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Reactivity of [M(η^4-P_2C_2tBu$_2$)] (M = Ge, Sn) with *tert*-Butylphosphaethyne, P≡C*t*Bu: Synthesis, Structural Characterisation and Computational Studies of the Novel Zwitterionic Organophosphorus Cage Compounds [MP_4C_4tBu$_4$] (M = Ge, Sn)

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Treatment of [M(η^4-P_2C_2tBu$_2$)] with the phosphaalkyne P≡C*t*Bu leads to the formation of the unusual zwitterionic cage compounds [M(P_4C_4tBu$_4$)] (M = Ge, Sn) which have been fully characterised in solution by multinuclear NMR spectroscopy and the solid-state structure of [GeP_4C_4tBu$_4$] has been elucidated by a single-crystal X-ray diffraction study. DFT calculations support the zwitterionic formulation and suggest the likely reaction pathway. Whilst [GeP_4C_4tBu$_4$] exhibits considerable stability, [SnP_4C_4tBu$_4$] shows gradual decomposition in solution within a matter of hours.

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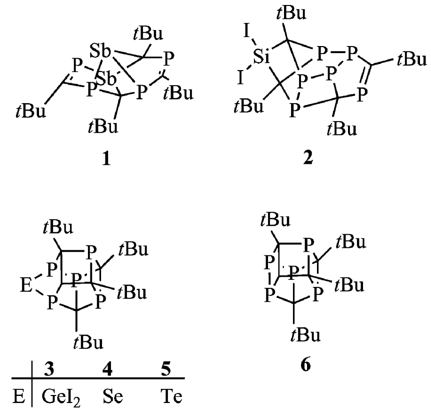
Introduction

Organo-phosphorus cage compounds have been the focus of considerable attention in recent years,[1] the two major synthetic routes generally involving oxidative coupling of polyphospholyl anions $C_nR_nP_{5-n}$ (n = 0–4) or the thermal or metal-mediated oligomerization of phosphaalkynes P≡CR.[2] Our interest in this area has been on the development of organo-phosphorus cages containing one or more additional heteroatoms and a number of examples of such cages have been described containing antimony **1**,[3] silicon **2** or germanium **3**[4] and selenium **4** or tellurium **5**[2n] as shown in Figure 1. Cage **1** was derived from the diphosphastibolyl anion [P_2SbC_2tBu$_2$]$^-$ and **2** and **3** from the triphospholyl anion [P_3C_2tBu$_2$]$^-$ (Scheme 1). The chalcogen-substituted organo-phosphorus systems **4** and **5** were prepared by an unusual facile insertion of the chalcogen into a specific P–P bond of the hexaphospha-pentaprismane **6**, the latter being itself derived from the oxidative coupling of two [P_3C_2tBu$_2$]$^-$ anions.[2l] In this paper we wish to describe the synthesis and characterisation of two new organophosphorus cage compounds [MP_4C_4tBu$_4$] (M = Ge, **7**; Sn, **8**) containing germanium and tin, by an unusual route involving the reaction of the phosphaalkyne P≡C*t*Bu with the group 14 1,3-diphosphacyclobutadienyl complexes [M(η^4-P_2C_2tBu$_2$)] (M = Ge, **9**;[5] Sn, **10**[6]).



Scheme 1.

Results and Discussion

Treatment of a pale yellow ether solution of [Ge(η^4-P_2C_2tBu$_2$)] (**9**) with a 2.5 to threefold excess of P≡C*t*Bu at –70 °C followed by warming to ambient temperature led to a deep red solution from which the unusual cage compound [GeP_4C_4tBu$_4$] (**7**), which could be isolated in 43% yield, after crystallisation from toluene, as a very dark red crystalline solid which melts without decomposition between 108 and 110 °C (Scheme 2). Compound **7** has been fully characterised by multinuclear NMR spectroscopy and in the solid state by a single-crystal X-ray diffraction study (see Figure 1, Table 1), which leads us to view it as a zwitterionic structure (vide infra). The analogous tin compound

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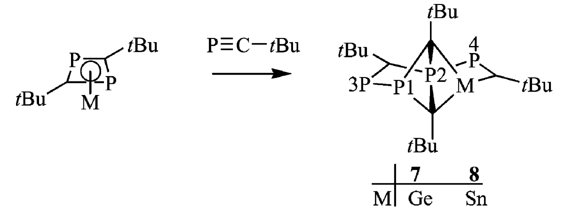
[$SnP_4C_4tBu_4$] **8** can be synthesised in the same way but, unlike **7** its comparative instability in solution has frustrated all attempts to isolate it in pure form and we have been unable to obtain structural characterisation although a full NMR spectroscopic study has been carried out. Moreover, attempts to form a stable derivative **8** by coordination of one or more P-lone pairs or the P=C double bonds to a metal fragment were unsuccessful.



Scheme 2.

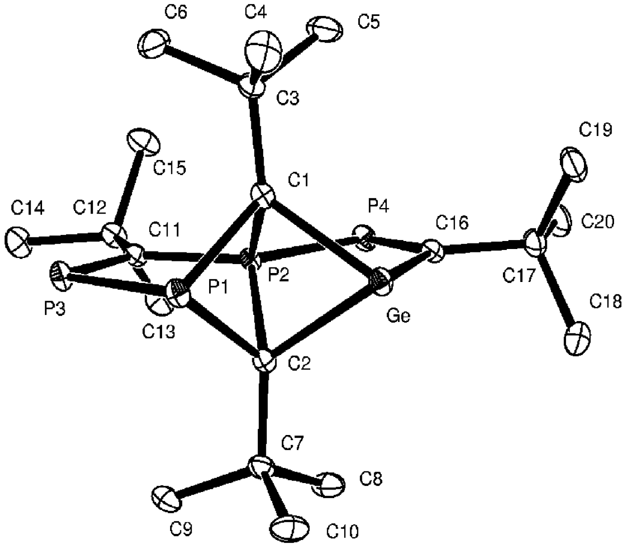


Figure 1. X-ray molecular structure of **7**. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths[a] [Å] and angles [°] in **7**.

Distances			
P3–C11	1.6914(12)	P(2)–P(4)	2.2018(16)
P3–P1	2.3196(16)	P(4)–C(16)	1.685(5)
C11–P2	1.8470(10)	C(16)–Ge	2.103(5)
C1–Ge	2.0633(5)	C(2)–P(1)	1.895(5)
C2–Ge	2.133(4)	P(1)–C(1)	1.8959(12)
C2–P2	1.804(4)	C(1)–P(2)	1.8081(10)
Angles			
P1–P3–C11	94.59(6)	C1–Ge–C2	66.76(12)
P3–C11–P2	107.61(5)	C1–Ge–C16	93.16(3)
P2–P4–C16	87.30(16)	C2–Ge–C16	94.35(17)
P4–C16–Ge	121.1(2)	P3–P1–C1	100.05(6)
C1–P1–C2	75.07(14)	C11–P2–P4	123.97(6)
P3–P1–C2	98.29(14)	C1–P2–P4	111.26(6)
C11–P2–C2	109.59(14)	C1–P2–C2	79.50(14)
C2–P2–P4	112.91(15)	C1–P2–C11	110.91(6)

[a] B3LYP/6-31+G*-computed bond lengths of **7** for comparison: P(3)–C(11) 1.690, P(3)–P(1) 2.363, C(11)–P(2) 1.879, C(1)–Ge 2.135, C(2)–Ge 2.135, C(2)–P(2) 1.823, P(2)–P(4) 2.244, P(4)–C(16) 1.700, C(16)–Ge 2.114, C(2)–P(1) 1.909, P(1)–C(1) 1.909, C(1)–P(2) 1.823.

Despite this, we feel confident that **7** and **8** are isostructural even in the absence of a crystal structure of the latter. Geometry optimization of **8** at the B3LYP/LANL2DZ(p) level resulted in a structure which is similar to that of **7**, however, the computed SnC_{16} bond is considerably longer (2.327 Å) than the usual SnC single bond. The weakness of this bond might be related to the instability of the compound. The multinuclear NMR spectra of the two compounds exhibit very similar features. The $^{31}P\{^1H\}$ NMR spectrum of **7** shows four multiplet resonances consistent with four distinct phosphorus environments. The two low field resonances at δ = 450.1 and 271.6 ppm are consistent with the phosphaalkenyl resonances P(3) and P(4) whilst the higher field resonances at 76 and 49.6 ppm are in the expected region for the saturated phosphorus centres P(1) and P(2). At this point there exists possible ambiguity in assigning these resonances. To facilitate the assignment, the chemical shifts were calculated at the B3LYP/cc-PVTZ//B3LYP/6-31+G* level for **7**. Further calculations have been carried out also at the B3LYP/6-311+G**//B3LYP/6-31+G*, B3LYP/6-31+G*//B3LYP/6-31+G* and B3PW91/6-31+G*//B3LYP/6-31+G* levels, the ordering and the chemical shift difference of the two signals remained unchanged for **7**. The data in Table 2 show that the P(3) signal should appear at δ = 200 ppm lower field than the P(4) signal, suggesting that P(3) should be assigned to the 450.1 ppm signal and the 271.6 ppm resonance should be attributed to P(4). Although the small difference between the P(1) and P(2) shifts does not allow decisive predictions *solely* on the basis of the computations of the chemical shifts, assignment of the phosphorus signals for P(1) and P(2) can be logically deduced from their mutual P-P coupling constants. Thus the resonance at δ = 450.1 ppm [attributed to P(3) on the basis of the computations] shows a large $^1J_{P,P}$ coupling (174.0 Hz) which is also exhibited by the resonance at δ = 49.6 ppm, suggesting that the latter signal belongs to P(1) which is directly bonded to P(3). The remaining resonance at δ = 76.0 ppm should be attributed to P(2), which is the neighbour of the unsaturated phosphorus P(4) (assigned to the 271.6 ppm signal) as evidenced by their common $^1J_{P,P}$ coupling (379.3 Hz). Further confirmation of this assignment can be obtained from the computation of the spin–spin coupling.

Table 2. NMR spectroscopic data for **7** and **8**. (The numbering of the P atoms is given in Scheme 2.)

	δ [ppm]		$^1J_{P-P}$ [Hz]		J_{P-Sn} [Hz]
	7[a]	**8**	**7**	**8**	**8**
P1	49.6 (73.1)	55.5	174.0	169.8	297
P2	76.0 (77.2)	84.6	379.2	394.5	12
P3	450.1 (507.6)	445.0	174.1	169.8	85
P4	271.6 (309.5)	284.8	379.3	394.4	–

[a] B3LYP/cc-PVTZ//B3LYP/6-31+G*-computed chemical shifts for **7** are given in parenthesis.

At the B3LYP/6-31+G* level values of 128 Hz and 338 Hz have been obtained for $^1J_{P(1)-P(3)}$ and $^1J_{P(2)-P(4)}$ respectively, in reasonable agreement with the observed

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data. It is expected that further information can be obtained from the $^{31}P\{^{1}H\}$ NMR spectrum of the tin analogue **8**, the chemical shifts and P–P couplings of which are almost identical to those in **7** (see Table 2). The similarity of the chemical shifts and J_{P-P} coupling constants is also predicted computationally at the B3LYP/3-21G(*)//B3LYP/LANL2DZ(p) level. A further informative feature is the appearance of ^{119}Sn satellites on some of the ^{31}P resonances. Of the two low-field resonances in the $^{31}P\{^{1}H\}$ NMR spectrum of **8**, only that at δ = 445 ppm [assigned to P(3) on the basis of the shifts computed for **7**] shows ^{119}Sn satellites (J_{P-Sn} of 85 Hz). This observation is completely unexpected, since P(3) is more distant from the Sn atom than P(4). Computation of the coupling constants of **8** at B3LYP/3-21G(*), however, results in values of 48 Hz for $J_{P(3)-Sn}$ and 6 Hz for $J_{P(4)-Sn}$ in agreement with the assignment proposed above (Table 2). A possible explanation might be that the zwitterionic electronic structure is responsible for the unusual coupling. It is also noteworthy that the coupling constants of the two tricoordinate phosphorus atoms [P(1) and P(2), each being separated from the tin atom by two bonds], are also markedly different. $J_{P(1)-Sn}$ (297 Hz) is much larger than $J_{P(2)-Sn}$ (12 Hz). The B3LYP/3-21G(*)//B3LYP/LANL2DZ(p) coupling constants also follow a similar trend [$J_{P(2)-Sn}$129 Hz and $J_{P(1)-Sn}$ 5 Hz], indicating that even with the small basis set the NMR properties of **8** are qualitatively properly predicted.

The ^{119}Sn NMR spectrum of **8** shows a doublet of doublets of doublets at δ = –206.8 ppm (rel. to $SnMe_4$). The two large couplings of 297 Hz and 85 Hz measured from the satellites in the $^{31}P\{^{1}H\}$ NMR spectrum are mirrored in the ^{119}Sn spectrum. In addition a smaller coupling of ca. 12 Hz is also visible, but the satellites representing this coupling are not visible in the $^{31}P\{^{1}H\}$ NMR spectrum, perhaps being obscured by the main signals. The chemical shift of δ = –206.8 ppm gives some precedent for the zwitterionic interpretation of **7** and **8**. This shift is very similar to that of δ = –221 ppm seen in the stannyl anion $[Sn(CH_2tBu)_3]^-$ which has also been structurally characterised as its potassium salt.[7] The ^{13}C and ^{1}H NMR spectra of **7** are similar to those of **8** and show resonances consistent with their proposed structures. The ^{1}H NMR spectra of both **7** and **8** show three resonances in the ratio of 1:1:2 thereby indicating that two of the *t*Bu groups have coincidental chemical shifts. This is reflected in the ^{13}C NMR spectra which show three resonances for the *t*Bu carbon atoms instead of four. Likewise, the GIAO B3LYP/cc-PVTZ//B3LYP/6-31+G* shieldings show that the two *t*Bu groups attached at the GeCP1C ring have equivalent chemical shifts, in agreement with the (pseudo) C_s arrangement of the molecule. In the case of **7** all carbon signals could be seen whereas in the case of **8** only one of the cage quaternary carbon atoms could be detected. The EI mass spectra of both compounds exhibit peaks for their molecular ions with the expected isotopic distribution patterns. Curiously, and in both cases, a peak was also seen at exactly 100 mass units above M^+ which corresponds to an extra $P\equiv CtBu$ unit. These extra peaks, which correspond to units of formula $[MP_5C_5tBu_5]$, are almost certainly the result of a facile capture of a phosphaalkyne unit by M^+ in the gas phase. This observation was consistently reproducible and also occurred on analytically pure samples of **7**. The molecular structure of **7** is shown in Figure 1 with important bond lengths and distances collected in Table 1. The distances P(3)–C(11) and P(4)–C(16) of 1.6914(12) and 1.685(5) Å respectively, are consistent with localised P=C double bonds which typically lie between 1.61 and 1.71 Å.[8]

The other P–C bond lengths in the structure which vary between 1.804(4) and 1.8959(12) Å are in the range for normal P–C single bonds which are expected to be in the region of around 1.85 Å.[2f] Examination of the structure reveals a trigonal pyramidal germanium centre and a distorted tetrahedral phosphorus P(2). In view of this situation, and in order to assign meaningful formal oxidation states to the P(2) and Ge centres we are inclined to describe the molecule as being zwitterionic in the sense of $P(2)^+$, Ge^-. Thus the molecule can be thought of as a phosphonium salt with a germyl anion as the counter anion.

The Ge–C bond lengths range between 2.0633(5) and 2.133(4) Å which are only marginally longer than those seen in other structurally characterised germyl anions e.g. 2.042 to 2.054 Å in $[Li(thf)_2][Ge(C_6H_4\text{-}o\text{–}NMe_2)_3]$[9] and 2.000 to 2.024 Å in $[Li(Et_2O)_3][Ge(C_6H_5)_3]$.[9] Two of the C–Ge–C bond angles in **7** are 94.35(17), 93.16(3)°. These angles are also typical of those seen in pyramidal germyl anions e.g. 96.847–99.241° in $[Li(thf)_2][Ge(C_6H_4\text{-}o\text{–}NMe_2)_3]$[9] and 97.284–98.985° in $[Li(Et_2O)_3][Ge(C_6H_5)_3]$.[10] The angle C(1)–Ge–C(2) of 66.76(12)° in $[GeP_4C_4tBu_4]$ is significantly smaller than the other two and is likely to be the result of the geometrical constraints imposed by the strained cage structure.

Mechanistic and Computational Aspects

To understand the formation and the structure of **7** density functional calculations were carried out. It is reasonable to consider that $[Ge(\eta^4\text{-}P_2C_2tBu_2)]$ reacts first with one molecule of $P\equiv CtBu$, and the intermediate so formed reacts with the second molecule of $P\equiv CtBu$. Since during the NMR monitoring of the reaction no signal was attributable to the intermediate, the second reaction step should be facile. It seemed reasonable that either the $P\equiv C$ triple bond or the phosphorus lone pair electrons can interact with the Ge atom, which is unshielded, and has electron deficiency. Thus, we have considered several ways to bind a $P\equiv CtBu$ unit to the Ge atom of $[Ge(\eta^4\text{-}P_2C_2tBu_2)]$, but upon optimisation the $P\equiv CtBu$ was repelled by the rest of the system. The only stable structure, resulting from a 1:1 ratio of the reactants was **9** (Figure 2), in which a C=P bond bridges the original four-membered ring. Furthermore, the energy of this structure was higher by 3.5 kcal/mol (B3LYP/6-31+G*) than that of the starting materials. We were also able to locate the transition structure corresponding to the loss of the $P\equiv CtBu$ unit from **9** resulting in $[Ge(\eta^4\text{-}P_2C_2tBu_2)]$ and $P\equiv CtBu$, and furthermore this transition structure lies only 11.0 kcal/mol above the energy of **9**.

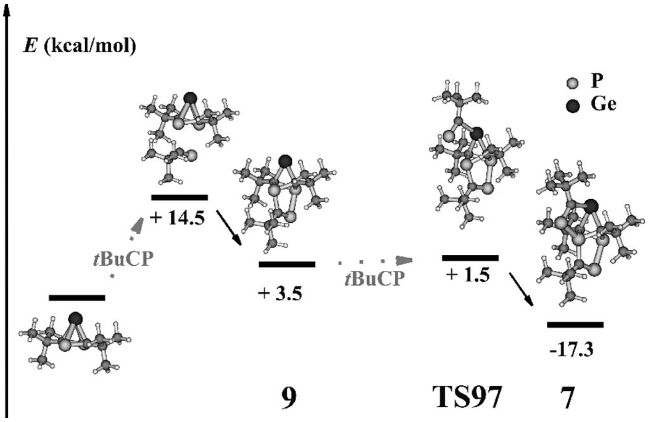

Figure 2. B3LYP/6-31+G* transition states and intermediate on the reaction path leading to the formation of **7**.

Addition of a second P≡C*t*Bu molecule to **9** furnishes **7** directly, and we were able to locate the corresponding transition structure **TS97**, which is only 18.8 kcal/mol less stable than the product (**7**), and is only slightly less stable than the energy of [Ge(η^4-$P_2C_2tBu_2$)] and two P≡C*t*Bu units. Because this second transition structure on the reaction path has a low energy, it is understandable that no intermediate has been observed during the experiments. We have also investigated the addition of the second P≡C*t*Bu molecule in a different regio-chemistry (with the P being attached to Ge). The product of this reaction is less stable than **7** (by 17.3 kcal/mol) and also the corresponding transition structure is less stable than **TS97** (by 8.9 kcal/mol).[11] Thus the computational studies of the entire reaction path are in accordance with the observed product, furthermore the low energy transition structures in both reaction steps are in agreement with the rather facile reaction observed at room temperature. Although the first reaction step is slightly endothermic (interaction with the solvent might influence the energetics somewhat), the stabilisation in the second step provides the necessary driving force for the reaction.

We have also investigated the computed electronic properties of the unusual zwitterionic product **7**. The B3LYP/6-31+G*-optimized structural parameters match favourably with the X-ray structural data (see footnote in Table 1). The electrostatic potential map of **7** is shown in Figure 3. and clearly supports the zwitterionic structure formulation. It is clearly evident that the phosphorus atoms (printed in red) carry a positive charge, while the germanium atom (shown in blue) is rather negative. This negative charge is understandable, since the HOMO[12] is located nearly entirely on the germanium atom. It is worthy noting that germanium is more electropositive than phosphorus (and carbon), thus **7** has an inverted charge distribution. Since tin is even more electropositive than germanium, the "charge inversion" is even larger in **8** than in **7** explaining the destabilization (see above) in case of **8**. The high energy HOMO[12] also makes the colour of **7** understandable, furthermore TD DFT computations at the B3LYP/6-31+G* level predict vertical excitation energies at 612 nm ($f = 0.0002$), 520 nm ($f = 0.0009$) and 476 nm ($f = 0.0034$), in agreement with the observed red colour of **7**.

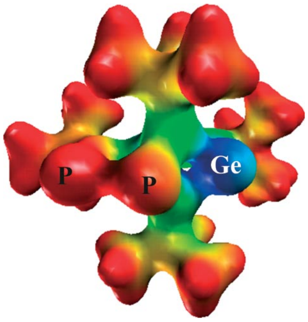

Figure 3. Electrostatic potential map of **7** computed at the B3LYP/6-31+G* level. Red colour denotes positive, blue negative charge.

Conclusions

We have found that the group-14 1,3-diphosphacyclobutadienyl complexes [M(η^4-$P_2C_2tBu_2$)] (M = Ge, Sn) react smoothly with the phosphaakyne P≡C*t*Bu to afford the group 14 organophosphorus cage compounds [$MP_4C_4tBu_4$] which have been characterised by multinuclear NMR spectroscopy, mass spectrometry and a single-crystal X-ray diffraction study in the case of **7**. Consideration of these data lead us to view the compounds as zwitterionic cages, with an inverted charge distribution at the group 14 element. These conclusions are fully supported by detailed density functional computational studies. Finally, there is a marked difference in the stability of **7** and **8**, with the latter showing considerable degradation in solution over a number of hours (in accordance with the increased charge inversion) whereas **7** appears to be stable in solution for at least several days with no apparent change in its NMR spectra.

It is worthy to note that zwitterionic structures are well known in solutions, (e.g. amino acids in water), however, these are stabilized by hydrogen bonds and rearrange in the gas phase by proton shift to their non ionic form. In the case of **7** and **8** – likewise in case of ylides (as $R_3P = CR'_2$) no such rearrangement is possible, however, in the present case the negative and positive charges are not stabilized as being localised in neighbouring atoms.

Experimental Section

General Remarks: All procedures were carried out using conventional Schlenk techniques under high purity argon in flame-dried glassware or in a Miller–Howe glovebox. Toluene and diethyl ether were dried by heating to reflux over NaK alloy for at least 10 h before being distilled under nitrogen. C_6D_6 was dried by over molten potassium before being vacuum transferred into a storage ampoule fitted with a greaseless tap. $^{31}P\{^1H\}$, ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX-300 spectrometer and were referenced to external 85% H_3PO_4, the residual ^1H resonances of the deuterated solvent and the ^{13}C resonances of the solvent

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respectively. ^{119}Sn NMR spectra were recorded with a Bruker AMX-500 spectrometer and were referenced to external $SnMe_4$. EI mass spectra were recorded with a VG Autospec instrument at 70 eV. Microanalyses were performed by Medac Ltd, Surrey, England. $[Ge(\eta^4\text{-}P_2C_2t\mathrm{Bu}_2)]$[5] and $[Sn(\eta^4\text{-}P_2C_2t\mathrm{Bu}_2)]$[6] were prepared according to the literature. P≡C*t*Bu was prepared by a modification[13] of the original literature procedure.[14]

$[GeP_4C_4t\mathrm{Bu}_4]$ (7): P≡C*t*Bu (0.22 g, 2.2 mmol, 355 µL) was added dropwise to a solution of $[Ge(\eta^4\text{-}P_2C_2t\mathrm{Bu}_2)]$ (0.2 g, 0.73 mmol) in diethyl ether (10 mL) at –70 °C with stirring. The resultant solution was warmed to room temperature and was stirred for 18 h during which time it became deep red in colour. Volatiles were removed in vacuo and the residue recrystallised from toluene at –85 °C to afford $[GeP_4C_4t\mathrm{Bu}_4]$ as a dark red solid m.p. 108–110 °C (0.15 g, 43%). The crystals so formed were suitable for an X-ray diffraction study. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ = 1.03 (s, 18 H, *t*Bu), 1.39 (s, 9 H, *t*Bu), 1.48 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (C_6D_6, 75.43 MHz, 298 K): δ = *t*Bu methyl groups: 30.97 (dd, $J_{P\text{–}C}$ = 5.07 and 9.41 Hz), 31.66 [dd, $J_{P\text{–}C}$ = 2.63 and 13.4 Hz, -C(CH$_3$)$_3$], 33.69 [dd, $J_{P\text{–}C}$ = 4.34 and 7.25 Hz, -C(CH$_3$)$_3$] ppm. *t*Bu quaternaries by refocused INEPT: 36.45 (dd, $J_{P\text{–}C}$ = 1.57 and 4.77 Hz), 41.27 [dd, -C(CH$_3$)$_3$, $J_{P\text{–}C}$ = 6.33 and 14.85 Hz], 49.92 [dd, -C(CH$_3$)$_3$, $J_{P\text{–}C}$ = 14.53 and 15.78 Hz]. Cage quaternaries by refocused INEPT: 114.39 (dd, $J_{P\text{–}C}$ = 4.6 Hz and 40 Hz), 227.14 (ddd, $J_{P\text{–}C}$ = 6.4, 58 and 70.4 Hz), 332.6 (ddd, $J_{P\text{–}C}$ = 4.5, 13.4 and 31.3 Hz), 333.3 (ddd, $J_{P\text{–}C}$ = 4.3, 13.3, 31.2 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 121.68 MHz, 298 K): δ = 49.6 [ddd, $^1J_{P(2)\text{–}P(4)}$ = 174.0, $^2J_{P(2)\text{–}P(1)}$ = 4.9, $^3J_{P(2)\text{–}P(3)}$ = 26.6 Hz, P(2)], 76.0 [ddd, $^1J_{P(1)\text{–}P(3)}$ = 379.2, $^2J_{P(1)\text{–}P(2)}$ = 4.9, $^3J_{P(1)\text{–}P(4)}$ = 12.4 Hz, P(1)], 271.6 [ddd, $^1J_{P(3)\text{–}P(1)}$ = 379.2, $^3J_{P(3)\text{–}P(2)}$ = 26.6, $^4J_{P(3)\text{–}P(4)}$ = 6.5 Hz, P(3)], 450.1 [ddd, $^1J_{P(4)\text{–}P(2)}$ = 174.0, $^3J_{P(4)\text{–}P(1)}$ = 12.4, $^4J_{P(4)\text{–}P(3)}$ = 6.5 Hz, P(4)] ppm. EI mass spectrum (main peaks) (70 eV): *m*/*z* (%) = 574 (26) [M + PC*t*Bu]$^+$, 474 (16) [M]$^+$, 417 (7) [M – *t*Bu]$^+$, 343 (55) [M – P$_2$C*t*Bu]$^+$, 305 (46) [M – PC$_2$*t*Bu$_2$]$^+$, 169 (45) [PC$_2$*t*Bu$_2$]$^+$, 57 (48) [*t*Bu]$^+$, 41 (100) [CH$_3$ – C=CH$_2$]$^+$. Microanalysis: $C_{20}H_{36}GeP_4$: calcd. C 50.79, H 7.67; found C 50.64, H 7.68.

$[SnP_4C_4t\mathrm{Bu}_4]$ (8): $[Sn(\eta^4\text{-}P_2C_2t\mathrm{Bu}_2)]$ (0.050 g, 0.16 mmol) was dissolved in C_6D_6 (ca. 0.6 mL) in an NMR tube and P≡C*t*Bu (0.040 g, 63 µL, 0.39 mmol) was added slowly with a micro-syringe and the solution was shaken periodically. Upon complete addition the solution became a deep red colour. ^{31}P{^{1}H} and ^{1}H NMR spectroscopic monitoring at this point showed only resonances corresponding to the product $[SnP_4C_4t\mathrm{Bu}_4]$ as well as excess P≡C*t*Bu and so it is reasonable to assume that initially the product is formed quantitatively. Over a period of hours, monitoring by ^{31}P{^{1}H} NMR spectroscopy shows considerable decomposition to a number of unidentified phosphorus containing products as well as starting material. Due to this facile decomposition, preparative scale attempts to isolate $[SnP_4C_4t\mathrm{Bu}_4]$ have been unsuccessful. A mass spectrum was obtained by examining a sample of the residue after removal of volatiles from a freshly prepared solution. ^{1}H NMR (C_6D_6, 298 K, 300 MHz): δ = 1.03 (s, 18 H, *t*Bu), 1.39 (s, 9 H, *t*Bu), 1.47 (s, 9 H, *t*Bu) ppm. ^{13}C NMR (75.43 MHz, C_6D_6, 298 K): δ = *t*Bu methyl groups: 31.4 (dd, $J_{P\text{–}C}$ = 6.77 and 9.8 Hz), 32.08 [dd, $J_{P\text{–}C}$ = 2.67 and 14.08 Hz, -C(CH$_3$)$_3$], 35.06 [dd, $J_{P\text{–}C}$ = 4.39 and 7.24 Hz, -C(CH$_3$)$_3$] ppm. *t*Bu quaternaries: 36.3 (dd, $J_{P\text{–}C}$ = 2.53 and 6.34 Hz), 41.6 [dd, -C(CH$_3$)$_3$, $J_{P\text{–}C}$ = 6.13 and 16.95 Hz], 49.90 [dd, -C(CH$_3$)$_3$, $J_{P\text{–}C}$ = 14.6 and 18.18 Hz]. Only one cage quaternary signal could be found: 117.0 (dd, $J_{P\text{–}C}$ = 5.42 Hz and 44.13 Hz). ^{31}P{^{1}H} NMR (C_6D_6, 298 K, 121.68 MHz): δ = 55.5 [ddd, P(2), $^1J_{P(2)\text{–}P(4)}$ = 169.9 Hz, $^2J_{P(2)\text{–}P(1)}$ = 2.86 Hz, $^3J_{P(2)\text{–}P(3)}$ = 25.7 Hz], 84.6 [ddd, P(1), $^1J_{P(1)\text{–}P(3)}$ = 394.5 Hz, $^2J_{P(1)\text{–}P(2)}$ = 3.0 Hz, $^3J_{P(1)\text{–}P(4)}$ = 14.0 Hz], 284.8 [ddd, P(3), $^1J_{P(3)\text{–}P(1)}$ = 394.4, $^3J_{P(3)\text{–}P(2)}$ = 25.7 Hz, $^4J_{P(3)\text{–}P(4)}$ = 6.3 Hz], 445.0 [ddd, P(4), $^1J_{P(4)\text{–}P(2)}$ = 169.8, $^3J_{P(4)\text{–}P(1)}$ = 14.2 Hz, $^4J_{P(4)\text{–}P(3)}$ = 6.6 Hz]. ^{119}Sn{^{1}H} (186.36 MHz, 298 K, C_6D_6): δ = –206.8 (ddd, $J_{P\text{–}Sn}$ = 297, 85 and 12 Hz) ppm. EI mass spectrum (main peaks) (70 eV): *m*/*z* (%) = 620 (7) [M + PC*t*Bu]$^+$, 520 (9) [M]$^+$, 400 (89) [M – Sn]$^+$, 169 (100) [PC$_2$*t*Bu$_2$]$^+$, 57 (70) [*t*Bu]$^+$, 41 (83) [CH$_3$–C=CH$_2$]$^+$.

X-ray Structure Determination of 7: X-ray quality crystals were obtained from a toluene solution at –85 °C. Intensity data were collected with a KappaCCD diffractometer and the structure was solved by direct methods and refined on F^2 using full-matrix least-squares with SHELX-97.[15] An empirical absorption correction was applied. The structure contains one toluene solvent molecule disordered across an inversion centre. Formula $C_{20}H_{36}GeP_4\cdot 0.5(C_7H_8)$, M = 519.03, T = 173(2) K, triclinic space group $P\bar{1}$, a = 9.5148(2) Å, b = 10.1061(2) Å, c = 16.3853(4) Å, α = 96.046(1)°, β = 95.661(1)°, γ = 117.485(1)°, V = 1370.46(6) Å^3, λ = 0.71073 Ä, Z = 2, $d_{\text{calcd.}}$ = 1.26 Mg m^{-3}, μ = 1.36 mm^{-1}, size = 0.3 × 0.3 × 0.3 mm, θ range 3.81 to 25.05°, reflections collected 10215, independent reflections: 4507 (R_{int} = 0.037), reflections with $I > 2\sigma(I)$ 4092, completeness to θ = 25.05° 93.0%, $T_{\max}$ = 0.691, $T_{\min}$ = 0.615, GooF on F^2 = 1.070, R [$I > 2\sigma(I)$]: R_1 = 0.052, wR_2 = 0.131, R (all data): R_1 = 0.058, wR_2 = 0.136 largest diff.peak and hole 1.38 and –0.98 e Å^3 (near disordered solvate).

CCDC-207900 (for **7**) contains supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computations: Density functional calculations were carried out by using the Gaussian 03 suite of programs.[16] Geometries were fully optimized at the B3LYP/3-21G(*) level of the density functional theory[17] followed by calculation of the second derivatives to characterise the stationary points obtained. For minima all eigenvectors of the second derivative matrix were positive, while for the transition structures a single negative eigenvector was obtained. In case of the transition structures subsequent IRC calculations located the minima corresponding to the transition state. Further optimizations were carried out at the B3LYP/6-31+G* level of the theory making use the B3LYP/3-21G(*) force constants. No further second derivative calculations were carried out at the B3LYP/6-31+G* optimized structures. NMR chemical shifts for **7** were computed at the B3LYP/cc-PVTZ//B3LYP/6-31+G* level.

The structures and the electrostatic potential surface were visualized by the MOLDEN program.[18]

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