

allowed to warm to room temperature. The crude compound was purified by flash chromatography on alumina eluting with CH₃CN to give analytically pure **Pru**(PF₆)₂ (200 mg, 83 %). ³¹P NMR (162 MHz, CD₂Cl₂): δ = −7.07 (s); MS (ES): *m/z* 922.9 [*M* − PF₆]⁺, 389.0 [*M* − 2PF₆]²⁺; UV/Vis (CH₃CN): λ_{max} [nm] (ε [dm³mol^{−1}cm^{−1}]): 450 (12000), 339 (10000), 285 (56000), 273sh (48000), 255 (35000), 235 (38000); elemental analysis (%) calcd for C₄₄H₃₃F₁₂N₆P₃Ru₁: C 49.49, H 3.11, N, 7.87; found C 49.77, H 3.21, N, 7.69.

1: A solution of **Pru**(PF₆)₂ (100 mg, 0.094 mmol) in CH₂Cl₂ (10 mL) was added to a stirred solution of [CpRu(CH₃CN)₂(CO)]PF₆^[4] (39.4 mg, 0.094 mmol) in CH₂Cl₂ (10 mL). After 24 h the solvent was evaporated under vacuum. The crude product was purified by column chromatography on alumina, eluting first with CH₃CN/Toluene (1/1) and then with CH₃CN to afford the pure product **1** (94.3 mg, 88 %). FT-IR (CH₃CN): ν̄ = 1996 cm^{−1} (C=O); ¹H NMR (400 MHz, CD₃CN, TMS): δ = 5.18 (s, 5H, C₅H₅), 5.14 (s, 5H, C₅H₅), 2.00 (d, *J*(P,H) = 1.20 Hz, 3H, CH₃CN), 1.97 (d, *J*(P,H) = 1.20 Hz, 3H, CH₃CN); ³¹P NMR (162 MHz, CD₃CN): δ = 48.77 (s), 48.67 (s); UV/Vis (CH₃CN): λ_{max} [nm] (ε [dm³mol^{−1}cm^{−1}]): 441 (14000), 284 (72000), 275 (75000), 235 (53500); elemental analysis (%) calcd for C₅₂H₄₁F₁₈N₇O₁P₄Ru₂: C 43.13, H 2.85, N 6.77; found C 43.52, H 2.96, N 6.54.

Photosubstitution of CH₃CN in **1**: The photochemical reaction was carried out with a 400 W high-pressure mercury lamp through a Toshiba Y-47 glass filter (λ > 450 nm). The exchange reaction was monitored by the intensity of the ¹H NMR resonance signals of the CH₃CN and Cp units.

3: 40 min irradiation of **1** in CD₃CN; yield 100%; spectroscopic data are identical to **1**.

4: 40 min irradiation of **1** in [D₅]pyridine; yield 92%; FT-IR (CH₃CN): ν̄ = 1979 cm^{−1} (C=O); ¹H NMR (400 MHz, CD₃CN, TMS): δ = 5.30 (s, 5H, C₅H₅), 5.24 (s, 5H, C₅H₅); ³¹P NMR (162 MHz, CD₃CN): δ = 51.26 (s), 51.16 (s).

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The Hexaphosphapentaprismane P₆C₄tBu₄: A “Jaws-Like” Cage Molecule That Bites!*

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Organophosphorus cage compounds are of considerable current interest.^[1] Two major synthetic routes to these compounds are the cyclooligomerization of phosphalkynes (often metal-mediated)^[2] and the coupling of polyphospholyl anions.^[3] Examples include 1) the tetraphosphacubane P₄C₄tBu₄ from the thermal oligomerization of PCtBu or treatment of [ZrCp₂(P₂C₂tBu₂)] with C₂Cl₆,^[4] and 2) the FeCl₃-mediated oxidative coupling of a mixture of the anions [1,2,4-P₃C₂tBu₂][−] (**1**) and [1,3-P₂C₃tBu₃][−] (**2**) to afford the pentaphospha cage compound P₅C₅tBu₅.^[5] More recently, we reported the structurally characterized hexaphospha cage compound P₆C₆tBu₆, which to date is the largest phosphalkyne 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 EI₄ (E = Si, Ge) leads to the two structurally different cage compounds P₆C₄tBu₄GeI₂ (**3**) and P₆C₄tBu₄SiI₂ (**4**).^[7] These cages are probably formed by two successive [2+2] cycloadditions of adjacent triphospholyl rings of the bis-η¹ intermediate (P₃C₂tBu₂)₂EI₂. We now report the synthesis of the related phosphorus–chalcogen cages P₆C₄tBu₄E (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 hexaphosphapentaprismane P₆C₄tBu₄ (**5**). Compound **5** was first synthesized by Breit, Mack, and Regitz by an indirect method, but more recently improved syntheses involving coupling of two (P₃C₂tBu₂)[−] 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 GeR₂, stannylene SnR₂ (R = N(SiMe₃)₂), and the plumbylene PbR₂ (R' = C₆H₃(NMe₂)₂) to afford the structurally characterized

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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

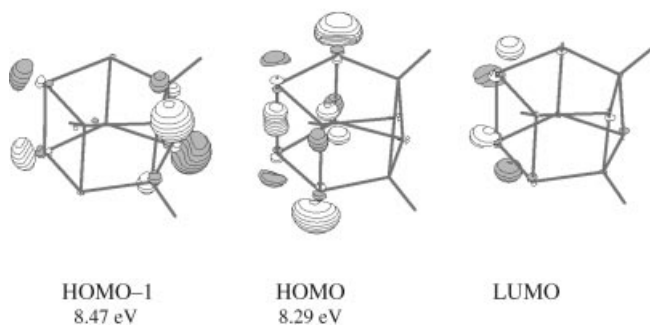


Figure 2. Frontier orbitals of **5H** at the HF/6-31G**/B3LYP/6-31G* level of theory.

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

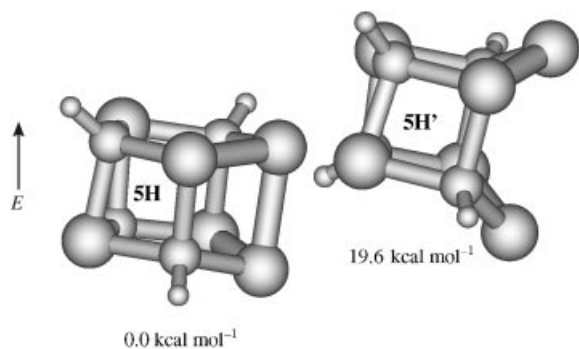


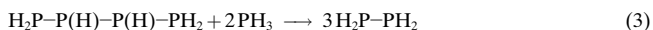
Figure 3. Structure and energy (UB3LYP/6-31G*) of **5H** and **5H'**.

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 C₄H₄P₆S 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 P₄ 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



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.

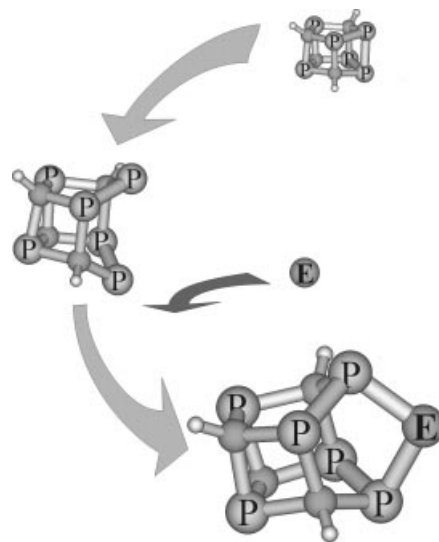


Figure 4.

Experimental Section

Spectroscopic data: **6**: ¹H NMR (300 MHz, [D₆]benzene, 25 °C): δ = 1.13 (s, 18 H, *t*Bu), 1.33 (s, 18 H, *t*Bu); ³¹P{¹H} NMR (121.68 MHz, [D₆]benzene, 25 °C, 85 % H₃PO₄): δ = 138.5 (m, ¹J(P,P) = 235 Hz, P3), 141.0 (m, ¹J(P,P) = 235 Hz, P2), 145.5 (m, P1); ⁷⁷Se NMR (95.39 MHz, [D₆]benzene, 25 °C,

Me₂Se): δ = 290 (tt, ¹J(P,Se) = 202, ²J(P,Se) = 22 Hz); MS (70 eV): *m/z* (%): 542 (6) [*M*]⁺, 485 (10) [*M* – *t*Bu]⁺, 231 (23) [*P*₃C₄*t*Bu₃]⁺; m.p. 245 °C; elemental analysis (%) found (calcd): C 44.56 (44.38), H 6.59 (6.70). **7**: ¹H NMR (300 MHz, [D₆]benzene, 25 °C): δ = 1.16 (s, 18H, *t*Bu), 1.41 (s, 18H, *t*Bu); ³¹P{¹H} NMR (121.68 MHz, [D₆]benzene, 25 °C, 85% H₃PO₄): δ = 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); ¹²⁵Te NMR (157.86 MHz, [D₆]benzene, 25 °C, Me₂Te): δ = 424.8 (tt, ¹J(P,Te) = 358, ²J(P,Te) = 57 Hz); MS (70 eV): *m/z* (%): 592 (43) [*M*]⁺, 535 (6) [*M* – *t*Bu]⁺, 464 (77) [*P*₆C₄*t*Bu₄]⁺, 231 (100) [*P*₃C₄*t*Bu₃]⁺; m.p. 264 °C; elemental analysis (%) found (calcd): C 41.40 (40.72), H 6.11 (6.15). **8**: ¹H NMR (300 MHz, [D₆]benzene, 25 °C): δ = 1.12 (s, 18H, *t*Bu), 1.28 (s, 18H, *t*Bu); ³¹P{¹H} NMR (121.68 MHz, [D₆]benzene, 25 °C, 85% H₃PO₄): δ = 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*Bu]⁺.

Crystal data: **6**: C₂₀H₃₆P₆Se, *M*_r = 541.27; crystal dimensions 0.2 × 0.1 × 0.05 mm, monoclinic, space group *C2/c* (No. 15); *a* = 13.780(2), *b* = 14.862(3), *c* = 12.1833(13) Å, β = 94.981(1)°, *V* = 2485.8(7) Å³, ρ_{calcd} = 1.45 g cm^{−3}; θ = 4.64–22.98°, MoK α radiation (λ = 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* > 2σ*I*); *R*₁ = 0.086, *wR*₂ = 0.141 (all data); Multi-scan absorption correction, μ = 1.90 mm^{−1}, *T*_{max} = 0.842, *T*_{min} = 0.789. **7**: C₂₀H₃₆P₆Te, *M*_r = 690.91; crystal dimensions 0.3 × 0.2 × 0.02 mm; triclinic, space group *P1* (No. 2); *a* = 10.4038(3), *b* = 14.8533(3), *c* = 16.5591(15) Å, α = 91.435(1), β = 94.981(1), γ = 99.001(2)°, *V* = 2526.4(1) Å³, ρ_{calcd} = 1.55 g cm^{−3}; θ = 3.76–27.91°, MoK α radiation (λ = 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* > 2σ*I*); *R*₁ = 0.062, *wR*₂ = 0.089 (all data); Multi-scan absorption correction, μ = 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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