

Impact of high π -density on the coordination properties of π -excess aromatic neutral $\sigma^2\text{P}$ ligands – $\text{P}(\pi)$ -donor bonds to Ag^+ and HgCl_2^\dagger Cite this: *Dalton Trans.*, 2014, 43, 51Received 15th October 2013,
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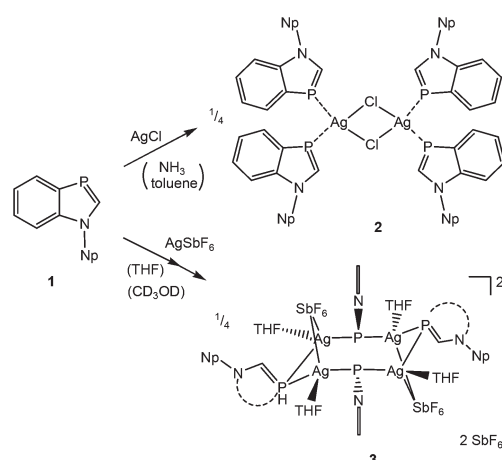
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Unprecedented coordination types of non-zerovalent d^{10} transition metals (AgX , HgCl_2) by π -excess aromatic $\text{P}=\text{C}$ ligands involving $\text{P}(\pi)$ -donor bond contributions were detected by structural and quantum chemical studies.

Trivalent phosphorus compounds are widely used ligands in coordination chemistry and homogenous late transition metal catalysis, but studies on ligands with dicoordinated ($\sigma^2\text{P}$) phosphorus are restricted almost completely to phosphabenzenes¹ and some phosphalkenes.² Complexes with π -excess-aromatic $\sigma^2\text{P}$ -azaphosphole ligands, apart from metal(0) complexes,^{3,4} are extremely sparsely documented,^{5,6} and only one, a 1,2-azaphosphole allylnickel chloride complex,⁶ has been characterized by crystal structure analysis. Complexes of the π -rich 1,3-azaphospholes with phosphorus in conjugation to nitrogen ($\text{N}=\text{C}=\text{P} \leftrightarrow \text{N}^+=\text{C}=\text{P}^-$) are still unknown for non-zerovalent transition metals. We report here the first examples with d^{10} metal cations; these 1,3-benzazaphosphole $\text{Ag}(\text{I})$ and HgCl_2 complexes display a hitherto unprecedented coordination pattern. Structurally characterized $\sigma^2\text{P}$ - $\text{Ag}(\text{I})$ complexes are very rare,^{7,8} and we are not aware of any $\text{Hg}(\text{II})$ complexes with $\sigma^2\text{P}$ -ligands.

Addition of toluene and NH_3 to an equimolar mixture of **1** and AgCl at -60°C and warming to r.t. led to the formation of an inversion-symmetric benzazaphosphole silver chloride complex with a central Ag_2Cl_2 ring (Scheme 1). Colourless crystals of **2** were obtained on overlaying a concentrated solution



Scheme 1 Formation of silver complexes of **1** (Np = neopentyl) and **3** (schematic structure presentation of **3**).

in THF with hexane. The crystal structure analysis (Fig. 1) displays distorted tetrahedral coordination of Ag^+ with an inter-planar angle of 80.8° between the Ag_2Cl_2 and the $\text{P3}-\text{Ag}-\text{P3}'$ planes. The $\text{P}-\text{Ag}$ bonds do not lie within the extended ligand ring plane, but are tilted away by 32.4 and 12.7° . The bond

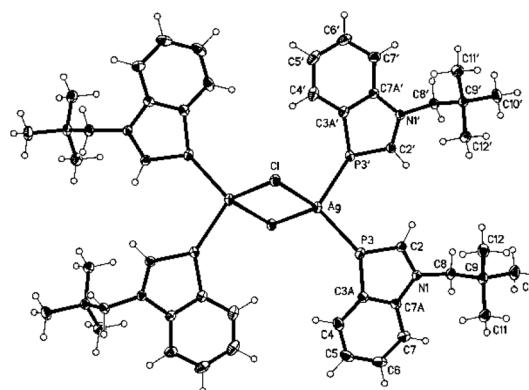


Fig. 1 Structure of **2** in the crystal (ellipsoids with 50% probability).

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† Electronic supplementary information (ESI) available: Syntheses and NMR spectra of **2**, **3**, and **5**, crystallographic details for **2** and **5** and quantum chemical calculations. CCDC 926714 and 926715. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52909f

lengths and angles within the ligand are only marginally changed (P-C3a slightly shortened) compared to **1**.⁹ A cationic silver complex of a different coordination type was formed in THF at room temperature from a mixture of **1** and AgSbF₆. Crystals of **3** were grown by slow concentration of a solution of the pale brown crude product in CD₃OD. They proved to be less stable than **2** and decomposed within a few days, but crystallographic analysis of freshly prepared crystals of **3** clearly revealed two [Ag₄(**1**)₄THF₄(SbF₆)₂]²⁺ clusters with μ-P coordination and four uncoordinated SbF₆⁻ counter-ions per unit cell (in space group *P2₁/c*). Full refinement was not possible, with the THF molecules and SbF₆⁻ ions being disordered (for details see ESI†). The sharp singlets lacking coupling with ^{107/109}Ag in the CD₃OD solution of silver complexes **2** and **3** indicate a rapid ligand exchange and thus kinetic lability. Complex formation is indicated mainly by upfield coordinated ³¹P chemical shifts, much stronger for the μ-P bridged **3** (Δδ = -76.7 ppm) than the terminally coordinated **2** (Δδ = -18.9 ppm). Characteristic features in the ¹³C NMR spectra are decreasing ¹J_{PC} coupling constants of C2 and C3a and downfield shifts of the C-2 signals, whereas proton NMR data are scarcely altered.

To find out if divalent mercury is also able to form complexes with 1,3-benzazaphospholes, the reaction of **1** with HgCl₂ in THF was explored. Oxidation of phosphorus to a λ⁵P heterocycle as reported for the reaction of 2,4,6-triphenylphosphabenzene with Hg(OAc)₂¹⁰ was not observed. The NMR spectra of the yellow solid, with a marked upfield ³¹P coordination chemical shift in C₆D₆ (Δδ³¹ = -84.8 ppm), indicated complex formation, but attempts to grow single crystals for a detailed structural characterization failed. A crystalline 1,3-benzazaphosphole–HgCl₂ complex was finally obtained from the recently reported σ³P,σ²P-hybrid benzazaphosphole **4**¹¹ and HgCl₂ in THF (Scheme 2). XRD analysis of the yellow single crystals of **5** (Fig. 2), grown from concentrated THF solution, showed a P,P'-chelate structure as expected. However, whereas in the recently reported Mo(0)(CO)₄(P,P')-chelate complex with **4** the zero-valent metal is only slightly (by 14.4°) tilted out of the ring plane with shorter ring-P–Mo than Ph₂P–Mo(0) distances and marginal changes within the ligand,¹¹ the HgCl₂ complex **5** coordinates mercury almost perpendicular to the benzazaphosphole ring plane with much longer Hg–P3 (2.6978(7) Å) than Hg–P1 bonds (2.4219(5) Å) and altered P–C and C–N bond lengths within the ring. The angle of the Hg–P vector to the ring plane of 80.3° (deviation from plane 2.62 Å) and the angles C2–P–Hg (86.40(8)) and C3a–P–Hg (98.92(8)), average

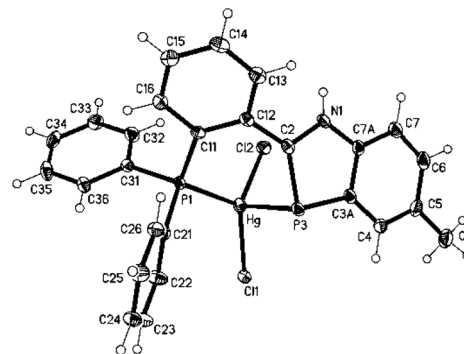
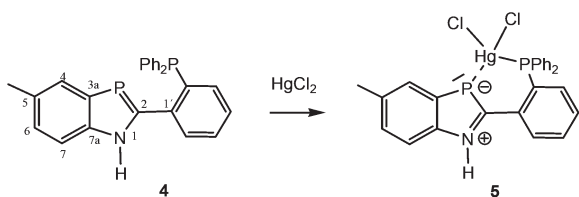


Fig. 2 Structure of **5** in the crystal (ellipsoids with 50% probability).

92.7°, hint at a π-donor bond from the ring-P atom to Hg(II). In combination with the elongated C2–P and shortened N–C2 bond (1.770(3) and 1.344(3) Å compared to 1.7173(17) and 1.369(2) Å in the Mo(0) complex¹¹) this implies a high weight for a zwitterionic P-coordinated phosphidomethylenimmonium “resonance structure” (cf. Scheme 2). The increased NH acidity favours N–H⋯Cl hydrogen bonds (H01⋯Cl(2)#1 2.42(3), N1⋯Cl(2)#1 3.238(2) Å, N–H⋯Cl 169(3)°) in the crystal packing and in solution, the latter indicated by a strongly downfield shifted NH proton signal (Δδ = 3.0 ppm). The coordination of HgCl₂ at the two P-atoms is indicated in solution by a downfield shift for the phosphanyl group Δδ = 31.0 ppm, similar to that of (Ph₃P)₂HgCl₂ (Δδ = 39 ppm¹²), and upfield shift for the ring-P atom, which is however much smaller than for the μ-bridging coordination in **3** and even smaller than for the two terminal benzazaphosphole ligands in **2**. The coordination at the ring-P atom is labile, displaying a rather sharp doublet by two-bond P–P-coupling but no ¹J(¹⁹⁹Hg³¹P) satellites, whereas the coordinated phosphanyl group exhibits a broad signal associated with the dynamic behaviour at the other P-atom.

The coordination of two benzazaphosphole ligands at each Ag(I) atom, the tilting of the P–Ag bond out of the ring plane in **2**, the μ-coordination mode in **3** and the unprecedented side-on coordination in the chelate complex **5** distinguish the complexes of the π-excess-type P=C–N ligands **1** and **4** from phosphabenzene complexes, which usually coordinate non-zero-valent transition metals within the ring plane.¹ To shed light on the background of these differences and to understand the unusual bonding in more detail, density functional calculations were carried out at the ωB97D/6-31G* level.¹³ First a second order perturbation analysis of the donor–acceptor interaction between NBOs at the crystal structures of **2** and **5** was performed. While in the case of **2** both P lone pairs at each atom exhibit about 60.5 kcal mol⁻¹ stabilization donating to Ag, an additional 6.4 kcal mol⁻¹ stabilization interaction was obtained for the (P=C bond)–Ag interaction in the case of the 32.4° tilted azaphosphole ring, showing some donor contribution of the π electron pair to the dative bonding. In the case of **5** the interaction between the σ³P lone pair and mercury amounts to 129.0 kcal mol⁻¹, while the interaction



Scheme 2 Synthesis of the chelate complex **5**.



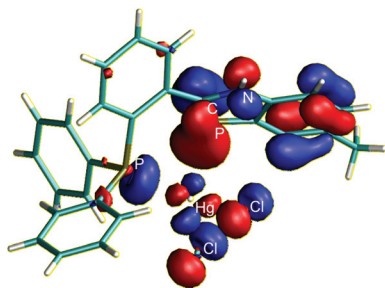


Fig. 3 The HOMO of 5 showing the involvement of one Hg d-orbital and the delocalised P=C π -orbital in the bonding.

between the σ^2P and mercury is only $12.1 \text{ kcal mol}^{-1}$. The small interaction with the mainly s-type¹⁴ σ^2P lone pair is in agreement with the near perpendicular position of the Hg atom with respect to the benzazaphosphole ring. The apparently lost (P lone pair)–Hg interaction, however, is amply compensated by the $40.0 \text{ kcal mol}^{-1}$ stabilization arising from the interaction between the P=C π -orbital and mercury. This interaction is also clearly seen on the HOMO of 5 with the involvement of both Hg and the mainly P=C bonded delocalised π orbital (the HOMO of the benzazaphosphole ligand) as is shown in Fig. 3.

The involvement of the (largely) P=C bonded orbital in the dative bonding is in agreement with the lengthening of the P=C distance (see above). It is noteworthy that no back-bonding from mercury to π^* type orbitals was detected. Optimization of the structure of 5 at the $\omega B97D/6-31G^*$ level resulted in a shift of the Hg atom from phosphorus towards the ring nitrogen, together with the formation of an intramolecular Cl...H bond (see Fig. S3.3 in the ESI†). This behaviour is in agreement with the conclusions drawn from the solution NMR data discussed above. To understand why mercury prefers to interact with the P=C bond rather than the P lone pair, further model calculations were carried out. In order to exclude the effect of any steric constraint caused by the interlocking of the two phosphorus atoms of 4, the structure of various $L(PMe_3)_2HgCl_2$ complexes was investigated, where L contained σ^2P in different bonding environments.

During the geometry optimization of the benzazaphosphole the $HgCl_2$ unit occupies an out-of-plane position similar to that in 5 (albeit with larger P–Hg distances), even if the geometry optimization is started from a structure where Hg lies in the plane of the benzazaphosphole¹⁵ ring. The complexes with the other ligands exhibit similar structural characteristics, with the exception of the in-plane complexed phosphabenzene ligand. The optimized structures can be seen in Fig. S3.4 of the ESI.† It is noteworthy that the σ^2P –Hg distance (between 2.57 and 3.49 Å) is related to the interaction energy between the π -system and mercury. Strongest interactions are obtained with ligands (L) having high energy (and localised) HOMO (Table 1) as can easily be explained by simple perturbation theory arguments.

Accordingly, while the phosphabenzene ligand with stabilized P=C π -orbitals (in agreement with the aromaticity) has a

Table 1 Interactions of various P=C ligands with $HgCl_2$

Ligands	ϵ_{HOMO} of L (eV)	$D_{\text{P-Hg}}$ (Å)	$\pi_{\text{P=C}} \rightarrow \text{Hg}$ (kcal mol^{-1})
PH=CH ₂	−9.50	3.49	8.6
	−8.93	2.99 ^a	9.6 ^b
	−8.65	2.95	21.5 ^c
HP=CH ₂ NH ₂	−7.46	2.79	62.1
	−7.40	3.11	33.2
	−7.08	2.57	149.2

^a $D_{\text{C-Hg}}$. ^b $\pi_{\text{P=C}} \rightarrow \text{Hg}$. ^c $n_{\text{P}} \rightarrow \text{Hg}$.

limited π -interaction and thus prefers the “classical” $n_{\text{P}} \rightarrow \text{Hg}$ bonding, the electron-rich P=C–N units (high energy HOMO) prefer the π interaction. The aromatic stabilization on the P=C π -orbital¹⁶ of the 1,3-azaphosphole (compared to the 1,3-azaphospholine), together with the delocalization, weakens the interaction with mercury. It should be noted that a phenyl mercury compound with intermolecular phenyl Hg π -interactions is known;¹⁷ however, its linear geometry is not distorted by the weak interaction.

In conclusion, we have presented the first complexes of π -rich σ^2P -aromatic 1,3-azaphosphole ligands with non-zero-valent late transition metals and revealed unprecedented significant π -donor contributions in the coordinative bond. Our findings suggest to search for related P(π)-donor complexes which open up new tuning possibilities in the highly important field of phosphorus-based late-transition metal catalysis.

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