# A Novel Coordination Mode for Cationic Phosphorus pπ Systems: $\mu^2$-Bridging Coordination of a Bis(phosphonio)isophosphindolium Cation

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1,3-Bis(triphenylphosphonio)isophosphindolium bromide reacts with CuBr to give a binuclear complex which is shown by X-ray crystallography to contain a $\mu^2$(P)-bridging cationic bis(triphenylphosphonio)isophosphindolium ligand.

The synthesis of isolable phosphenium cations $R_2P^+$ where a formal electron sextet at the two-coordinate phosphorus is stabilised by strongly π-donating substituents R (*e.g.* amino groups) marked a pioneering step in the still developing field of the chemistry of higher main group elements in low coordination states.[1] Even though coordination of phosphenium ions to transition metals *via* the phosphorus lone-pair was achieved some time ago, the number of known complexes is still very limited and is confined to compounds with zero valent metals ($Mo^0$,[1] $W^0$,[1] $Fe^0$,[1] $Ni^0$[2]). In the course of our investigation into the coordination chemistry of bis(phosphonio)isophosphindolium cations[3] (Scheme 1), whose two-coordinate phosphorus has been characterised as a phosphenium centre stabilised by two ylidyl substituents,[3] we recently described the stable gold complex **2** as the first phosphenium complex of a coinage metal.[4] Here, we report on the reaction of **1** with copper(I) bromide which leads to the formation of a binuclear complex featuring a hitherto unprecedented $\mu^2$(P)-bridging coordination of a phosphenium-type ligand to two metals.

Addition of 1 equiv. of CuBr (390 mg) to a solution of **1** (2.00 g) in methanol (50 cm$^3$) and stirring for 5 h at 20 °C produced a yellow solution and a dark yellow precipitate which was subsequently identified as the binuclear complex **3** (Scheme 1). According to a $^{31}$P NMR spectroscopic assay, 50% of unreacted **1** was still present in the supernatant solution. The crude product was recrystallised by dropwise addition of $CH_2Cl_2$ to the boiling reaction mixture until all solids were completely dissolved, followed by slow cooling to −30 °C. The separated orange crystals were collected by filtration (1.13 g, 70% with respect to CuBr) and dried in a stream of dry argon. Characterisation of **3** was achieved by $^1$H and $^{31}$P NMR spectroscopy,† satisfactory elemental (C, H) analyses and single crystal X-ray diffractometry.‡ Complete conversion of **1** into **3** was observed in the reaction of the ligand with 2 equiv. of CuBr under similar conditions. Complex **3** was also obtained together with several unidentified oxidation products when **1** was treated with a methanolic solution of $CuBr_2$. The reaction was immediate, and the precipitated **3** was isolated in 35% yield after filtration and drying in vacuum.

The molecular structure of **3** in the solid state is composed of discrete binuclear complexes $LCu_2Br_3$ (L = cation of **1**) whose key feature is a planar, four-membered ring consisting of the P(1)-atom of the $\mu^2$-coordinated ligand L, a μ-bromine, and the two trigonal planar (sum of valence angles 360°) Cu atoms (Fig. 1). The coordination spheres of both metals exhibit notable differences [Fig. 1(*b*)]. The P(1)–Cu(1) [2.351(1) Å] and the opposite Cu(2)–Br(3) distances [2.422(2) Å] are considerably larger than the neighbouring P(1)–Cu(2) [2.255(2) Å] and Cu(1)–Br(3) [2.371(1) Å] bond lengths, respectively. At the same time, the Br(1)–Cu(1)–Br(3) angle [136.7(1)°] opposite to the longer Cu(1)–P(1) bond is substantially widened and exceeds the corresponding angle at Cu(2) [Br(2)–Cu(2)–Br(3) 127.7(1)°] by 9°. This leads to an irregular, Y-shaped coordination geometry at Cu(1), which is, however, still less pronounced than in the copper selenolate $[(cHex_3P)CuSeC(SiMe_3)_3]_2$ (cHex = cyclohexyl) where a P–Cu–Se angle of 151.4° was found.[5]

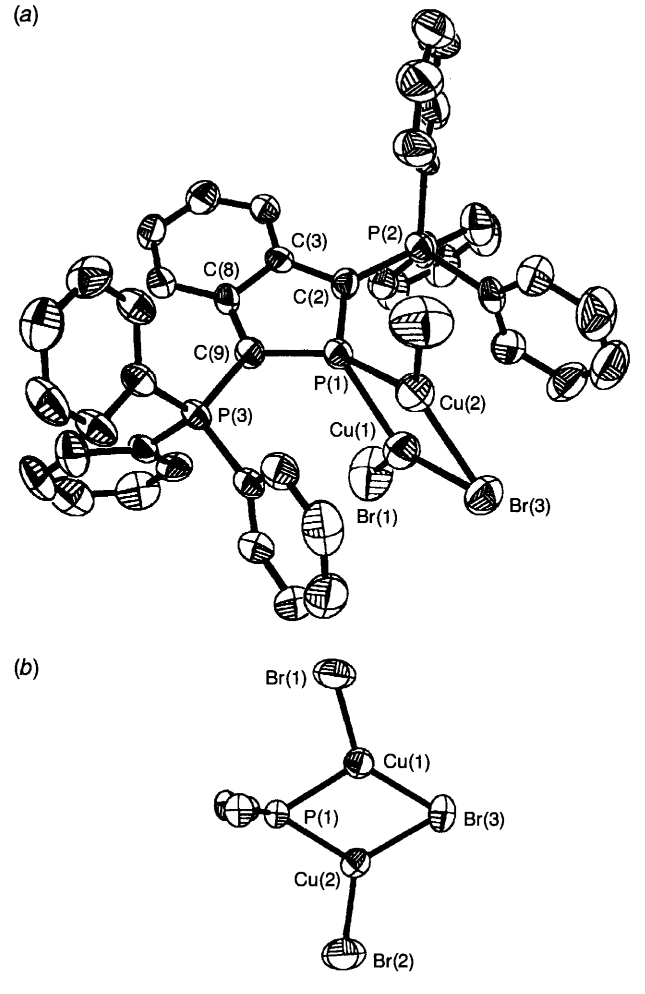
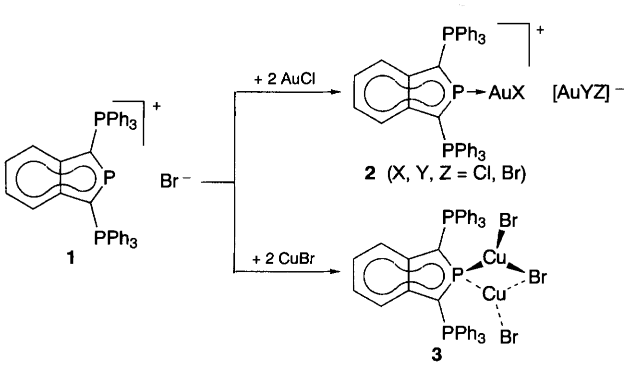


**Fig. 1** (*a*) ORTEP view of the structure of **3** in the crystal with 50% thermal ellipsoids (*b*) reduced representation of the metal environment in **3**. Selected bond distances (Å) and angles (°): Cu(1)–Br(1) 2.262(2), Cu(1)–Br(3) 2.371(1), Cu(2)–Br(2) 2.289(2), Cu(2)–Br(3) 2.422(2), P(1)–Cu(1) 2.351(1), P(1)–Cu(2) 2.255(2), P(1)–C(2) 1.728(7), P(1)–C(9) 1.730(7), P(2)–C(2) 1.749(7), P(3)–C(9) 1.737(7), C(2)–C(3) 1.432(9), C(8)–C(9) 1.444(10), Cu(1)–Br(3)–Cu(2) 61.6(1), Br(1)–Cu(1)–P(1) 107.1(1), P(1)–Cu(1)–Br(3) 116.2(1), Br(1)–Cu(1)–Br(3) 136.7(1), P(1)–Cu(2)–Br(2) 114.4(1), P(1)–Cu(2)–Br(3) 117.9(1), Br(2)–Cu(2)–Br(3) 127.7(1), C(2)–P(1)–C(9) 93.5(3).



**Scheme 1**

The small endocyclic angles at the bridging P(1) and Br(3) atoms of **3** [Cu(1)–P(1)–Cu(2) 64.3(1), Cu(1)–Br(3)–Cu(2) 61.6(1)°] lead to a markedly shorter Cu–Cu distance [2.454(2) Å] as compared to $[Cu_2Br_4]^{2-}$ [6] or $[\{(cHex)_3P\}_2Cu_2(\mu\text{-}Br)_2]$ **4**[7] ($r_{Cu\cdots Cu}$ 2.66–3.07 Å). More remarkable is the orientation of the isophosphindole plane in **3** which is orthogonal to the $PCu_2Br$ moiety, but shows a 10° tilt away from the line bisecting the Cu(1)–P(1)–Cu(2) angle towards the P(1)–Cu(1) vector [Fig. 1(*b*)]. The bonding parameters within the isophosphindolium moiety and the propeller-shaped arrangement of the $Ph_3P$ groups which enclose the metal atoms above and beneath the coordination plane at van der Waals distances are in good agreement with the corresponding features of the cations in **1** and the gold complex **2**, respectively.[4]

As the cationic ligand L contains a delocalised 10π-electron system extending over both anellated rings,[8] the bonding in the $Cu_2P$ unit of **3** may be rationalised in a similar way as in the topologically related aryl copper compounds and aryl cuprates,[9] where two metal centres are bridged by $\mu^2$(C)-coordinated aryl moieties. Within a qualitative MO picture,[9] the dominating Cu–P bonding interaction should then result from $L(\sigma) \rightarrow M$ electron transfer from the σ(P) orbital ('lone pair') into the symmetric combination of empty Cu 4s orbitals. Additional bonding contributions originate from $L(\pi) \rightarrow M$ interactions of occupied ligand π orbitals with the antisymmetric combination of Cu 4s orbitals, and from $M \rightarrow L(\pi)$ 'back donation' from filled Cu 3d orbitals into empty π* levels. Accordingly, the bonding in the $Cu_2P$ core may be classified as a 3-centre–2-electron bond which is further stabilised by interactions between the metals and the ligand π system.[9] This view is supported by the observed P–Cu bond distances for **3**, as well as by the similarity of the C–C and P–C bond lengths in **3** and **1**.[4] In particular, the Cu(1)–P(1) bond in **3** is much longer than expected for an electron-precise (*i.e.* 2-centre–2-electron) Cu–P bond involving three-coordinate copper (*cf.* $r_{P-Cu}$ = 2.18 Å for **4**,[7] even if a $\mu^2$-coordinated ligand should form somewhat longer bonds, see ref. 10) but is similar to distances of electron-deficient bonds in $\mu^3$-phosphido copper complexes (2.32–2.36 Å).[11] Furthermore, the formation of two electron-precise Cu–P bonds as observed for $\mu^2$(P)-bridging phospholides is anticipated to induce a breakdown of the cyclic π-conjugation in the ligand,[12a] thus leading to a marked increase of the endocyclic P–C bond distances in the complex.[12b] The asymmetric bridging of the $Cu_2$ pair by L in **3** is precedented by a similar asymmetry of the aryl bridges in the tetrameric compound, $[(2.4.6\text{-}Pr^i{}_3C_6H_2)Cu]_4$,[13] suggesting that: (i) the σ and π electrons of L contribute unequally to the two P–Cu bonds,[9,13] and (ii) the L–M π interactions are apparently weaker than the $L(\sigma) \rightarrow M$ interaction. Since the latter induces an increased electron density between the metal centres, the short metal–metal distance which is similar to Cu–Cu distances in copper aryls (2.37–2.45 Å)[9] is explained.

The observed structural features of **3** may be seen as experimental evidence that concerning its ligand properties, the bis(phosphonio)isophosphindolium cation in **1** constitutes a transition between a unique phosphenium cation and a phospholide anion. On one hand, the increased nucleophilicity of the cation in **1**, as compared to aminophosphenium ions, promotes the $L(\pi) \rightarrow M$ charge transfer which is a prerequisite for the $\mu^2$-coordination mode. On the other hand, owing to the presence of a positive charge resulting from the formal replacement of two hydrogens in a phospholide by $R_3P^+$ substituents, the π-nucleophilicity is significantly weaker than in phospholide anions. The bonding situation in **3** is no longer adequately described in terms of two electron-precise metal–phosphorus bonds, but rather on the basis of electron-deficient three-centre bonds as in organometallic aryl copper compounds. When the different endocyclic Cu–Br bond distances are considered also, **3** resembles an intimate-contact ion pair consisting of a phosphenium-like $[L(CuBr)]^+$ and a $[Cu'Br_2]^-$ fragment which are held together by additional Cu′–P and Br–Cu interactions. This view is corroborated by the discovery that solutions of **3** consist of an equilibrium mixture which contains, beside the binuclear complex and the free salt **1**, a small amount of a mononuclear isophosphindolium complex. A full account of these studies, as well as the characterisation of the analogous reaction products of **1** with CuI and CuCl and the chemical properties of the obtained complexes, will be reported elsewhere.

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## Footnotes

† *Selected data* for **3**: $^{31}P\{^1H\}$ NMR (−60 °C, $CH_2Cl_2$, ext. 85% $H_3PO_4$): 142.3 (t) and 12.7 (d, *J* 76.3 Hz).

‡ *Crystal data* for **3**: a suitable single crystal was grown from $CH_2Cl_2$–MeOH solution at ambient temperature; $C_{44}H_{34}Br_3Cu_2P_3\cdot 2CH_2Cl_2$, triclinic, space group $P\bar{1}$, (no. 2), $a$ = 12.825(2), $b$ = 13.087(2), $c$ = 14.288(2) Å, $\alpha$ = 85.88(1), $\beta$ = 84.92(1), $\gamma$ = 87.78(1)°, $V$ = 2381.3(6) Å$^3$, $Z$ = 2, $D_c$ = 1.66 g cm$^{-3}$, $\mu$(Mo-K$\alpha$) = 3.77 mm$^{-1}$, Nicolet R3m diffractometer, ω-scan, $2\theta_{max}$ 50.10°; 8868 reflections measured, 8312 symmetry-independent reflections ($R_{int}$ = 0.073), full-matrix least-squares refinement on $F^2$ (program SHELXL-93, G. M. Sheldrick, Universität Göttingen, 1993) with 523 variables. H-atoms are in calculated positions and were treated as riding atoms. $R_1$ = 0.068 [$I > 2\sigma(I)$]; $wR_2$ = 0.180, residual electron density between 0.753 and −0.801 e Å$^{-3}$. An empirical absorption correction was applied with the program DIFABS (N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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