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Low temperature isolation of a dinuclear silver complex of the cyclotetraphosphane [ClP(μ-PMes*)]$_2$†

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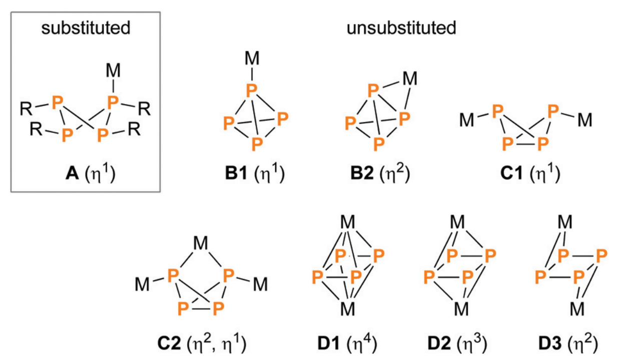
The reaction of the cyclotetraphosphane [ClP(μ-PMes*)]$_2$ (1, Mes* = 2,4,6-tri-*tert*-butylphenyl) with Ag[Al(OR^F)$_4$] (R^F = CH(CF$_3$)$_2$) resulted in a labile, dinuclear silver complex of 1, which eliminates AgCl above −30 °C. Its properties were investigated by spectroscopic methods, single crystal X-ray diffraction and DFT calculations.

Introduction

Ring systems composed of Group 15 elements (pnictogens) are an intriguing aspect of main group chemistry.[1] Especially, those comprising a binary N_2E_2 (E = P, As, Sb, Bi) scaffold represent versatile reagents in pnictogen chemistry.[2] Metal complexes of such ring systems were investigated to quite some extent,[3–5] including studies about their potential application in catalysis[6] and even anti-tumour studies.[7] Interestingly, despite the indisputable importance of phosphorus compounds as ligands in catalysis,[8] the coordination chemistry of homologous P_4 ring systems (cyclotetraphosphanes) has received much less attention. Examples include mainly P_4R_4 systems (**A**, Scheme 1; R = organic substituent) which coordinate to transition metal fragments such as metal carbonyls,[9–13] metal halides[14] or phosphane substituted metal complexes.[15] The coordination chemistry of unsubstituted P_n scaffolds, on the other hand, is more versatile;[16,17] in particular, there are numerous examples of coordination to P_4, which can adopt either a tetrahedral (**B1**, **B2**),[18–22] bicyclic (**C1**, **C2**)[23–26] or rectangular/square planar structure (**D1–D3**)[27–31] in the complex (Scheme 1). Likewise, the coordination chemistry of the *cyclo*-P_5^- moiety was well investigated; it found application in a variety of syntheses ranging from "simple" molecules such as Cp*FeP_5 (Cp* = pentamethylcyclopentadiene)[32,33] to chain-like poly-cations[34,35] or spherical macromolecules.[36–39]



Scheme 1 Common coordination patterns of various P_4 scaffolds.

Results and discussion

Pursuing our interest in the chemistry of the recently reported cyclotetraphosphane [ClP(μ-PMes*)]$_2$ (**1**),[40] we explored its reactivity towards silver salts of the weakly coordinating anions $[Al(OR^F)_4]^-$ ($R^F = CH(CF_3)_2$) and $[B(C_6F_5)_4]^-$.[41,42] Taking advantage of the bulky, weakly coordinating anion and naked Ag^+ ion – in terms of both stabilization and halide abstraction abilities – we hoped to find access to the dark red cyclotetraphosphenium ion [ClP(μ-PMes*)$_2$P]$^+$ (**2**$^+$), which had previously been observed as an intermediate during the reaction of **1** and the Lewis acid $GaCl_3$ (Scheme 2, top).[43] However, when mixing Ag[Al(OR^F)$_4$] (**4**) and **1** in a 1 : 1 ratio in CH_2Cl_2 at low temperatures, no precipitation of AgCl was observed. Instead, crystallization at −80 °C afforded colourless crystals that were identified as CH_2Cl_2 solvate of a dimeric silver complex of **1** (**5**[Al(OR^F)$_4$]$_2$, Scheme 2, bottom; yield of isolated substance: 28%).

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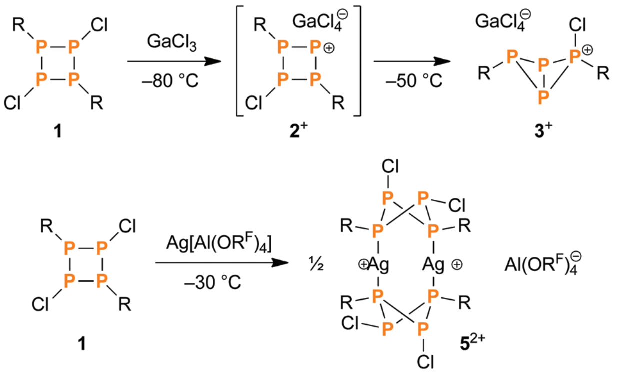


Scheme 2 Top: the reaction of cyclophosphane **1** with $GaCl_3$ led to the formation of the intermediate $\mathbf{2}^+$. Bottom: the reaction of **1** and **4** at low temperatures yielded the dinuclear silver complex $\mathbf{5}^{2+}$ (R = Mes*).

Molecular structure

Most interestingly, both chlorine atoms remained at the P_4 scaffold; nonetheless two rather long Ag⋯Cl contacts were observed, which are shorter than the sum of van der Waals radii (Ag1–Cl2A 3.496(1) Å, Ag1–Cl2A′ 3.641(2) Å; *cf.* $\sum r_{vdW}$ = 4.35 Å)[44] as revealed by single crystal X-ray diffraction (Fig. 1). The P–Ag bond lengths (P1A–Ag1 2.394(2) Å, P3a–Ag1′ 2.391(2) Å) compare well to the sum of the covalent radii (2.39 Å),[45] whereas the Ag–Ag distance (3.0511(7) Å) lies between the sum of the covalent (2.56 Å)[45] and van der Waals radii (5.06 Å).[44] The silver atoms are almost linearly coordinated (177.52(5)°) and lie in a perfect plane with the Mes* substituted P atoms. Strikingly, the configuration at P2 is inverted in comparison with the starting material, where both chlorine atoms are arranged in an equatorial position with respect to the P_4 ring system. The dinuclear silver complex is nicely shielded by all four Mes* substituents: the Ag atoms and the equatorial Cl atoms (Cl2A, Cl2A′) are protected by the *ortho-t*Bu groups, while the axial Cl atoms (Cl1A, Cl1A′) are sandwiched between the phenyl rings (Fig. S1, ESI†). A similar coordination pattern was previously observed in $[(Cy_4P_4)_2Sb_2Cl_2]^{2+}$ (Cy = cyclohexyl), where a planar Sb_2Cl_2 scaffold is coordinated by two Cy_4P_4 rings.[46] To the best of our knowledge, it is the only other example of a dinuclear metal complex capped by two P_4 ring systems.

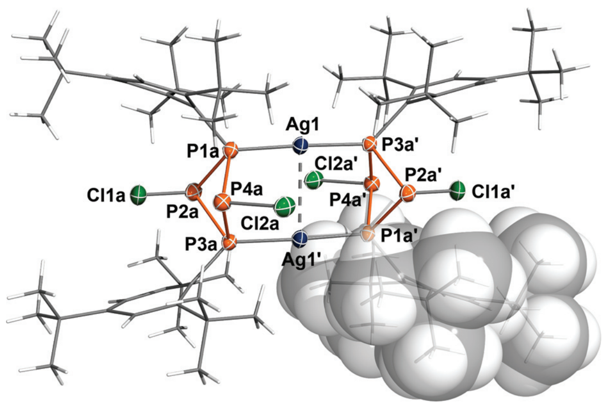


Fig. 1 Molecular structure of $\mathbf{5}^{2+}$. Ellipsoids are set at 50% probability (173 K). The cation is situated on a crystallographic inversion centre and thus displays C_i symmetry. Selected bond lengths [Å] and angles [°]: P1a–Ag1 2.394(2), P1a–P2a 2.235(2), P1a–P4a 2.242(2), P2a–Cl1a 2.059(2), P2a–P3a 2.232(2), P3a–Ag1′ 2.391(2), P3a–P4a 2.252(2), P4a–Cl2a 2.069(2), Ag1–Ag1′ 3.0511(7), P3a′–Ag1–P1a 177.52(5), P1a–Ag1–Ag1′ 90.68(4), P3a′–Ag1–Ag1′ 87.24(4).

Spectroscopic characterization

The low temperature ^{31}P NMR spectrum (−60 °C) of $\mathbf{5}[Al(OR^F)_4]_2$ showed a complex AA′BB′MM′M″M‴XX′ spin system (Fig. 2). The A and B part were assigned to the inequivalent Cl substituted P atoms (axially substituted: 126.9 ppm, equatorially substituted: 122.1 ppm), the M part to the Mes* substituted P atoms (16.8 ppm) and the X part to the Ag nuclei. The $^1J(^{31}P–^{31}P)$ coupling constants amount to −205 ($^1J_{AM}$) and −248 Hz ($^1J_{BM}$); the $^1J(^{31}P–^{107}Ag)$ coupling is −468 Hz ($^1J_{MX}$), which compares to reported (unsigned) coupling constants of other two-coordinate complexes such as $[(Ph_3P)_2Ag]^+$ (552 Hz) or $[(p\text{-}Tol_3P)_2Ag]^+$ (496 Hz).[47,48] Due to the complex multiplet structure and generally low solubility of $\mathbf{5}[Al(OR^F)_4]_2$, the signal to noise ratio of the NMR spectrum was rather poor, which is why only the large ^1J coupling constants could be determined unambiguously, while all smaller coupling constants have higher uncertainties. Nonetheless, the experimental data agree well with calculated NMR shifts and coupling constants (Table S3†).

In the solid state Raman spectrum (at −60 °C), characteristic bands of the $[P_4Ag]_2$ fragment are observed at 464 cm^{-1} (P–P stretching within the P_4 scaffold), 493 cm^{-1} (P–Cl stretching) and 514 cm^{-1} (P–C stretching). Further intense signals in the Raman spectrum can be attributed to the Mes* moieties (*e.g.* 563, 603 cm^{-1}: *t*Bu deformation; 739 cm^{-1}: phenyl ring deformation; 1007, 1018 cm^{-1}: Me deformation; 1130 cm^{-1}: combination of ring and CH deformation; 1582 cm^{-1}: ring stretching; 2900–3000 cm^{-1}: CH stretching of Me groups) and the $[Al(OR^F)_4]^-$ anion (*e.g.* 563 cm^{-1}: CF deformation;

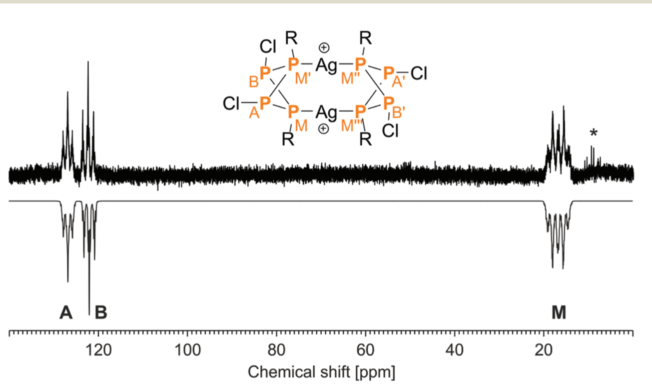


Fig. 2 Experimental (up) and simulated (down) ^{31}P NMR spectrum of $\mathbf{5}^{2+}$. Starred lines are due to slow elimination of AgCl even at low temperatures.

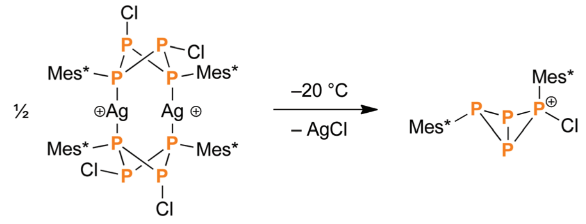
746 cm^{-1}: symmetrical AlO_4 stretching; 818 cm^{-1}: combination of deformation at O and CF_3; 1364, 1386 cm^{-1}: CH deformation; 2873 cm^{-1}: CH stretching). The assignments of the signals were made on the basis of computed vibrational data.

Computational study

To further investigate the bonding situation in $\mathbf{5}^{2+}$, density functional theory (DFT) calculations were performed.† According to NBO analysis,[49] there is no significant bonding interaction between the two Ag atoms, as already indicated by the nearly linear coordination of the Ag centres. Furthermore, both Wiberg bond index (0.31) and natural bond index (0.56) indicate a low covalent character of the Ag–P bonds; accordingly, the natural Lewis representation comprises two distinguished Ag^+ cations and two neutral cyclophosphane moieties. Second order perturbation analysis reveals two stabilizing interactions per Ag^+ cation between the empty s-orbital and the lone pairs (LPs) of the flanking P atoms (346.2 kJ mol^{-1} each), which is consistent with a classical dative bond from P to Ag (Fig. 3). The natural partial charge of each Ag centre is $+0.59e$, while each of the four coordinating P atoms bears a charge of $+0.17e$. Hence, the formal charge transfer amounts to $-0.41e$ per Ag^+ ion.

Intramolecular elimination of AgCl

When the reaction mixture of the cyclophosphane **1** and the silver salt **4** was allowed to warm to temperatures above −30 °C, precipitation of a white solid was observed, indicating elimination of AgCl. *In situ* ^{31}P NMR spectroscopy revealed that the intermediately formed silver complex $\mathbf{5}^{2+}$ decomposed above that temperature (Fig. S3†), yielding the bicyclic cation $[Mes^*P_4(Cl)Mes^*]^+$ ($\mathbf{3}^+$, Scheme 3), which had previously been obtained by reacting **1** with $GaCl_3$ (Scheme 2, top).[43] The same reaction outcome was observed when warming a solution of pure $\mathbf{5}[Al(OR^F)_4]_2$. In this respect, $\mathbf{5}[Al(OR^F)_4]_2$ can be viewed as an isolable intermediate, which demonstrates that the eventual AgCl elimination does not occur *via* direct attack of a silver ion, but rather *via* complexation and a subsequent intramolecular elimination reaction.



$\mathbf{5}^{2+}$ $\mathbf{3}^+$

Scheme 3 Above −30 °C, the silver complex $\mathbf{5}^{2+}$ eliminates AgCl, which leads to the formation of the bicyclic phosphino–phosphonium cation $\mathbf{3}^+$.

Interestingly, when treating **1** with $Ag[B(C_6F_5)_4]$ (**6**) under the same reaction conditions, precipitation of AgCl was observed even at −80 °C, leading once more to the formation of $\mathbf{3}^+$, as indicated by ^{31}P NMR spectroscopy. However, an intermediate similar to the cyclotetraphosphenium cation $\mathbf{2}^+$ could not be observed in any of these reactions.

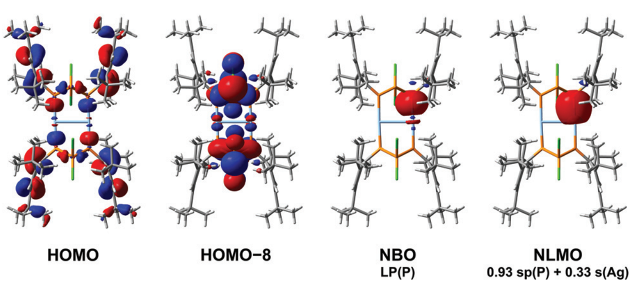


Fig. 3 Left: molecular orbitals (MOs) of $\mathbf{5}^{2+}$. The HOMO shows contributions to the LPs at the coordinating P atoms, the HOMO−8 encompasses the LPs at Cl and the other P atoms as well as bonding within the P_4 ring systems. Right: natural bond orbital (NBO) representation of a LP at phosphorus and the corresponding natural localized molecular orbital (NLMO), which consists mainly of a formal sp hybrid orbital at P (86%) and an s orbital at Ag (11%), thus illustrating the bonding between these two centres.

Conclusions

In conclusion, we present a thermally labile dinuclear silver complex capped by two P_4 ring systems, which eliminates AgCl at temperatures above −30 °C. Thus it can be considered an intermediate of the chloride abstraction from $[ClP(\mu\text{-}PMes^*)]_2$, demonstrating that the reaction occurs *via* an intramolecular rather than an intermolecular process.

Acknowledgements

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