

Copper(I) mediated oligomerisation of a phosphalkyne†

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The oligomerisation of *tert*-butylphosphalkyne, ${}^t\text{BuC}\equiv\text{P}$, mediated by Cu(I) complexes yields an unprecedented C_4P_5 cage compound, which is stabilised in a matrix of copper(I) iodide.

Following the successful isolation of *tert*-butylphosphalkyne **1** by Becker *et al.*,¹ the first compound featuring a carbon–phosphorus triple bond which is stable at room temperature, its coordination chemistry^{2,3} as well as its element organic chemistry^{3,4} has been widely explored. One focus of these explorations was the oligomerisation of **1**, since this reaction yields a range of novel carbon–phosphorus cage compounds, often stereoselectively.⁵ The oligomerisation of **1** can be induced by a variety of methods, such as thermal activation and reactions with Lewis acids. For the latter strategy, which often proceeds in a more controlled fashion than thermal oligomerisation, both main group and transition metal Lewis acids have been used.⁶ The resulting carbon–phosphorus cage compounds feature multiple phosphorus atoms that can act as coordination sites for transition metals.⁷ This suggested to us that the rigid cages could act as building blocks for supramolecular aggregates. Our group has recently synthesised a variety of supramolecular aggregates using group 10 metals and P_n -ligand complexes as building blocks,⁸ so it was of interest to see if the function of the latter could possibly also be fulfilled by carbon–phosphorus cage compounds. Since we previously successfully used the Lewis acidic copper(I) halides for the synthesis of supramolecular assemblies, we decided to explore the reactivity of **1** with similar complexes. It can be expected that the metal halide serve as both a Lewis acid to initiate the oligomerisation of **1** and at the same time function as a supramolecular matrix⁹ to stabilise any resulting unusual carbon–phosphorus cages.

The reaction of *tert*-butylphosphalkyne **1** with CuI in CH_3CN leads to the formation of a red solution, which shows a singlet in its ${}^{31}\text{P}\{\text{H}\}$ NMR spectrum at -58.1 ppm.‡ This value is shifted downfield in comparison to free **1** ($\delta = -68.0$ ppm in C_6D_6) which indicates an initial complexation of **1** by the copper(I) halide. After two days a solid which precipitated out of the solution, was obtained as small needle shaped crystals if the reaction solution is not agitated. This crystalline material was identified as $[\text{H}({}^t\text{BuC})_4\text{P}_5(\text{CuI})_3(\text{CH}_3\text{CN})_x]_n$ ($x = 1, 3$) ($2 \cdot x\text{CH}_3\text{CN}$) by single-crystal X-ray structure determinations.§ During several different attempts to repeat the reaction we occasionally obtained small

amounts of red crystals as a side product which was identified as $[({}^t\text{BuCP})_4\text{Cu}_2\text{I}_2]_2$ (**3**).

Complexes **2** and **3** are insoluble in common organic solvents which made it impossible to investigate their NMR spectroscopic properties.

The crystal structure of **2**§ is depicted in Fig. 1 and 2. It shows a novel ${}^t\text{Bu}_4\text{C}_4\text{HP}_5$ cage that coordinates to three CuI units of a ladder-like motif, in such a way that a one-dimensional coordination polymer is obtained. The polymeric strands are oriented along the crystallographic *c*-axis. The ${}^t\text{Bu}_4\text{C}_4\text{HP}_5$ cage in **2** (Fig. 1) has not been previously observed as an oligomer of **1**. Since the composition of the cage molecule is not a multiple of the phosphalkyne **1** it is obvious that the stoichiometry of the cage cannot be described by a simple oligomerisation of **1**. We assume that the cage was formed by an initial pentamerisation reaction of **1** followed by the elimination of a *t*BuC moiety, which probably was caused by the steric crowding in the CuI matrix, and a subsequent protonation of the vacant coordination site. The cage structure in **2** can be described as a P_5C_3 cubane where a CH^tBu unit is inserted into a P–P bond. All bonds in the cage are in the

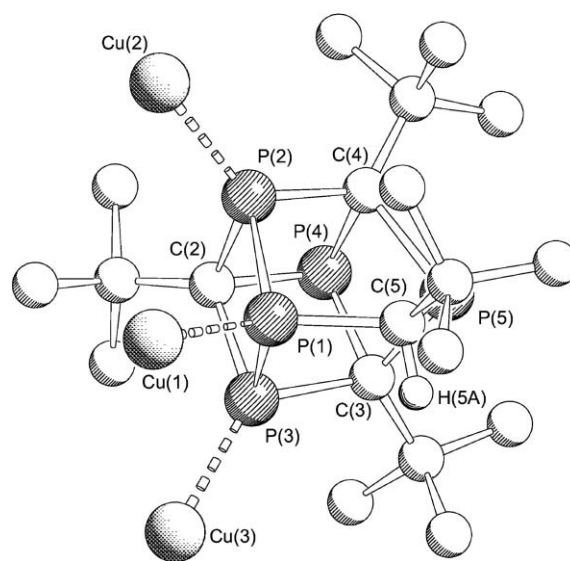


Fig. 1 C_4P_5 cage of **2** showing the coordination mode to the copper atoms. Hydrogen atoms at the *tert*-butyl substituents have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)–P(1) 2.259(3), Cu(2)–P(2) 2.230(3), Cu(3)–P(3) 2.256(3), P(1)–P(2) 2.233(4), P(1)–P(3) 2.193(5), P(1)–C(5) 1.854(10), P(2)–C(2) 1.897(10), P(2)–C(4) 1.852(9), P(3)–C(2) 1.912(9), P(3)–C(3) 1.901(10), P(4)–C(2) 1.875(10), P(4)–C(3) 1.923(10), P(4)–C(4) 1.971(10), P(5)–C(3) 1.891(12), P(5)–C(4) 1.943(11), P(5)–C(5) 1.830(10); Cu(1)–P(1)–P(2) 114.1(1), Cu(1)–P(1)–P(3) 114.3(2), Cu(1)–P(1)–C(5) 136.2(4), P(2)–P(1)–P(3) 81.5(2), P(2)–P(1)–C(5) 99.9(3), P(3)–P(1)–C(5) 96.8(4), Cu(2)–P(2)–P(1) 112.6(2).

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† Electronic supplementary information (ESI) available: Experimental details for the removal of CuI from **2** and the ${}^{31}\text{P}$ NMR data of the resulting products. See DOI: 10.1039/b712161j

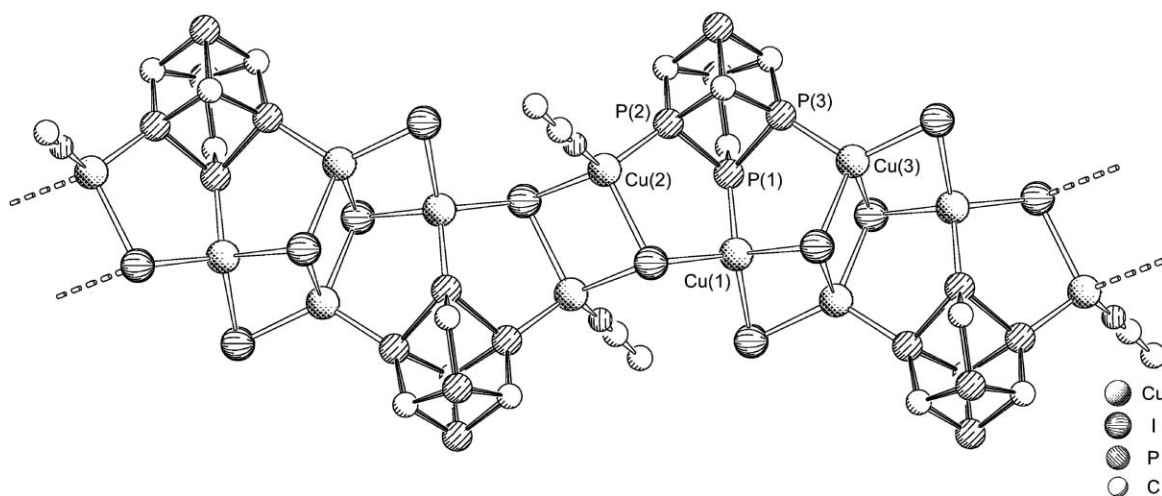


Fig. 2 Polymeric strand in **2** oriented along the crystallographic *c*-axis; *tert*-butyl groups and protons have been omitted for clarity.

range of normal single bonds. The high strain within the cage is reflected in bond angles at the carbon atoms which can be as acute as 87.7(5) for P(4)–C(4)–P(5). Coordination of the C₄P₅ cage to three copper atoms is achieved *via* the P atoms P(1), P(2) and P(3). The copper atoms Cu(1) and Cu(3) are included in ladder-like Cu₄I₄ units, Cu(2) is part of a Cu₂I₂ ring. These subunits are connected in such a way that a one-dimensional polymeric strand is formed (Fig. 2). All copper atoms show a tetrahedral coordination environment and the bond lengths in the CuI-network are within normal ranges.

The molecular structure of **3**, which has a crystallographically imposed inversion symmetry, is depicted in Fig. 3 and consists of a C₄P₄ cage which was already spectroscopically described as an uncoordinated cage by Regitz and co-workers as the product of a reaction sequence starting with the oligomerisation of **1** induced by

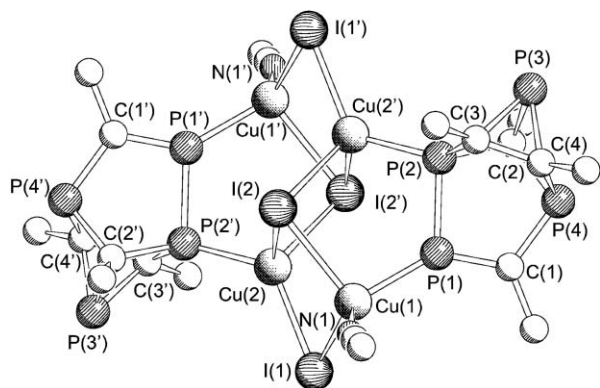
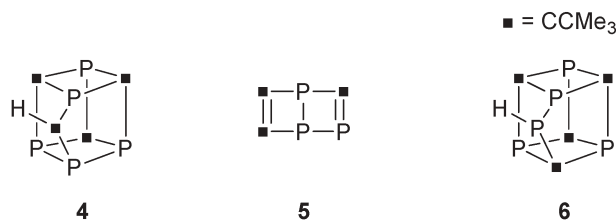


Fig. 3 The molecular structure of **3**; hydrogen atoms and methyl groups at the *tert*-butyl groups have been omitted for clarity. Symmetry code: 2 – *x*, 2 – *y*, –*z*. Selected bond lengths (Å) and angles (°): I(1)–Cu(1) 2.599(2), I(1)–Cu(2) 2.587(1), I(2)–Cu(1) 2.739(2), I(2)–Cu(2) 2.725(2), I(2)–Cu(2') 2.704(2), Cu(1)–P(1) 2.233(3), Cu(1)–N(1) 2.017(8), Cu(2)–P(2') 2.256(3), P(1)–C(1) 1.693(9), P(1)–P(2) 2.180(3), P(2)–C(2) 1.842(9), P(2)–C(3) 1.863(10), P(3)–C(2) 1.956(9), P(3)–C(3) 1.905(10), P(3)–C(4) 1.897(10), P(4)–C(1) 1.862(9), P(4)–C(2) 1.840(9), P(4)–C(4) 1.889(10), C(3)–C(4) 1.578(10); Cu(1)–I(1)–Cu(2) 69.77(5), Cu(1)–I(2)–Cu(2) 65.77(4), Cu(1)–I(2)–Cu(2') 93.90(4), Cu(2)–I(2)–Cu(2') 84.58(5), I(1)–Cu(1)–I(2) 107.96(5), I(1)–Cu(1)–P(1) 119.44(8).

AlCl₃.¹⁰ In **3** two of these cages are coordinated to a ladder-like Cu₄I₄ unit, which is terminated by two molecules of CH₃CN. All bonds within the cage compound can be described as single bonds, except the bond between C(1) and P(1) (1.693(9) Å) which is formally a double bond.

To test if the method of Cu(I) assisted self assembly of **1** can be used as a synthetic method for the preparation of free carbon phosphorus cages, we tried to remove the metal atoms from the cage. Cu(I) halides are known to form very stable cyano complexes and the method to extract CuI from a phosphorus adduct was recently imaginatively used to obtain a new allotrope of phosphorus.¹¹ Indeed, if **2** is suspended in a mixture of an aqueous NaCN solution and Et₂O, after 5 h all of the orange powder has dissolved and the ether phase shows a pale yellow colour (*cf.* ESI†). The ³¹P NMR spectrum of the Et₂O phase is complex and can be attributed to three major products, one of them being the expected free C₄P₅-cage **4** (Scheme 1) found in **2**. Its ³¹P NMR spectrum shows five multiplets in a range from 190 to –33 ppm with a coupling pattern that can be assigned to the free cage **4** (see ESI†). Unexpectedly, the spectrum also showed signals attributable to two other carbon–phosphorus compounds, which could be identified as **5** and **6** by their ³¹P NMR spectra (Scheme 1). Binger *et al.* obtained the triphospha-Dewar-benzene **5** by a reaction of (COT')Hf(^tBu₃C₃P₃) with C₂Cl₆ (COT' = 1,4-(Me₃Si)₂C₈H₆) and the reported NMR spectroscopic data matches our observations.¹² In addition to the spectroscopic identification the structure of **6** was confirmed by X-ray crystallography (Fig. 4), which has a crystallographically imposed mirror symmetry. The formation of the novel cage compound **6**, which is a valence isomer of **4**, gives rise to the assumption that the free cage **4**



Scheme 1 Compounds **4–6**.

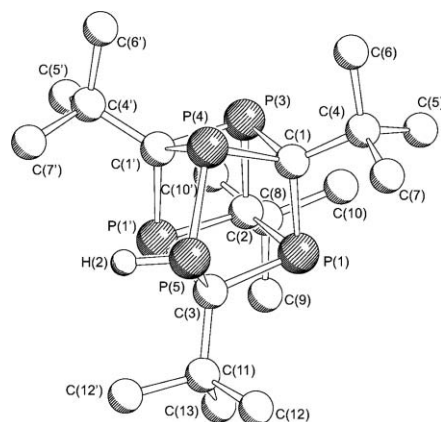


Fig. 4 Molecular structure of **6**; hydrogen atoms have been omitted for clarity. Symmetry code: $x, 1 - y, z$. Selected bond lengths (Å) and angles (°): P(4)–P(5) 2.157(2), P(5)–C(3) 1.884(5), P(1)–C(1) 1.896(4), P(1)–C(2) 1.893(3), P(1)–C(3) 1.895(3), P(3)–C(1) 1.901(4), P(3)–C(2) 1.871(5), P(4)–C(1) 1.891(4), C(4)–C(1) 1.539(5), C(2)–C(8) 1.536(7), C(3)–C(11) 1.562(7); C(2)–P(1)–C(3) 87.74(16), P(1)–C(1)–P(3) 93.42(17), C(2)–P(1)–C(3) 87.74(16), C(2)–P(3)–C(1) 86.21(16), C(2)–P(3)–P(4) 101.90(16), C(1)–P(3)–C(1') 86.21(16), P(1)–C(3)–P(1') 91.8(2), C(1)–P(4)–C(1') 86.21(16), C(3)–P(5)–P(4) 92.88(16).

undergoes rearrangement reactions, when the CuI matrix is removed.

In summary we have shown that the oligomerisation of **1** in the presence of CuI can be used for the synthesis of new carbon–phosphorus cage compounds. Preliminary investigations on the extraction of CuI from the insoluble supramolecular aggregates have shown that it should be possible to remove CuI from the reaction products and isolate the free cage compounds, which partially undergo subsequent transformation, after removal of the CuI matrix.

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Notes and references

† Typical experimental procedure: To a solution of CuI (460 mg, 2.59 mmol) in 35 ml of CH₃CN was added *tert*-butylphosphaalkyne **1** (472 mg, 4.72 mmol) under an atmosphere of dry N₂. The mixture showed a red colour immediately. ³¹P NMR spectrum of the solution: δ_P (161 MHz; CD₃CN; H₃PO₄) –58.1 (s). After a period of 4 days without agitation, orange, microcrystalline 2-*x*CH₃CN ($x = 1, 3$) (60 mg, 7%) precipitated (Found: C, 24.1; H, 4.0. C₂₀H₃₇Cu₃I₃P₅ requires C, 23.9; H, 3.7%); $\tilde{\nu}$ /cm⁻¹: 1957, 2898, 2861, 1629, 1522, 1473, 1391, 1362, 1260, 1210, 1195, 1087, 1042, 1021, 1002, 930, 899, 872, 795, 718, 699, 584, 529, 464. Occasionally a few deep red crystals of **3** were also obtained.

§ Two different kinds of crystals for **2** were found. Both show the same cage core, but differ in the number of solvent molecules in the crystal

lattice. For both structures a CH₃CN molecule which coordinates to a Cu atom is found, but in the second structure two additional molecules of CH₃CN are found in the crystal lattice in between two strands of the coordination polymer. The structure solution of 2-3CH₃CN was not satisfactory due to the poor quality of the crystals obtained (unit cell: $a = 11.647(2)$, $b = 13.348(3)$, $c = 14.588(3)$ Å, $\alpha = 97.47(3)$, $\beta = 103.034(3)$, $\gamma = 114.73(3)^\circ$). All single crystals were mounted in an inert oil and transferred to the cold stream of a Oxford Diffraction CCD area-detector diffractometer using Cu-K α radiation ($\lambda = 1.54178$ Å). Crystal data for 2-CH₃CN: C₂₂H₄₀Cu₃I₃NP₅, $M = 1044.75$, triclinic, space group $P\bar{1}$, $a = 11.693(2)$, $b = 12.892(2)$, $c = 13.172(3)$ Å, $\alpha = 89.99(1)$, $\beta = 64.79(2)$, $\gamma = 77.48(1)^\circ$, $V = 1744.2(6)$ Å³, $T = 103(1)$ K, $Z = 2$, $\mu(\text{Cu-K}\alpha) = 25.236$ mm⁻¹, 11103 reflections measured, 3742 unique ($R_{\text{int}} = 0.0487$) which were used in all calculations. The final $R_1 [I > 2\sigma(I)]$ was 0.0368. Crystal data for 3-2CH₃CN: C₄₄H₇₈Cu₄I₄N₂P₈, $M = 1644.64$, monoclinic, space group $P2_1/c$, $a = 15.505(3)$, $b = 11.642(2)$, $c = 18.001(3)$ Å, $\beta = 111.43(2)^\circ$, $V = 3025(1)$ Å³, $T = 104(1)$ K, $Z = 2$, $\mu(\text{Cu-K}\alpha) = 19.841$ mm⁻¹, 13212 reflections measured, 3267 unique ($R_{\text{int}} = 0.0466$) which were used in all calculations. The final $R_1 [I > 2\sigma(I)]$ was 0.0391. Crystal data for 6-0.5C₇H₈: C_{23.5}H₄₁P₅, $M = 478.41$, monoclinic, space group $C2/m$, $a = 23.7888(3)$, $b = 11.2636(2)$, $c = 10.3868(1)$ Å, $\beta = 108.202(1)^\circ$, $V = 2643.85(6)$ Å³, $T = 123(2)$ K, $Z = 4$, $\mu(\text{Cu-K}\alpha) = 3.259$ mm⁻¹, 25696 reflections measured, 2385 unique ($R_{\text{int}} = 0.1366$) which were used in all calculations. The final $R_1 [I > 2\sigma(I)]$ was 0.0810. The disordering of the toluene molecule in the crystal lattice of **6** over two positions leads to a somewhat elevated wR_2 value. CCDC 656701–656703. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712161j

- G. Becker, G. Gresser and W. Uhl, *Z. Naturforsch., Teil B*, 1981, **36**, 16.
- J. F. Nixon, *Chem. Soc. Rev.*, 1995, 319.
- M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1484.
- (a) *Phosphorus: The Carbon Copy*, ed. K. B. Dillon, F. Mathey and J. F. Nixon, John Wiley, Chichester, 1998; (b) F. Mathey, *Angew. Chem., Int. Ed.*, 2003, **42**, 1578.
- (a) R. Streubel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 436; (b) L. Weber, *Adv. Organomet. Chem.*, 1997, **41**, 1; (c) A. Mack and M. Regitz, in *Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks*, ed. K. K. Laali, J. A. I. Press, Stamford, CT, 1999, p. 199; (d) J. F. Nixon in *Carbocyclic and Heterocyclic Cage Compounds and Their Building Blocks*, ed. K. K. Laali, J. A. I. Press, Stamford, CT, 1999, p. 257.
- A. Mack and M. Regitz, *Chem. Ber.*, 1997, **130**, 823.
- (a) P. Kramkowski and M. Scheer, *Angew. Chem., Int. Ed.*, 1999, **38**, 3183; (b) P. Kramkowski and M. Scheer, *Eur. J. Inorg. Chem.*, 2000, 1869; (c) D. Himmel, M. Seitz and M. Scheer, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1220.
- J. Bai, A. V. Virovets and M. Scheer, *Angew. Chem., Int. Ed.*, 2002, **41**, 1737; J. Bai, E. Leiner and M. Scheer, *Angew. Chem., Int. Ed.*, 2002, **41**, 783; J. Bai, A. V. Virovets and M. Scheer, *Science*, 2003, **300**, 781; M. Scheer, L. Gregoriades, J. Bai, M. Sierka, G. Brunklaus and H. Eckert, *Chem.–Eur. J.*, 2005, **11**, 2163; M. Scheer, J. Bai, B. P. Johnson, R. Merkle, A. V. Virovets and C. E. Anson, *Eur. J. Inorg. Chem.*, 2005, 4023; M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder and I. Krossing, *Angew. Chem., Int. Ed.*, 2006, **45**, 5689; B. P. Johnson, F. Dielmann, G. Balázs, M. Sierka and M. Scheer, *Angew. Chem., Int. Ed.*, 2006, **45**, 2473.
- For examples of polyphosphorus cages stabilised in a CuI matrix, see: (a) A. Pfitzner and E. Freundenthaler, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1647; (b) A. Pfitzner and E. Freundenthaler, *Z. Naturforsch., Teil B*, 1997, **52**, 199.
- B. Breit, U. Bergsträßer, G. Maas and M. Regitz, *Angew. Chem.*, 1992, **104**, 1043; B. Breit and M. Regitz, *Chem. Ber.*, 1996, **129**, 489.
- A. Pfitzner, M. F. Bräu, J. Zweck, G. Brunklaus and H. Eckert, *Angew. Chem., Int. Ed.*, 2004, **43**, 4228.
- P. Binger, S. Leininger, K. Gather and U. Bergsträßer, *Chem. Ber.*, 1997, **130**, 1491.