Low temperature isolation of a dinuclear silver complex of the cyclotetraphosphane \([\text{ClP}(\mu-\text{PMes}*)]_2\)\(^{\dagger}\)

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The reaction of the cyclotetraphosphane \([\text{ClP}(\mu-\text{PMes}*)]_2\) (1, Mes\(^*\) = 2,4,6-tri-tert-butylphenyl) with Ag[Al(OR\(^7\))\(_4\)] (RF = CH(CF\(_3\))\(_2\)) resulted in a labile, dinuclear silver complex of 1, which eliminates AgCl above \(-30^\circ\)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 \(\text{N}_2\text{E}_2\) (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 \(\text{P}_4\) ring systems (cyclotetraphosphanes) has received much less attention. Examples include mainly \(\text{P}_3\text{R}_4\) systems (A, Scheme 1; \(\text{R} = \text{organic substituent}\)) which coordinate to transition metal fragments such as metal carboxyls,\(^9\)–\(^13\) metal halides\(^14\) or phosphane substituted metal complexes.\(^15\) The coordination chemistry of unsubstituted \(\text{P}_n\) scaffolds, on the other hand, is more versatile;\(^16,17\) in particular, there are numerous examples of coordination to \(\text{P}_n\), which can adopt either a tetrahedral (B\(_1\), B\(_2\)),\(^18\)–\(^22\) bicyclic (C\(_1\), C\(_2\))\(^23\)–\(^26\) or rectangular/square planar structure (D\(_1\)–D\(_3\))\(^27\)–\(^31\) in the complex (Scheme 1). Likewise, the coordination chemistry of the \(\text{cyclo-P}_5\)\(^-\) moiety was well investigated; it found application in a variety of syntheses ranging from “simple” molecules such as \(\text{Cp}^*\text{FeP}_5\) (\(\text{Cp}^* = \text{pentamethylcyclopentadiene}\))\(^32,33\) to chain-like poly-cations\(^34,35\) or spherical macromolecules.\(^36\)–\(^39\)

Results and discussion

Pursuing our interest in the chemistry of the recently reported cyclotetraphosphane \([\text{ClP}(\mu-\text{PMes}*)]_2\) (1),\(^40\) we explored its reactivity towards silver salts of the weakly coordinating anions \([\text{Al}(\text{OR})\(_7\)]\(_4\)\(^-\) (RF = CH(CF\(_3\))\(_2\)) and \([\text{B}(\text{C}_6\text{F}_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 cyclotetraphosphonium ion \([\text{ClP}(\mu-\text{PMes}*)_2\text{P}^+\)]\(^2-\) (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\(^7\))]\(_4\) (4) and 1 in a 1 : 1 ratio in CH\(_2\)Cl\(_2\) at low temperatures, no precipitation of AgCl was observed. Instead, crystallization at \(-80^\circ\)C afforded colourless crystals that were identified as CH\(_2\)Cl\(_2\) solvate of a dimeric silver complex of 1 (5[Al(OR\(^7\))]\(_4\)), Scheme 2, bottom; yield of isolated substance: 28%).

\(^{\dagger}\)Electronic supplementary information (ESI) available: Experimental and computational details, crystallographic and spectroscopic data. CCDC 1417701. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03928b
Molecular structure

Most interestingly, both chlorine atoms remained at the P₄ 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. \( \sum r_{\text{vdw}} = 4.35 \) 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 (2.56 Å)\(^{45}\) and van der Waals radii (5.06 Å).\(^{44}\) Most interestingly, both chlorine atoms remained at the P₄ positions, whereas the Ag–Ag distance (3.0511(7) Å) is shorter than the sum of van der Waals radii (3.641 Å).\(^{45}\) The silver atoms are almost linearly coordinated (177.52(5)°) and lie in a perfect plane with the Mes* substituted P atoms (16.8 ppm). The M part to the Mes* substituted P atoms (axially substituted: 126.9 ppm), the X part to the Ag nuclei. The \( J_{\text{1P-2P}} \) 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 \([\text{P₄Ag}]^2⁺\) fragment are observed at 464 cm\(^{-1}\) (P–P stretching within the P₄ 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\(^{-1}\); tBu 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 \([\text{Al(ORF)}]^-\) anion (e.g. 563 cm\(^{-1}\); CF deformation; 651 cm\(^{-1}\); ORF deformation; 687 cm\(^{-1}\); ORF deformation; 944 cm\(^{-1}\); ORF deformation; 1646 cm\(^{-1}\); ORF deformation; 2921 cm\(^{-1}\); ORF deformation; 3044 cm\(^{-1}\); ORF deformation; 3108 cm\(^{-1}\); ORF deformation; 3133 cm\(^{-1}\); ORF deformation; 3164 cm\(^{-1}\); ORF deformation; 3198 cm\(^{-1}\); ORF deformation).
746 cm⁻¹: symmetrical AlO₃ stretching; 818 cm⁻¹: combination of deformation at O and CF₃; 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 5²⁺, 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 +0.17, 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 ³¹P NMR spectroscopy revealed that the intermediated formed silver complex 5²⁺ decomposed above that temperature (Fig. S3†), yielding the bicyclic cation [Mes*P₄(Cl)Mes*⁺] (3⁺, Scheme 3), which had previously been obtained by reacting 1 with GaCl₃ (Scheme 2, top).⁴³ The same reaction outcome was observed when warming a solution of pure 5[Al(OR)₃]₂. In this respect, 5[Al(OR)₃]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.

Interestingly, when treating 1 with Ag[B(C₆F₅)₄] (6) under the same reaction conditions, precipitation of AgCl was observed even at −80 °C, leading once more to the formation of 3⁺, as indicated by ³¹P NMR spectroscopy. However, an intermediate similar to the cyclotetraphosphenium cation 2⁺ could not be observed in any of these reactions.

Conclusions

In conclusion, we present a thermally labile dinuclear silver complex capped by two P₄ ring systems, which eliminates AgCl at temperatures above −30 °C. Thus it can be considered an intermediate of the chloride abstraction from [ClP(µ-PMes*)]₂, demonstrating that the reaction occurs via an intramolecular rather than an intermolecular process.

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Notes and references

1. L. Stahl, Coord. Chem. Rev., 2000, 210, 203–250.
2. G. He, O. Shynkaruk, M. W. Lui and E. Rivard, Chem. Rev., 2014, 114, 7815–7880.
3. M. S. Balakrishna, V. S. Reddy, S. S. Krishnamurthy, J. F. Nixon and J. C. T. R. B. St. Laurent, Coord. Chem. Rev., 1994, 129, 1–90.
4. G. G. Briand, T. Chivers and M. Krahn, Coord. Chem. Rev., 2002, 233–234, 237–254.
5. M. S. Balakrishna, D. J. Eisler and T. Chivers, Chem. Soc. Rev., 2007, 36, 650–664.
6. D. W. Stephan, Angew. Chem., Int. Ed., 2000, 39, 314–329.
7. D. Suresh, M. S. Balakrishna, K. Rathinasamy, D. Panda and S. M. Mobin, Dalton Trans., 2008, 2812–2814.
8 Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis, ed. P. C. J. Kamer and P. W. N. M. Van Leeuwen, John Wiley & Sons, 2012.
9 H. G. Ang, J. S. Shannon and B. O. West, Chem. Commun., 1965, 10–11.
10 W. A. Fowles and D. K. Jenkins, Chem. Commun., 1965, 61–62.
11 M. A. Bush, V. R. Cook and P. Woodward, Chem. Commun., 1967, 630–631.
12 N. H. Tran Huy, Y. Inubushi, L. Ricard and F. Mathey, Organometallics, 1997, 16, 2506–2508.
13 N. H. Tran Huy, Y. Lu and F. Mathey, Organometallics, 2011, 30, 1734–1737.
14 C. S. Cundy, M. Green, F. G. A. Stone and A. Tauntong-Rigby, J. Chem. Soc. A, 1968, 1776–1778.
15 I. G. Phillips, R. G. Ball and R. G. Cavell, Inorg. Chem., 1992, 31, 1633–1641.
16 M. Scheer, G. Balázs and A. Seitz, Chem. Rev., 2010, 110, 4236–4256.
17 B. M. Cossart, N. A. Piro and C. C. Cummins, Chem. Rev., 2010, 110, 4164–4177.
18 O. J. Scherer, Comments Inorg. Chem., 1987, 6, 1–22.
19 I. Krossing, J. Am. Chem. Soc., 2001, 123, 4603–4604.
20 V. Mirabello, M. Caporali, V. Gallo, L. Gonsalvi, D. Gudat, W. Frey, A. Ienco, M. Latronico, P. Mastrorilli and M. Peruzzini, Chem. – Eur. J., 2012, 18, 11238–11250.
21 S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo and M. Scheer, Angew. Chem., Int. Ed., 2013, 52, 10887–10891.
22 F. Spitzer, M. Sierka, M. Latronico, P. Mastrorilli, A. V. Virovets and M. Scheer, Angew. Chem., Int. Ed., 2015, 54, 4392–4396.
23 S. Heinl and M. Scheer, Chem. Sci., 2014, 5, 3221–3225.
24 C. Schwarzmaier, A. Y. Timoshkin, G. Balázs and M. Scheer, Angew. Chem., Int. Ed., 2014, 53, 9077–9081.
25 S. Pelties, D. Herrmann, B. de Bruin, F. Hartl and R. Wolf, Chem. Commun., 2014, 7014–7016.
26 C. Schwarzmaier, S. Heinl, G. Balázs and M. Scheer, Angew. Chem., Int. Ed., 2015, 54, 13116–13121.
27 W. W. Seidel, O. T. Summerscales, B. O. Patrick and M. D. Fryzuk, Angew. Chem., Int. Ed., 2009, 48, 115–117.
28 A. S. P. Frey, F. G. N. Cloke, P. B. Hitchcock and J. C. Green, New J. Chem., 2011, 35, 2022.
29 A. Velian and C. C. Cummins, Chem. Sci., 2012, 3, 1003.
30 C. Camp, L. Maron, R. G. Bergman and J. Arnold, J. Am. Chem. Soc., 2014, 136, 17652–17661.
31 S. Yao, N. Lindenmaier, Y. Xiong, S. Inoue, T. Szilvási, M. Adelhardt, J. Sutter, K. Meyer and M. Driess, Angew. Chem., Int. Ed., 2015, 54, 1250–1254.
32 O. J. Scherer and T. Brück, Angew. Chem., Int. Ed. Engl., 1987, 26, 59–59.
33 M. Baudler, S. Akpapoglou, D. Ouzounis, F. Wasgestian, B. Meinigke, H. Budzikiewicz and H. Münster, Angew. Chem., Int. Ed. Engl., 1988, 27, 280–281.
34 S. Welsch, L. J. Gregoriades, M. Sierka, M. Zabel, A. V. Virovets and M. Scheer, Angew. Chem., Int. Ed., 2007, 46, 9323–9326.
35 C. Heinl, S. Heinl, D. Lüdeker, G. Brunklaus, W. Kremer and M. Scheer, Inorg. Chim. Acta, 2014, 422, 218–223.
36 M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets and C. E. Anson, Eur. J. Inorg. Chem., 2005, 5, 4023–4026.
37 M. Scheer, A. Schindler, R. Merkle, B. P. Johnson, M. Linseis, R. F. Winter, C. E. Anson and A. V. Virovets, J. Am. Chem. Soc., 2007, 129, 13386–13387.
38 C. Schwarzmaier, A. Schindler, C. Heinl, S. Scheuermayer, E. V. Peresypkina, A. V. Virovets, M. Neumeier, R. Gschwind and M. Scheer, Angew. Chem., Int. Ed., 2013, 52, 10896–10899.
39 F. Dielmann, C. Heinl, F. Hastedt, E. V. Peresypkina, A. V. Virovets, R. M. Gschwind and M. Scheer, Angew. Chem., Int. Ed., 2014, 53, 13605–13608.
40 J. Bresien, C. Hering, A. Schulz and A. Villinger, Chem. – Eur. J., 2014, 20, 12607–12615.
41 I. Krossing and A. Reisinger, Coord. Chem. Rev., 2006, 250, 2721–2744.
42 I. Krossing and I. Raabe, Angew. Chem., Int. Ed., 2004, 43, 2066–2090.
43 J. Bresien, K. Faust, A. Schulz and A. Villinger, Angew. Chem., Int. Ed., 2015, 54, 6926–6930.
44 S. Alvarez, Dalton Trans., 2013, 42, 8617–8636.
45 P. Pyykö and M. Atsumi, Chem. – Eur. J., 2009, 15, 12770–12779.
46 E. Conrad, N. Burford, U. Werner-Zwanziger, R. McDonald and M. J. Ferguson, Chem. Commun., 2010, 46, 2465–2467.
47 R. E. Bachman and D. F. Andretta, Inorg. Chem., 1998, 37, 5657–5663.
48 E. L. Muetterties and C. W. Alegranti, J. Am. Chem. Soc., 1972, 94, 6386–6391.
49 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, NBO 6.0, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.