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Copper(I) and silver(I) complexes of carbaphosphazene-anchored N-heterocyclic carbene ligands

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ABSTRACT

Carbaphosphazene-anchored imidazolium salts are synthesized by treating a six-membered dichlorodiphenyldicarbaphosphazene of the formula $(ClCN)_2(Ph_2PN)$ with N-Me, N-*tert*-Bu and N-Dipp imidazoles (Dipp = 2,6-diisopropylphenyl) in toluene. While Dipp and *tert*-Bu substituted imidazolium salts undergo a facile reaction with Ag_2O in CH_2Cl_2 to form carbene complexes, **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** and **[DPCP-(NHC:^{Dipp}AgCl)$_2$]**, no pure products are found in case of Me substituted salt. Under similar conditions, Cu_2O with the N-Dipp substituted imidazolium salt gives **[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]**, a $[Cu^{I}Cl_2]^-$ complex with the imidazolium ion as counter cation. However, a carbaphosphazene-anchored NHC complex of Cu, **[DPCP-(NHC:^{Dipp}CuCl)$_2$]**, is also synthesized by heating a mixture of Cu_2O and the N-Dipp imidazolium salt at 60 °C in acetonitrile. The complexes **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]**, **[DPCP-(NHC:^{Dipp}CuCl)$_2$]** and **[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]** are structurally characterized. In all these compounds the imidazole rings are coplanar with the carbaphosphazene ring.

1. Introduction

Cyclophosphazenes are one of the most extensively studied inorganic ring systems. In addition to the polymerization reactions leading to unique inorganic –P=N– polymers [1], nucleophilic substitution reactions [2] at the phosphorus center in six-membered $N_3P_3Cl_6$ and eight-membered $N_4P_4Cl_8$ rings have generated rich chemistry. Robust nature of the NP ring and high reactivity of P–Cl bonds have facilitated the installation of various coordinating groups thereby making these inorganic heterocycles an important class of ligands [3]. Replacement of one or two of the phosphorous atoms in N_3P_3 ring by main-group elements or transition metals [4] has resulted in several new classes of heterocycles among which thionylphosphazenes [5] and carbaphosphazenes [6] are well studied. Even though the nucleophilic substitution reactions at the carbon and phosphorus centers of carbaphosphazenes have been thoroughly investigated [7], there are only four articles reported in the literature on the coordination chemistry of these inorganic/organic hybrid heterocycles [8]. N-heterocyclic carbenes (NHCs) have been the theme of interest in recent years, which has been reflected in number of articles being published every year. Their metal complexes have been employed as catalysts in a wide variety of reactions [9]. Therefore, we have chosen these ligand groups for anchoring onto carbaphosphazenes. Herein we report the synthesis and structural characterization of novel copper(I) and silver(I) complexes of carbaphosphazene-anchored N-heterocyclic carbene ligands.

2. Results and discussion

The imidazolium salts were prepared by treating dichlorodiphenyldicarbaphosphazene, $[(ClCN)_2(Ph_2PN)]$, (**DPCP-Cl$_2$**) [10] with excess of appropriate imidazole in toluene at room temperature for *tert*-Bu and Me substituted imidazoles [11], and at reflux temperature for 2,6-diisopropylphenyl (Dipp) substituted imidazole (Scheme 1). The imidazolium salts **[DPCP-(Imid$^{Bu\text{-}t}$)$_2$]Cl$_2$**, **[DPCP-(Imid^{Me})$_2$]Cl$_2$** and **[DPCP-(Imid^{Dipp})$_2$]Cl$_2$**, which were collected as precipitates, were washed with THF, dried under vacuum and characterized by NMR. ^{1}H NMR spectrum has been quite useful in characterizing these salts. In all the cases, a significant down-field shift in imidazole protons, especially N–C**H**–N proton (shifted from $\delta \sim 7.5$ to $\delta \sim 12$ ppm), has been observed. The singlet resonance in ^{31}P NMR also moved to down-field region by ~5 ppm compared to **DPCP-Cl$_2$**. It is noteworthy that N-substituted imidazoles form quaternary ammonium salts with chlorocarbaphosphazenes in contrast to trialkyl amines, including bicyclic compounds like quinuclidine and diazabicyclooctane (DABCO), which undergo C–N bond cleavage [12].

Our attempts to synthesize free carbenes (or *in situ* generation) from these imidazolium salts using standard deprotonating agents

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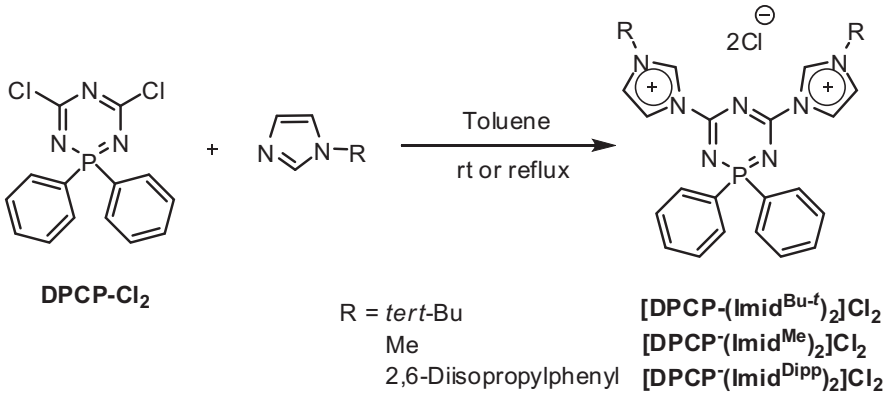
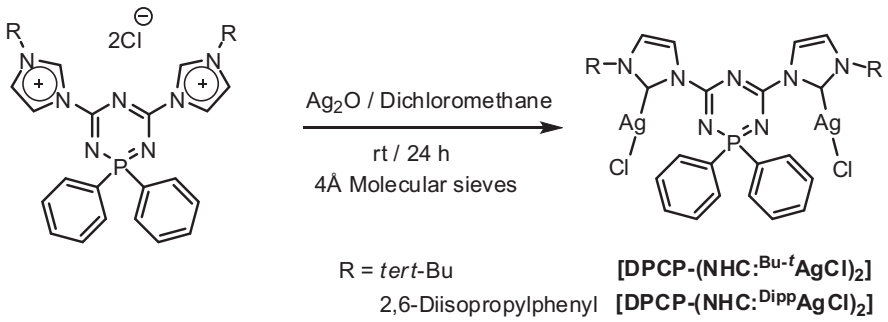


Scheme 1. Synthesis of imidazolium salts.



Scheme 2. Synthesis of Ag:NHCs.

like $KN(SiMe_3)_2$, *tert*-BuOK etc. were unsuccessful. Silver oxide has been widely used to synthesize silver NHCs, which are very good carbene transfer agents for a wide range of transition metals [13]. In view of this reaction, we treated the imidazolium salts, **[DPCP-(Imid^{R})$_2$]Cl$_2$** with excess of Ag_2O in presence of molecular sieves in dichloromethane. In case of **DPCP-(Imid$^{Bu\text{-}t}$)$_2$]Cl$_2$** and **[DPCP-(Imid^{Dipp})$_2$]Cl$_2$**, a facile reaction took place, and the complexes **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** and **[DPCP-(NHC:^{Dipp}AgCl)$_2$]** were obtained in good yields. However, **[DPCP-(Imid^{Me})$_2$]Cl$_2$** gave a mixture of products (from ^{1}H and ^{31}P NMR data) and no pure substances were isolated in this case. The complexes **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** and **[DPCP-(NHC:^{Dipp}AgCl)$_2$]** were characterized by multinuclear NMR. The absence of N–C**H**–N resonance and the presence of other imidazole protons in ^{1}H NMR spectra confirm the formation of the carbene complexes. ^{31}P NMR spectrum showed a singlet in slightly upfiled region compared to the salts. Solutions of complexes **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** and **[DPCP-(NHC:^{Dipp}AgCl)$_2$]** are photosensitive and turned black within a few minutes of exposure to light. However, they showed only a slow decomposition when exposed to air in the absence of light (Scheme 2).

Solid state structure of **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** was confirmed by single crystal X-ray diffraction studies. An ORTEP diagram along with selected bond parameters is given in Fig. 1. **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** crystallizes in *P*cnb space group. The two imidazole rings and the carbaphosphazene ring are coplanar. C–Ag–Cl bond is almost linear and Ag is weakly coordinated by skeletal N of carbaphosphazene (Ag–N distance is 2.725 Å). A thorough search on CCDC resulted in reports of a few carbene–Ag complexes with imido nitrogen closer to Ag [14]. All the bond parameters are as with the Ag–NHC complexes [14] and carbaphosphazenes reported in the literature [10,12].

Reactivity of these imidazolium salts toward Cu_2O has also been explored. Stirring **[DPCP-(Imid^{Dipp})$_2$]Cl$_2$** with excess of Cu_2O in dichloromethane at RT for 24 h did not give the expected NHC–Cu(I) complex, instead, it resulted in the formation of an ionic complex containing $[DPCP\text{-}(Imid^{Dipp})_2]^{2+}$, $[Cu^{I}Cl_2]^{-}$ and Cl^{-} ions (Scheme 3).

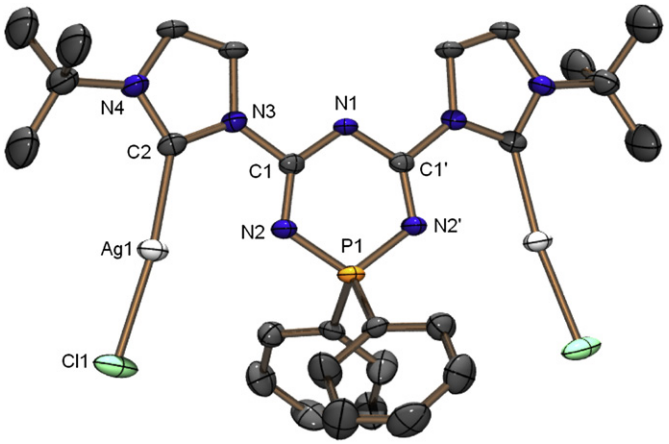
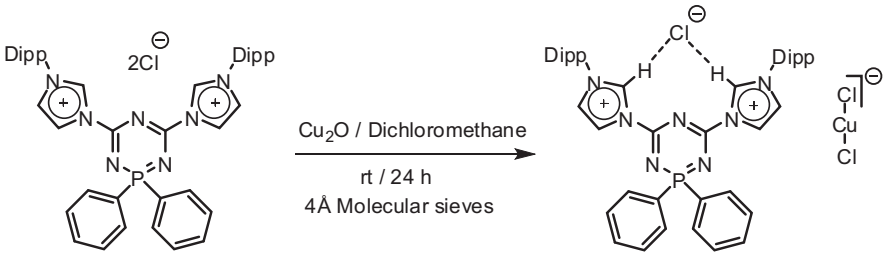


Fig. 1. Molecular structure of **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]**. All hydrogen atoms and one set of disordered methyl carbons from each *tert*-Bu group are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths [Å]: Ag1–C2 2.080(7), Ag1–Cl1 2.335(2), N3–C2 1.371(9), N4–C2 1.346(9), N3–C1 1.429(8), P1–N2 1.627(6), N2–C1 1.284(8), C1–N1 1.350(8), Ag1···N2 2.725. Selected bond angles [°]: C2–Ag1–Cl1 171.5(2), N4–C2–N3 102.9(6), N4–C2–Ag1 135.6(6), N3–C2–Ag1 121.4(5), C2–N3–C1 124.4(6), C4–N3–C1 124.7(6), N2–P1–N2′ 110.2(4), C1–N2–P1 116.1(5), N2–C1–N1 131.2(7), N1–C1–N3 111.1(6), N2–C1–N3 117.6(6), C1–N1–C1′ 115.0(8).



Scheme 3. Reaction of Dippimidazolium salt with Cu_2O in CH_2Cl_2.

This complex is readily soluble in chloroform while the parent imidazolium salt dissolves only when heated. It is colorless and highly air sensitive. When a solution of the complex in chloroform was exposed to air, it immediately turned green. While this observation indicates the presence of Cu(I), the ^1H, ^{13}C and ^{31}P NMR spectra, which are almost the same as those of **[DPCP-(Imid^{Dipp})$_2$]Cl$_2$**, support the presence of [DPCP-(Imid^{Dipp})$_2$]$^{2+}$ ion. The structure of the complex **[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]** was confirmed by single crystal X-ray studies. Single crystals, suitable for X-ray diffraction, were grown from a solution of chlorobenzene at RT. An ORTEP diagram along with selected bond parameters is given in Fig. 2. The two imidazole rings and the carbaphosphazene ring are coplanar. There are three chloride ions in the molecule and two of them coordinate to Cu in an almost linear fashion (Cl–Cu–Cl = 174°). The third chloride ion is planked between two imidazole rings through weak C–H···Cl interaction (Av. H···Cl = 2.488 Å) and is 1.224 Å away from the mean plane of the imidazolium and carbaphosphazene rings.

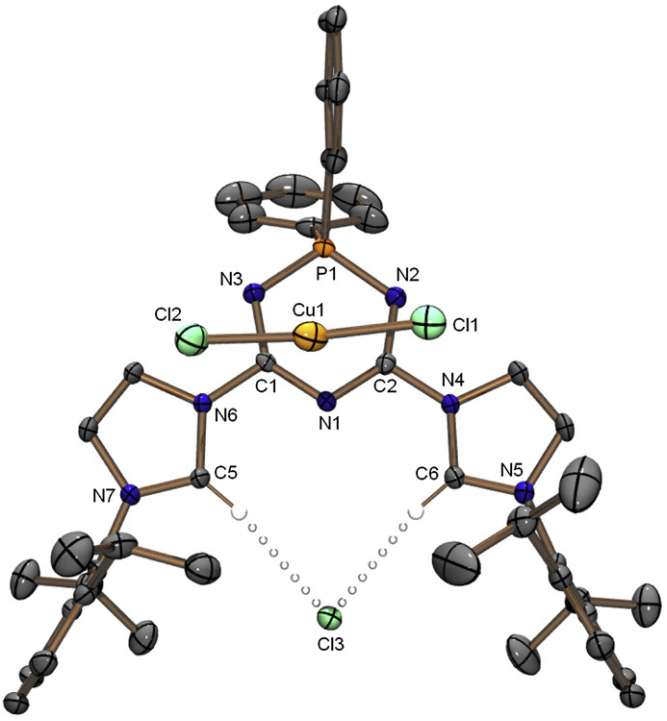


Fig. 2. Molecular structure of **[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]**. All hydrogen atoms, except those connected to chloride ion, are omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths [Å]: Cu1–Cl1 2.1036(7), Cu1–Cl2 2.0979(8), P1–N3 1.6349(18), P1–N2 1.6356(18), N1–C1 1.328(3), N1–C2 1.334(3), N3–C1 1.301(2), N2–C2 1.302(2), N6–C1 1.426(2), N4–C2 1.426(2), N4–C6 1.348(2), N5–C6 1.321(3), N7–C5 1.321(3), N6–C5 1.345(2), Av. H···Cl 2.488. Selected bond angles [°]: Cl2–Cu1–Cl1 174.38(3), N3–P1–N2 109.73(9), P1–N2–C2 115.28(15), N2–C2–N1 132.55(19), C1–N1–C2 114.27(16), N3–C1–N1 132.47(18), C6–N4–C2 125.68(17), N5–C6–N4 107.43(17), C5–N6–C1 125.71(17), N7–C5–N6 106.81(17), N1–C2–N4 112.95(16), N2–C2–N4 114.48(18), N3–C1–N6 114.18(17), N1–C1–N6 113.33(16).

However, Cu(I) carbene complex, **[DPCP-(NHC:^{Dipp}CuCl)$_2$]**, was eventually synthesized by treating a mixture of **[DPCP-(Imid^{Dipp})$_2$]Cl$_2$** and excess of Cu_2O in acetonitrile at 60 °C for 5 h in the presence of 4 Å molecular sieves (Scheme 4). The complex was characterized by NMR analysis. ^1H NMR shows two singlets for imidazole and the other peaks related to the expected structure. The absence of N–C**H**–N resonance confirms the formation of carbene. ^{31}P NMR spectrum was compared with that of the parent imidazolium salt and an upfield shift (by ~6 ppm) of chemical shift value was observed. The complex **[DPCP-(NHC:^{Dipp}CuCl)$_2$]** is air sensitive and its solutions turn to bluish green when exposed to air.

The crystal structure of **[DPCP-(NHC:^{Dipp}CuCl)$_2$]** shows copper in an almost linear geometry (Fig. 3). Basically the molecule is isostructural with **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]**. The imidazole rings are coplanar with the carbaphosphazene ring. All the bond parameters are as with the similar structures reported in the literature [15].

Surprisingly, **[DPCP-(Imid$^{Bu\text{-}t}$)$_2$]Cl$_2$** and **[DPCP-(Imid^{Me})$_2$]Cl$_2$**, even under reflux conditions and extending the reaction time up to 24 h, did not give any pure compound in acetonitrile. Both resulted in a mixture of compounds. ^1H and ^{31}P NMR showed that the unreacted imidazolium salt was the major component.

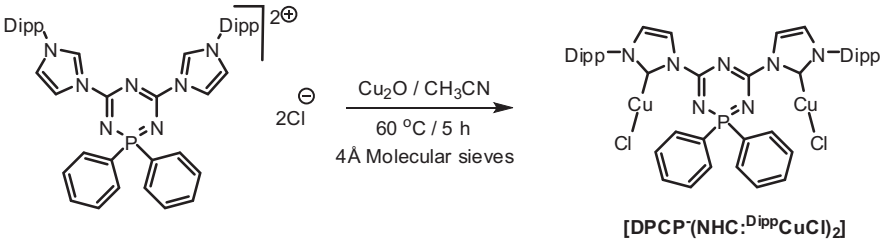
3. Conclusion

In summary, dichlorodiphenylcarbaphosphazene, [(ClCN)$_2$-(Ph$_2$PN)], undergoes a facile reaction with N-substituted imidazoles to give imidazolium salts, which upon treatment with Ag_2O or Cu_2O, form Ag- and Cu-NHCs respectively. The complexes **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]**, **[DPCP-(NHC:^{Dipp}AgCl)$_2$]** and **[DPCP-(NHC:^{Dipp}-CuCl)$_2$]** are the first examples of carbaphosphazene-anchored NHCs. Crystal structures of **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** and **[DPCP-(NHC:^{Dipp}CuCl)$_2$]** reveal that the imidazole rings are coplanar with the carbaphosphazene ring, though there is not much interaction between the metal and the skeletal nitrogen. Currently, transmetallation reactions of these complexes with Ni and Pd reagents are being explored.

4. Experimental section

4.1. General considerations

All manipulations, except syntheses of imidazoles, were carried out under N_2 atmosphere using a Schlenk line and a glove box. N-substituted imidazoles were prepared by following literature procedures [16]. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker 400 MHz instrument. Elemental analyses were performed using Thermo Scientific Flash 2000 elemental analyzer.



Scheme 4. Synthesis of Cu:NHC.

4.2. Synthesis of dichlorodiphenylcarbaphosphazene, [(ClCN)$_2$(Ph$_2$PN)], (**DPCP-Cl$_2$**) [10]

Ph_2PCl (11.60 g, 52.57 mmol) was chlorinated using dry chlorine in chlorobenzene (30 mL) at a moderate rate till the solution turned bright yellow. After removal of chlorobenzene in vacuo, crystalline trichlorodiphenylphosphine was obtained, which was re-dissolved in 1,2-dichloroethane (70 mL). Sodium dicyanamide (4.68 g, 52.56 mmol) was added to the mixture and refluxed for 20 h, brought to room temperature (RT) and filtered using a frit. The filtrate was concentrated to one third of its volume and kept at 0 °C overnight to obtain colorless crystals (12.20 g, 73%). mp: 103–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (m, 6H, ph–H), 7.56 (m, 4H, ph–H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.25, 134.28, 131.67, 131.26, 129.40, 128.75, 127.49 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 37.93 (s) ppm.

4.3. Synthesis of [DPCP-(Imid^{Me})$_2$]Cl$_2$

To a solution of **DPCP-Cl$_2$** (1.00 g, 3.10 mmol) in toluene (20 mL) was added slowly 1-methylimidazole (0.65 g, 7.92 mmol) using syringe. White precipitate was formed immediately upon addition. The mixture was allowed to stir for 3 h at RT and filtered. The precipitate was washed with hot THF (2 × 30 mL) to obtain analytically pure sample of **[DPCP-(Imid^{Me})$_2$]Cl$_2$** (1.40 g, 91%). mp: >200 °C dec. (lit. 190–195) [11]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.05 (s, 2H, imidazole–NCHN), 8.34 (s, 2H, imidazole–NC**H**CHN), 8.21 (s, 2H, imidazole–NCHC**H**N), 7.72 (m, 6H, Ph–H), 7.60 (m, 4H, Ph–H), 4.26 (s, 6H, NCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.27, 139.70, 135.11, 131.35, 129.99, 129.84, 127.46, 126.18, 125.80, 118.56, 37.53 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 42.94 (s) ppm.

4.4. Synthesis of [DPCP-(Imid$^{Bu\text{-}t}$)$_2$]Cl$_2$

The procedure given for the synthesis of **[DPCP-(Imid^{Me})$_2$]Cl$_2$** was followed. Yield: 92%. mp: 170–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.00 (s, 2H, imidazole–NCHN), 8.47 (s, 2H, imidazole–NC**H**CHN), 8.10 (s, 2H, imidazole–NCHC**H**N), 7.73 (m, 6H, Ph–H), 7.62 (m, 4H, Ph–H), 1.90 [s, 18H, $C(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.86, 137.69, 134.90, 131.27, 129.76, 129.03, 128.22, 127.61, 122.01, 119.29, 62.83, 30.35 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 41.89 ppm (s).

4.5. Synthesis of [DPCP-(Imid^{Dipp})$_2$]Cl$_2$

It was prepared by following the procedure given for synthesis of **[DPCP-(Imid^{Me})$_2$]Cl$_2$**, except that the reaction mixture was refluxed for 3 h. Yield: 93%. mp: >270 °C dec. ^{1}H NMR (400 MHz,

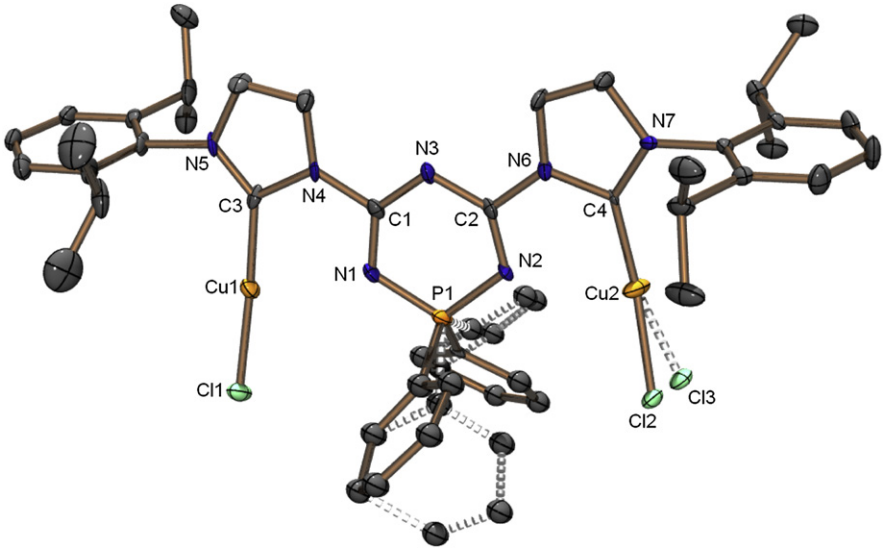


Fig. 3. Molecular structure of **[DPCP-(NHC:^{Dipp}CuCl)$_2$]**. All hydrogen atoms and one set of disordered methyl carbons of one of the isopropyl groups are omitted for clarity. One set of the other disordered moieties are shown with dashed bonds. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths [Å]: Cu1–C3 1.870(7), Cu1–Cl1 2.129(2), Cu2–C4 1.845(6), Cu2–Cl2 2.123(4), Cu2–Cl3 2.176(4), P1–N1 1.624(6), P1–N2 1.642(5), N1–C1 1.309(8), N2–C2 1.289(8), N3–C1 1.322(8), N3–C2 1.355(8), N4–C1 1.419(9), N4–C3 1.392(8), N5–C3 1.315(9), N6–C2 1.394(8), C4–N6 1.393(8), N7–C4 1.328(7), Cu1···N1 2.537, Cu2···N2 2.566. Selected bond angles [°]: C3–Cu1–Cl1 176.1(2), C4–Cu2–Cl2 166.1(2), C4–Cu2–Cl3, 165.7(2), N1–P1–N2 109.8(3), C1–N1–P1 116.3(5), N1–C1–N3 131.1(7), C1–N3–C2 115.6(6), N2–C2–N3 131.2(6), C2–N2–P1 115.9(5), N2–C2–N6 114.8(6), N3–C2–N6 114.0(6), C2–N6–C4 123.5(6), N7–C4–N6 102.9(5), N7–C4–Cu2 134.9(5), N6–C4–Cu2 122.1(4), N1–C1–N4 115.1(6), N3–C1–N4 113.8(6), C3–N4–C1 123.2(6), N4–C3–N5 102.6(6), N5–C3–Cu1 136.4(5), N4–C3–Cu1 120.7(5).

$CDCl_3$): δ 12.72 (s, 2H, imidazole–NCHN), 8.93 (s, 2H, imidazole–NC**H**CHN), 8.00 (m, 4H, imidazole–NCHC**H**N & Ar–H), 7.15–7.78 (set of multiplets, 14H, Ar–H & Ph–H), 2.37 [m, 4H, C**H**$(CH_3)_2$], 1.22 [d, 12H, CH(C**H**$_3)_2$], 1.12 [d, 12H, CH(C**H**$_3)_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.88, 144.90, 135.06, 132.00, 131.83, 131.72, 130.31, 130.01, 129.87, 129.18, 128.37, 127.74, 126.20, 125.44, 124.70, 120.29, 29.02, 24.33 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 43.04 (s) ppm.

4.6. Synthesis of *[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]*

A mixture of **[DPCP-(Imid$^{Bu\text{-}t}$)$_2$]Cl$_2$** (0.24 g, 0.42 mmol), Ag_2O (0.14 g, 0.60 mmol) and 4 Å molecular sieves (~1.00 g) was stirred at RT in dichloromethane (25 mL) for 24 h in the absence of light. The reaction mixture was then filtered through a pad of celite, the volatiles were removed from the filtrate and the residue was recrystallized from dichloromethane/hexane mixture to obtain colorless crystals overnight at RT (0.25 g, 76%). mp: >166 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H, imidazole–NC**H**CHN), 8.14 (m, 4H, Ph–H), 7.61 (m, 6H, Ph–H), 7.27 (s, 2H, imidazole–NCHC**H**N), 1.82 [s, 18H, C$(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.73, 133.95, 131.38, 131.26, 129.66, 129.52, 129.19, 125.45, 119.42, 118.74, 59.06, 31.70 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 38.13 (s) ppm. Anal. Calcd for $C_{28}H_{32}Ag_2Cl_2N_7P$: C, 42.88; H, 4.11; N, 12.50. Found: C, 42.76; H, 4.20; N, 12.53.

4.7. Synthesis of *[DPCP-(NHC:^{Dipp}AgCl)$_2$]*

It was prepared by following the procedure given for synthesis of **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]**. Yield: 89%. mp: 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 2H, imidazole–NC**H**CHN), 8.06 (m, 4H, Ph–H), 7.60 (m, 6H, Ph–H), 7.45 (m, 2H, Ar–H), 7.23 (d, 4H, Ar–H), 7.06 (d, 2H, imidazole–NCHC**H**N), 2.45 [m, 4H, C**H**$(CH_3)_2$], 1.23 [d, 12H, CH(C**H**$_3)_2$], 1.10 [d, 12H, CH(C**H**$_3)_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.87, 146.66, 145.39, 135.33, 134.06, 134.03, 131.30, 131.19, 130.9, 129.73, 129.59, 129.16, 128.37, 124.54, 123.87, 120.40, 28.47, 24.69, 24.44 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 38.26 (s) ppm. Anal. Calcd for $C_{44}H_{48}Ag_2Cl_2N_7P$: C, 53.25; H, 4.87; N, 9.88. Found: C, 53.20; H, 4.91; N, 9.81.

4.8. Reaction of *[DPCP-(Imid^{Dipp})$_2$]Cl$_2$* with Cu_2O in dichloromethane

A mixture of **[DPCP-(Imid^{Dipp})$_2$]Cl$_2$** (0.20 g, 0.25 mmol), Cu_2O (0.055 g, 0.38 mmol) and 4 Å molecular sieves (~1 g) was stirred at RT in dichloromethane (25 mL) for 24 h. The reaction mixture was then filtered through a pad of celite, the volatiles were removed from the filtrate and the residue was recrystallized from dichloromethane/hexane mixture to obtain colorless crystals of **[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]** overnight at RT (0.17 g, 98% based on Cl). mp: 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.31 (s, 2H, imidazole–NCHN), 8.70 (s, 2H, imidazole–NC**H**CHN), 8.01 (m, 4H, Ph–H), 7.76 (m, 6H, Ph–H), 7.45 (t, 2H, Ar–H), 7.36 (s, 2H, imidazole–NCHCHN), 7.25 (d, 4H, Ar–H), 2.45 [m, 4H, C**H**$(CH_3)_2$], 1.24 [d, 12H, CH(C**H**$_3)_2$], 1.12 [d, 12H, CH(C**H**$_3)_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.71, 145.07, 141.02, 135.11, 132.03, 131.92, 130.25, 129.98, 129.83, 127.49, 126.82, 126.21, 125.58, 124.72, 123.97, 119.87, 28.96, 24.38 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 43.41 (s) ppm. Anal. Calcd for $C_{44}H_{50}Cl_3CuN_7P$: C, 60.20; H, 5.74; N, 11.17. Found: C, 60.23; H, 5.79; N, 11.10.

4.9. Synthesis of *[DPCP-(NHC:^{Dipp}CuCl)$_2$]*

A mixture of **[DPCP-(Imid^{Dipp})$_2$]Cl$_2$** (0.21 g, 0.26 mmol), Cu_2O (0.057 g, 0.39 mmol) and 4 Å molecular sieves (~1 g) in acetonitrile (25 mL) was heated at 60 °C for 5 h. It was then filtered through a pad of celite and the yellow colored filtrate was stored at RT to obtain pale yellow crystals, which were filtered off. Reducing the volume of the mother liquor to half gave a further crop of yellow crystals. Overall yield is 83% (0.20 g), mp: >246 °C dec. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (s, 2H, imidazole–NC**H**CHN), 8.17 (m, 4H, Ph–H), 7.62 (m, 6H, Ph–H), 7.47 (t, 2H, Ar–H), 7.27 (d, 4H, Ar–H), 7.00 (m, 2H, imidazole–NCHC**H**N), 2.51 [m, 4H, C**H**$(CH_3)_2$], 1.29 [d, 12H, CH(C**H**$_3)_2$], 1.14 [d, 12H, CH(C**H**$_3)_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.28, 145.39, 135.22, 133.85, 131.50, 131.39, 130.71, 130.00, 129.51, 129.37, 128.71, 124.48, 124.40, 119.48, 28.55, 24.76, 24.30 ppm. ^{31}P (161 MHz, $CDCl_3$): δ 37.67 (s) ppm. Anal. Calcd for $C_{44}H_{48}Cl_2Cu_2N_7P$: C, 58.47; H, 5.35; N, 10.85. Found: C, 58.51; H, 5.40; N, 10.81.

Table 1
Crystal data for compounds **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]**, **[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]** and **[DPCP-(NHC:^{Dipp}CuCl)$_2$]**.

	[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]·2$CHCl_3$·CH_2Cl_2	**[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]**·2C_6H_5Cl	**[DPCP-(NHC:^{Dipp}CuCl)$_2$]**·CH_3CN
Empirical formula	$C_{31}H_{36}Ag_2Cl_{10}N_7P$	$C_{56}H_{60}Cl_5CuN_7P$	$C_{46}H_{51}Cl_2Cu_2N_8P$
Formula wt	1107.88	1102.87	944.90
Temp (K)	150(2)	150(2)	150(2)
Cryst syst	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbcn*	*P*2/n	*P*
a (Å)	13.3570(4)	15.5595(2)	9.5478(3)
b (Å)	19.8355(6)	15.7611(3)	14.8445(9)
c (Å)	17.3347(6)	23.7077(4)	18.4794(10)
α (deg)	90	90	68.820(5)
β (deg)	90	105.052(2)	79.290(4)
γ (deg)	90	90	79.874(4)
V (Å^3)	4592.7(3)	5614.48(16)	2382.7(2)
Z	4	4	2
ρ_{calcd} (Mg m^{-3})	1.602	1.305	1.317
μ (mm^{-1})	1.500	0.698	1.078
F(000)	2200	2296	980
cryst size (mm)	0.30 × 0.22 × 0.12	0.40 × 0.20 × 0.19	0.32 × 0.24 × 0.11
θ range (deg)	2.80–29.42	2.73–29.37	2.78–29.36
No. of collected/ unique rflns	13,432/5488 (*R*(int) = 0.0318)	34,377/13,173 (*R*(int) = 0.0330)	17,806/10,833 (*R*(int) = 0.0534)
No. of data/restraints/ params	5488/23/229	13,173/0/639	10,833/0/515
*R*1, *wR*2 ($I > 2\sigma(I)$)[a]	0.0617, 0.2240	0.0461, 0.0981	0.0883, 0.2199
*R*1, *wR*2 (all data)[a]	0.1300, 0.2529	0.0714, 0.1114	0.1832, 0.2439
GOF	1.004	1.056	0.936
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.706/−1.206	0.593/−0.664	2.613/−0.861

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

5. Structural determination

Single crystals were mounted on a glass fibre in paraffin oil and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. Data collection was performed on an OXFORD XCALIBUR diffractometer, equipped with CCD area detector, using graphite-monochromated MoK_α ($\lambda = 0.71073$ Å) radiation and a low-temperature device. All calculations were performed using SHELXS-97 and SHELXL-97 [17]. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically (except acetonitrile molecules in **[DPCP-(NHC:^{Dipp}-CuCl)$_2$]**). The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks in case of **[DPCP-(NHC:$^{Bu\text{-}t}$AgCl)$_2$]** and **[(DPCP-(Imid^{Dipp})$_2$Cl][Cu^{I}Cl$_2$]**. However, in case of **[DPCP-(NHC:^{Dipp}CuCl)$_2$]**, two peaks (Q1 = 2.61 and Q2 = 2.44), each one located in between one of the imidazole carbons and Cl of another molecule, were found. While Q1 is 1.590 Å away from one of carbons of one imidazole ring and 1.841 Å away from Cl3, Q2 is 1.606 Å away from one of carbons of another imidazole ring and 2.124 Å away from Cl1.

All the datasets were collected to 2Θ values $>50^\circ$ but they were cut off to $2\Theta = 50^\circ$ during the refinement. Relevant data concerning crystallographic data, data collection, and refinement details are summarised in Table 1.

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Appendix A. Supplementary material

CCDC 877872, 877873 and 877874 contain the 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 or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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