The surprising and stereoselective formation of P_2C_{10} cages by the reduction of Cp*PCl$_2$†

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Reactions of Cp*PCl$_2$ with Group 13 reducing agents result in a cascade of P–C, P–P and C–C bond forming reactions and the stereoselective formation of P_2C_{10} cages.
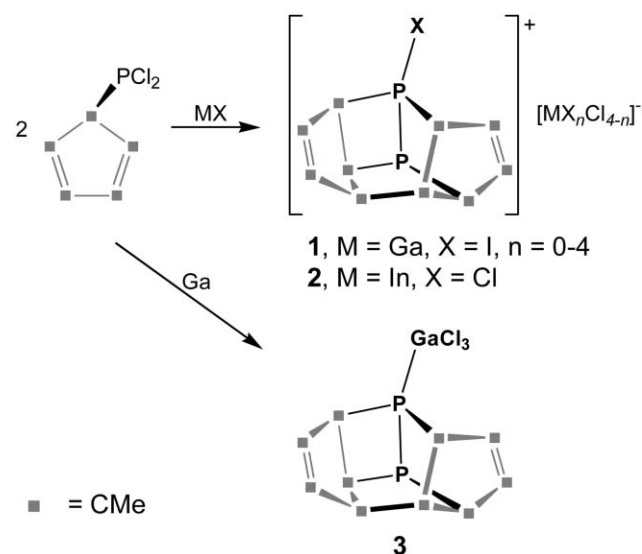
The last decade has witnessed spectacular advances in molecular main group cluster chemistry. Amongst the most eye catching have been the metalloid type clusters containing $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$, $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$ and more recently $Sn_{15}(NRR')_6$ complexes reported from the groups of Schnöckel, Lappert and Power.[1–3] In parallel, important milestones have been reached in phosphorus–carbon clusters which have been synthesised with various P : C ratios, and which have been shown to possess fascinating coordination chemistry;[4–6] the synthesis of such clusters often involves phosphaalkynes as a starting point which limits the general accessibility of the materials. As part of our ongoing studies towards synthesising cage complexes containing the p-block elements,[7,8] we have discovered facile syntheses of elaborate P_2C_{10} cages, both as a neutral species and as part of a cation, by reductive coupling of Cp*PCl$_2$ using Group 13 reagents.

The cations of **1** and **2** were synthesised in quantitative yield‡ by stirring solutions of MX (Scheme 1; M = Ga, X = I, **1**; M = In, X = Cl, **2**) with Cp*PCl$_2$ at room temperature for 30 minutes; the compounds formed colourless crystals upon layering chlorinated solutions of the compounds with hexane.§ The neutral compound **3** was synthesized by reacting a toluene solution of Cp*PCl$_2$ with excess gallium metal at 50 °C for 10 days and could be isolated in 78% yield.

Single crystal X-ray crystallographic studies showed the molecular structures of **1** and **2** to be isomorphous, consisting of ion-separated $[MX_4]^-$ anions and cationic cages of molecular C_1 symmetry comprising two P centres (one of which is ligated by a halogen atom) and ten CMe units (see Fig. 1 for a diagram of the cationic unit of **1**). In both cations, the two phosphorus atoms are joined by a single bond {P(1)–P(2) 2.178(6) in **1**; 2.153(2) Å in **2**}, two of the C–C contacts are formally unsaturated {C(1)–C(5) 1.36(2), C(8)–C(9) 1.36(2) in **1**; C(1)–C(5) 1.346(7), C(8)–C(9) 1.340(7) Å in **2**} whereas the remainder are saturated. It should be

noted that several of the C–C single bonds are rather longer than normal C–C bonds {up to 1.64(2) Å}, presumably on account of the high degree of steric crowding and the imposed tight bond angles {as acute as 88.6(8)°} in the cations. Both phosphorus atoms and the six saturated carbon centres are formally chiral, and in addition, the cation possesses a helical twist. In this respect, it is of note that both **1** and **2** crystallised in chiral space groups ($P2_1$ and $P2_12_12_1$ for **1** and **2** respectively). For **1**, each individual crystal represents a single enantiomer, although the overall mixture contains a mixture of two enantiomers; in contrast, **2** crystallises as a racemic twin. The observation of just one enantiomeric pair from the many possible combinations is presumably a manifestation of both the reaction pathway to form the P_2C_{10} units and the geometric constraints of the cage. In contrast to the cationic cages **1** and **2** the neutral compound **3** crystallises in the centrosymmetric space group $P2_1/c$ so that both enantiomers exist in the same crystal. The molecular structure of the $C_{10}P_2$ cage in **3** (Fig. 2) is similar to the cationic cages **1** and **2**. Minor differences between the cationic and electroneutral compounds are the slightly elongated P–P bond (P(1)–P(2) 2.178(6) in **1**; 2.153(2) in **2**; 2.186(1) Å in **3**) and the longer C–P(1) bonds in **3** (average P(1)–C 1.884 in **1**; 1.855 in **2**; 1.900 Å in **3**), which can be explained by the different electronic situation of the P(1) atom.

The P_2C_{10} frameworks of **1–3** adopt a quite different geometry from the lantern-like structure of $P_6C_6Bu^t_6$ observed in the largest

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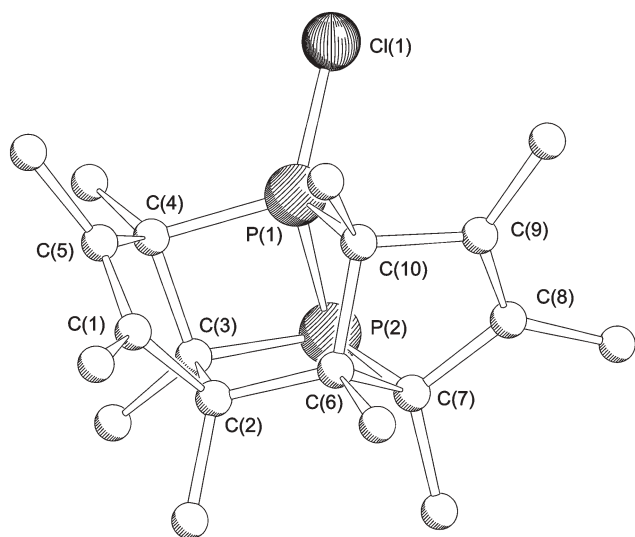
Scheme 1 Synthesis of compounds **1–3**.

Fig. 1 The molecular structure of **2**; all hydrogen atoms and the [InCl$_4$]$^-$ anion have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(2)–C(7) 1.911(4), P(2)–C(3) 1.926(4), P(2)–P(1) 2.153(2), P(1)–C(4) 1.854(4), P(1)–C(10) 1.855(4), P(1)–Cl(1) 1.977(2), C(3)–C(2) 1.570(6), C(3)–C(4) 1.585(7), C(6)–C(2) 1.580(6), C(6)–C(7) 1.583(6), C(6)–C(10) 1.598(6), C(4)–C(5) 1.491(6), C(7)–C(8) 1.513(6), C(9)–C(8) 1.340(7), C(9)–C(10) 1.532(6), C(1)–C(5) 1.346(7), C(1)–C(2) 1.514(7); C(7)–P(2)–C(3) 93.1(2), C(7)–P(2)–P(1) 88.3(2), C(3)–P(2)–P(1) 71.2 (25), C(4)–P(1)–C(10) 111.3(2), C(4)–P(1)–P(2) 86.4 (2), C(10)–P(1)–P(2) 99.1(2), C(2)–C(3)–C(4) 102.1(4), C(2)–C(3)–P(2) 109.9(3), C(4)–C(3)–P(2) 102.8(3), C(2)–C(6)–C(7) 111.1(3), C(2)–C(6)–C(10) 114.0(3), C(7)–C(6)–C(10) 97.9(3), C(5)–C(4)–C(3) 103.8(4), C(5)–C(4)–P(1) 111.8(3), C(3)–C(4)–P(1) 87.3(3), C(8)–C(7)–C(6) 103.2(3), C(8)–C(7)–P(2) 108.2(3), C(6)–C(7)–P(2) 102.1(3), C(8)–C(9)–C(10) 110.3(4), C(9)–C(8)–C(7) 110.4(4), C(81)–C(8)–C(7) 121.6(4), C(9)–C(10)–C(6) 102.1(3), C(9)–C(10)–P(1) 101.3(3), C(6)–C(10)–P(1) 99.3(3), C(5)–C(1)–C(2) 112.7(4), C(1)–C(5)–C(4) 110.5(4), C(1)–C(2)–C(3) 102.0(3), C(1)–C(2)–C(6) 113.0(4), C(3)–C(2)–C(6) 106.0(3). The corresponding figure and selected bond lengths and angles for **1** are given in the electronic supplementary information.†

phosphalkyne oligomer (hexamer) structurally characterised to date.[9] A clear chemical difference between the P$_2$C$_{10}$ and P$_6$C$_6$ units is the presence of unsaturated C=C bonds in **1–3** whereas P$_6$C$_6$Bu$^t_6$ contains formally saturated, P–P, P–C and C–C contacts; presumably this is on account of the higher reactivity of P=C *vs.* C=C, leading to the more open structures of **1–3**.

In solution, the carbon–phosphorus cages remain intact, each giving two peaks in the ^{31}P NMR spectrum (δ = 29.0 {P(2)} and 68.7 {P(1)} ppm, $^1J_{PP}$ 231.1 Hz for **1**; 24.7 {P(2)} and 126.5 {P(1)} ppm, $^1J_{PP}$ 245.6 Hz for **2**; −10.8 ({P(1)} and 17.8 {P(2)} $^1J_{PP}$ 149.1 Hz for **3**) and ten sets of peaks for the chemically inequivalent CMe centres in both the ^{1}H and ^{13}C NMR spectra, each of which has been assigned by HMQC, HMBC and selectively ^{31}P decoupled ^{1}H NMR spectroscopy experiments.

Presumably, the cationic and neutral cage compounds have been formed from the reductive coupling of two Cp*P units. This observation is surprising in view of the detailed investigations on the reduction of Cp*PCl$_2$ from the group of Jutzi.[10,11] They investigated the reduction of Cp*PX$_2$ (X = Cl, Br) with a range of alkali- and alkaline earth-metals under various reaction conditions and identified several P–P bonded products by
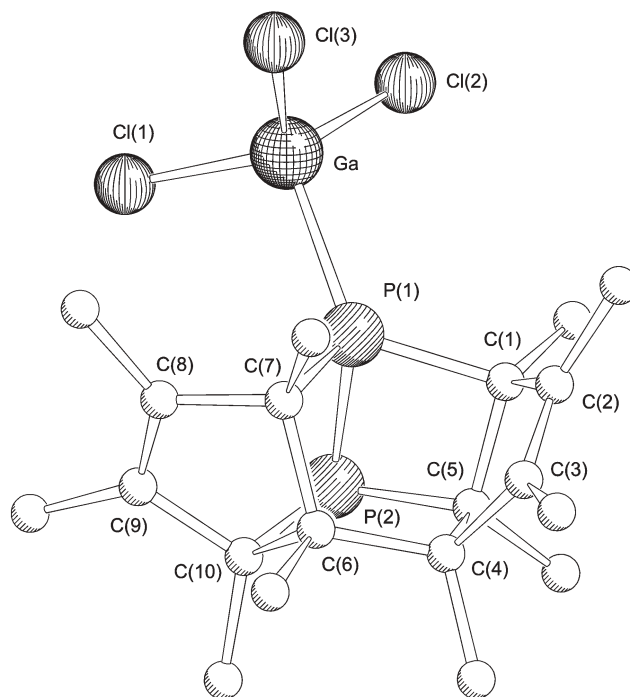

Fig. 2 The molecular structure of **3**; all hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ga–Cl(3) 2.1717(8), Ga–Cl(1) 2.1725(7), Ga–Cl(2) 2.1773(9), Ga–P(1) 2.3917(7), P(1)–C(1) 1.899(2), P(1)–C(7) 1.900(2), P(1)–P(2) 2.1858(9), P(2)–C(10) 1.907(2), P(2)–C(5) 1.907(2), C(1)–C(2) 1.496(3), C(1)–C(5) 1.565(3), C(2)–C(3) 1.347(3), C(3)–C(4) 1.532(3), C(4)–C(5) 1.580(3), C(4)–C(6) 1.588(3), C(6)–C(10) 1.568(3), C(6)–C(7) 1.577(3), C(7)–C(8) 1.522(3), C(8)–C(9) 1.337(3), C(9)–C(10) 1.513(3); C(1)–P(1)–C(7) 107.20(9), C(1)–P(1)–P(2) 81.59(7), C(7)–P(1)–P(2) 94.22(7), C(10)–P(2)–C(5) 94.22(9), C(10)–P(2)–P(1) 90.81(7), C(5)–P(2)–P(1) 75.26(7), C(2)–C(1)–C(11) 117.6(2), C(2)–C(1)–C(5) 104.2(2), C(2)–C(1)–P(1) 111.4(1), C(5)–C(1)–P(1) 92.3(1), C(3)–C(2)–C(1) 110.8(2), C(2)–C(3)–C(4) 111.7(2), C(3)–C(4)–C(5) 101.6(2), C(3)–C(4)–C(6) 112.6(2), C(5)–C(4)–C(6) 106.6(2), C(1)–C(5)–C(4) 102.1(2), C(1)–C(5)–P(2) 100.5(1), C(4)–C(5)–P(2) 108.5(1), C(10)–C(6)–C(7) 97.6(2), C(10)–C(6)–C(4) 110.4(2), C(7)–C(6)–C(4) 114.8(2), C(8)–C(7)–C(6) 102.5(2), C(8)–C(7)–P(1) 101.3(1), C(6)–C(7)–P(1) 103.4(1), C(9)–C(8)–C(7) 109.8(2), C(8)–C(9)–C(10) 109.9(2), C(9)–C(10)–C(6) 103.5 (2), C(9)–C(10)–P(2) 107.8(1), C(6)–C(10)–P(2) 101.3(1).

^{1}H, ^{13}C and ^{31}P NMR spectroscopies, most notably the *trans* diphosphene Cp*P=PCp*. In all of these products, the Cp* group remains as an innocent spectator ligand. Given these extensive investigations, the observed stereoselective P–C (two), P–P (one) and C–C (one) bond forming reactions required to generate the cation of **1** and **2** or the neutral cage **3** are highly surprising, in particular the selectivity of the cascade of reactions that are involved.

In summary, we have shown that phosphorus–carbon cage compounds may be accessed using the readily accessible route of reduction of Cp*PCl$_2$ using low oxidation state Group 13 halides or elemental gallium; we are continuing to investigate the coordination chemistry of these cages and in particular reactions which lead to the partial opening of the cage by cleavage of the P–P bond.

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