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Synthesis, crystal and molecular structures of the novel, structurally different, cage compounds $P_6C_4Bu^t_4SiI_2$ and $P_6C_4Bu^t_4GeI_2$, resulting from *intra*-molecular coupling of two 1,2,4-triphospholyl rings

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Treatment of EI_4 (E = Si or Ge) with 2 equivalents of $K[P_3C_2Bu^t_2]$ affords the novel cage compounds $P_6C_4Bu^t_4SiI_2$ and $P_6C_4Bu^t_4GeI_2$ respectively, whose molecular structures, determined spectroscopically and by single crystal X-ray diffraction studies, are different both in solution and in the solid state.

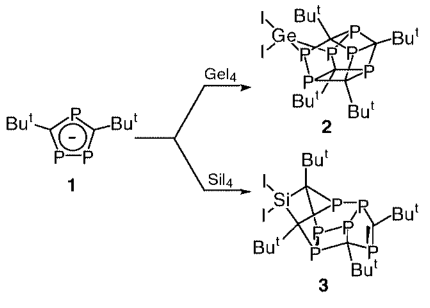
Phosphorus substituted analogues of the aromatic cyclopentadienyl anion, $C_nR_nP_{5-n}$ ($n = 0$–4), are of considerable current interest.[1] In particular, the 3,5-di-*tert*-butyl-1,2,4-triphospholyl anion, $P_3C_2Bu^t_2{}^-$ **1**, has been used in the preparation of a range of transition metal complexes[2–7] in which a variety of bonding modes have been observed such as in $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (M = Fe or Ru), $[M(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}C_5Me_5)\{W(CO)_5\}]$ (M = Fe or Ru) and *trans*-$[M(\eta^1\text{-}P_3C_2Bu^t_2)_2(PEt_3)_2]$ (M = Pt or Pd).

In contrast however, examples of main group element compounds derived from **1** are comparatively rare and to date are restricted to a handful of examples, namely $[In(\eta^5\text{-}P_3C_2Bu^t_2)]$, $P_3C_2Bu^t_2CH(SiMe_3)_2$, $[Tl(\eta^5\text{-}P_3C_2Bu^t_2)]$, $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ and $[M(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ (M = Sn or Pb).[8–11] We therefore decided to examine the reaction of **1** (in the form of its recently synthesised potassium salt),[9] with silicon and germanium tetraiodides.

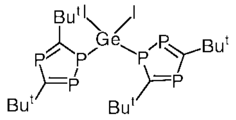
Surprisingly, although the resulting products both have the anticipated formulae $P_6C_4Bu^t_4EI_2$ (E = Ge **2**, E = Si **3**) in which two iodides may have been expected to have been replaced by $\eta^1\text{-}P_3C_2Bu^t_2$ ligands, they actually contain two different novel $P_6C_4Bu^t_4$ cages which arise from different *intra*-molecular coupling reactions of the adjacent 1,2,4-triphospholyl rings.

Thus, treatment of 2 equivalents of **1** with EI_4 (E = Si or Ge) led to the moisture sensitive compounds **2** (E = Ge) and **3** (E = Si), respectively (Scheme 1), which were recrystallised from diethyl ether (**3**, orange crystals, mp 190 °C; yield 55%) or hot heptane (**2**, red crystals, mp 275 °C; yield 52%). Both compounds exhibited the expected parent ions in their mass spectra (*m/z* 789 for **2**; 744 for **3**), however the solution $^{31}P\{^1H\}$ and ^1H NMR spectroscopic data are only consistent with the proposed cage structures, which were subsequently confirmed by single crystal X-ray diffraction studies (*vide infra*).

The ^1H NMR spectrum of **2** shows only two singlets for the two different types of Bu^t groups, while the $^{31}P\{1H\}$ NMR spectrum, which has been fully analysed and successfully simulated as an AA′MM′XX′ spin system,† confirms the symmetric structure and as expected contains no resonances involving unsaturated phosphorus atoms. The formation of the cage compound **2** clearly results from the anticipated bis-($\eta^1\text{-}P_3C_2Bu^t_2$)–$GeI_2$ intermediate **4** which then rapidly undergoes two further intramolecular [2 + 2] cycloaddition reactions generating four new P–C bonds.



Scheme 1



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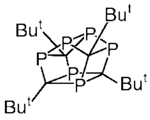

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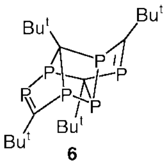

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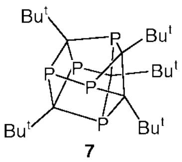

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The molecular structure of **2**‡ which is shown in Fig. 1, shows some similar features to the recently reported hexaphosphaprismane $P_6C_4Bu^t_4$ **5** synthesised by Regitz and coworkers[12] *via* an unusual light-induced valence isomerisation reaction of **6**, but is different from the $P_5C_5Bu^t_5$ cage structure **7** constructed by oxidative coupling of $P_3C_2Bu^t_2$ and $P_2C_3Bu^t_3$ ring anions.[13] Presumably the steric effect of the large iodide ligands attached to Ge in the presumed intermediate **4** facilitates the ring coupling reaction leading to **2**.

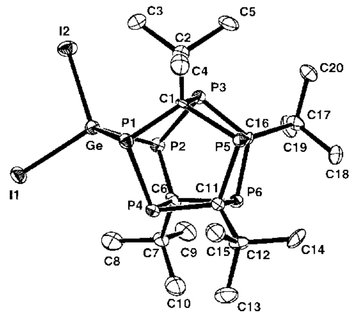

Fig. 1

The molecular structure of **3**, determined by a single crystal X-ray diffraction study,‡ which is shown in Fig. 2, unexpectedly shows that the Si is attached to two *carbon* atoms within the cage, resulting in a much more asymmetric structure than observed for **2** involving a P=C double bond between P(6) and C(4) and a five-atom phosphorus network P(1)–P(2)–P(3)–P(4)–P(5). In accord with the above structure, the 1H NMR spectrum exhibits four distinct resonances for the non-equivalent Bu^t groups, while $^{31}P\{1H\}$ NMR spectrum of **3** consists of

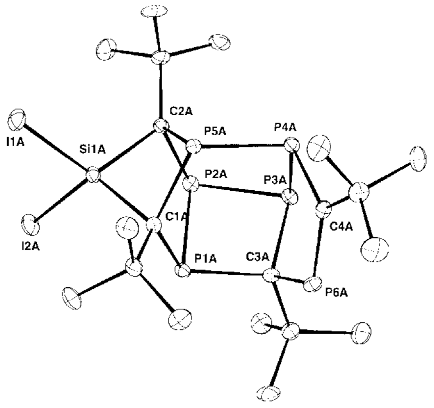

Fig. 2

six distinct resonances exhibiting several $^{1}J_{(PP)}$ couplings in the range 110–300 Hz. The lowest field signal (δ 357.0) which is in the region typical of P=C bonds and involves only small couplings clearly corresponds to P(6). The two highest field resonances ($\delta = -19.1$ and -24.4) which exhibit a single large coupling, can readily be assigned to P(5) and P(1), respectively. The remaining resonances at δ 124.1, 78.4 and 24.6 can be attributed to P(2), P(3) and P(4), respectively.

The mechanism of formation of **3** is currently unknown but it seems likely that the first step involves Si–P bond formation. Attempts to form the novel silylene or germylene species $P_6C_4Bu^t{}_4E$: (E = Si, **8** , E = Ge, **9**) by treatment of **2** and **3** with sodium napthalenide in THF, led in each case to regeneration of the $P_3C_2Bu^t{}_2$ ring anion **1**.

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Notes and references

† *Spectroscopic data*: for **2**: NMR (C_6D_6, 298 K): δ_H(300 MHz) 1.33 (s, 18H, Bu^t), 1.03 (s, 18H, But). δ_p(121.68 MHz) 37.23 (m, P(1), ^{2}JP(1)P(2)) -40.42, ^{1}J(P(1)P(4)) +294.99, ^{2}J(P(1)P(5)) +9.93, ^{2}J(P(1)P(3)) -10.73, ^{3}J(P(1)P(6)) +2.12 Hz) 145.91 (m, P(4), ^{3}JP(4)P(3)) +0.30, ^{2}JP(4)P(6)) +18.92 Hz), 217.34 (m, P(5), ^{2}J(P(5)P(6)) +6.16, ^{2}J(P(5)P(4)) -10.06 Hz). Microanalysis: Found: C, 31.5; H, 4.4. Calc.: C, 30.5; H, 4.6%.

For **3**: NMR (C_6D_6, 298 K): δ_H(300 MHz) 1.30 (s, 9H, Bu^t), 1.33 (s, 9H, Bu^t), 1.40 (s, 9H, Bu^t), 1.44 (s, 9H, Bu^t). δ_P(121.68 MHz) 357.0 (m, P(6), ^{2}JP(6)P(4)) 19 Hz, ^{2}J(P(6)P(1)) = 20, ^{3}J(P(6)P(2)) 19, ^{3}JP(6)P(5)) 11 Hz), 124.1 (m, P(2), ^{1}JP(2)P(3)) 291, ^{1}J(P(2)P(1)) 303, ^{3}J(P(2)P(5)) 11, ^{2}J(P(2)P(4)) = 11, ^{3}J(P(2)P(6)) 19 Hz), 88.4 (ddd, P(3), ^{1}J(P(3)P(2)) 291, ^{1}JP(3)P(4)) 150, ^{2}JP(3)P(1)) 12 Hz), 24.6 (m, P(4), ^{2}JP(4)P(6)) 19, ^{1}JP(4)P(3)) 150, ^{3}JP(4)P(1)) 8, ^{2}JP(4)P(2)) 11, ^{1}JP(4)P(5)) 110 Hz), -19.1 (dqt, P(5), ^{2}JP(6)P(5)) ^{2}JP(5)P(2)) 11, ^{3}JP(5)P(1)) 11 Hz, ^{1}JP(5)P(4)) 110 Hz), -24.4 (m, P(1), ^{2}JP(1)P(3)) 12, ^{2}JP(1)P(6)) 20, ^{3}JP(1)P(4)) 8, ^{3}JP(1)P(5)) 11, ^{1}JP(1)P(2)) 303 Hz). Microanalysis. Found: C, 33.1; H, 5.2. Calc.: C, 32.3, H, 4.9%.

‡ *Crystal data*: for **2**: $C_{20}H_{36}P_6GeI_2$, $M = 788.70$, monoclinic, space group $P2_1/n$ (no. 14), $a = 11.8196(12)$, $b = 17.491(3)$, $c = 13.850(3)$ Å, $\beta = 95.009(14)°$, $V = 2852.4(8)$ Å^3; $T = 173(2)$ K, $Z = 4$, $\mu = 3.58$ mm^{-1}, $\lambda = 0.71073$ Å, 5261 reflections collected, 5021 independent ($R_{int} = 0.0458$), $R_1 = 0.046$, $wR_2 = 0.089$ for $I > 2\sigma I$, $R_1 = 0.090$, $wR_2 = 0.108$ for all data.

For **3**: $C_{20}H_{36}P_6SiI_2$: $M = 744.2$, monoclinic, space group $P2_1$ (no. 4), $a = 11.827(4)$, $b = 15.837(9)$, $c = 15.626(5)$ Å, $\beta = 94.87(3)°$, $V = 2916(2)$ Å^3; $T = 173(2)$ K, $Z = 4$, $\mu = 2.54$ mm^{-1}, $\lambda = 0.71073$ Å, 9137 reflections collected, 8776 independent ($R_{int} = 0.020$), $R_1 = 0.033$, $wR2 = 0.065$ for $I > 2\sigma I$, $R_1 = 0.042$, $wR_2 = 0.070$ for all data.

The G. M. Sheldrick, SHELX-97 suite of programs for crystal structure analysis, University of Gottingen, Gottingen, Germany, 1997, were used to elucidate both structures.

CCDC 182/1601. See http://www.rsc.org/suppdata/cc/b0/b001632m/ for crystallographic files in .cif format.

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