Copper(1) mediated oligomerisation of a phosphaalkyne†

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The oligomerisation of tert-butylphosphaalkyne, 1BuC≡P, mediated by Cu(I) complexes yields an unprecedented C₈P₃ cage compound, which is stabilised in a matrix of copper(I) iodide.

Following the successful isolation of tert-butylphosphaalkyne 1 by Becker et al., the first compound featuring a carbon–phosphorus triple bond which is stable at room temperature, its coordination chemistry 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. 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. The resulting carbon–phosphorus cage compounds feature multiple phosphorus atoms that can act as coordination sites for transition metals. 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 P₃-ligand complexes as building blocks. 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 will act as both a Lewis acid to initiate the oligomerisation of 1 and the same time function as a supramolecular matrix to stabilise any resulting unusual carbon–phosphorus cages.

The reaction of tert-butylphosphaalkyne 1 with CuI in CH₂CN leads to the formation of a red solution, which shows a singlet in its 31P{[1H]} NMR spectrum at −58.1 ppm.† This value is shifted downfield in comparison to free 1 (δ = −68.0 ppm in CD₂Cl₂) 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 [[(CH₂CN)₅Cu(CuI)₅](CH₂CN)₆] (x = 1, 3) (2:1:CH₂CN) 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 [(1BuCP)₂Cu₄I₈] (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 1BuC≡PH₃ 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 1BuC≡PH₃ 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 phosphaalkyne 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 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 P₃C₈ cubane where a CH₄Bu unit is inserted into a P-P bond. All bonds in the cage are in the

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Fig. 1 C₈P₃ 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 (°): Cu(I)(P(1)) 2.259(3), Cu(I)(P(2)) 2.230(3), Cu(I)(P(3)) 2.256(3), Cu(I)(P(4)) 2.233(4), Cu(I)(P(5)) 2.193(5), P(1)–C(5) 1.854(10), P(2)–C(6) 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(I)(P(1))–P(2) 114.1(1), Cu(I)(P(1))–P(3) 114.3(2), Cu(I)(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).
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 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 the 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[Bu₃C₃P₃] 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

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

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), P(4)–P(2) 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).

Scheme 1 Compounds 4–6.
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


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(6), (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)) 1.891(4), (C(4)–C(1)–P(3)) 1.539(5), (C(2)–C(8)–C(11)) 1.562(7); (C(1)–P(1)–C(3)) 87.74(16), (P(1)–C(1)–P(3)) 93.42(17), (C(2)–P(1)–C(3)) 1.891(4), (C(4)–C(1)–P(3)) 1.539(5), (C(2)–C(8)–C(11)) 1.562(7).