allowed to warm to room temperature. The crude compound was purified by flash chromatography on alumina eluting with CH_3CN to give analytically pure **Pru**$(PF_6)_2$ (200 mg, 83 %). ^{31}P NMR (162 MHz, CD_2Cl_2): $\delta = -7.07$ (s); MS (ES): m/z 922.9 $[M-PF_6]^+$, 389.0 $[M-2PF_6]^{2+}$; UV/Vis (CH_3CN): λ_{max} [nm] (ε [$dm^3mol^{-1}cm^{-1}$]): 450 (12000), 339 (10000), 285 (56000), 273sh (48000), 255 (35000), 235 (38000); elemental analysis (%) calcd for $C_{44}H_{33}F_{12}N_6P_3Ru_1$: C 49.49, H 3.11, N, 7.87; found C 49.77, H 3.21, N, 7.69.

1: A solution of **Pru**$(PF_6)_2$ (100 mg, 0.094 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of $[CpRu(CH_3CN)_2(CO)]PF_6$[4] (39.4 mg, 0.094 mmol) in CH_2Cl_2 (10 mL). After 24 h the solvent was evaporated under vacuum. The crude product was purified by column chromatography on alumina, eluting first with CH_3CN/Toluene (1/1) and then with CH_3CN to afford the pure product **1** (94.3 mg, 88 %). FT-IR (CH_3CN): $\tilde{\nu} = 1996\ cm^{-1}$ (C≡O); ^1H NMR (400 MHz, CD_3CN, TMS): $\delta = 5.18$ (s, 5H, C_5H_5), 5.14 (s, 5H, C_5H_5), 2.00 (d, J(P,H) = 1.20 Hz, 3H, CH_3CN), 1.97 (d, J(P,H) = 1.20 Hz, 3H, CH_3CN); ^{31}P NMR (162 MHz, CD_3CN): $\delta = 48.77$ (s), 48.67 (s); UV/Vis (CH_3CN): λ_{max} [nm] (ε [$dm^3mol^{-1}cm^{-1}$]): 441 (14000), 284 (72000), 275 (75000), 235 (53500); elemental analysis (%) calcd for $C_{52}H_{41}F_{18}N_7O_1P_4Ru_2$: C 43.13, H 2.85, N 6.77; found C 43.52, H 2.96, N 6.54.

Photosubstitution of CH_3CN in **1**: The photochemical reaction was carried out with a 400 W high-pressure mercury lamp through a Toshiba Y-47 glass filter ($\lambda > 450$ nm). The exchange reaction was monitored by the intensity of the ^1H NMR resonance signals of the CH_3CN and Cp units.

3: 40 min irradiation of **1** in CD_3CN; yield 100 %; spectroscopic data are identical to **1**.

4: 40 min irradiation of **1** in [D_5]pyridine; yield 92 %; FT-IR (CH_3CN): $\tilde{\nu} = 1979\ cm^{-1}$ (C≡O); ^1H NMR (400 MHz, CD_3CN, TMS): $\delta = 5.30$ (s, 5H, C_5H_5), 5.24 (s, 5H, C_5H_5); ^{31}P NMR (162 MHz, CD_3CN): $\delta = 51.26$ (s), 51.16 (s).

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The Hexaphosphapentaprismane $P_6C_4tBu_4$: A "Jaws-Like" Cage Molecule That Bites!**

Mahmoud M. Al-Ktaifani, Daniel P. Chapman, Matthew D. Francis, Peter B. Hitchcock, John F. Nixon,* and László Nyulászi*

Organophosphorus cage compounds are of considerable current interest.[1] Two major synthetic routes to these compounds are the cyclooligomerization of phosphaalkynes (often metal-mediated)[2] and the coupling of polyphospholyl anions.[3] Examples include 1) the tetraphosphacubane $P_4C_4tBu_4$ from the thermal oligomerization of PC*t*Bu or treatment of $[ZrCp_2(P_2C_2tBu_2)]$ with C_2Cl_6;[4] and 2) the $FeCl_3$-mediated oxidative coupling of a mixture of the anions $[1,2,4\text{-}P_3C_2tBu_2]^-$ (**1**) and $[1,3\text{-}P_2C_3tBu_3]^-$ (**2**) to afford the pentaphospha cage compound $P_5C_5tBu_5$.[5] More recently, we reported the structurally characterized hexaphospha cage compound $P_6C_6tBu_6$, which to date is the largest phosphaalkyne oligomer known.[6]

We were interested in expanding this area to include cages containing an additional heteroatom, and recently we showed that treatment of **1** with EI_4 (E = Si, Ge) leads to the two structurally different cage compounds $P_6C_4tBu_4GeI_2$ (**3**) and $P_6C_4tBu_4SiI_2$ (**4**).[7] These cages are probably formed by two successive [2+2] cycloadditions of adjacent triphospholyl rings of the bis-η^1 intermediate $(P_3C_2tBu_2)_2EI_2$. We now report the synthesis of the related phosphorus – chalcogen cages $P_6C_4tBu_4E$ (E = S, Se, Te), with full structural characterization (E = Se, Te) or NMR spectroscopic characterization (E = S). These compounds were obtained by an unprecedented reaction involving the facile specific insertion of the chalcogen atom into a P–P bond of the hexaphosphaprismane $P_6C_4tBu_4$ (**5**). Compound **5** was first synthesized by Breit, Mack, and Regitz by an indirect method, but more recently improved syntheses involving coupling of two $(P_3C_2tBu_2)^-$ anions were independently developed by Nixon et al. and Zenneck et al.[1b,8]

In view of the ease and specificity of the insertion reactions of several carbene-like species into **5**, we have likened this behavior to that of the well-known shark "Jaws". This novel feature of its reactivity is further exemplified by the ready reaction of **5** with the stable germylene GeR_2, stannylene SnR_2 ($R = N(SiMe_3)_2$), and the plumbylene PbR'_2 ($R' = C_6H_3(NMe_2)_2$) to afford the structurally characterized

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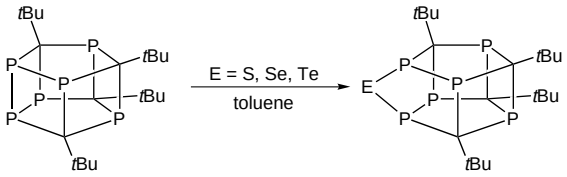
insertion products $P_6C_4tBu_4GeR_2$, $P_6C_4tBu_4SnR_2$, and $P_6C_4tBu_4PbR'_2$.[9, 10]

Treatment of **5** with elemental S, Se, or Te in toluene at room temperature (S, Se) or 60 °C (Te) readily affords the new cage compounds $P_6C_4tBu_4E$ (**6**–**8**) by specific insertion of the heteroatom into the unique P–P bond which joins the two component $P_3C_2tBu_2$ ring systems [Eq. (1))]. All the com-



5

6: E = Se
7: E = Te
8: E = S

pounds are stable towards air and moisture and are thermally robust, melting without decomposition above 240 °C. Each exhibits a molecular-ion peak in its EI mass spectrum, and the multinuclear solution spectra of **6, 7**, and **8** are fully consistent with their proposed cage structures, which were subsequently confirmed by single-crystal X-ray diffraction studies on **6** and **7** (vide infra).

The ^{1}H NMR spectrum of **6**, which is typical, displays two singlets for the two inequivalent *t*Bu groups. The $^{31}P\{^1H\}$ NMR spectrum consists of three complex multiplets arising from an AA′MM′XX′ spin system, but despite their complexity the large $^1J_{P,P}$ coupling constant of 235 Hz can be clearly distinguished. A $^1J_{P,Se}$ coupling of 202 Hz was observed both in the ^{77}Se NMR spectrum and for the satellites in the $^{31}P\{^1H\}$ spectrum.

The molecular structure of **6** (Figure 1 a) is very similar to that of **3**[7] and can be formally viewed as arising from simple substitution of the GeI_2 moiety with a selenium atom. The P-Se-P angle of 91.69(9)° is marginally smaller than usual, but the P–Se bond lengths of 2.2615(19) Å in **6** lie in the expected range for single bonds. Compound **7** (Figure 1 b), which as expected has a molecular structure similar to that of **6**, is only the third structurally characterized compound containing a P-Te-P structural motif, along with $[(CO)_4Cr(\mu\text{-}PtBu_2)_2Te]$[11] (**11**) and $[(MeCH)_2N_2P]_2Te$[12] (**12**). The P-Te-P angle in **7** (85.94(3)°) lies between those of **11** (81.4°) and **12** (94.5°), while the P–Te bond lengths of 2.4728(9) and 2.4790(5) Å are comparable with those of 2.481(1) and 2.491(1) Å in **11** and 2.56 Å in **12**.

Solution NMR data for **7** are also consistent with the above structure and are similar to those of **6**; the $^1J_{P,P}$ coupling constant is 240 Hz. The ^{125}Te satellites in the $^{31}P\{^1H\}$ NMR spectrum yielded a $^1J_{P,Te}$ value of 358 Hz, which was confirmed by the ^{125}Te NMR spectrum, which in addition gave a $^2J_{P,Te}$ coupling constant of 57 Hz. As expected, coupling constants involving tellurium are generally around two to three times greater than the corresponding couplings involving selenium.[13]

To better understand why only the unique central P–P bond is specifically involved in these insertion reactions, quantum

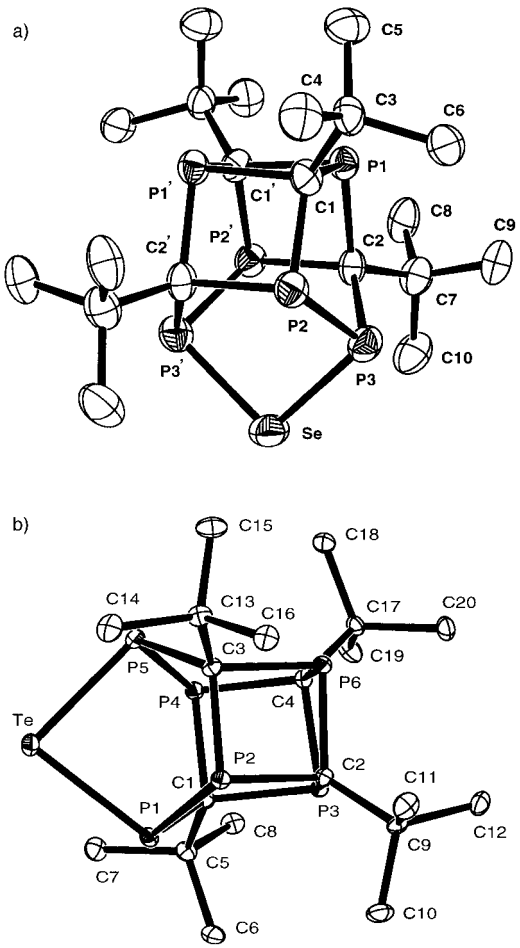
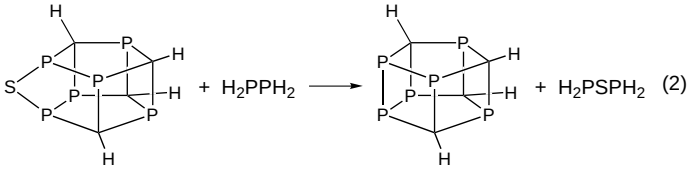


Figure 1. View of the molecule of **6** (a) and **7** (b) in the crystal.

chemical calculations were carried out.[14] Optimization of the parent hexaphosphapentaprismane $P_6C_4H_4$ (**5H**) at the B3LYP/6-31G* level of theory resulted in a structure similar to that obtained from the X-ray diffraction study on **5**.[8a] The calculated length of the central P–P bond in **5H** is 2.331 Å (2.2809(6) Å in **5**), while the other P–P bond length is 2.297 Å (2.2200(6) Å in **5**); this indicates slight weakening of the central P–P bond. In the hypothetical tetraphosphane $H_2PPHPHPH_2$, the central P–P bond is calculated to be slightly shorter than the terminal bonds (2.248 and 2.274 Å, respectively), while in $Me_2PPMePMePMe_2$ all three P–P bonds are nearly identical in length. The Wiberg bond index in **5H** is slightly larger for the central P–P bond (0.964) than for the two other P–P bonds (0.957). It seems therefore that the two types of P–P bonds in **5H** have similar strengths. Likewise, the three P–P bonds in tetraphosphane do not differ much in energy. For the isodesmic reaction shown in Equation (2), a net stabilization of only 1.4 kcal mol^{-1} was



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obtained, and this indicates that the two P–P bonds in tetraphosphane have similar strengths.

The electronic structure of **5H**, as evidenced by the shape of the HF/6-31G*//B3LYP/6-31G* frontier orbitals shown in Figure 2, indicates that the central P–P unit is involved not

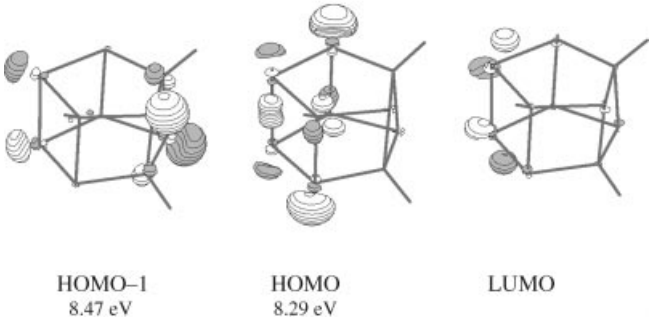

Figure 2. Frontier orbitals of **5H** at the HF/6-31G*//B3LYP/6-31G* level of theory.

only in both the HOMO and LUMO but also in HOMO – 1.[15] This is strong evidence that the central P–P bond is likely to be involved in a bond-cleavage reaction of **5H**. Interestingly, the lowest B3LYP/6-31G* harmonic frequency (224 cm^{-1}) involves a vibration in which the unique central P–P bond length is changing while the other atoms of the cage show hardly any movement.

The triplet state of **5H** is only 18.6 kcal mol^{-1} higher in energy (UB3LYP/6-31G*) than **5H** itself, and the cage opens at the central P–P bond. A search for a singlet biradical (UB3LYP/6-31G*) resulted in **5H′**, which has a similar geometry to and almost the same energy as the triplet (Figure 3); however, the formal S^2 value of the UB3LYP

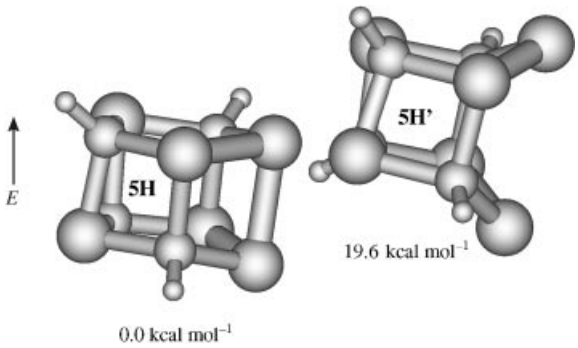

Figure 3. Structure and energy (UB3LYP/6-31G*) of **5H** and **5H′**.

wavefunction is 1.03. Optimization at the UMP2/6-31G* level resulted in a similar structure, again with an S^2 value of 1.03 instead of 0.0, which is the expected value for the singlet state. The energy difference (MP2CAS(2,2)/6-31G*//B3LYP/6-31G*) of 19.6 kcal mol^{-1} between **5H** and **5H′** provides support for the above energy difference between the closed and opened structures.

As evidenced by the structural data and Wiberg bond indices discussed above, there is no significant difference in the electronic nature of P–P single bonds in general and that of the unique P–P bond in the hexaphosphapentaprismane **5** in particular. However, opening the latter bond might cause the rest of the molecule to relax, so that the product is stabilized relative to **5**. Since the P–P bond energy is about 50 kcal mol^{-1},[16] and **5H′** is less stable than **5H** by 19.6 kcal mol^{-1}, the destabilization of the central P–P bond in **5** can be estimated to be about 30 kcal mol^{-1}. The destabilization is also in accord with the rules set up by Böcker and Häser[17] for four-membered phosphorus ring systems.

Thus, the product stability plays a decisive role in reactions which involve opening of the central P–P bond in **5**. Calculating the relative energies of the pentaprismane-based $C_4H_4P_6S$ isomers, we found the lowest energy for **8H**, in which the sulfur atom inserted into the central P–P bond. The structure in which the sulfur atom inserted into the other P–P bond of **5H** is higher in energy by 13.88 kcal mol^{-1}, and possible isomers in which the sulfur atom is doubly bonded to the other phosphorus atoms of the P_4 unit in **5H** are all at least 20 kcal mol^{-1} less stable than **8H**. The isodesmic reaction shown in Equation (3), which is endothermic by

$$H_2P–P(H)–P(H)–PH_2 + 2\,PH_3 \longrightarrow 3\,H_2P–PH_2 \quad (3)$$

30.8 kcal mol^{-1}, also clearly shows that the stability of the product relative to the reactant is the driving factor that opens the unique central P–P bond of **5**. The destabilization energy deduced from the isodesmic reaction also favorably matches that deduced above for the central P–P bond of **5** and thus offers a ready explanation for its unexpected reactivity. The overall reaction sequence involving the reactant cage compound, the biradical intermediate, and the product cage is shown pictorially in Figure 4.

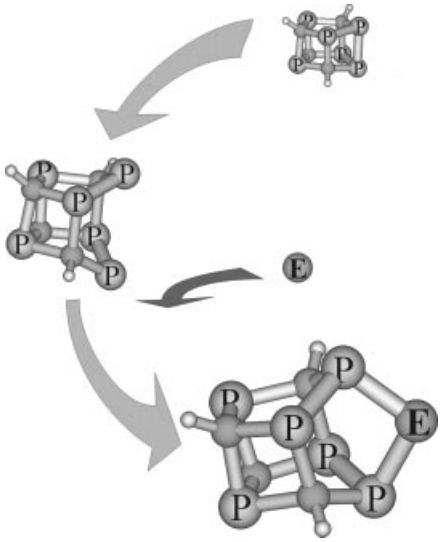

Figure 4.

Experimental Section

Spectroscopic data: **6**: ^{1}H NMR (300 MHz, [D_6]benzene, 25 °C): $\delta = 1.13$ (s, 18H, *t*Bu), 1.33 (s, 18H, *t*Bu); ^{31}P{^{1}H} NMR (121.68 MHz, [D_6]benzene, 25 °C, 85 % H_3PO_4): $\delta = 138.5$ (m, ^1J(P,P) = 235 Hz, P3), 141.0 (m, ^1J(P,P) = 235 Hz, P2), 145.5 (m, P1); ^{77}Se NMR (95.39 MHz, [D_6]benzene, 25 °C,

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Me_2Se): $\delta = 290$ (tt, $^1J(P,Se) = 202$, $^2J(P,Se) = 22$ Hz); MS (70 eV): m/z (%): 542 (6) $[M]^+$, 485 (10) $[M - t\mathrm{Bu}]^+$, 231 (23) $[P_3C_2t\mathrm{Bu}_2]^+$; m.p. 245 °C; elemental analysis (%) found (calcd): C 44.56 (44.38), H 6.59 (6.70). **7**: ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.16$ (s, 18H, *t*Bu), 1.41 (s, 18H, *t*Bu); ^{31}P{^{1}H} NMR (121.68 MHz, [D$_6$]benzene, 25 °C, 85 % H_3PO_4): $\delta = 91.5$ (m, $^1J(P,P) = 240$ Hz, P1, P5), 134.0 (m, P3, P6), 146.8 (m, $^1J(P,P) = 240$ Hz, P2, P4); ^{125}Te NMR (157.86 MHz, [D$_6$]benzene, 25 °C, Me_2Te): $\delta = 424.8$ (tt, $^1J(P,Te) = 358$, $^2J(P,Te) = 57$ Hz); MS (70 eV): m/z (%): 592 (43) $[M]^+$, 535 (6) $[M - t\mathrm{Bu}]^+$, 464 (77) $[P_6C_4t\mathrm{Bu}_4]^+$, 231 (100) $[P_3C_2t\mathrm{Bu}]^+$; m.p. 264 °C; elemental analysis (%) found (calcd): C 41.40 (40.72), H 6.11 (6.15). **8**: ^{1}H NMR (300 MHz, [D$_6$]benzene, 25 °C): $\delta = 1.12$ (s, 18H, *t*Bu), 1.28 (s, 18H, *t*Bu); ^{31}P{^{1}H} NMR (121.68 MHz, [D$_6$]benzene, 25 °C, 85 % H_3PO_4): $\delta = 138.7$ (m, $^1J(P,P) = 239.6$ Hz, P3), 156.0 (m, $^1J(P,P) = 235$ Hz, P2), 154.9 (m, P1); MS (70 eV): m/z (%): 494 (100) $[M]^+$, 437 (15) $[M - t\mathrm{Bu}]^+$.

Crystal data: **6**: $C_{20}H_{36}P_6Se$, $M_r = 541.27$; crystal dimensions $0.2 \times 0.1 \times 0.05$ mm, monoclinic, space group $C2/c$ (No. 15); $a = 13.780(2)$, $b = 14.862(3)$, $c = 12.1833(13)$ Å, $\beta = 94.981(1)°$, $V = 2485.8(7)$ Å^3, $\rho_{calcd} = 1.45\ g\,cm^{-3}$; $\theta = 4.64 - 22.98°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K, 5013 reflections, 1708 independent reflections ($R_{int} = 0.095$); $R_1 = 0.057$, $wR_2 = 0.128$ ($I > 2\sigma I$); $R_1 = 0.086$, $wR_2 = 0.141$ (all data); Multi-scan absorption correction, $\mu = 1.90\ mm^{-1}$, $T_{max} = 0.842$, $T_{min} = 0.789$. **7**: $C_{20}H_{36}P_6Te$, $M_r = 690.91$; crystal dimensions $0.3 \times 0.2 \times 0.02$ mm; triclinic, space group $P\bar{1}$ (No. 2); $a = 10.4038(3)$, $b = 14.8533(3)$, $c = 16.5591(15)$ Å, $\alpha = 91.435(1)$, $\beta = 94.981(1)$, $\gamma = 99.001(2)°$, $V = 2526.4(1)$ Å^3, $\rho_{calcd} = 1.55\ g\,cm^{-3}$; $\theta = 3.76 - 27.91°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 173(2)$ K, 43231 reflections, 12034 independent reflections ($R_{int} = 0.058$); $R_1 = 0.039$, $wR_2 = 0.081$ ($I > 2\sigma I$); $R_1 = 0.062$, $wR_2 = 0.089$ (all data), Multi-scan absorption correction, $\mu = 1.56\ mm^{-1}$, $T_{max} = 0.829$, $T_{min} = 0.756$.

Diffraction data for both structures were recorded on a Kappa CCD instrument. Both structures were solved and refined by using the SHELX-97 suite of programs for crystal structure analysis (G. M. Sheldrick, University of Göttingen, Germany, **1997**). Structures were refined by full-matrix least-squares methods on $|F^2|$. Hydrogen atoms were placed in calculated positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161083 and -161084. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Figures 2 and 3 were drawn with the program MOLDEN.[18]

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