups in **3** and thus they are readily methylated. The electron-rich amine-substituted cyclodiphosphazanes undergo quaternization with ease, while less basic alkoxy- substituted ring resist quaternization. The quaternization of both the phosphorus atoms with amine-substituted rings is difficult, and needs the highly electrophilic methyl triflate for di-quaternization. This is

probably due to the cationic nature of the cyclodiphosphazane ring after the first quaternization which reduces the basicity of the second phosphorus atom.[46-48]

Chart 1

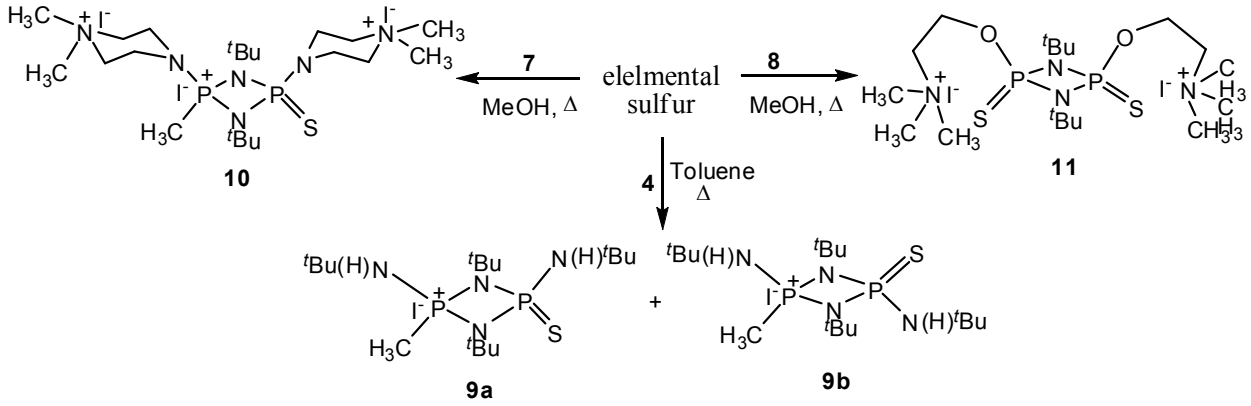


The ^{31}P NMR spectra of **4**, **5** and **7** showed two singlets at 80.4 and 19.6 ppm, 82.2 and 21.1 ppm and 87.1 and 35.1 ppm, respectively, for the trivalent- and methylated-phosphorus centers. The ^{1}H NMR spectra of **4** and **7** consists of singlets for the P–*CH*$_3$ protons at 1.65 and 1.23 ppm, whereas **5** showed a doublet centered at 2.10 ppm with a $^{2}J_{PH}$ coupling of 14.9 Hz. The ^{31}P NMR spectra of **6** and **8** showed single resonances at 39.6 and 132.9 ppm, respectively, indicating the symmetric nature of phosphorus atoms. Owing to the poor quality of crystals only poor data was obtained for **6** (See supporting information) while the molecular structure of **4** was reported earlier.[32]

Reactions with chalcogens. The reaction of **4** with elemental sulfur in a 1:1 molar ratio in toluene afforded a mixture of *cis*- and *trans*-[{(^{t}BuNHPS)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu)}](I) (**9a** and

9b) isomers (Scheme 1) in a 3:2 ratio as substantiated by its ^{31}P NMR spectrum. Attempts to separate the *cis* and *trans* isomers have been unsuccessful. The ^{31}P NMR spectrum consists of two doublets centered at 36.6 and 38.2 ppm which are assigned to the P(S) centers, while the P(CH_3) centers appear as doublets, respectively, at 23.4 and 25.8 ppm, with $^2J_{PP}$ values of 38.8 and 32.0 Hz. The reactions of **7** and **8** with elemental sulfur in 1:1 and 1:2 molar ratios gave monosulfide, *cis*-[{($Me_2NC_4H_8N$)P(S)(μ-N^{t}Bu)$_2$P(CH_3)($NC_4H_8NMe_2$)}($I)_3$] (**10**) and bis(sulfide), *cis*-[{(μ-N^{t}BuPS)$_2$($OCH_2CH_2NMe_3)_2$}($I)_2$] (**11**) in quantitative yield. Reaction of mono-quaternized phosphorus compounds with chalcogens to form the corresponding chalcogenides is expected under refluxing conditions.[49-53] The ^{31}P NMR spectrum of **10** showed two singlets at 48.1 and 35.7 ppm for the P(S) and P(CH_3) centers, respectively. The ^{31}P NMR spectrum of **11** consists of a single resonance at 48.5 ppm.

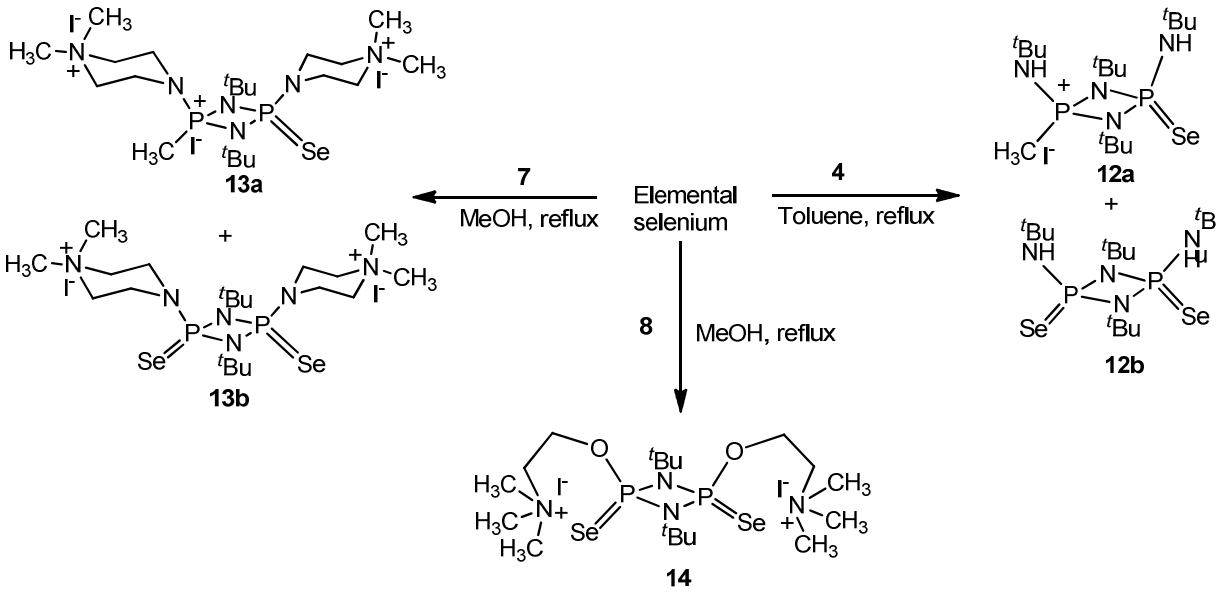
Scheme 1. Reactions of cyclodiphosphazane derivatives **4**, **7** and **8** with elemental sulfur



Interestingly, the reactions between **4** or **7** and elemental selenium in equimolar ratios led to the formation of a 3:1 mixture of mono- and bis(selenide) derivatives as per the ^{31}P NMR spectroscopic data. Fractional crystallization resulted in the isolation of **12a** in pure form. The separation of bis(selenide) (**12b**) by the same method has been unsuccessful. However, mono(selenide), *cis*-[{($Me_2NC_4H_8NPSe$)(μ-N^{t}Bu)$_2$(P(CH_3)NC_4H_8N-Me_2)}]($I)_3$ (**13a**) and

bis(selenide), *cis*-[{(μ-N^{t}BuPSe)$_2$(NC$_4$H$_8$NMe$_2$)$_2$}](I)$_2$ (**13b**) were separated by fractional crystallization. The ^{31}P NMR spectrum of **12a** consists of two doublets centered at 24.1 and 25.8 ppm for P(Se) and P(CH$_3$) centers, respectively, with a $^1J_{SeP}$ coupling of 906 Hz. The bis(selenide) (**12b**) showed a single resonance at 23.3 ppm with a $^1J_{SeP}$ coupling of 872 Hz (lit: δ_P = 26.7 ppm, $^1J_{SeP}$ = 880 Hz in THF-d_8).[54] The ^{31}P NMR spectrum of **13a** showed two doublets centered at 41.1 and 39.6 ppm for the P(Se) and P(CH$_3$) centers, respectively. The $^1J_{SeP}$ coupling of **13a** is 910 Hz and the $^2J_{PP}$ coupling is 28.8 Hz. The bis(selenide) **13b** shows a single resonance at 40.5 ppm with a $^1J_{SeP}$ coupling of 890 Hz. The $^1J_{SeP}$ value in **13b** is slightly lower than that reported for *cis*-[{(μ-N^{t}BuPSe)$_2$(NC$_4$H$_8$NMe)$_2$}] ($^1J_{SeP}$ = 917 Hz).[41] Under similar conditions, the reaction between **3** and selenium powder in a 1:2 molar ratio afforded exclusively the bis(selenide) *cis*-[{(μ-N^{t}BuPSe)$_2$(OCH$_2$CH$_2$NMe$_3$)$_2$}](I)$_2$ (**14**) in 80% yield (Scheme 2).

Scheme 2. Reactions of cyclodiphosphazane derivatives **4**, **7** and **8** with elemental selenium



The ^{31}P NMR spectrum of **14** showed a sharp singlet at 42.7 ppm with a $^1J_{SeP}$ coupling of 930 Hz. The chalcogenide derivatives, **10**, **11**, **13a**, **13b** and **14** are soluble in water and dimethyl sulphoxide, while **9a**, **9b**, **12a** and **12b** are soluble only in common organic solvents. The ^{1}H

NMR spectral and microanalyses data for **9-14** are in accordance with the proposed structures. Further, the molecular structures of **12a**, **13b** and **14** have been confirmed by single crystal X-ray diffraction studies.

Molecular structures of *cis*-[{^{t}BuN(H)P(Se)(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu}](I) (12a), *cis*-[{(Me$_2$NC$_4$H$_8$N)P(Se)(μ-N^{t}Bu)$_2$P(Se)(NC$_4$H$_8$NMe$_2$)}](I)$_2$ (13b) and *cis*-[{Me$_3$NCH$_2$CH$_2$O)P(μ-N^{t}Bu)$_2$P(OCH$_2$CH$_2$NMe$_3$)}](I)$_2$ (14).

Perspective views of the molecular structures of **12a**, **13b** and **14** along with the atom labeling schemes are shown in Figures 1-4. The crystallographic data and the details of the structure determination are given in Table 1, while the selected bond lengths [Å] and bond angles [°] are listed in Table 3.

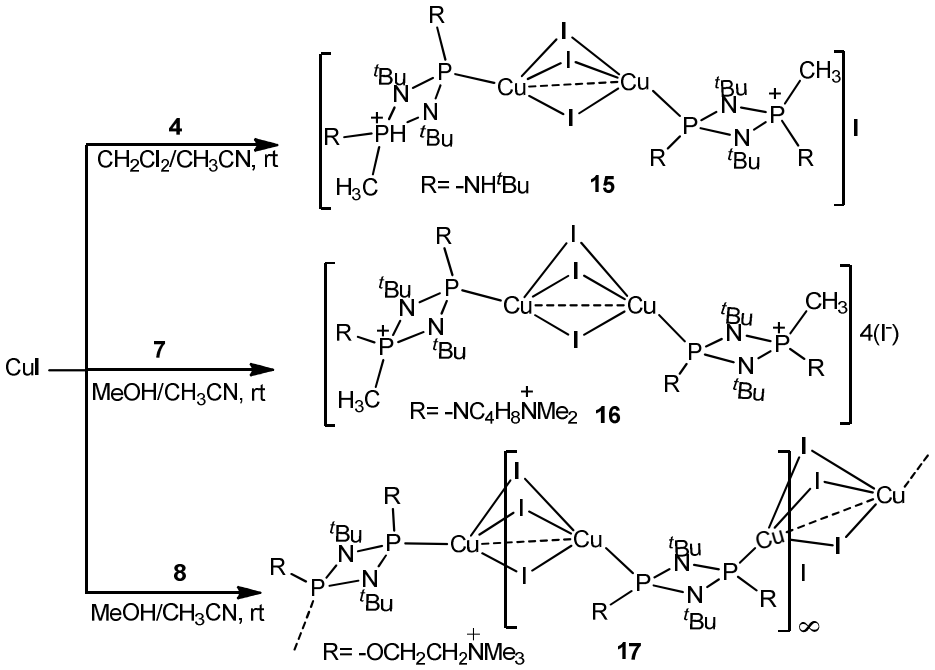
The asymmetric unit of **12a** consists of two independent molecules with similar conformations which differ primarily in the orientations of the ^{t}Bu groups (Fig 1b) as well as in the folding of the diazadiphosphetidine rings along the N---N axis (7.4(2)° for molecule 1 and 9.0(2)° for molecule 2. The hydrogen atoms in the ^{t}BuNH groups of **12a** are in an *endo-endo* orientation with respect to the P_2N_2 ring while the two non-identical phosphorus centers, P1 and P2, are in pseudo-tetrahedral environments. The geometries around the ring nitrogen atoms are nearly planar (sum of angles at N1 = 357.79° and at N2 = 358.66°), whereas the *exo*-cyclic nitrogen atoms exhibit distorted pyramidal geometries. The *endo*-cyclic P–N bond lengths vary from 1.653(2) Å (P2–N1) to 1.713(2) Å (P1–N2) which are longer than the *exo*-cyclic P–N bond distances (P1–N3, 1.618(3) and P2–N4, 1.592(3) Å). The P1-Se1 and P2–C17 bond lengths are 2.0798(8) Å and 1.770(3) Å, respectively.

The asymmetric units, of **13b** and **14** consist of two and one molecules, respectively, and one molecule of water as solvent of crystallization. The amido groups, [-NC$_4$H$_8$NMe$_2$] are in a

thermodynamically stable chair conformation and are in a mutually *cis* orientation with respect to the P_2N_2 ring. The rigid four-membered P_2N_2 rings are folded along the N---N′ axis by a dihedral angle of 14.9(2)° and 11.1(2)° for the two independent molecules in **13b** and 5.2(1)° in **14.** The P1–Se1 and P2–Se2 bond distances in **13b** are 2.0822(12) Å and 2.0773(13) Å and they are marginally longer than those reported for *cis*-{^{t}Bu(H)N(Se)P(μ-N^{t}Bu)$_2$P(Se)N(H)^{t}Bu} [P–Se = 2.078(1) and 2.070(1) Å].[55] The *endo*-cyclic nitrogen atoms in **14** are almost planar with the sum of the bond angles around nitrogen being ~358°. The *exo*-cyclic nitrogen atoms as well as the phosphorus atoms are in distorted tetrahedral environments. The average *endo*-cyclic P–N and *exo*-cyclic P–O bond distances in **14** are 1.6845 Å and 1.6014 Å. The P1–Se1 (2.0635(7) Å) and P2–Se2 (2.0672(7) Å) bond distances in **14** vary slightly as do the *exo*-cyclic N–C bonds [(1.493(3) Å (N4–C16) to 1.517(5) Å (N4–C15)].

Copper(I) complexes. The reactions of copper iodide with **4** or **7** in a 1:1 molar ratio in a mixture of dichloromethane/acetonitrile (1:1) or methanol/acetonitrile (1:1) afforded binuclear complexes, *cis*-[{Cu_2(μ-I)$_3$(^{t}BuN(H)P)(μ-N^{t}Bu)$_2$(P(CH_3)N(H)^{t}Bu)]$_2$}(I)] (**15**) and *cis*-[{Cu_2(μ-I)$_3$[($Me_2NC_4H_8N$)P(μ-N^{t}Bu)$_2$P(CH_3)($NC_4H_8NMe_2$)]$_2$}($I)_5$] (**16**), respectively. Treatment of **8** with CuI in a 1:2 molar ratio afforded a one-dimensional zigzag coordination polymer [{Cu_2(μ-I)$_3$(μ-N^{t}BuP)$_2$($OCH_2CH_2NMe_3$)$_2$}I]$_\infty$ (**17**) as shown in Scheme 3.

Scheme 3. Reactions of **4**, **7** and **8** with CuI

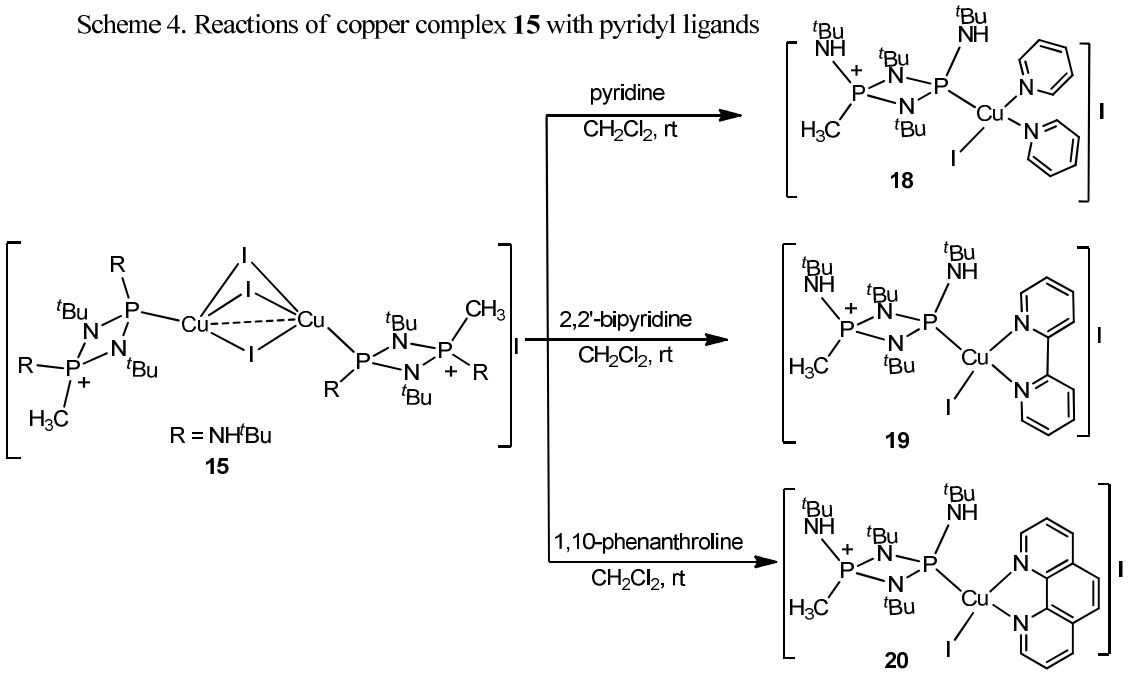


The copper(I) complex **15** showed good solubility in common organic solvents, whereas the complexes **16** and **17** are soluble only in dimethyl sulphoxide. The ^{31}P NMR spectra of **15** and **16** showed broad singlets at 78.5 and 69.2 ppm for the coordinated phosphorus centers and the quaternized phosphorus atoms also appear as singlets at 20.3 and 38.9 ppm. The coordination polymer **17** showed a broad singlet at 107.1 ppm. The molecular structure of binuclear copper(I) complex **15** is confirmed by a single crystal X-ray diffraction study.

Mixed-Ligand Complexes of *cis*-[{Cu$_2$(μ-I)$_3$[(^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu)]$_2$}(I)] (15). The binuclear copper(I) complex **15** was further reacted with different pyridyl ligands to produce various mixed-ligand complexes. Treatment of **15** with excess of pyridine at room temperature afforded the mixed-ligand complex, *cis*-[{(C$_5$H$_5$N)$_2$CuI(^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu)}(I)] (**18**). The ^{31}P NMR spectrum of **18** showed broad singlets at 72.3 and 21.4 ppm, respectively, for the coordinated phosphorus and P(CH$_3$) centers. Similarly, the reactions of **15** with 2,2′-

bipyridine or 1,10-phenanthroline produced the mononuclear complexes *cis*-[(2,2′-bpy)Cu(I){^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu}]I (**19**) and *cis*-[(1,10-phen)Cu(I){^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu}]I (**20**) as yellow crystalline solids (Scheme 4). The ^{31}P NMR spectra of **19** and **20** showed broad singlets at 79.4 and 79.3 ppm for the Cu–P centers, whereas the ^{31}P signals due to the P–CH$_3$ centers appear as broad singlets at 20.6 and 19.7 ppm, respectively. The ^{1}H NMR spectral data of **18**-**20** are consistent with the proposed structures. The molecular structures of **19** and **20** are confirmed by single crystal X-ray diffraction studies.

Scheme 4. Reactions of copper complex **15** with pyridyl ligands



The molecular structures of **15**, **19** and **20** along with the atom labeling scheme are shown in Figures 4-9. The crystallographic data and the details of the structure determination are given in Tables 1 and 2 while the selected bond lengths [Å] and bond angles [°] are listed in Tables 3 and 4.

The structure of **15** consists of a central [Cu$_2$(μ-I)$_3$] unit with each copper atom being coordinated to three bridging iodine atoms and one phosphorus atom. The bond angles around

Cu1 vary from 98.63(1)° (I2–Cu1–I3) to 128.96(3)° (I2–Cu1–P1) while at Cu2 the bond angles range from 98.92(1)° (I1–Cu2–I2) to 125.38(3)° (I2–Cu2–P3) clearly indicating the distorted tetrahedral geometry around the copper centers. The two P_2N_2 rings deviate from planarity by an angle of 1.51(4)° and 3.3(1)°, respectively. The Cu1–P1 and Cu2–P3 bond lengths are 2.2137(8) Å and 2.2037(8) Å, respectively. The Cu–I bond lengths differ significantly and vary from 2.6395(5) Å (I2–Cu2) to 2.7655(5) Å (I3–Cu2). The Cu···Cu distance of 2.555 Å is quite short and comparable with other complexes containing the $[Cu_2(\mu\text{-}I)_3]$ unit but without any other bridging ligands.[56-59] The interesting aspect in the molecular structure of **15** is the presence of strong intra- and intermolecular hydrogen bonding between the iodide ion and the NH protons. The bond angles around the hydrogen atoms of the amido moieties ranges from 165º (N4–H4···I4) to 176º (N8–H8···I4) while the bond lengths vary from 2.73 Å (N–H3···I4) to 2.90 Å (N–H4···I4). The presence of the intermolecular hydrogen bonding interactions leads to the formation of a one-dimensional polymeric structure in the crystal lattice (Figure 5).

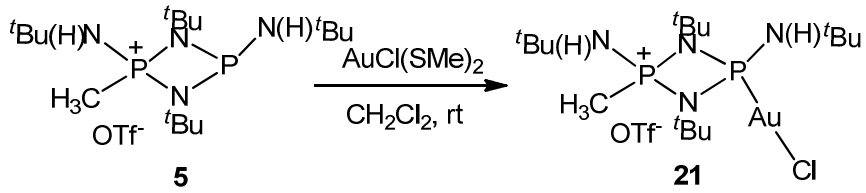
The yellow crystals of **19** suitable for single crystal X-ray diffraction study were obtained through slow evaporation of a dichloromethane-petroleum ether solution at room temperature. The amido [^{t}BuNH-] groups are *cis*-oriented with respect to the P_2N_2 ring. The phosphorus atom, two nitrogen atoms of 2,2′-bipyridine and one iodine atom form a distorted tetrahedral geometry about the copper atom. The largest deviation from the ideal geometry is reflected by the N5–Cu1–N6 (79.32(17)°) and P1–Cu1–N5 (126.28(14)°) bond angles which are markedly different from the undistorted tetrahedral value of 109.4°. The Cu1–P1 bond length is 2.1962(11) Å. The Cu–N bond distances are identical (Cu1–N5, 2.086(4); Cu1–N6, 2.082(4) Å) and the Cu1–I1 bond length is 2.6159(6) Å. Similar to the complex **15**, the molecular structure of **19** also shows the presence of intra- and intermolecular C–H···I and N–H···I hydrogen bonding. The H···I

distances for the N–H1···I2 and N–H4···I2 interactions are 2.83 Å with N–H···I angles of 155° (N1–H1···I2) and 175° (N4–H4···I2) while for the C19–H19···I2 interaction, the values are 2.95 Å and 160°. These interactions in the solid-state structure of **19** lead to the formation of a two-dimensional polymeric sheet-like structure as shown in Figure 7.

Complex **20** is isostructural with **19** and the patterns of bond lengths and bond angles are similar. The iodide ion shows intramolecular N–H···I hydrogen bonding and makes a short intermolecular C–H···I contact with the 1,10-phenonthroline ligand (N1–H1···I2, 2.69 Å, 170°; N4–H4···I2, 2.67 Å, 180°; C17–H17A···I1, 3.06 Å, 161°). The existence of both inter- and intramolecular hydrogen bonding leads to the formation of a one-dimensional polymeric structure as shown in Figure 9. The dihedral angle of the diazadiphosphetidine ring is 4.8(1)° in **19** and 4.1(2)° in **20**.

Gold(I) complex. Slow addition of $AuCl(SMe_2)$ to **5** in a 1:1 molar ratio gave a mononuclear gold complex *cis*-[^{t}BuN(H)P{AuCl}(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu]OTf (**21**) (Scheme 5). The ^{31}P NMR spectrum of **21** showed two singlets at 67.5 and 31.9 ppm, respectively, for coordinated- and methylated-phosphorus atoms. The molecular structure of **21** is confirmed by a single crystal X-ray diffraction study.

Scheme 5. Gold(I) complexes of cyclodiphosphazane derivative **5**



5 **21**

In the molecular structure of **21** (Figure 10), the geometry around Au(I) is linear with Cl1–Au1–P1 = 176.26(4)°. The P_2N_2 ring is almost planar with the fold about the N---N axis being 1.8(3)°. The Au1–P1 and Au1–Cl1 bond lengths are 2.2154(12) Å and 2.2961(12) Å, respectively. The molecular structure of **21** shows strong hydrogen bonding between the exocyclic N–H and one oxygen atom of the triflate ion (N1–H1···O2 = 2.06 Å, N4–H4···O2 = 2.05 Å; N1–H1···O2 = 162°, N4–H4···O2 = 162°).

Conclusions

The reactions of cyclodiphosphazane derivatives with methyl iodide and their subsequent reactions with elemental sulfur and selenium have been reported. Interestingly, the reactions of various cyclodiphosphazanes with methyl iodide showed preferential quaternization of nitrogens leaving at least one of the phosphorus atoms undisturbed which is very useful in coordination chemistry to generate metal complexes with catalytic applications. Further these compounds are moderately water soluble even after complex formation. The X-ray structures of the copper(I) complexes have shown extensive intra- and intermolecular hydrogen bonding which is very important in biological applications, especially with DNA interactions. The water solubility and ability to form hydrogen bonding would make these systems ideal for anticancer studies. Further work in this direction is under active investigation in our laboratory.

Experimental Section

General Procedures. All experimental manipulations were carried out under dry nitrogen or argon atmosphere, using standard Schlenk techniques unless otherwise stated. Solvents were dried and distilled prior to use by conventional methods. The cyclodiphosphazane derivatives, *cis*-{^{t}BuN(H)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu} (**1**),[60] *cis*-{MeN(C$_4$H$_8$N)P(μ-N^{t}Bu)$_2$P(NC$_4$H$_8$Me)} (**2**)[41]

$\{Me_2NCH_2CH_2O)P(\mu\text{-}N^tBu)_2P(OCH_2CH_2NMe_2)\}$ (**3**)[30] and $AuCl(SMe_2)$[61] were prepared according to the published procedures. Sulfur and selenium were purchased from commercial sources. CuI and all pyridyl derivatives were purchased from Aldrich and were used without further purification.

Instrumentaion. The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were obtained on Varian VXR 400 or Bruker AV 400 spectrometers operating at frequencies of 400 and 162 MHz, respectively. Tetramethylsilane and 85% H_3PO_4 were used as an internal and external standards for ^1H and $^{31}P\{^1H\}$ NMR, respectively. Positive shifts lie downfield of the standard in all the cases. Microanalyses were carried out on a Carlo Erba Model 1106 elemental analyzer. The mass spectra were recorded using Waters Q-Tof micro (YA-105). Melting points of all complexes were determined on a Veego melting point apparatus and are uncorrected.

Synthesis of *cis*-[{^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu}]I (4). To a solution of *cis*-$\{^tBuN(H)P(\mu\text{-}N^tBu)_2PN(H)^tBu\}$ (0.50 g, 1.43 mmol) in petroleum ether (10 mL) was added methyl iodide (1 mL) also in petroleum ether (15 mL) dropwise over a period of 10 min at room temperature during which time the solution turned turbid. The reaction mixture was heated under reflux for 2 h. The solution was brought to room temperature and the product was separated by filtration. The product was washed several times with cold petroleum ether and dissolved in dichloromethane, layered with 2 mL of petroleum ether, and placed at -25 °C for 18 h to afford **4** as a white crystalline compound. Yield: 90% (0.633 g). Mp: 198-200 °C. Anal. Calcd. for $C_{17}H_{41}N_4P_2I$: C, 41.63; H, 8.42; N, 11.42%. Found: C. 41.47; H, 8.58; N, 11.32%. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.05 (d, $^2J_{PH}$ = 14.4 Hz, *NH*, 1H), 2.30 (d, $^2J_{PH}$ = 13.2 Hz, *NH*, 1H), 1.65 (s, *CH*$_3$, 3H), 1.60 (s, ^{t}*Bu*, 9H), 1.34 (s, ^{t}*Bu*, 18H), 1.32 (s, ^{t}*Bu*, 9H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 80.4 (s), 19.6 (s).

Synthesis of *cis*-[{^{t}BuN(H)P(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu}]OTf (5). To a solution of *cis*-{^{t}BuN(H)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu} (0.50 g, 1.43 mmol) in petroleum ether (10 mL) was added methyl triflate (0.24 g, 1.46 mmol) also in petroleum ether (15 mL) dropwise over a period of 10 min at room temperature during which time the solution turned turbid. The reaction mixture was stirred at room temperature for 4 h and the product was separated by filtration. The product was washed several times with cold petroleum ether and dissolved in dichloromethane, layered with 2 mL of petroleum ether, and placed at –20 °C for 18 h to afford **5** as a white crystalline compound. Yield: 86% (0.632 g). Mp: 206-208 °C. Anal. Calcd. for $C_{18}H_{41}F_3N_4O_3P_2S$: C, 42.18; H, 8.06; N, 10.93; S, 6.26%. Found: C. 41.52; H, 7.46; N, 11.39; S, 6.67%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.42 (br s, *NH*, 1H), 6.56 (br s, *NH*, 1H), 2.10 (d, $^2J_{PH}$ = 14.9 Hz, *CH$_3$*, 3H), 1.51 (s, ^{t}*Bu*, 9H), 1.46 (s, ^{t}*Bu*, 18H), 1.32 (s, ^{t}*Bu*, 9H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 82.2 (s), 21.1 (s). MS (EI): 363.28 (M–OTf).

Synthesis of *cis*-[{^{t}BuN(H)P(CH$_3$)(μ-N^{t}Bu)$_2$P(CH$_3$)N(H)^{t}Bu}](OTf)$_2$ (6). To a solution of *cis*-{^{t}BuN(H)P(μ-N^{t}Bu)$_2$PN(H)^{t}Bu} (0.50 g, 1.43 mmol) in petroleum ether (10 mL) was added methyl triflate (0.5 g, 3.02 mmol) in the same solvent (20 mL) dropwise at room temperature during which time the solution turned turbid. The reaction mixture was stirred at room temperature for 4 h and the product was separated by filtration. The residue was washed several times with cold petroleum ether and dissolved in dichloromethane, layered with 2 mL of petroleum ether, and placed at -20 °C for 18 h to afford **6** as a white crystalline compound. Yield: 92% (0.632 g). Mp: >260 °C. Anal. Calcd. for $C_{20}H_{44}F_6N_4O_6P_2S_2$: C, 35.50; H, 6.55; N, 8.28; S, 9.48%. Found: C. 35.72; H, 6.37; N, 8.47; S, 9.78%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.97 (br s, *NH*, 2H), 2.90 (d, $^2J_{PH}$ = 6.3 Hz, *CH$_3$*, 6H), 1.63 (s, ^{t}*Bu*, 18H), 1.54 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ): 39.6 (s).

Synthesis of *cis*-[{($Me_2NC_4H_8N$)P(μ-N^{t}Bu)$_2$P(CH_3)($NC_4H_8NMe_2$)}](I)$_3$ (7). Methyl iodide (2 mL) in dichloromethane (15 mL) was added to a stirred solution of **2** (0.90 g, 2.23 mmol) also in dichloromethane (10 mL) over a period of 10 min. The clear solution turned turbid immediately after the addition of methyl iodide. The reaction mixture was stirred at room temperature for further 4 h during which time the product was precipitated. The residue was separated by filtration, washed several times with dichloromethane and dried under vacuum to afford **7** as white crystalline solid. Yield: 85% (1.57 g, 1.90 mmol). Mp: 212-214 °C. Anal. Calcd. for $C_{21}H_{49}I_3P_2N_6$: C, 30.45; H, 5.96; N, 10.15%. Found: C. 30.36; H, 5.68; N, 10.22%. ^{1}H NMR (400 MHz, D_2O, δ): 3.80-3.29 (m, C_4H_8, 16H), 3.27 (s, NMe_2, 6H), 3.19 (s, NMe_2, 6H), 1.38 (s, ^{t}*Bu,* 18H), 1.37 (s, CH_3, 3H). ^{31}P{^{1}H} NMR (161.8 MHz, D_2O, δ): 87.1 (s), 35.1 (s).

Synthesis of *cis*-[{(μ-N^{t}BuP)$_2$($OCH_2CH_2NMe_3$)$_2$}(I)$_2$] (8). This was synthesized by a procedure similar to that of **7** using **3** (1.12 g, 2.94 mmol) and MeI (3 mL). Yield: 95% (1.86 g, 2.79 mmol). Mp: 148-150 °C. Anal. Calcd. for $C_{18}H_{44}N_4P_2O_2I_2$: C, 32.54; H, 6.67; N, 8.43%. Found: C. 32.43; H, 6.66; N, 8.42%. ^{1}H NMR (400 MHz, D_2O, δ): 4.35 (t, J_{HH} = 9.8 Hz, OCH_2, 4H), δ 3.62 (t, J_{HH} = 8.4 Hz, NCH_2, 4H), 3.21 (s, NMe_3, 18H), 1.31 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, D_2O, δ): 132.9 (s).

Synthesis of [{(^{t}BuNHPS)(μ-N^{t}Bu)$_2$(P(CH_3)NH^{t}Bu)}(I)] (9). A mixture of **4** (0.10 g, 0.204 mmol) and elemental sulfur (0.007 g, 0.204 mmol) in toluene (20 mL) was heated under reflux for 16 h. The reaction mixture was allowed to cool to room temperature and all the volatiles were removed under vacuum. The residue was washed with petroleum ether to give **9** as a crystalline compound. Yield: 90% (0.959 g). Mp: 208-210 °C. Anal. Calcd. for $C_{17}H_{41}N_4P_2SI$: C, 39.08; H, 7.91; N, 10.72%. Found: C. 39.37; H, 7.78; N, 10.60%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.15 (d, $^2J_{PH}$ = 12.6 Hz, *NH*, 1H), 2.42 (d, $^2J_{PH}$ = 8.8 Hz, *NH*, 1H), 1.70 (s, CH_3, 3H), 1.56 (s, ^{t}*Bu*, 9H),

1.32 (s, ^{t}Bu, 18H), 1.28 (s, ^{t}Bu, 9H). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 38.2 (d, $^{2}J_{PP}$ = 32.3 Hz *trans*-P-S), 24.1 (d, $^{2}J_{PP}$ = 32.3 Hz, *trans*-P-CH_3); 36.6 (d, $^{2}J_{PP}$ = 38.8 Hz, *cis*-P-S), 24.1 (d, $^{2}J_{PP}$ = 38.8 Hz, *cis*-P-CH_3).

Synthesis of *cis*-[{$(Me_2NC_4H_8N)P(S)(\mu$-$N^{t}Bu)_2P(CH_3)(NC_4H_8NMe_2)$}$(I)_3$] (10). A mixture of **5** (0.240 g, 0.290 mmol) and elemental sulfur (0.010 g, 0.290 mmol) in methanol (20 mL) was heated under reflux for 10 h. The reaction mixture was allowed to attain room temperature and all the volatiles were removed under vacuum. The residue was washed with petroleum ether to give **10** as a crystalline compound. Yield: 85% (0.212 g). Mp: 216-218 °C. Anal. Calcd. for $C_{21}H_{49}N_6P_2I_3S$: C, 29.31; H, 5.74; N, 9.76%. Found: C. 29.26; H, 5.68; N, 9.48%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.71-3.47 (m, C_4H_8, 16H), 3.38 (s, NMe_2, 6H), 3.27 (s, NMe_2, 6H), 1.38 (d, $^{2}J_{PH}$ = 4 Hz, CH_3, 3H), 1.35 (s, ^{t}Bu, 18H). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, DMSO-d_6, δ): 48.1 (s), 35.7 (s).

Synthesis of *cis*-[{$(\mu$-$N^{t}BuPS)_2(OCH_2CH_2NMe_3)_2$}$(I)_2$] (11). This was synthesized by a procedure similar to that of **10** using **8** (0.121 g, 0.182 mmol) and elemental sulfur (0.012 g, 0.364 mmol). Yield: 82% (0.109 g). Mp: 174-176 °C. Anal. Calcd. for $C_{18}H_{44}O_2N_4P_2S_2I_2$: C, 29.68; H, 6.09; N, 7.69; S, 8.80%. Found: C. 29.59; H, 6.02; N, 7.43; S, 8.65%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 4.48 (br s, CH_2, 4H), 3.69 (br s, CH_2, 4H), 3.17 (s, NMe_3, 18H), 1.48 (s, ^{t}Bu, 18H). $^{31}P\{^{1}H\}$ NMR (161.8 MHz, DMSO-d_6, δ): δ 48.5 (s).

Synthesis of *cis*-[{$(^{t}BuNHPSe)(\mu$-$N^{t}Bu)_2(P(CH_3)NH^{t}Bu)$}$(I)$] (12a). This was synthesized by a procedure similar to that of **9** using **4** (0.112 g, 0.228 mmol) and elemental selenium (0.018 g, 0.228 mmol). Yield: 70% (0.908 g, 0.160 mmol). Mp: 212-214 °C. Anal. Calcd. for $C_{17}H_{41}N_4P_2ISe$: C, 35.86; H, 7.25; N, 9.84%. Found: C. 35.73; H, 7.18; N, 9.72%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.85 (d, $^{2}J_{PH}$ = 12.4 Hz, *NH*, 1H), 2.34 (d, $^{2}J_{PH}$ = 10.2 Hz, *NH*, 1H), 1.72 (s,

CH$_3$, 3H), 1.56 (s, ^{t}*Bu*, 9H), 1.32 (s, ^{t}*Bu*, 18H), 1.28 (s, ^{t}*Bu*, 9H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 25.8 (d, $^2J_{PP}$ = 25.6 Hz), 24.1 (d, $^2J_{PP}$ = 25.6 Hz, $^1J_{SeP}$ = 906 Hz).

Synthesis of *cis*-[{(Me$_2$NC$_4$H$_8$NPSe)(μ-N^{t}Bu)$_2$(P(CH$_3$)NC$_4$H$_8$NMe$_2$)}(I)$_3$] (13a). This was synthesized by a procedure similar to that of **10** using **7** (0.200 g, 0.241 mmol) and elemental selenium (0.019 g, 0.241 mmol). Yield: 65% (0.157 g). Mp: 212-214 °C. Anal. Calcd. for $C_{21}H_{49}N_6P_2I_3Se$: C, 27.80; H, 5.44; N, 9.26%. Found: C. 27.67; H, 5.58; N, 9.41%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.85-3.52 (m, C_4H_8, 16H), 3.36 (s, *NMe*$_2$, 6H), 3.22 (s, *NMe*$_2$, 6H), 1.48 (d, $^2J_{PH}$ = 4 Hz, *CH*$_3$, 3H), 1.35 (s, ^{t}*Bu,* 18H). ^{31}P{^{1}H} NMR (161.8 MHz, DMSO-d_6, δ): 41.1 (d, $^2J_{PP}$ = 28.8 Hz), 39.6 (d, $^2J_{PP}$ = 28.8 Hz, $^1J_{SeP}$ = 910 Hz).

***cis*-[{(μ-N^{t}BuPSe)$_2$(NC$_4$H$_8$NMe$_2$)}(I)$_2$] (13b).** Mp: 188-190 °C. Anal. Calcd. for $C_{20}H_{46}N_6P_2I_2Se_2$: C, 28.45; H, 5.49; N, 9.95%. Found: C. 28.62; H, 5.28; N, 9.79%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 3.88 (br s, *CH*$_2$, 8H), 3.34 (br s, *CH*$_2$ 8H), 2.78 (s, *NMe*$_2$, 6H), 1.78 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, DMSO-d_6, δ): 40.5 (s, $^1J_{SeP}$ = 890 Hz).

Synthesis of *cis*-[{(μ-N^{t}BuPSe)$_2$(OCH$_2$CH$_2$NMe$_3$)$_2$}(I)$_2$] (14). This was synthesized by a procedure similar to that of **10** using **8** (0.121 g, 0.181 mmol) and elemental selenium (0.029 g, 0.364 mmol). Yield: 80% (0.119 g, 0.145 mmol). Mp: 182-184 °C. Anal. Calcd. for $C_{18}H_{44}N_4P_2O_2I_2Se_2$: C, 26.29; H, 5.39; N, 6.81%. Found: C. 26.45; H, 5.42; N, 6.79%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 4.28- (t, J_{HH} = 8.8 Hz, *OCH*$_2$, 4H), 3.68 (t, J_{HH} = 8.2 Hz, *NCH*$_2$, 4H), 3.30 (s, *NCH*$_3$, 18H), δ 1.49 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, DMSO-d_6, δ): 42.7 (s, $^1J_{SeP}$ = 930 Hz).

Synthesis of *cis*-[{Cu$_2$(μ-I)$_3$[(^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu)]$_2$}(I)] (15). A solution of CuI (0.026 g, 0.139 mmol) in acetonitrile (5 mL) was added dropwise to a well-stirred solution of **4** (0.068 g, 0.139 mmol) in dichloromethane (5 mL). The reaction mixture was stirred for a further

4 h at room temperature. The solution was filtered through celite and concentrated to 5 mL under reduced pressure. The concentrated solution was stored at room temperature for 48 h to afford **15** as colorless crystals. Yield: 90% (0.085 g). Mp: 208-210 °C (dec). Anal. Calcd. for $C_{34}H_{82}N_8P_4Cu_2I_4$: C, 29.98; H, 6.07; N, 8.23%. Found: C. 29.88; H, 6.18; N, 8.12%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.85 (d, $^2J_{PH}$ = 5.6 Hz, *NH*, 1H), 2.52 (d, $^2J_{PH}$ = 14.8 Hz, *NH*, 1H), 1.61 (s, *CH*$_3$, 3H), 1.59 (s, ^{t}*Bu*, 9H), 1.55 (s, ^{t}*Bu*, 18H), 1.32 (s, ^{t}*Bu*, 9H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 80.4 (s), 19.6 (s).

Synthesis of *cis*-[{Cu$_2$(μ-I)$_3$[(Me$_2$NC$_4$H$_8$N)P(μ-N^{t}Bu)$_2$P(CH$_3$)(NC$_4$H$_8$NMe$_2$)]$_2$}(I)$_5$] (16). To a solution of **7** (0.063 g, 0.076 mmol) in 6 mL of methanol was added a solution of CuI (0.014 g, 0.076 mmol) in acetonitrile (4 mL). The reaction mixture was stirred at room temperature for 4 h. All the volatiles were removed under vacuum and the resulting solid washed with diethyl ether to afford **16** as an analytically pure crystalline solid. Yield: 78% (0.061 g). Mp: 232-234 °C (dec). Anal. Calcd. for $C_{42}H_{98}P_4N_{12}I_6Cu_2I_2$: C, 24.75; H, 4.84; N, 8.25%. Found: C. 24.65; H, 4.96; N, 8.17%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): δ 3.90-3.11 (m, C_4H_8, 22H), 1.46 (s, *CH*$_3$, 3H), 1.46 (s, ^{t}*Bu*, 18H), 1.42 (s, *CH*$_3$, 3H). ^{31}P{^{1}H} NMR (161.8 MHz, DMSO-d_6, δ): δ 69.2 (br s, Cu-P), 38.9 (s, P-CH_3).

Synthesis of *cis*-[{Cu$_2$(μ-I)$_3$(μ-N^{t}BuP)$_2$(OCH$_2$CH$_2$NMe$_3$)$_2$}$_n$(I)$_n$] (17). This was synthesized by a procedure similar to that of **15** using **8** (0.020 g, 0.030 mmol) and CuI (0.011 g, 0.060 mmol). Yield: 73% (0.023 g). Mp: 240-242 °C (dec). Anal. Calcd. for $C_{18}H_{44}N_4P_2O_2I_4Cu_2$: C, 20.68; H, 4.24; N, 5.36%. Found: C. 20.45; H, 4.42; N, 5.49%. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 4.43 (br s, *OCH*$_2$, 4H), 3.60 (br s, *NCH*$_2$, 4H), 3.15 (br s, *NCH*$_3$, 18H), δ 1.48 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161.8 MHz, DMSO-d_6, δ): 107.1 (br s).

Synthesis of *cis*-[{$(C_5H_5N)_2$CuI(^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH_3)NH^{t}Bu)}(I)] (18). A solution of pyridine (2 mL) in dichloromethane (5 mL) was added dropwise to **15** (0.040 g, 0.029 mmol) also in dichloromethane (8 mL) at room temperature and the reaction mixture was stirred for 3 h. All the volatiles were removed under vacuum and the residue was dissolved in dichloromethane, layered with petroleum ether and stored at -30 °C to give yellow crystals of **18**. Yield: 88% (0.019 g). Mp: 162-164 °C (dec). Anal. Calcd. for $C_{27}H_{51}N_6P_2CuI_2$: C, 38.65; H, 6.13; N, 10.02%. Found: C. 38.68; H, 6.28; N, 9.85%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.85-7.75 (m, *Py*, 5H) 7.12 (br s, *NH*, 1H), 2.45 (br s, *NH*, 1H), 1.64 (s, *CH$_3$*, 3H), 1.58 (s, ^{t}*Bu*, 18H), 1.55 (s, ^{t}*Bu*, 9H), 1.32 (s, ^{t}*Bu*, 9H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 72.4 (br s, Cu-P), 21.5 (s, P-CH_3).

Synthesis of *cis*-[{(2,2′-bpy)CuI(^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH_3)NH^{t}Bu)}(I)] (19). To a solution of **15 (**0.048 g, 0.035 mmol**)** in dichloromethane (5 mL) was added dropwise a solution of 2,2′-bipyridine (0.011 g, 0.070 mmol) in the same solvent (5 mL) at room temperature. The reaction mixture was stirred for further 6 h, concentrated to 4 mL and layered with petroleum ether (2 mL). The clear yellow colored solution was stored at room temperature for 48 h to obtain **19** as yellow orange crystals. Yield: 83% (0.049 g). Mp: 210-212 °C (dec). Anal. Calcd. for $C_{27}H_{49}I_2N_6P_2Cu$: C, 38.74; H, 5.90; N, 10.04%. Found: C. 38.67; H, 5.78; N, 10.14%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.96-7.42 (m, *bpy*, 8H), 7.15 (br s, *NH*, 1H), 2.85 (br s, *NH*, 1H), 1.71 (s, *CH$_3$*, 3H), 1.64 (s, ^{t}*Bu*, 9H), 1.59 (s, ^{t}*Bu*, 18H), 1.28 (s, ^{t}*Bu*, 9H). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$, δ): 79.4 (br s, Cu-P), 20.6 (br s, P-CH_3).

Synthesis of *cis*-[{(1,10-phen)CuI(^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH_3)NH^{t}Bu)}(I)] (20). This was synthesized by a procedure similar to that of **19** using **15** (0.048 g, 0.035 mmol) and 1,10-phenanthroline (0.013 g, 0.070 mmol). Yield: 88% (0.053 g). Mp: 222-224 °C (dec). Anal. Calcd. for $C_{29}H_{49}I_2N_6P_2Cu$: C, 40.45; H, 5.74; N, 9.76%. Found: C. 40.52; H, 5.68; N, 9.72%. ^{1}H

NMR (400 MHz, $CDCl_3$, δ): 8.35-7.68 (m, *phen*, 8H) 7.05 (br s, *NH*, 1H), 2.30 (br s, *NH*, 1H), 1.68 (s, CH_3, 3H), 1.58 (s, ^tBu, 9H), 1.42 (s, ^tBu, 18H), 1.32 (s, ^tBu, 9H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 79.3 (br s, Cu-P), 19.7 (br s, P-CH_3).

Synthesis of *cis*-[{^{t}BuNHP(AuCl)(μ-N^{t}Bu)$_2$P(CH$_3$)NH^{t}Bu}(OTf)] (21). To a solution of **5** (0.030 g, 0.058 mmol) in dichloromethane (5 mL) was added dropwise a solution of [(Me_2S)AuCl] (0.0176 g, 0.058 mmol) in the same solvent (10 mL) at room temperature. The reaction mixture was stirred for 4 h. The clear solution obtained was concentrated to a small bulk under reduced pressure and layered with petroleum ether to obtain **21** as a colorless crystalline solid. Yield: 81% (0.035 g). Mp: 176-179 °C (dec). Anal. Calcd. for $C_{18}H_{41}F_3N_4O_3P_2SAuCl$: C, 29.02; H, 5.55; N, 7.52; S, 4.30%. Found: C. 29.62; H, 5.92; N, 7.05; S 4.72%. ^1H NMR (400 MHz, $CDCl_3$, δ): 6.71 (d, $^2J_{PH}$ = 6.9 Hz, *NH*, 1H), 6.13 (d, $^2J_{PH}$ = 9.5 Hz, *NH*, 1H), 2.23 (d, $^2J_{PH}$ = 15.2 Hz, CH_3, 3H), 1.53 (s, ^tBu, 18H), 1.52 (s, ^tBu, 9H), 1.51 (s, ^tBu, 9H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 67.5 (s), 31.9 (s).

X-ray Crystallography

Crystals obtained in the present investigation were mounted in a CryoLoop™ with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. For each, a full sphere of data was collected using 3 sets of 400 frames, each of width 0.5° in ω, collected at φ = 0.00, 90.00 and 180° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = -30.00 and 210.00°using the SMART[62] or APEX2[63] software packages. The raw data were reduced to *F2* values using the SAINT software[64] and global refinements of unit cell parameters employing 4622–9890 reflections chosen from the full data set were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption correction as well as a correction for any crystal deterioration during the

data collection (SADABS).[65] The structures were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package.[66,67] Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Crystallographic Data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 991947 (Compound **12a**), 991948 (Compound **13b**), 991949 (Compound **14**), 991950 (Compound **15**), 991951 (Compound **19**), 991952 (Compound **20**), 991953 (Compound **21**).

References

1. K. H. Shaughnessy, *Chem. Rev.*, 2009, **109**, 643-710.
2. M. Stradiotto, K. D. Hesp and R. J. Lundgren, *Angew. Chem. Int. Ed.*, 2010, **49**, 494-512.
3. J. Bravo, S. Bolano, L. Gonsalvi and M. Peruzzini, *Coord. Chem. Rev.*, 2010, **254**, 555-607.
4. N. Pinault and D. W. Bruce, *Coord. Chem. Rev.*, 2003, **241**, 1-25.
5. J. Boulanger, H. Bricout, S. Tilloy, A. Fihri, C. Len, F. Hapiot and E. Monflier, *Cat. Commun.*, 2012, **29**, 77-81.
6. Y. S. Wagh, D. N. Sawant, K. P. Dhake and B. M. Bhanage, *Catal. Sci. Technol.*, 2012, **2**, 835-840.
7. J. Schulz, I. Cisarova and P. Stepnicka, *Organometallics*, 2012, **31**, 729-738.
8. D. J. Darensbourg, C. G. Ortiz and J. Yarbrough, *Inorg. Chem.*, 2003, **42**, 6915-6922.
9. D. P. Paterniti, L. W. Francisco and J. D. Atwood, *Organometallics*, 1999, **18**, 123-127.
10. T. Malmstrom and C. Andersson, *Chem. Commun.*, 1996, 1135-1136.
11. A. Avey, D. M. Schut, T. J. R. Weakley and D. R. Tyler, *Inorg. Chem.*, 1993, **32**, 233-236.
12. R. Garcia-Alvarez, M. Zablocka, P. Crochet, C. Duhayon, J.-P. Majoral and V. Cadierno, *Green Chem.*, 2013, **15**, 2447-2456.
13. S. Vigo, R. Andres, P. Gomez-Sal, J. de la Mata and E. de Jesus, *J. Organomet. Chem.*, 2012, **717**, 88-98.

14. R. B. DeVasher, J. M. Spruell, D. A. Dixon, G. A. Broker, S. T. Griffin, R. D. Rogers and K. H. Shaughnessy, *Organometallics*, 2005, **24**, 962-971.
15. K. H. Shaughnessy and R. S. Booth, *Org. Lett.*, 2001, **3**, 2757-2759.
16. A. T. Ekubo, M. R. J. Elsegood, A. J. Lake and M. B. Smith, *Inorg. Chem.*, 2009, **48**, 2633-2638.
17. A. T. Ekubo, M. R. J. Elsegood, A. J. Lake and M. B. Smith, *Inorg. Chem.*, 2010, **49**, 3703-3705.
18. K. L. Luska, K. Z. Demmans, S. A. Stratton and A. Moores, *Dalton Trans.*, 2012, **41**, 13533-13540.
19. M. Terada and M. Kouchi, *Tetrahedron*, 2006, **62**, 401-409.
20. H. Remmele, A. Kollhofer and H. Plenio, *Organometallics*, 2003, **22**, 4098-4103.
21. F. Zaragoza, *J. Org. Chem.*, 2002, **67**, 4963-4964.
22. D. A. Krogstad, A. Guerriero, A. Ienco, G. Manca, M. Peruzzini, G. Reginato and L. Gonsalvi, *Organometallics*, 2011, **30**, 6292-6302.
23. B. R. James and F. Lorenzini, *Coord. Chem. Rev.*, 2010, **254**, 420-430.
24. R. Schibli, K. V. Katti, W. A. Volkert and C. L. Barnes, *Inorg. Chem.*, 2001, **40**, 2358-2362.
25. C. D. Swor, K. R. Hanson, L. N. Zakharov and D. R. Tyler, *Dalton Trans.*, 2011, **40**, 8604-8610.
26. A. D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza and M. Peruzzini, *Coord. Chem. Rev.*, 2004, **248**, 955-993.
27. M. S. Balakrishna, D. J. Eisler and T. Chivers, *Chem. Soc. Rev.*, 2007, **36**, 650-664.
28. G. S. Ananthnag, S. Kuntavalli, J. T. Mague and M. S. Balakrishna, *Inorg. Chem.*, 2012, **51**, 5919-5930.
29. M. S. Balakrishna, R. Venkateswaran and J. T. Mague, *Dalton Trans.*, 2010, **39**, 11149-11162.
30. P. Chandrasekaran, J. T. Mague and M. S. Balakrishna, *Inorg. Chem.*, 2005, **44**, 7925-7932.
31. M. S. Balakrishna, D. Suresh, A. Rai, J. T. Mague and D. Panda, *Inorg. Chem.*, 2010, **49**, 8790-8801.

32. D. Suresh, M. S. Balakrishna, K. Rathinasamy, D. Panda and S. M. Mobin, *Dalton Trans.*, 2008, 2812-2814.
33. A. Nordheider, T. Chivers, O. Schon, K. Karaghiosoff, K. S. Athukorala Arachchige, A. M. Z. Slawin and J. D. Woollins, *Chem. Eur. J.*, 2014, **20**, 704-712.
34. T. Roth, H. Wadepohl, D. S. Wright and L. H. Gade, *Chem. Eur. J.*, 2013, **19**, 13823-13837.
35. A. Nordheider, T. Chivers, R. Thirumoorthi, K. S. Athukorala Arachchige, A. M. Z. Slawin, J. D. Woollins and I. Vargas-Baca, *Dalton Trans.*, 2013, **42**, 3291-3294.
36. A. Nordheider, T. Chivers, R. Thirumoorthi, I. Vargas-Baca and J. D. Woollins, *Chem. Commun.*, 2012, **48**, 6346-6348.
37. H. Bladt, S. Gonzalez Calera, J. M. Goodman, R. J. Less, V. Naseri, A. Steiner and D. S. Wright, *Chem. Commun.*, 2009, 6637-6639.
38. S. Gonzalez Calera, D. J. Eisler, J. M. Goodman, M. McPartlin, S. Singh and D. S. Wright, *Dalton Trans.*, 2009, 1293-1296.
39. N. S. Kumar, K. P. Kumar, K. V. P. Pavankumar, P. Kommana, J. J. Vittal and K. C. Kumaraswamy, *J. Org. Chem.*, **2004**, **69**, 1880.
40. G. R. Lief, D. F. Moser, L. Stahl and R. J. Staples, *J. Organomet.Chem.*, 2004, **689**, 1110-1121.
41. M. S. Balakrishna, D. Suresh and J. T. Mague, *Eur. J. Inorg. Chem.*, 2011, 4201-4210.
42. J. A. Dobado, H. Martinez-Garcia, José Molina Molina and M. R. Sundberg, *J. Am. Chem. Soc.*, 2000, **122**, 1144-1149.
43. T. Leyssens and D. Peeters, *J. Org. Chem.*, 2008, **73**, 2725-2730.
44. R. Murugavel, S. Krishnamurthy, J. Chandrasekhar and M. Nethaji, *Inorg. Chem.*, 1993, **32**, 5447-5453.
45. P. von Rague Schleyer and A. J. Kos, *Tetrahedron*, 1983, **39**, 1141-1150.
46. K. P. Kumar, M. Chakravarty and K. C. K. Swamy, *Z. Anorg. Allg. Chem.*, 2004, **630**, 2063-2070.
47. G. Gangadhararao and K. C. Kumara Swamy, *Tetrahedron*, 2014, **70**, 2643-2653.
48. K. C. K. Swamy, K. P. Kumar and N. N. B. Kumar, *J. Org. Chem.*, 2006, **71**, 1002-1008.
49. G. G. Briand, T. Chivers and M. Krahn, *Coord. Chem. Rev.*, 2002, **233â€“234**, 237-254.
50. P. Kommana and K. C. Kumara Swamy, *Inorg. Chem.*, 2000, **39**, 4384-4385.

51. C.-C. Chang, R. C. Haltiwanger, M. L. Thompson, H.-J. Chen and A. D. Norman, *Inorg. Chem.*, 1979, **18**, 1899-1904.
52. K. C. K. Swamy, P. Kommana, M. Vijjulatha and K. P. Kumar, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2001, **169**, 31-34.
53. T. Chivers, M. Krahn and M. Parvez, *Chem. Commun.*, 2000, 463-464.
54. T. Chivers, M. Krahn, M. Parvez and G. Schatte, *Inorg. Chem.*, 2001, **40**, 2547-2553.
55. T. Chivers, M. Krahn and G. Schatte, *Inorg. Chem.*, 2002, **41**, 4348-4354.
56. G. A. Bowmaker, A. Camus, P. C. Healy, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1989, **28**, 3883-3888.
57. A. S. Batsanov, Y. T. Struchkov, L. Y. Ukhin and N. A. Dolgopolova, *Inorg. Chim. Acta*, 1982, **63**, 17-22.
58. W. J. Gee and S. R. Batten, *Cryst. Growth Des.*, 2013, **13**, 2335-2343.
59. A. K. Nurtaeva and E. M. Holt, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 594-597.
60. I. Schranz, L. Stahl and R. J. Staples, *Inorg. Chem.*, 1998, **37**, 1493-1498.
61. M. Brandys, M. C. Jennings and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 2000, 4601-4606.
62. Bruker-AXS, *SMART, Version 5.625, Madison, WI*, 2000.
63. *APEX2, version 2.1-0, Bruker-AXS, Madison, WI,*, 2006.
64. Bruker-AXS, *SAINT+, Version 6.35A, Madison, WI*, 2002.
65. G. Sheldrick, M., *SADABS, Version 2.05. University of Göttingen, Germany*, 2002.
66. G. M. Sheldrick, *SHELXS97 and SHELXL97. University of Göttingen, Germany*, 1997.
67. Bruker-AXS, *SHELXTL, Version 6.10, Madison, WI*, 2000.

Table 1. Crystallographic information for compounds **12a**, **13b**, **14** and **15**

	12a	**13b**	**14**	**15**
Formula	$C_{24}H_{49}N_4P_2Se{\cdot}I$	$C_{40}H_{94}N_{12}OP_4Se_4{\cdot}(I)_4$	$C_{18}H_{44}I_2N_4O_2P_2Se_2{\cdot}(I)_2{\cdot}H_2O$	$C_{34}H_{82}Cu_2I_3N_8P_4{\cdot}I{\cdot}CH_3CN$
Fw	661.47	1706.59	840.25	1402.68
crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
space group	P1 (No. 1)	P2/c (No. 13)	C2/c (No. 15)	$P2_1/c$ (No. 14)
a, Å	9.3436(6)	32.556(3)	12.1752(9)	10.3950(7)
b, Å	10.3905(7)	9.5372(10)	14.2395(11)	29.9149(18)
c, Å	16.706(1)	21.679(2)	36.578(3)	17.8929(11)
α, deg	93.176(1)	90	90	90
β, deg	104.556(1)	107.558(2)	94.632(1)	95.847(1)
γ, deg	91.995(1)	90	90	90
V, Å^3	1565.43(17)	6417.5(11)	6321.0(8)	5535.1(6)
Z	2	4	8	4
ρ_{calc}, gcm^{-3}	1.403	1.766	1.766	1.683
μ (MoKα), mm^{-1}	2.305	4.350	4.419	3.148
F (000)	676	3336	3280	2776
crystal size mm	0.14 × 0.15 × 0.20	0.13 × 0.15 × 0.16	0.9 × 0.19 × 0.22	0.06 × 0.15 × 0.20
T, K	100	100	100	100
θ range, deg	2.3-28.3	2.0-28.3	2.2-28.3	2.1-26.8
Total no. reflns	27720	110101	55219	30384
No. of indep. reflns	14366 [R_{int} = 0.025]	15994 [R_{int} = 0.069]	7868 [R_{int} = 0.037]	26164, [R_{int} = 0.0959]
R1[a]	0.0272	0.0494	0.0250	0.0362
wR_2[b]	0.0561	0.1038	0.0579	0.0703
GOF (F^2)	0.98	1.15	1.13	0.95

Table 2. Crystallographic information for compounds **19**, **20** and **21**

	19	**20**	**21**
Formula	$C_{27}H_{49}CuIN_6P_2{\cdot}I$	$C_{29}H_{49}CuI_2N_6P_2{\cdot}I$	$C_{17}H_{41}AuClN_4P_2{\cdot}CF_3O_3S$
Fw	837.00	861.03	744.96
crystal system	Orthorhombic	Orthorhombic	Triclinic
space group	$P2_12_12_1$ (No. 19)	$Pca2_1$ (No. 29)	P-1 (No. 2)
a, Å	14.1715(6)	24.7202(11)	9.714(3)
b, Å	14.6142(6)	10.1169(4)	10.396(3)
c, Å	16.8817(7)	14.2381(6)	17.440(6)
α, deg	90	90	81.865(4)
β, deg	90	90	85.488(4)
γ, deg	90	90	62.617(4)
V, Å^3	3496.3(3)	3560.8(3)	1547.9(9)
Z	4	4	2
ρ_{calc}, gcm^{-3}	1.590	1.606	1.598
μ (MoKα), mm^{-1}	2.508	2.465	5.051
F (000)	1672	1720	740
crystal size mm	0.13 × 0.14 × 0.15	0.11 × 0.16 × 0.26	0.11 × 0.23 × 0.23
T, K	100	100	150
2θ range, deg	2.3-28.3	2.0-29.0	2.2-29.5
Total no. reflns	61743	62138	27070
No. of indep. reflns	8681 [R_{int} = 0.053]	9502 [R_{int} = 0.043]	8002 [R_{int} = 0.060]
R1[a]	0.0379	0.0221	0.0327
wR_2[b]	0.0869	0.0470	0.0873
GOF (F^2)	1.07	1.05	1.03

Table 3. Selected bond distances and bond angles for **12a**, **13b**, **14** and **15**

12a				**13b**			
bond distances [Å]		bond angles [°]		bond distances [Å]		bond angles [°]	
Se1–P1	2.0797(11)	Se1–P1–N1	117.60(12)	Se1–P1	2.0822(12)	Se1–P1–N1	122.73(14)
P1–N1	1.703(3)	Se1–P1–N2	116.97(12)	Se2–P2	2.0773(13)	Se1–P1–N2	118.44(14)
P1–N3	1.618(3)	Se1–P1–N3	116.48(13)	P1–N2	1.708(4)	Se1–P1–N3	110.42(14)
P1–N2	1.713(2)	N1–P1–N2	81.95(16)	P1–N3	1.662(4)	N1–P1–N2	83.79(19)
P2–N2	1.660(3)	N1–P1–N3	108.81(17)	P1–N1	1.674(4)	N1–P1–N3	107.3(2)
P2–N4	1.592(4)	N2–P1–N3	110.04(17)	P2–N5	1.652(4)	N2–P1–N3	111.6(2)
P2–N1	1.652(4)	N1–P2–N2	85.12(17)	P2–N1	1.705(4)	Se2–P2–N1	117.14(14)
		N1–P2–N4	114.10(18)	P2–N2	1.685(4)	Se2–P2–N2	121.57(14)
						Se2–P2–N5	110.26(15)
						N1–P2–N2	83.51(19)
						N1–P2–N5	113.9(2)
14				**15**			
bond distances [Å]		bond angles [°]		bond distances [Å]		bond angles [°]	
Se1–P1	2.0635(7)	O1–P1–Se1	107.53(7)	I1–Cu1	2.7313(7)	Cu1–I1–Cu2	55.51(1)
Se2–P2	2.0672(7)	N1–P1–Se1	122.44(8)	I1–Cu2	2.7555(7)	Cu1–I2–Cu2	57.11(1)
P1–O1	1.6014(19)	N2–P1–Se1	123.61(8)	I2–Cu1	2.7050(7)	Cu1–I3–Cu2	55.370(18)
P1–N1	1.681(2)	O1–P1–N1	108.80(10)	I2–Cu2	2.6395(7)	I1–Cu1–I2	97.93(2)
P1–N2	1.692(2)	O1–P1–N2	108.01(10)	I3–Cu1	2.7342(7)	I1–Cu1–I3	102.51(2)
P2–O2	1.6015(18)	N1–P1–N2	84.24(10)	I3–Cu2	2.7655(7)	I1–Cu1–P1	118.65(4)
P2–N1	1.684(2)	O2–P2–Se2	113.06(7)	Cu1–P1	2.2137(13)	I2–Cu1–I3	98.63(2)
P2–N2	1.679(2)	N2–P2–Se2	122.78(8)	Cu2–P3	2.2037(12)	I2–Cu1–P1	128.96(4)
O1–C9	1.448(3)	N1–P2–Se2	121.99(8)	Cu1–Cu2	2.5553(8)	I3–Cu1–P1	105.91(4)
O2–C14	1.447(3)	O2 P2 N2	103.54(10)			Cu1–P1–N1	117.42(12)
N3–C12	1.502(3)	O2 P2 N1	106.62(10)				
N3–C11	1.504(3)	N2 P2 N1	84.51(10)				
N3–C10	1.517(3)						

Table 4. Selected bond distances and bond angles for **19**-**21**

19				**20**			
bond distances [Å]		bond angles [°]		bond distances [Å]		bond angles [°]	
I1–Cu1	2.6159(8)	I1–Cu1–P1	110.14(5)	I1–Cu1	2.6067(5)	I1–Cu1–P1	108.49(3)
Cu1–P1	2.1963(16)	I1–Cu1–N5	103.41(18)	Cu1–P1	2.1939(10)	I1–Cu1–N5	107.16(9)
Cu1–N5	2.086(6)	I1–Cu1–N6	110.79(19)	Cu1–N5	2.085(3)	I1–Cu1–N6	106.35(9)
Cu1–N6	2.082(6)	P1–Cu1–N5	126.28(18)	Cu1–N6	2.108(3)	P1–Cu1–N5	124.70(9)
P1–N1	1.645(5)	P1–Cu1–N6	122.84(19)	P1–N1	1.640(3)	P1–Cu1–N6	126.22(9)
P1–N2	1.744(6)	N5–Cu1–N6	79.3(2)	P1–N2	1.751(3)	N5–Cu1–N6	80.27(12)
P1–N3	1.758(6)	Cu1–P1–N1	122.1 (2)	P1–N3	1.756(3)	Cu1–P1–N1	124.38(12)
P2–C17	1.843(7)	Cu1–P1–N2	117.6(2)			Cu1–P1–N2	117.91(11)
		Cu1–P1–N3	117.4(2)			Cu1–P1–N3	115.71(11)

21			
bond distances [Å]		bond angles [°]	
Au1–Cl1	2.2960(11)	P1–Au1–Cl1	176.26(3)
Au1–P1	2.2155(11)	P1–N2–P2	96.05(13)
P2–C17	1.784(3)	Au1–P1–N1	116.94(10)
P1–N1	1.621(3)	Au1–P1–N2	115.06(9)
P2–N4	1.606(3)	C17–P2–N4	111.29(17)
P1–N2	1.726(3)		
P2–N2	1.664(3)		

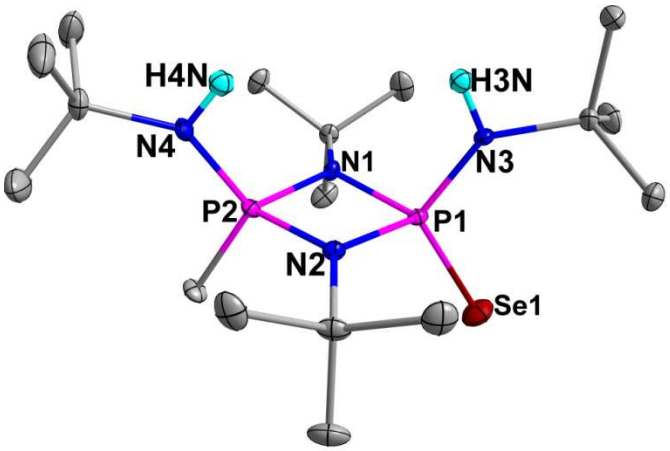


Figure 1. The molecular structure of *cis*-[{(^{t}BuNHPSe)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu)}(I)] (**12a**). All hydrogen atoms (except H3N and H4N), the iodide ion and solvent toluene molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

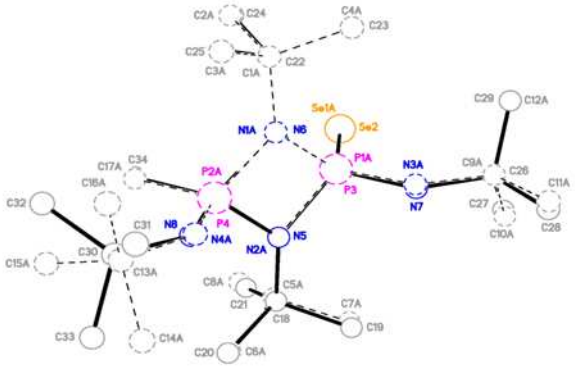


Figure 1b. Overlay of molecule 2 (solid lines) of **12a** on molecule 1 (dotted lines) showing the conformational differences.

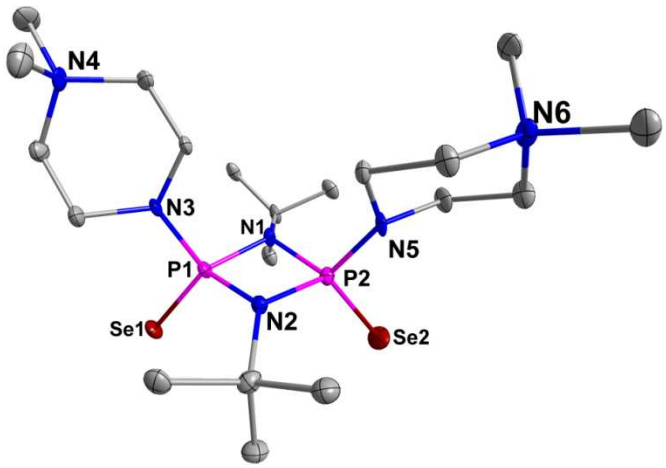


Figure 3. The molecular structure of *cis*-[{(μ-N^{t}BuPSe)$_2$(NC$_4$H$_8$NMe$_2$)}(I)$_2$] (**13b**). All hydrogen atoms, iodide ions and solvent water molecules are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

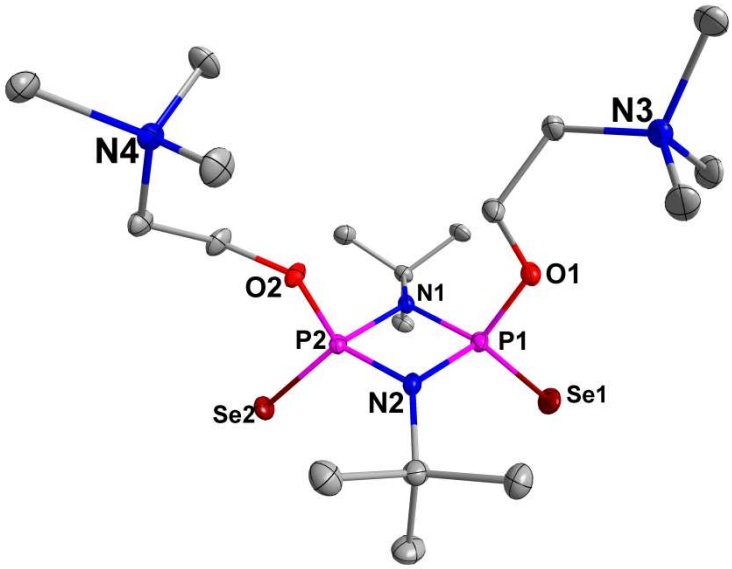


Figure 4. The molecular structure of *cis*-[{(μ-N^{t}BuPSe)$_2$(OCH$_2$CH$_2$NMe$_3$)$_2$}(I)$_2$] (**14**). All hydrogen atoms, iodide atoms and solvent water molecules were omitted for clarity. Thermal ellipsoids are drawn at 50% probability level.

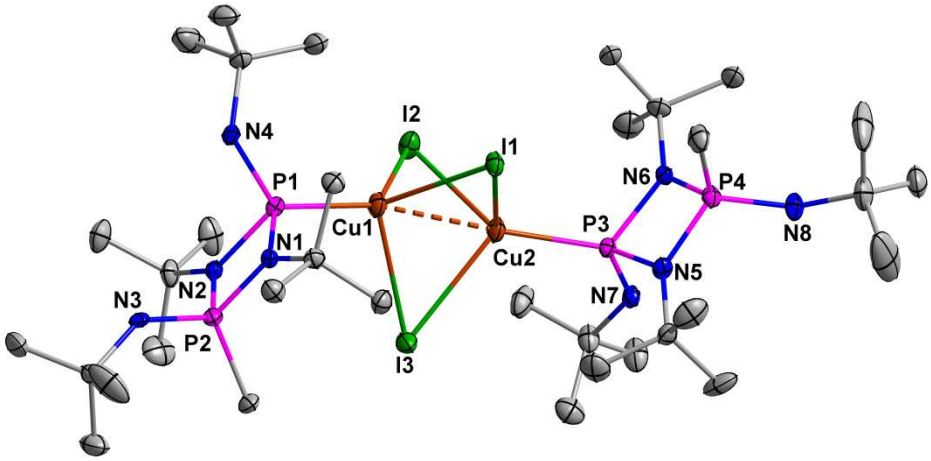


Figure 4. The molecular structure of *cis*-[{$Cu_2(\mu\text{-}I)_3[(^t\text{BuNHP})(\mu\text{-}N^t\text{Bu})_2(P(CH_3)NH^t\text{Bu})]_2$}(I)] (**15**). All hydrogen atoms, the iodide ion and solvent acetonitrile molecule are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

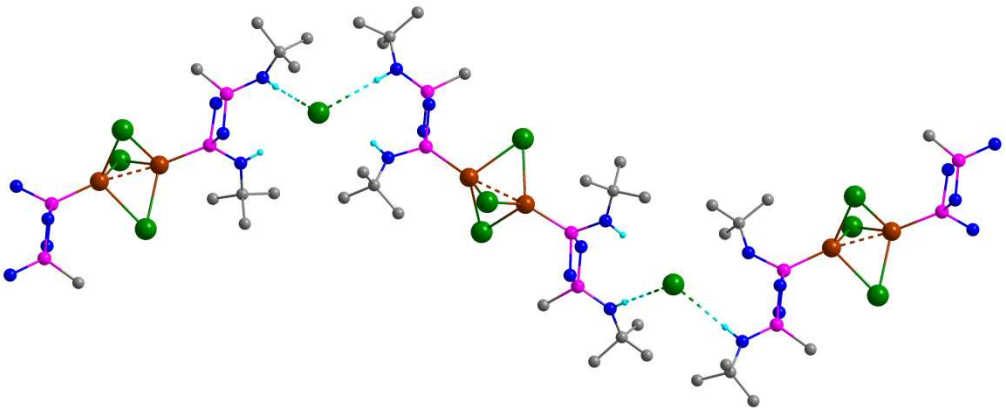


Figure 5. Ball and stick model of the molecular structure of *cis*-[{$Cu_2(\mu\text{-}I)_3[(^t\text{BuNHP})(\mu\text{-}N^t\text{Bu})_2(P(CH_3)NH^t\text{Bu})]_2$}(I)] (**15**) showing the intermolecular hydrogen bonding.

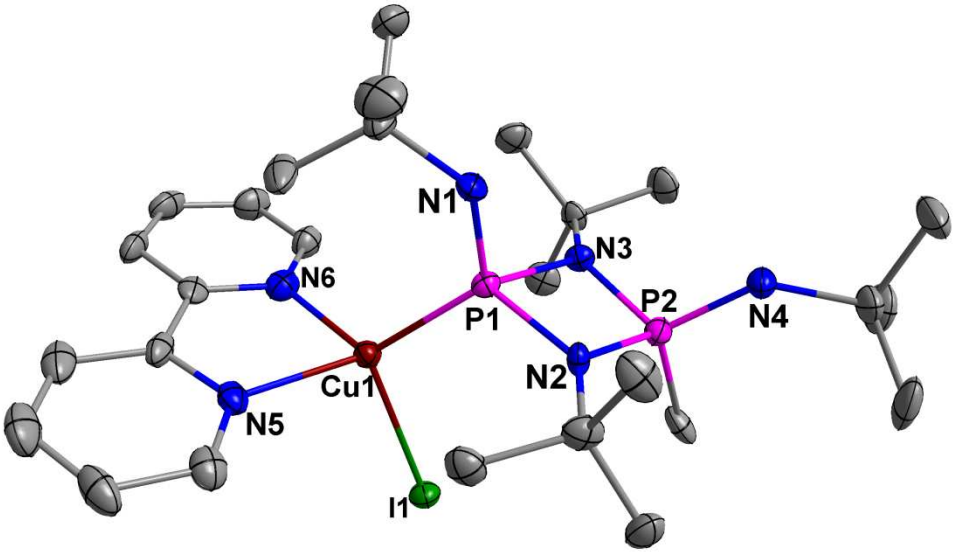


Figure 6. The molecular structure of *cis*-[{(2,2′-bpy)CuI(ᵗBuNHP)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu)}(I)] (**19**). All hydrogen atoms and the iodide ion are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

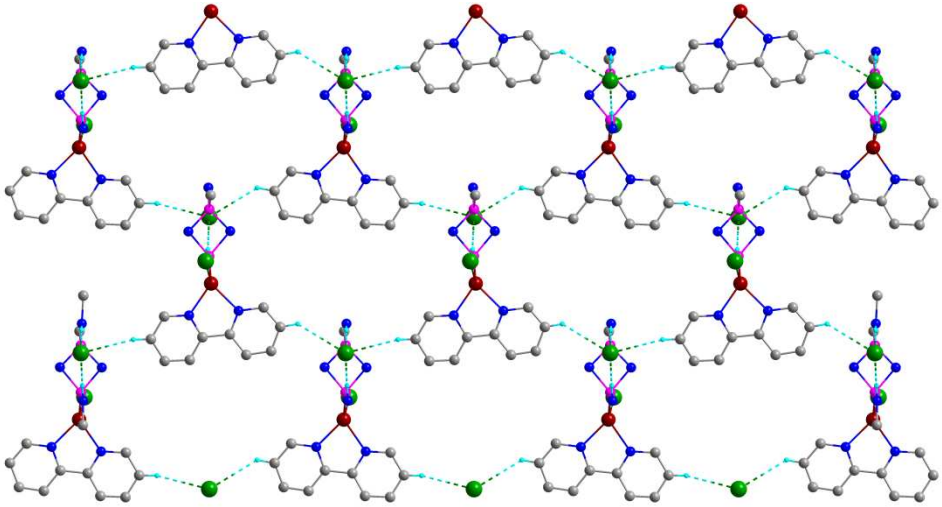


Figure 7. Ball and stick model of the packing of *cis*-[{(2,2′-bpy)CuI(ᵗBuNHP)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu)}(I)] (**19**) showing the intra- and intermolecular hydrogen bonding.

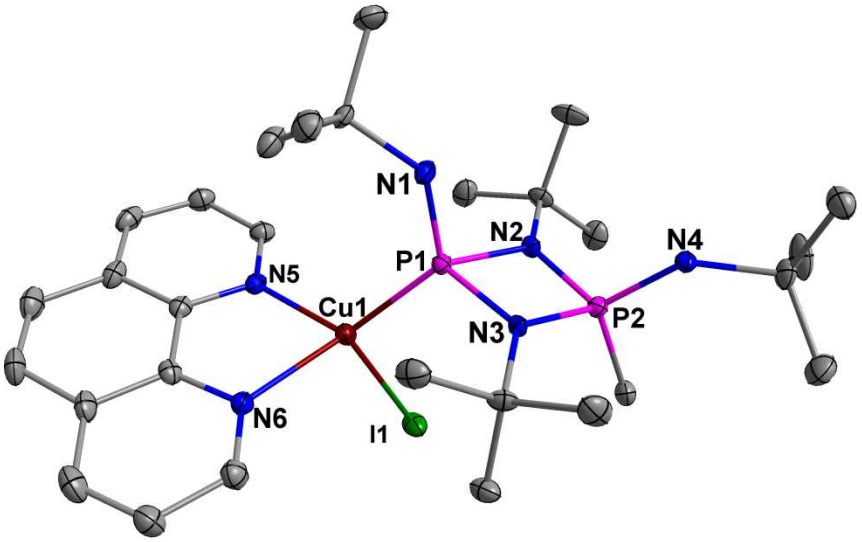


Figure 8. The molecular structure of *cis*-[(1,10-phen)CuI{^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu}]I (**20**). All hydrogen atoms and the iodide ion are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

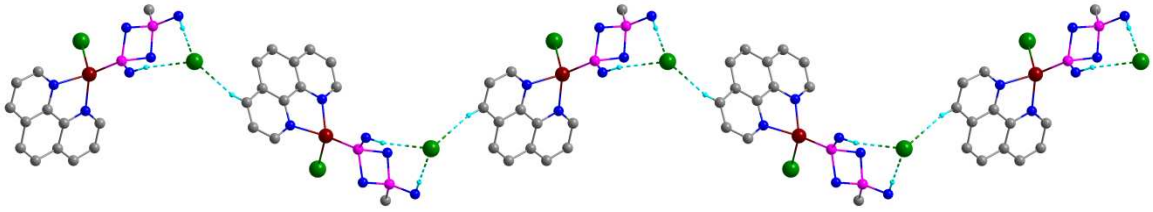


Figure 9. Ball and stick model of *cis*-[(1,10-phen)CuI{^{t}BuNHP-(μ-N^{t}Bu)$_2$P(CH$_3$)NH^{t}Bu}]I (**20**) showing the intra- and intermolecular hydrogen bonding.

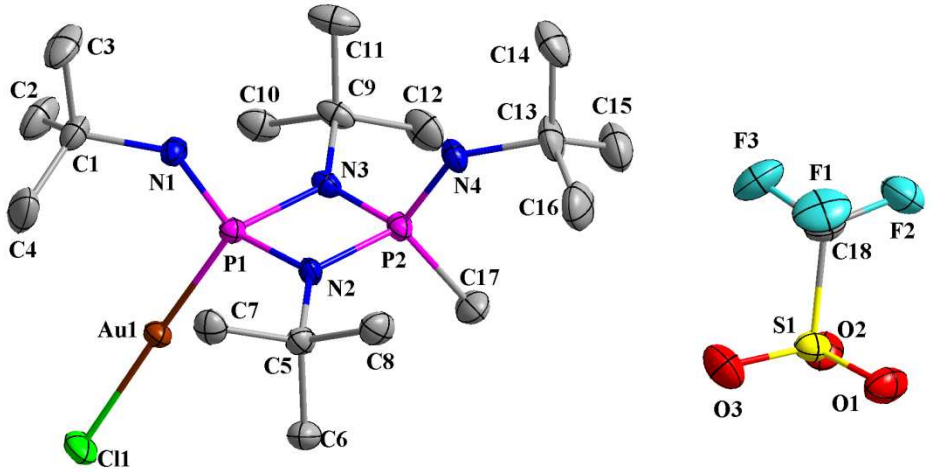


Figure 10. The molecular structure of *cis*-[(AuCl){^{t}BuNHP)(μ-N^{t}Bu)$_2$(P(CH$_3$)NH^{t}Bu}]OTf (**21**). All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Synopsis for contents page

Quaternization and oxidation reactions of cyclodiphosphazane derivatives and their copper(I) and gold(I) complexes

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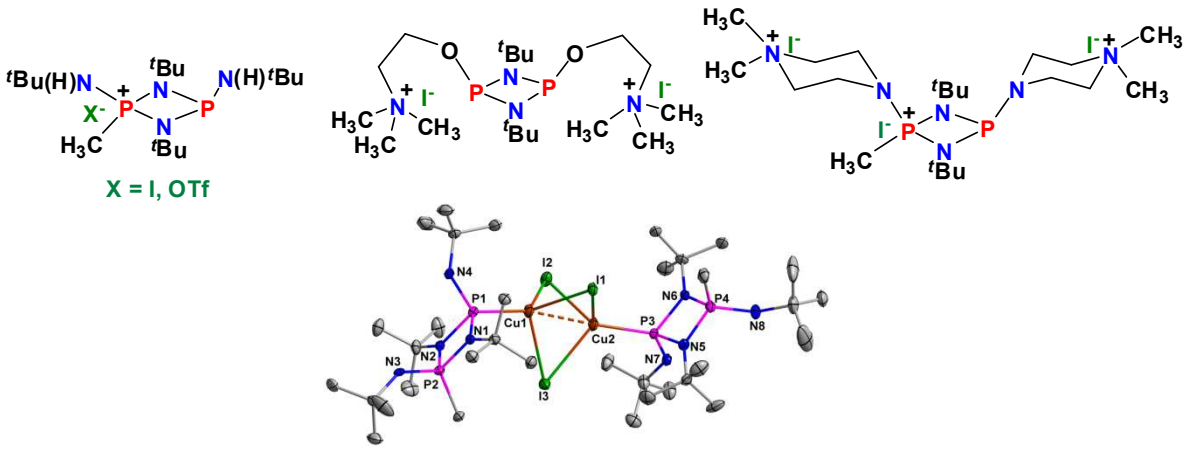

Quaternization reactions of various cyclodiphosphazanes and their transition metal (Cu^{I} and Au^{I}) complexes are described

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