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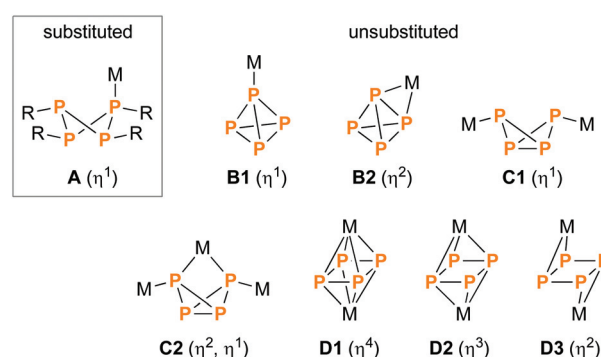
Low temperature isolation of a dinuclear silver complex of the cyclotetraphosphane [CIP( $\mu$ -PMes\*)]<sub>2</sub><sup>†</sup>Jonas Bresien,<sup>a</sup> Axel Schulz<sup>\*a,b</sup> and Alexander Villinger<sup>a</sup>

The reaction of the cyclotetraphosphane [CIP( $\mu$ -PMes\*)]<sub>2</sub> (**1**, Mes\* = 2,4,6-tri-*tert*-butylphenyl) with Ag[Al(OR<sup>F</sup>)<sub>4</sub>] (R<sup>F</sup> = CH(CF<sub>3</sub>)<sub>2</sub>) 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.

such as Cp\*FeP<sub>5</sub> (Cp\* = pentamethylcyclopentadiene)<sup>32,33</sup> to chain-like poly-cations<sup>34,35</sup> or spherical macromolecules.<sup>36–39</sup>

## Introduction

Ring systems composed of Group 15 elements (pnictogens) are an intriguing aspect of main group chemistry.<sup>1</sup> Especially, those comprising a binary N<sub>2</sub>E<sub>2</sub> (E = P, As, Sb, Bi) scaffold represent versatile reagents in pnictogen chemistry.<sup>2</sup> Metal complexes of such ring systems were investigated to quite some extent,<sup>3–5</sup> including studies about their potential application in catalysis<sup>6</sup> and even anti-tumour studies.<sup>7</sup> Interestingly, despite the indisputable importance of phosphorus compounds as ligands in catalysis,<sup>8</sup> the coordination chemistry of homologous P<sub>4</sub> ring systems (cyclotetraphosphanes) has received much less attention. Examples include mainly P<sub>4</sub>R<sub>4</sub> systems (**A**, Scheme 1; R = organic substituent) which coordinate to transition metal fragments such as metal carbonyls,<sup>9–13</sup> metal halides<sup>14</sup> or phosphane substituted metal complexes.<sup>15</sup> The coordination chemistry of unsubstituted P<sub>n</sub> scaffolds, on the other hand, is more versatile;<sup>16,17</sup> in particular, there are numerous examples of coordination to P<sub>4</sub>, which can adopt either a tetrahedral (**B1**, **B2**),<sup>18–22</sup> bicyclic (**C1**, **C2**)<sup>23–26</sup> or rectangular/square planar structure (**D1–D3**)<sup>27–31</sup> in the complex (Scheme 1). Likewise, the coordination chemistry of the *cyclo*-P<sub>5</sub><sup>–</sup> moiety was well investigated; it found application in a variety of syntheses ranging from “simple” molecules

Scheme 1 Common coordination patterns of various P<sub>4</sub> scaffolds.

## Results and discussion

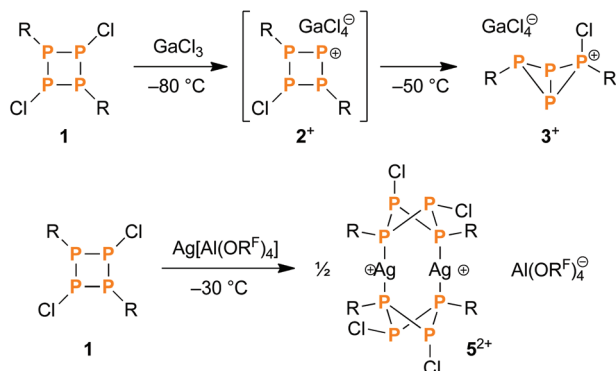
Pursuing our interest in the chemistry of the recently reported cyclotetraphosphane [CIP( $\mu$ -PMes\*)]<sub>2</sub> (**1**),<sup>40</sup> we explored its reactivity towards silver salts of the weakly coordinating anions [Al(OR<sup>F</sup>)<sub>4</sub>]<sup>–</sup> (R<sup>F</sup> = CH(CF<sub>3</sub>)<sub>2</sub>) and [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>–</sup>.<sup>41,42</sup> Taking advantage of the bulky, weakly coordinating anion and naked Ag<sup>+</sup> ion – in terms of both stabilization and halide abstraction abilities – we hoped to find access to the dark red cyclotetraphosphonium ion [CIP( $\mu$ -PMes\*)<sub>2</sub>P]<sup>+</sup> (**2**<sup>+</sup>), which had previously been observed as an intermediate during the reaction of **1** and the Lewis acid GaCl<sub>3</sub> (Scheme 2, top).<sup>43</sup> However, when mixing Ag[Al(OR<sup>F</sup>)<sub>4</sub>] (**4**) and **1** in a 1 : 1 ratio in CH<sub>2</sub>Cl<sub>2</sub> at low temperatures, no precipitation of AgCl was observed. Instead, crystallization at –80 °C afforded colourless crystals that were identified as CH<sub>2</sub>Cl<sub>2</sub> solvate of a dimeric silver complex of **1** ([5[Al(OR<sup>F</sup>)<sub>4</sub>]<sub>2</sub>], Scheme 2, bottom; yield of isolated substance: 28%).

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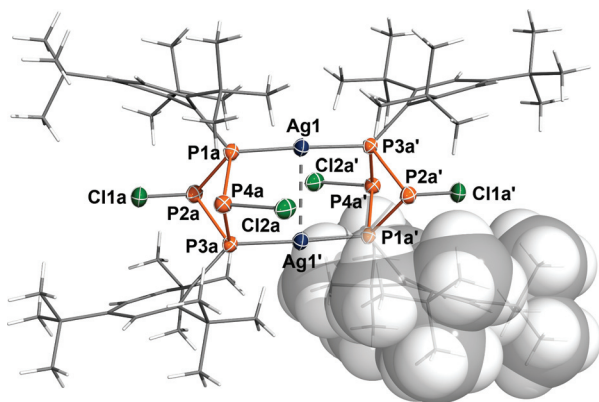




**Scheme 2** Top: the reaction of cyclophosphane **1** with  $\text{GaCl}_3$  led to the formation of the intermediate  $2^+$ . Bottom: the reaction of **1** and **4** at low temperatures yielded the dinuclear silver complex  $5^{2+}$  ( $R = \text{Mes}^*$ ).

### Molecular structure

Most interestingly, both chlorine atoms remained at the  $\text{P}_4$  scaffold; nonetheless two rather long  $\text{Ag}\cdots\text{Cl}$  contacts were observed, which are shorter than the sum of van der Waals radii ( $\text{Ag1}-\text{Cl2A}$  3.496(1) Å,  $\text{Ag1}-\text{Cl2A}'$  3.641(2) Å; cf.  $\sum r_{\text{vdW}} = 4.35$  Å)<sup>44</sup> as revealed by single crystal X-ray diffraction (Fig. 1). The P–Ag bond lengths ( $\text{P1A}-\text{Ag1}$  2.394(2) Å,  $\text{P3A}-\text{Ag1}'$  2.391(2) Å) compare well to the sum of the covalent radii (2.39 Å),<sup>45</sup> whereas the Ag–Ag distance (3.0511(7) Å) lies between the sum of the covalent (2.56 Å)<sup>45</sup> and van der Waals radii (5.06 Å).<sup>44</sup> The silver atoms are almost linearly coordinated ( $177.52(5)^\circ$ ) and lie in a perfect plane with the  $\text{Mes}^*$  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  $\text{P}_4$  ring system. The dinuclear silver complex is nicely shielded by all



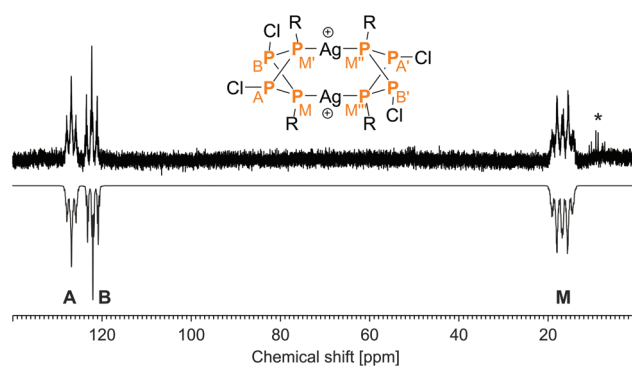
**Fig. 1** Molecular structure of  $5^{2+}$ . Ellipsoids are set at 50% probability (173 K). The cation is situated on a crystallographic inversion centre and thus displays  $C_i$  symmetry. Selected bond lengths [Å] and angles [ $^\circ$ ]:  $\text{P1a}-\text{Ag1}$  2.394(2),  $\text{P1a}-\text{P2a}$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

four  $\text{Mes}^*$  substituents: the Ag atoms and the equatorial Cl atoms ( $\text{Cl2A}$ ,  $\text{Cl2A}'$ ) are protected by the *ortho*-*t*Bu groups, while the axial Cl atoms ( $\text{Cl1A}$ ,  $\text{Cl1A}'$ ) are sandwiched between the phenyl rings (Fig. S1, ESI<sup>†</sup>). A similar coordination pattern was previously observed in  $[(\text{Cy}_4\text{P}_4)_2\text{Sb}_2\text{Cl}_2]^{2+}$  ( $\text{Cy} = \text{cyclohexyl}$ ), where a planar  $\text{Sb}_2\text{Cl}_2$  scaffold is coordinated by two  $\text{Cy}_4\text{P}_4$  rings.<sup>46</sup> To the best of our knowledge, it is the only other example of a dinuclear metal complex capped by two  $\text{P}_4$  ring systems.

### Spectroscopic characterization

The low temperature  $^{31}\text{P}$  NMR spectrum ( $-60$  °C) of  $5[\text{Al}(\text{OR}^{\text{F}})_4]_2$  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  $\text{Mes}^*$  substituted P atoms (16.8 ppm) and the X part to the Ag nuclei. The  $^1J(^{31}\text{P}-^{31}\text{P})$  coupling constants amount to  $-205$  ( $^1J_{\text{AM}}$ ) and  $-248$  Hz ( $^1J_{\text{BM}}$ ); the  $^1J(^{31}\text{P}-^{107}\text{Ag})$  coupling is  $-468$  Hz ( $^1J_{\text{MX}}$ ), which compares to reported (unsigned) coupling constants of other two-coordinate complexes such as  $[(\text{Ph}_3\text{P})_2\text{Ag}]^+$  (552 Hz) or  $[(p\text{-Tol}_3\text{P})_2\text{Ag}]^+$  (496 Hz).<sup>47,48</sup> Due to the complex multiplet structure and generally low solubility of  $5[\text{Al}(\text{OR}^{\text{F}})_4]_2$ , 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<sup>†</sup>).

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



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



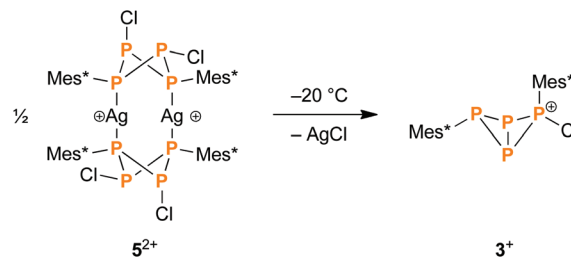
746  $\text{cm}^{-1}$ : symmetrical  $\text{AlO}_4$  stretching; 818  $\text{cm}^{-1}$ : combination of deformation at O and  $\text{CF}_3$ ; 1364, 1386  $\text{cm}^{-1}$ : CH deformation; 2873  $\text{cm}^{-1}$ : CH stretching). The assignments of the signals were made on the basis of computed vibrational data.

### Computational study

To further investigate the bonding situation in  $5^{2+}$ , density functional theory (DFT) calculations were performed.<sup>†</sup> According to NBO analysis,<sup>49</sup> 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  $\text{Ag}^+$  cations and two neutral cyclophosphane moieties. Second order perturbation analysis reveals two stabilizing interactions per  $\text{Ag}^+$  cation between the empty s-orbital and the lone pairs (LPs) of the flanking P atoms (346.2  $\text{kJ mol}^{-1}$  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  $\text{Ag}^+$  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  $-30\text{ }^\circ\text{C}$ , precipitation of a white solid was observed, indicating elimination of AgCl. *In situ*  $^{31}\text{P}$  NMR spectroscopy revealed that the intermediately formed silver complex  $5^{2+}$  decomposed above that temperature (Fig. S3<sup>†</sup>), yielding the bicyclic cation  $[\text{Mes}^*\text{P}_4(\text{Cl})\text{Mes}^*]^+$  (**3**<sup>+</sup>, Scheme 3), which had previously been obtained by reacting **1** with  $\text{GaCl}_3$  (Scheme 2, top).<sup>43</sup> The same reaction outcome was observed when warming a solution of pure  $5[\text{Al}(\text{OR}^F)_4]_2$ . In this respect,  $5[\text{Al}(\text{OR}^F)_4]_2$  can be viewed as an isolable intermediate, which demonstrates that the eventual AgCl elimination does not occur *via* direct attack of a silver



**Scheme 3** Above  $-30\text{ }^\circ\text{C}$ , the silver complex  $5^{2+}$  eliminates AgCl, which leads to the formation of the bicyclic phosphino–phosphonium cation **3**<sup>+</sup>.

ion, but rather *via* complexation and a subsequent intramolecular elimination reaction.

Interestingly, when treating **1** with  $\text{Ag}[\text{B}(\text{C}_6\text{F}_5)_4]$  (**6**) under the same reaction conditions, precipitation of AgCl was observed even at  $-80\text{ }^\circ\text{C}$ , leading once more to the formation of **3**<sup>+</sup>, as indicated by  $^{31}\text{P}$  NMR spectroscopy. However, an intermediate similar to the cyclotetraphosphenium cation **2**<sup>+</sup> could not be observed in any of these reactions.

## Conclusions

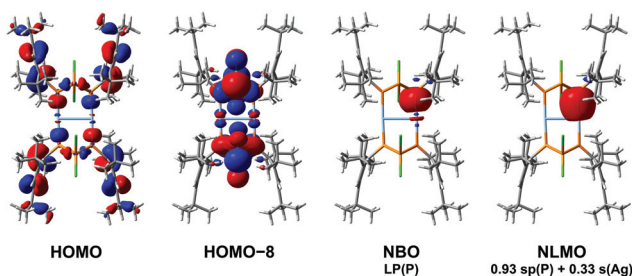
In conclusion, we present a thermally labile dinuclear silver complex capped by two  $\text{P}_4$  ring systems, which eliminates AgCl at temperatures above  $-30\text{ }^\circ\text{C}$ . Thus it can be considered an intermediate of the chloride abstraction from  $[\text{ClP}(\mu\text{-PMes}^*)]_2$ , demonstrating that the reaction occurs *via* an intramolecular rather than an intermolecular process.

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**Fig. 3** Left: molecular orbitals (MOs) of  $5^{2+}$ . 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  $\text{P}_4$  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.



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