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# Copper(I), silver(I) and gold(I) complexes of *N*-heterocyclic carbene-phosphinidene

Venkata A. K. Adiraju, Muhammed Yousufuddin, H. V. Rasika Dias\*

Department of Chemistry and Biochemistry, The University of Texas at Arlington,

Arlington, Texas 76019, USA

TEL: (+1) 817 272 3813

E-mail: <u>dias@uta.edu</u>

Homepage: <a href="http://www.uta.edu/chemistry/faculty/directory/Dias.php">http://www.uta.edu/chemistry/faculty/directory/Dias.php</a>

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**Abstract:** N-heterocyclic carbene stabilized phosphinidene IMes•PPh has been used as a bridging ligand to isolate a group of closely related molecules involving all three coinage metal ions. The bis-copper(I) chloride, bis-silver(I) chloride and bis-copper(I) bromide adducts of IMes•PPh crystallize as halide ion bridged octanuclear molecules while the [IMes•PPh](AuCl)<sub>2</sub> adduct remains monomeric. These molecules feature long P-C(carbene) bonds in the range 1.822(3)-1.843(4) Å, near typical P-C single bond length region.

### Introduction:

*N*-heterocyclic carbene stabilized phosphinidenes<sup>1-4</sup> represent an interesting class of molecules that can be regarded as polarized phosphaalkenes as illustrated by resonance structures **1A-1C** in Figure 1.<sup>5-10</sup> Indeed, IMes•PPh (*N*-heterocyclic carbene stabilized phosphinidenes of the type **1** shown in Figure 1 with R = 2,4,6-trimethylphenyl (Mes) and R' = phenyl) reacts with BH<sub>3</sub> forming 1:2 adducts consistent with the dominant resonance form **1A-B** and the ability of phosphorus to serve as a four-electron donor via the use of two lone pairs.<sup>7</sup> Furthermore, the steric and electronic properties of *N*-heterocyclic carbene stabilized phosphinidenes could potentially be altered using the substituents on the phosphorus and by varying the carbene fragment.<sup>5, 11</sup> However, metal coordination properties of this interesting class of molecules have not been explored widely. Recently, Larocque and Lavoie described the use of IMes•PPh to isolate a monometallic transition metal adduct RuCl<sub>2</sub>[IMes•PPh](PPh<sub>3</sub>)(CHPh).<sup>12</sup> Tamm and co-workers utilized IPr•PSiMe<sub>3</sub> (*N*-heterocyclic carbene stabilized phosphinidenes of the type **1** shown in Figure 1 with R = 2,6-diisopropylphenyl and R' = SiMe<sub>3</sub>) as a

precursor to obtain *N*-heterocyclic carbene-phosphinidyne metal complexes of the type [IPr•P]ML<sub>n</sub> (ML<sub>n</sub> = ( $\eta^6$ -*p*-cymene)RuCl and ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)RhCl) as well as bi- and trimetallic systems.<sup>9</sup> Hudnell and co-workers described the use of carbonyl decorated *N*-heterocyclic carbenes to stabilize phenylphosphinidene moiety to obtain molecules that show features of the canonical phosphaalkene end of the continuum illustrated in Figure 1 (i.e., bonding dominated by the resonance form similar to **1C** with short P-C bond and low-field <sup>31</sup>P resonance).<sup>5</sup>



**Figure 1.** Several resonance structures of *N*-heterocyclic carbene stabilized phosphinidene (R and R' are usually alkyl or aryl substituents)

One area of activity in our laboratory has been the study of Cu(I), Ag(I) and Au(I) chemistry involving various donors and their catalytic and photophysical properties.<sup>13-24</sup> *N*-heterocyclic carbene stabilized phosphinidenes are attractive for us because they offer a good ligand template to stabilize homo- and possibly hetero-bimetallic systems involving these and other metal ions. Here we present the use of IMes•PPh as a supporting ligand to stabilize bis(group 11 metal) adducts involving CuCl, AgCl and AuCl, as well as the related CuBr system (Figure 2), and their structural features.



Figure 2. Bis(group11 metal) complexes of IMes•PPh

# **Results and discussion:**

Treatment of IMes•PPh with slight excess of 2 eg of CuCl in THF resulted in {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub>, which was isolated as a white solid in 62% yield. The  ${}^{31}P{}^{1}H$ } NMR spectrum of {[IMes•PPh](CuCl)<sub>2</sub>]<sub>4</sub> displayed a singlet at  $\delta$  -54.8 ppm which is upfield of the corresponding signal of the free ligand IMes•PPh ( $\delta$  -23.0 ppm).<sup>2</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the crude reaction mixture of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub> indicated the existence of one major phosphorus containing species. The <sup>13</sup>C signal corresponding to NCN carbon of {[IMes•PPh](CuCl)<sub>2</sub>]<sub>4</sub> was observed at  $\delta$  153.1 ppm. which is an up-field shift of about 17 ppm from that of the related resonance of IMes•PPh (which was observed at  $\delta$  170.0 ppm). For comparison, <sup>13</sup>C signal of NCN moiety and <sup>13</sup>P resonance of [IMes•PPh](BH<sub>3</sub>)<sub>2</sub> appear at  $\delta$  152.3 and 4 ppm, respectively.<sup>7</sup> The reaction of IMes•PPh with 2 eq of CuBr afforded {[IMes•PPh](CuBr)<sub>2</sub>}<sub>4</sub>. <sup>1</sup>H, <sup>13</sup>P and <sup>13</sup>C NMR data of {[IMes•PPh](CuBr)<sub>2</sub>}<sub>4</sub> were not very different from that of the CuCl analog suggesting the formation of a similar product.

We have also investigated the reactivity of IMes•PPh towards heavier group 11 metal chlorides, AgCl and AuCl. The metal adducts {[IMes•PPh](AgCl)<sub>2</sub>]<sub>4</sub> and [IMes•PPh](AuCl)<sub>2</sub> were synthesized by treating IMes•PPh with slight excess of 2 eg of The  ${}^{31}P{}^{1}H$  chemical shift of the appropriate metal(I) chloride in THF. {[IMes•PPh](AgCl)<sub>2</sub>]<sub>4</sub> ( $\delta$  -50.0 ppm) is only about 5 ppm downfield of the copper analog {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub> while the related [IMes•PPh](AuCl)<sub>2</sub> displayed its <sup>31</sup>P{<sup>1</sup>H} resonance at  $\delta$  -4.0 ppm, which is very different from the chemical shift of the lighter member analogs. Two-coordinate  $[(Mes_3P)_2M]BF_4$  series (M = Cu, Au, Au) is known the <sup>31</sup>P chemical shifts show a similar trend.<sup>25</sup> For example, gold adduct shows the highest <sup>31</sup>P chemical shift value (at  $\delta$  6.1 ppm) among the three [(Mes<sub>3</sub>P)<sub>2</sub>M]BF<sub>4</sub> adducts. Silver and copper adducts show relatively up-field, chemical shifts at  $\delta$  -27.5 and -30.2 (average for two propeller isomers) ppm, respectively. In the three [IMes•PPh](MCI)<sub>2</sub> (M= Cu, Ag, Au) adducts, [IMes•PPh](AuCl)<sub>2</sub> has the most down-field shifted (deshielded) <sup>1</sup>H signal of NCH protons. This is perhaps an indication of [IMes•PPh](AuCl)<sub>2</sub> having an *N*-heterocyclic carbene stabilized phenylphosphinidene ligand with most polarized resonance form **1A-B** (Figure 1). It is known that gold(I) forms the strongest bonds to phosphorus in the Cu(I), Ag(I) and Au(I) series.<sup>26</sup> Gold is also the most electronegative element of the group 11 triad.

Solid samples of [IMes•PPh](AuCl)<sub>2</sub> adduct can be handled in open air for several hours without signs of decomposition while the related silver and copper adducts decompose easily under similar conditions. [IMes•PPh](AuCl)<sub>2</sub> is soluble in THF and chlorinated solvents like CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> but insoluble in hexane. The analogous

copper and silver adducts do not show good solubility in THF or hexane but they are soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>.



**Figure 3.** Molecular structure of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub>. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P1–C1 1.837(3), P1–Cu1 2.1828(7), P1–Cu2 2.2110(7), P2–Cu3 2.2052(7), P2–Cu4 2.1932(7), Cu1–Cl1 2.1272(7), Cu2–Cl2 2.3232(7), Cu2–Cl3 2.3105(7), Cu3–Cl2 2.3018(7), Cu3–Cl3 2.3933(7), Cu4–Cl4 2.2949(7), Cu1–P1–Cu2 121.90(3), Cu4–P2–Cu3 114.14(3), P1–Cu1–Cl1 167.45(3), P1–Cu2–Cl2 131.85(3), P1–Cu2–Cl3 133.66(3), P2–Cu3–Cl3 129.92(3), P2–Cu3–Cl2 135.28(3), P2–Cu4–Cl4 135.41(3).



**Figure 4.** Molecular structure of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub> showing coordination geometries at phosphorus and copper sites (hydrogen atoms have been omitted for clarity)

We have also investigated the solid state structures of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub>, {[IMes•PPh](AgCl)<sub>2</sub>}<sub>4</sub>, [IMes•PPh](AuCl)<sub>2</sub> and {[IMes•PPh](CuBr)<sub>2</sub>}<sub>4</sub> using X-ray crystallography. X-ray quality crystals were obtained using CH<sub>2</sub>Cl<sub>2</sub>-hexane. The crystal structure of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub> is illustrated in Figure 3. X-ray crystal structural data confirmed the formation of a molecule with 1:2 IMes•PPh:CuCl stoichiometry, but more interestingly, the overall molecule is a more complex octanuclear species with a center of symmetry. It features four tetrahedral phosphorus centers but two of the copper sites are linear and two-coordinate while the other six copper atoms are three-coordinate, and adopt trigonal planar geometry, resulting from the presence of either terminal or bridging chlorides. The coordination geometries of phosphorus, copper and chloride sites are highlighted in Figure 4.



**Figure 5.** Molecular structure of {[IMes•PPh](CuBr)<sub>2</sub>}<sub>4.</sub> Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P1–C1 1.834(5), P1–Cu1 2.1867(13), P1–Cu2 2.2205(13), P2–Cu3 2.2117(12), P2–Cu4 2.2006(13), Cu1–Br1 2.2512(8), Cu2–Br2 2.4400(8), Cu2–Br3 2.4323(7), Cu3–Br2 2.4248(7), Cu3–Br3 2.4922(7), Cu4–Br4 2.4140(7), Cu1–P1–Cu2 122.97(6), Cu4–P2–Cu3 113.27(5), P1–Cu1–Br1 165.42(4), P1–Cu2–Br2 133.17(4), P1–Cu2–Br3 130.22(4), P2–Cu3–Br3 129.62(4), P2–Cu3–Br2 132.64(4), P2–Cu4–Br4 131.91(4).

The copper(I) bromide and silver(I) chloride adducts aggregate in very similar fashion forming octanuclear species { $[IMes \cdot PPh](CuBr)_2$ }<sub>4</sub> and { $[IMes \cdot PPh](AgCl)_2$ }<sub>4</sub> as illustrated in Figures 5 and 6. They are all isomorphous and crystallize with two molecules of dichloromethane per octanuclear species. The central Ag<sub>2</sub>Cl<sub>2</sub> core shows a Ag•••Ag contact at 3.2626(5) Å, which is within the van der Waals separation of two silver atoms. Structural features of { $[IMes \cdot PPh](CuCl)_2$ }<sub>4</sub> and { $[IMes \cdot PPh](CuBr)_2$ }<sub>4</sub> are similar except for the obvious differences in Cu-X (X = Cl, Br) distances and Cu-X-Cu and X-Cu-X angles due to the size disparity between Cl and Br.



**Figure 6.** Molecular structure of {[IMes•PPh](AgCl)<sub>2</sub>}<sub>4</sub>. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P1–C1 1.825(3), P1–Ag1 2.3573(8), P1–Ag2 2.3884(8), P2–Ag3 2.3766(8), P2–Ag4 2.3596(8), Ag1–Cl1 2.3405(8), Ag2–Cl2 2.5643(9), Ag2–Cl3 2.5115(8), Ag3–Cl2 2.5215(9), Ag3–Cl3 2.5912(9), Ag4–Cl4 2.4957(9), Ag4–Ag4 3.2626(5), Ag1–P1–Ag 2 116.41(3), Ag4–P2–Ag3 107.54(3), P1–Ag1–Cl1 169.98(3), P1–Ag2–Cl2 128.77(3), P1–Ag2–Cl3 136.10(3), P2–Ag3–Cl3 129.23(3), P2–Ag3–Cl2 134.95(3), P2–Ag4–Cl4 137.39(3).

The gold adduct crystallized as discrete dinuclear species [IMes•PPh](AuCl)<sub>2</sub> with no close intermolecular Au-Cl contacts (Figure 7). The phosphorus atom adopts a

tetrahedral geometry while the gold centers are two-coordinate and feature familiar linear geometry.<sup>27</sup> Both experimental data and computational studies show that there is a tendency for group 11 metal adducts like CI-M-PR<sub>3</sub> to form oligomers.<sup>26</sup> The copper and silver systems are known to aggregate via the formation of M<sub>2</sub>Cl<sub>2</sub> units while the gold adducts prefer to interact via close Au•••Au interactions.<sup>28</sup> {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub>, {[IMes•PPh](AgCl)<sub>2</sub>}<sub>4</sub> also display this tendency as noted above. [IMes•PPh](AuCl)<sub>2</sub> however remains monomeric and shows no close Au•••Au contacts, perhaps due to steric reasons.

Comparison of metric parameters of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub>, {[IMes•PPh](AqCl)<sub>2</sub>}<sub>4</sub> and [IMes•PPh](AuCl)<sub>2</sub> show that P-M (M = Cu, Ag, Au) and M-Cl(terminal) bond distances follow the trend expected based on covalent radii of Cu(I), Ag(I), and Au(I).<sup>14,</sup> <sup>29</sup> P-M and M-CI distances involving copper(I) are the shortest while the corresponding distances of the silver adduct are the longest. The P-C(carbene) distances of  $\{[Mes \cdot PPh](CuCl)_2\}_4, \{[Mes \cdot PPh](AgCl)_2\}_4 \text{ and } [Mes \cdot PPh](AuCl)_2 \text{ are } av. 1.837(3), \}$ av.1.823(3) and 1.843(4) Å, respectively. Although, these values point to the longest P-C(carbene) bond in the gold adduct, the difference in distances between the three adducts are small and not-significant at the  $3\sigma$ -level of esds. They are all much closer to the typical P-C single bond distance of 1.87 Å while typical P=C bonds show distances at 1.67 Å.<sup>30</sup> Furthermore, P-C(carbene) (range 1.822(3)-1.843(4) Å) and P-C(Ph) 1.828(4)-1.846(5) Å) distances of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub>, (range {[IMes•PPh](CuBr)<sub>2</sub>}<sub>4</sub>, {[IMes•PPh](AgCl)<sub>2</sub>}<sub>4</sub> and [IMes•PPh](AuCl)<sub>2</sub> are very similar to each other in these adducts indicating that they all features IMes•PPh moieties with essentially **1A-B** character (Figure 1) and typical P-C(carbene) single bonds. For comparison, free IMes•PPh has a shorter P-C(carbene) bond (1.763(6) Å)<sup>2</sup> while the corresponding bond length of [IMes•PPh](BH<sub>3</sub>)<sub>2</sub> (1.856(2) Å) is comparable to those observed for bis(group 11 metal) adducts.



**Figure 7.** Molecular structure of [IMes•PPh](AuCl)<sub>2</sub>. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): P–C1 1.843(4), P–Au1 2.2380(10), P–Au2 2.2452(10), Au1–Cl1 2.2969(10), Au2–Cl2 2.2979(10), Au1•••Au2 3.691, Au1–P–Au2 110.83(4),N1-C1-N2 105.8(3), P–Au1–Cl1 174.41(4), P–Au2–Cl2 178.44(4).

In summary, we describe the use of IMes•PPh as a good bridging ligand for group 11 metal ions, and to isolate a group of closely related molecules involving copper, silver and gold. The copper(I) chloride, silver(I) chloride and copper(I) bromide complexes of IMes•PPh form interesting halide bridged octanuclear molecules while the  $[IMes•PPh](AuCl)_2$  adduct remains monomeric. Preliminary data suggest that  $\{[IMes•PPh](CuCl)_2\}_4$  reacts with IMes•PPh to produce a new product, presumably [IMes•PPh]CuCl or its aggregate. Further studies are underway to explore metal coordination chemistry of *N*-heterocyclic carbene stabilized phosphinidenes and their applications.

**Experimental details:** All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a drybox. Solvents were purchased from commercial sources, purified using an Innovative Technology SPS-400 PureSolv solvent drying system or by distilling over conventional drying agents and degassed by the freeze-pump-thaw method twice prior to use. Glassware was ovendried at 150 °C overnight. NMR spectra were recorded at 25 °C on JEOL Eclipse 500 (<sup>1</sup>H, 500.16 MHz; <sup>13</sup>C, 125.78 MHz) and 300 spectrometers (<sup>31</sup>P, 121.66 MHz). Proton and carbon chemical shifts are reported in ppm versus Me<sub>4</sub>Si. <sup>31</sup>P NMR chemical shifts were referenced relative to external 85% H<sub>3</sub>PO<sub>4</sub>. Elemental analyses were performed by Intertek QTI Laboratory (Whitehouse, NJ). Melting points were obtained on a Mel-Temp II apparatus and were not corrected. All materials were obtained from commercial vendors with the exception of IMes•PPh, which was synthesized by using the published procedure.<sup>2</sup>

**{[IMes•PPh](CuCl)**<sub>2</sub>**}**<sub>4</sub>**:** IMes•PPh (0.050 g, 0.121 mmol) and CuCl (0.026 g, 0.267 mmol) were stirred in THF (10 mL) at -75 °C for 1 h. The mixture was then allowed to warm to the room temperature and stirred for overnight. The solvent was removed under reduced pressure and dichloromethane (10 mL) was added to the residue. The mixture was flilterd thorough Celite *via* canula and the filtrate was concentrated to 3 mL under reduced pressure. Hexane (1 mL) was added to it and kept at room temperature to obtain colorless crystals of {[IMes•PPh](CuCl)<sub>2</sub>}<sub>4</sub>. Yield: 0.046 g (62%). M.p.: 176–180 °C (dec.). <sup>1</sup>H NMR (500.16 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  7.26-7.22 (m, 4H, *H*<sub>Arom</sub>), 7.18 (td, 1H, *J* = 1.8, 7.5 Hz, *H*<sub>Arom</sub>), 6.98-6.94 (m, 6H, *H*<sub>Arom</sub>/NC*H*), 2.36 (s, 6H, *p*-CH<sub>3</sub>), 2.03 (s, 12H, *o*-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}</sup> NMR (125.57 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  153.10 (d, *J* = 24.0 Hz,

NCN), 142.13, 139.49 (d, J = 15.6 Hz), 134.58, 131.83, 130.90, 129.69, 128.30 (d, J = 9.6 Hz), 127.36 (d, J = 30.0 Hz), 125.08, 21.40 (s, p-CH<sub>3</sub>), 18.70 (s, o-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.66 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  -54.8 (br). Anal. Calcd for C<sub>108</sub>H<sub>116</sub>Cl<sub>8</sub>Cu<sub>8</sub>N<sub>8</sub>P<sub>4</sub> (contains 0.7 eq. of CH<sub>2</sub>Cl<sub>2</sub>): C, 44.63; H, 4.26; N, 3.59. Found: C, 44.84; H, 3.98; N, 3.69

{[IMes·PPh](CuBr)<sub>2</sub>}<sub>4</sub>: IMes·PPh (0.050 g, 0.121 mmol) and CuBr (0.038 g, 0.267 mmol) were stirred in THF (10 mL) at -75 °C for 1 h. The mixture was then allowed to warm to the room temperature and stirred for overnight. The solvent was removed under reduced pressure and dichloromethane (10 mL) was added to the residue. The mixture was flilterd thorough Celite via canula and the filtrate was concentrated to 3 mL under reduced pressure. Hexane (1 mL) was added to it and kept at room temperature to obtain colorless crystals of {[IMes•PPh](CuBr)<sub>2</sub>}<sub>4</sub>. Yield: 0.038 g (45%). M.p.: 212–216 °C (dec.). <sup>1</sup>H NMR (500.16 MHz, CDCl<sub>3</sub>, 25 °C): δ 7.28-7.24 (m, 2H, H<sub>Arom</sub>), 7.13 (s, 2H, NCH), 7.09 (t, J = 6.9 Hz, 1H,  $H_{Arom}$ ), 6.90 (s, 4H,  $H_{Arom}$ ), 6.86 (t, J = 7.2 Hz, 2H,  $H_{Arom}$ ), 2.33 (s, 6H, *ρ*-CH<sub>3</sub>), 2.01(s, 12H, *ο*-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.57 MHz, CDCl<sub>3</sub>, 25 °C): δ 154.30 (d, J = 31.2 Hz, NCN), 141.68, 139.43 (d, J = 15.6 Hz), 134.30, 131.66, 130.81, 130.44, 128.99, 127.78 (d, J = 9.6 Hz), 124.38, 21.48 (s, p-CH<sub>3</sub>), 18.85 (s, o-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.66 MHz, CDCl<sub>3</sub>, 25 °C): δ -55.8 (br). Anal. Calcd for C<sub>108</sub>H<sub>116</sub>Br<sub>8</sub>Cu<sub>8</sub>N<sub>8</sub>P<sub>4</sub> (contains 0.5 eq. of CH<sub>2</sub>Cl<sub>2</sub>): C, 42.88; H, 3.98; N, 3.57. Found: C, 43.21; H, 3.57; N, 3.99.

{[IMes·PPh](AgCl)<sub>2</sub>}<sub>4</sub>: IMes·PPh (0.050 g, 0.121 mmol) and AgCl (0.038 g, 0.267 mmol) were stirred in THF (10 mL) at -75 °C for 1 h. The mixture was then allowed to warm to the room temperature and stirred for overnight. The solvent was removed under reduced pressure and dichloromethane (10 mL) was added to the residue. The mixture was flilterd thorough Celite via canula and the filtrate was concentrated to 2 mL under reduced pressure. Hexane (0.5 mL) was added to it and kept at room temperature to obtain colorless crystals of {[IMes•PPh](AqCl)<sub>2</sub>]<sub>4</sub>. Yield: 0.051 q (60%). M.p.: 190–194 °C (dec.). <sup>1</sup>H NMR (500.16 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.49 (dd, 2H, J = 7.5, 11.4 Hz,  $H_{Arom}$ ), 7.18 (td, 1H, J = 1.2, 7.5 Hz,  $H_{Arom}$ ), 7.10 (s, 2H, NCH), 7.04-7.00 (m, 2H, H<sub>Arom</sub>) 6.76 (s, 4H, H<sub>Arom</sub>), 2.25 (s, 6H, p-CH<sub>3</sub>), 2.03(s, 12H, o-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.57 MHz, CDCl<sub>3</sub>, 25 °C): δ 156.80 (d, J = 50.6 Hz, NCN), 141.91, 139.95 (d, J = 17.3 Hz), 134.28, 131.47, 130.60, 129.27, 127.85 (d, J = 28.2 Hz), 127.76 (d, J = 11.6 Hz), 124.21, 21.48 (s, p-CH<sub>3</sub>), 18.85 (s, o-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.66 MHz, CDCl<sub>3</sub>, 25 °C): δ -50.0 (s). Anal. Calcd for C<sub>108</sub>H<sub>116</sub>Ag<sub>8</sub>Cl<sub>8</sub>N<sub>8</sub>P<sub>4</sub> (contains 0.3 eq. of CH<sub>2</sub>Cl<sub>2</sub>): C, 44.54; H, 4.08; N, 3.78. Found: C, 44.42; H, 3.49; N, 3.58.

**[IMes•PPh](AuCI)**<sub>2</sub>: IMes•PPh (0.050 g, 0.121 mmol) and AuCI (0.062 g, 0.267 mmol) were stirred in THF (10 mL) at -75 °C for 1 h. The mixture was then allowed to warm to the room temperature and stirred for overnight. The solvent was removed under reduced pressure and dichloromethane (10 mL) was added to the residue. The mixture was flilterd thorough Celite *via* canula and the filtrate was concentrated to 2 mL under reduced pressure. Hexane (1 mL) was added to it and kept at room temperature to obtain colorless crystals of [IMes•PPh](AuCI)<sub>2</sub>. Yield: 0.048 g (45%). M.p.: 245–248 °C

(dec.). <sup>1</sup>H NMR (500.16 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  7.43 (ddd, 2H, *J* = 1.2, 8.0, 14.9 Hz, *H*<sub>Arom</sub>), 7.36-7.33 (m, 1H, *H*<sub>Arom</sub>), 7.35 (s, 2H, NC*H*), 7.09 (td, 2H, *J* = 2.9, 8.0 Hz, *H*<sub>Arom</sub>), 7.00 (s, 4H, *H*<sub>Arom</sub>), 2.40 (s, 6H, *p*-C*H*<sub>3</sub>), 2.06 (s, 12H, *o*-CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.57 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$  148.10 (d, *J* = 2.4 Hz, NCN), 142.68, 138.61 (d, *J* = 16.8 Hz), 134.87, 131.85, 131.43, 130.75, 128.35 (d, *J* = 13.2 Hz), 128.27 (d, *J* = 51.6 Hz), 126.35, 21.42 (s, *p*-CH<sub>3</sub>), 18.90 (s, o-CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.66 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$ -4.0 (s). Anal. Calcd for C<sub>27</sub>H<sub>29</sub>Au<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>P: C, 36.96; H, 3.33; N, 3.19. Found: C, 36.98; H, 3.05; N, 3.04.

**X-ray crystallographic data:** A suitable crystal covered with a layer of hydrocarbon/paratone-N oil was selected and mounted on a Cryo-loop, and immediately placed in the low temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker D8 Quest with a Photon 100 CMOS detector equipped with a Oxford Cryosystems 700 series cooler, a Triumph monochromator, and a Mo K $\alpha$  fine-focus sealed tube ( $\lambda$  = 0.71073 Å). Intensity data were processed using the Saint Plus program. All the calculations for the structure determination were carried out using the SHELXTL package (version 6.14). Initial atomic positions were located by direct methods using XT, and the structures of the compounds were refined by the least-squares method using XL. Absorption corrections were applied by using SADABS. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons. All the non-hydrogen atoms were refined anisotropically. Further details are given in Tables 1. The CCDC 1030195-1030198 contain the supplementary crystallographic data. These data can be obtained free of charge *via* 

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http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic

Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK).

Formula	C <sub>108</sub> H <sub>116</sub> Cl <sub>8</sub> Cu <sub>8</sub> N <sub>8</sub> P <sub>4</sub> • 2(CH <sub>2</sub> Cl <sub>2</sub> )	C <sub>108</sub> H <sub>116</sub> Cl <sub>8</sub> Ag <sub>8</sub> N <sub>8</sub> P <sub>4</sub> • 2(CH <sub>2</sub> Cl <sub>2</sub> )	$C_{27}H_{29}Au_2CI_2N_2P$	C <sub>108</sub> H <sub>116</sub> Br <sub>8</sub> Cu <sub>8</sub> N <sub>8</sub> P <sub>4</sub> • 2(CH <sub>2</sub> Cl <sub>2</sub> )
FW	2611.73	2966.37	877.32	2967.41
Temperature (K)	100	100	100	100
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	P2(1)/n	P2(1)/n	P2(1)/c	P2(1)/n
Cell Dimensions	a = 17.8559(14) Å	a = 17.9942(16) Å	a = 14.2115(11) Å	a = 17.9154(14) Å
	b = 16.5326(13) Å	b = 16.6328(15) Å	b = 11.7065(9) Å	b = 16.5873(13) Å
	c = 19.4749(15) Å	c = 19.7649(18) Å	c = 16.6136(13) Å	c = 19.6521(16) Å
	α= 90°	α= 90°	α= 90°	α= 90°
	β=94.917(2)°	β= 94.399(2)°	β= 98.0400(19)°	β= 94.218(2)°
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
$V(\text{\AA})^3$	5727.9(8)	5898.1(9)	2736.8(4)	5824.2(8)
Z	2	2	4	2
d <sub>calcd</sub> (g cm <sup>-3</sup> )	1.514	1.670	2.129	1.692
abs coeff (mm <sup>-1</sup> )	1.841	1.674	10.981	4.371
F (000)	2664	2952	1648	2952
θ range (deg)	2.717-28.281	2.843-29.575	3.027-33.141	2.727-28.282
refins collected	74308	83311	48639	73695
R <sub>int</sub> (Ind reflns)	0.0371(14193)	0.0308(16516)	0.0441(10423)	0.0701(14448)
data/restr/params	14193/0/652	16516/0/652	10423/0/313	14448/0/652
GOF on F <sup>2</sup>	1.036	1.013	1.057	1.041
<i>R</i> 1 [ <i>l</i> > 2σ( <i>l</i> )]/all data	0.0375/0.0557	0.0392/0.0564	0.0348/0.0506	0.0560/0.0824
wR2 [/ > 2σ(/)]/all data	0.0983/0.1099	0.1212/0.1380	0.0838/0.0905	0.1451/0.1695

 Table 1. Crystallographic data

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# TOC Figure:



IMes•PPh serves as a good bridging ligand for group 11 metal ions affording molecules with diverse solid state structures