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Chalcogenation of the 1,4-C_2P_4 Ring: Oxidation, Isomerization, Insertion, and Ring Contraction

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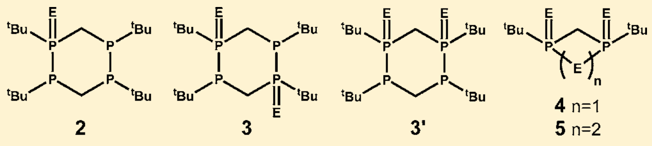
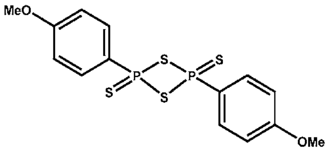
Ⓢ *Supporting Information*



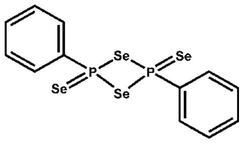
ABSTRACT: The reaction of $H_2C(PCl_2)_2$ with 4 equiv of ${}^tBuMgCl$ in tetrahydrofuran (THF) produces 1,4-$(CH_2)_2(P^tBu)_4$, **1**, in about 65% yield. This six-membered ring reacts directly with elemental sulfur or selenium in toluene at low temperatures to give the mono- and dichalcogenides 1,4-$(CH_2)_2(P^tBuE)(P^tBu)_3$ (E = S, **2a**, E = Se, **2b**) and 1,4-$(CH_2)_2$-2,5-$(P^tBuE)_2(P^tBu)_2$ (E = S, **3a**, E = Se, **3b**). X-ray structural determinations showed that **3a** and **3b** are isostructural in the solid state; the six-membered C_2P_4 ring exhibits a twist-boat geometry with chalcogen substituents in syn positions in each case. Density functional theory (DFT) calculations for the three possible isomers of disubstitution were performed to elucidate the factors that favor the 2,5-isomer. Thermal isomerism was observed in solutions of **3b** or **3a** in toluene at 60 and 95 °C, respectively, to give the corresponding 2,6-isomers. With an excess of chalcogen in toluene at reflux, the four-membered rings $(H_2C)(P^tBuE)_2E$ (E = S, **4a**, E = Se, **4b**) were obtained and identified by multinuclear NMR spectroscopy and single crystal X-ray crystallography, which showed the ${}^tBu$ groups in a *trans* orientation with respect to the CP_2E ring. With a large excess of chalcogen, the five-membered rings $(H_2C)(P^tBuE)_2E_2$ (E = S, **5a**, E = Se, **5b**) were also observed; the X-ray structure of **5b** revealed a half-envelope conformation for the CP_2Se_2 ring. The direct reaction of **4a** with sulfur in boiling toluene does not produce **5a**, whereas **5b** is formed slowly and in low yields from **4b** and selenium under similar conditions. On the basis of DFT calculations of the relative energies of likely intermediates, chalcogen insertion into the P−P bonds of **3a** and **3b** to give eight-membered $C_2P_4E_2$ rings, followed by monomerization, is proposed as a feasible pathway for the formation of the four-membered CP_2E heterocycles **4a** and **4b**.

■ INTRODUCTION

A variety of organophosphorus-chalcogen heterocycles are known, including three-, four-, five-, six-, eight-, and ten-membered ring systems.[1,2] The most important examples are the four-membered rings known as the Lawesson's (**LR**) and Woollins' Reagents (**WR**), which have wide-ranging applications in synthetic chemistry, for example, as efficient thionation and selenation reagents, respectively.[3,4] This class of organophosphorus-chalcogen heterocycle is formed, inter alia, from the reactions of cyclophosphanes $(RP)_5$ with an excess of chalcogen, but that approach leads to a complex mixtures of products (vide infra). Consequently, specific high-yield syntheses have been developed for **LR** and **WR**. The former is prepared by heating a mixture of P_4S_{10} with anisole in a high-boiling solvent,[5] while the selenium analogue is obtained in high yield by reaction of $PhPCl_2$ with Na_2Se and is now commercially available.[6]



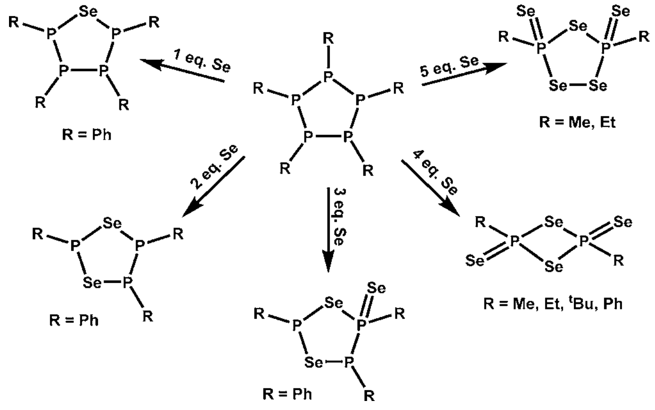
LR



WR

The complexity of the reaction of cyclopolyphosphanes with chalcogens is illustrated in Scheme 1 for $(RP)_5$ (R = Ph, alkyl) and selenium.[2,7,8] With 1 or 2 equiv of chalcogen the formal replacement of PR units by Se occurs initially with retention of the five-membered ring. Subsequently, in reactions with larger amounts of selenium, oxidation of the three-coordinate phosphorus centers takes place followed by ring contraction to give four-membered heterocycles as well as five-membered rings that incorporate a −Se−Se− linkage. Karaghiosoff et al. showed that the combination of ${}^{31}P$ and ${}^{77}Se$ NMR spectroscopy facilitates the identification of intermediates in the selenation of the more reactive methylated pentamer $(MeP)_5$.[8]

Scheme 1



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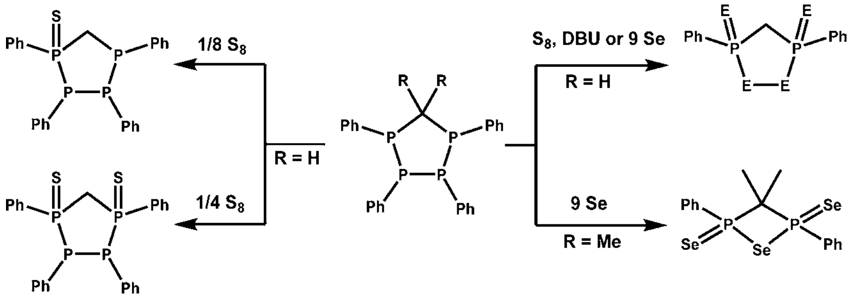
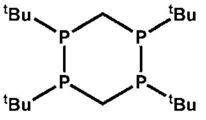
Scheme 2



The reactivity of carbacyclophosphanes toward chalcogens has also been investigated, in particular for the tetraphospholanes $(PhP)_4CH_2$ and $(PhP)_4C(CH_3)_2$. As illustrated in Scheme 2, the major products retain the PCP framework.[9,10] Baudler et al. showed that treatment of $(PhP)_4CH_2$ with 1 or 2 equiv of sulfur in boiling benzene results in oxidation of the geminal phosphorus centers.[9] With a large excess of chalcogen, however, Woollins et al. identified products that result from replacement of PhP groups by selenido or dichalcogenido (−E−E−) units, but with the PCP scaffold intact.[10] In addition, several carbon-free heterocycles (not shown in Scheme 2) were characterized as minor products on the basis of NMR (^{31}P and ^{77}Se).

The chemical properties and reactivity of the related six-membered 1,4-C_2P_4 ring system are largely unknown. Only a single reaction of an ^{i}Pr derivative $[1,4\text{-}(H_2C)_2(P^iPr)_4]$ with elemental sulfur has been reported, and it is claimed to result in oxidation of all four phosphorus centers.[11] This six-membered dicarbacyclotetraphosphane ring $[1,4\text{-}(H_2C)_2(PR)_4]$ can be synthesized by using a variety of methods and the ^{i}Pr, ^{t}Bu, and Ph derivatives have all been previously reported. The syntheses require formal insertion of a methylene group into the CP_4 ring[12a] or addition to an acyclic $[RPPR]^{2-}$ dianion.[12b] Reductive coupling of $H_2C(PRCl)_2$ with Na/K alloy[12c] or from slow addition of KPHPh to CH_2Cl_2[12d] has also been reported. The simplest method, which is only applicable for the ^{t}Bu derivative, involves the direct reaction of $H_2C(PCl_2)_2$ with ^{t}BuMgCl.[12e]

In view of the presence of two PCP structural braces on opposite sides of the 1,4-C_2P_4 ring and the resulting relatively high symmetry, we envisaged that this heterocycle might provide an informative model for identifying the intermediates involved in the chalcogenation of polyphosphorus ring systems and, hence, could lead to an understanding of the overall reaction pathway. Consequently, we have carried out a comprehensive investigation of the chalcogenation of $1,4\text{-}(H_2C)_2(P^tBu)_4$ to determine (a) the conditions under which monochalcogenides are formed exclusively, (b) which isomer is preferred upon disubstitution, and (c) the outcome of reactions with an excess of chalcogen. For comparative purposes, chalcogenation has been carried out with sulfur as well as selenium at both ambient and elevated temperatures, using a variety of stoichiometries. The focus, however, is on the selenium systems because of the additional information that is derived from the presence of NMR-active ^{77}Se nuclei ($I = 1/2$; 7.6%) and the current interest in organophosphorus−selenium heterocycles.[2,4]



1

EXPERIMENTAL SECTION

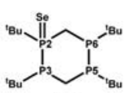
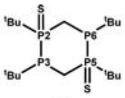
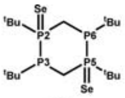
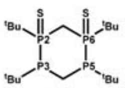
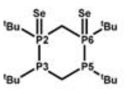
Reagents and General Procedures. All reactions and the manipulation of products were performed under an atmosphere of argon using standard Schlenk techniques. The compounds $[H_2C(PCl_2)_2]$ (Strem Chemicals, >90%), ^{t}BuMgCl (Aldrich, 1.0 M solution in THF), and elemental Se (Aldrich, 200 mesh, 99.5+%) were used as received. Elemental sulfur (Fisher, laboratory grade) was sublimed under vacuum prior to use. The solvents hexanes, toluene, diethyl ether, and tetrahydrofuran (THF) were dried by distillation over sodium/benzophenone under an argon atmosphere prior to use.

Spectroscopic Methods. The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were obtained in toluene-d_8 at 298 K on a Bruker DRX 400 spectrometer operating at 399.46, 100.46, 161.59, and 76.13 MHz, respectively. ^{1}H and ^{13}C-DEPT135 NMR spectra are referenced to the solvent signal, and the chemical shifts are reported relative to $(CH_3)_4Si$. ^{31}P NMR spectra are referenced externally to an 85% solution of H_3PO_4 at 0 ppm, and ^{77}Se NMR spectra to an external reference of Ph_2Se_2 in $CDCl_3$ at 463 ppm. The atom numbering scheme for NMR parameters is shown in Table 1. Low resolution mass spectra (EI/CI) were obtained with a Thermo Finnigan SSQ7000 mass spectrometer with a direct insertion probe; ammonia was used as the ionization gas for CI. For the more thermally sensitive compounds (**4b**, **5b**), mass spectra were obtained with a Bruker Autoflex III Smartbeam MALDI mass spectrometer using α-Cyano-4-hydroxycinnamic acid (HCCA) as a matrix. High resolution CI mass spectra were obtained on a Waters Micromass GCT Premier mass spectrometer equipped with a time-of-flight analyzer, using ammonia as the ionization gas. Elemental analyses were performed on a PerkinElmer 2400 elemental analyzer, equipped to measure C, H, and N.

Spectroscopic Modeling. All reported ^{31}P{^{1}H} NMR parameters for second-order spin systems were derived by iterative simulation of experimental data obtained at a ^{31}P Larmor frequency of 161.59 MHz using gNMR version 5.0.6.0 (Table 1).[13] In all cases spectra collected in toluene-d_8 at room temperature provided sufficiently good data for modeling; in the case of **2a**, low concentrations in a mixture of products and the use of reagent toluene precluded a reliable fit. However, a tentative fit for **2a** is provided in the Supporting Information for comparison with **2b**. The signs of the P−P coupling constants reported in Table 1 have been established by assigning the $^1J_{PP}$ coupling constants as negative.[14]

X-ray Crystallography. Crystallographic data for **1**, **3a**, **3b**, **4a**, **4b**, **5b** are summarized in Table 2. In each case, crystals were coated with Paratone 8277 oil and mounted on a nylon loop. Diffraction data were collected on a Nonius KappaCCD diffractometer using monochromated Mo Kα radiation (λ = 0.71073 Å) at −100 °C. An absorption correction was applied during the data collection using the SORTAV program.[15] The structures were solved by direct methods using SHELXS-97 and refined using SHELXL-97.[16a,b] After full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in idealized locations using the appropriate riding models. The structure of **4a** exhibits a 54:46 positional disorder in C1 and S_{endo}. The structure of **4b** shows a similar disorder with a 95:5 ratio; the atomic positions and thermal parameters of the minor component were constrained using SADI and EADP

Table 1. $^{31}P\{^1H\}$ NMR Parameters[a,b] for 2b, 3a, 3b, 3a′, and 3b′

	 2b	 3a	 3b	 3a'	 3b'
δ (ppm)	45.5 [2] -28.7 [3] -9.1 [5] -23.7 [6]	63.0 [2,5] -26.7 [3,6]	48.3 [2,5] -24.5 [3,6]	67.0 [2,6] -20.1 [3,5]	55.4 [2,6] -12.0 [3,5]
$^1J_{PP}$ (Hz)	-321 [2,3] -216 [5,6]	-296 [2,3] -296 [5,6]	-304 [2,3] -304 [5,6]	-315 [2,3] -315 [5,6]	-308 [2,3] -308 [5,6]
$^2J_{PP}$ (Hz)	11 [2,6] 8 [3,5]	17 [2,6] 17 [3,5]	16 [2,6] 16 [3,5]	25 [2,6] 25 [3,5]	34 [2,6] 34 [3,5]
$^3J_{PP}$ (Hz)	-2 [2,5] -24 [3,6]	-1 [2,5] -42 [3,6]	-3 [2,5] -43 [3,6]	0 [2,5] 0 [3,6]	0 [2,5] 0 [3,6]
$^1J_{PSe}$ (Hz)	700	–	715	–	725
$^2J_{PSe}$ (Hz)	0	–	0	–	25
Spin System	AGMX	AA'XX'	AA'XX'	AA'XX'	AA'XX'

[a] Numbers in square brackets refer to the phosphorus atom numbers in the line drawings (see ref 33). [b] All parameters were derived by iterative fitting of experimental data at 161.59 MHz.

Table 2. Crystallographic Data for 1, 3a, 3b, 4a, 4b, 5b

	1	3a	3b	4a	4b	5b
empirical formula	$C_{18}H_{40}P_4$	$C_{18}H_{40}P_4S_2$	$C_{18}H_{40}P_4Se_2$	$C_9H_{20}P_2S_3$	$C_9H_{20}P_2Se_3$	$C_9H_{20}P_2Se_4$
formula weight	538.3	444.5	538.3	286.4	427.1	506.3
crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	$C2/c$	$Pbca$	$Pbca$	$Cmca$	$Ibca$	$P2_1/n$
a, Å	16.0430(11)	13.3650(2)	13.7730(6)	9.3820(4)	8.0410(2)	14.2600(4)
b, Å	12.5350(10)	17.7920(3)	17.7200(3)	7.8780(8)	18.8488(6)	7.5740(5)
c, Å	11.6060(6)	20.7570(3)	20.6690(7)	19.2020(15)	19.2235(7)	15.8620(5)
α, deg.	90.00	90.00	90.00	90.00	90.00	90.00
β, deg.	102.024(4)	90.00	90.00	90.00	90.00	109.819(2)
γ, deg.	90.00	90.00	90.00	90.00	90.00	90.00
V, Å^3	2282.7(3)	4935.81(1)	5044.43(3)	1419.25(2)	2913.58(16)	1611.70(12)
Z	4	8	8	2	8	4
T, K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
ρ_{calcd}, mg/m^3	1.107	1.196	1.418	1.340	1.947	2.085
μ(Mo$K\alpha$), mm^{-1}	0.328	0.476	3.186	0.714	7.761	9.276
cryst. size, mm^3	0.24 × 0.16 × 0.12	0.20 × 0.22 × 0.12	0.10 × 0.08 × 0.08	0.08 × 0.08 × 0.08	0.08 × 0.08 × 0.04	0.10 × 0.08 × 0.08
F(000)	832	1920	2208	608	1648	960
θ range, deg.	2.08 to 30.26	2.1 to 27.6	2.1 to 27.5	3.5 to 27.5	2.12 to 27.65	3.0 to 27.5
no. of rflns collected	3319	37218	18295	1465	11797	13007
no. of unique rflns	2895	5679	5476	855	1706	3674
R_{int}	0.022	0.054	0.056	0.020	0.053	0.086
no. of rflns ($I > 2\sigma(I)$)	2895	5101	4427	783	1484	2731
$R1$ ($I > 2\sigma(I)$)	0.0539	0.0359	0.0452	0.0455	0.0324	0.0516
$wR2$ (all data)	0.173	0.095	0.121	0.135	0.0749	0.103
GOF on F^2	1.244	1.081	1.172	1.348	1.185	1.085
completeness	0.971	0.996	0.997	0.985	0.995	0.994

commands because of their close proximity to the atoms of the major component.

Computational Details. The structures considered in these studies were optimized using the ADF DFT package, version 2012.01).[17−19] The adiabatic local density approximation (ALDA) was used for the exchange-correlation kernel[20,21] and the differentiated static LDA expression was used with the Vosko−Wilk−Nusair parametrization.[22] Calculations of model geometries were gradient-corrected with the exchange and correlation functionals proposed in 1991 by Perdew and Wang (PW91).[23,24] The structures were refined using a triple-ζ all-electron basis set with two polarization functions and applying the zeroth order regular approximation (ZORA)[25−29] formalism with the specially adapted basis sets. The validity of all optimized structures was confirmed by calculating frequencies, and all calculated energies have been corrected for zero point energies.

Synthesis of 1,4-$(H_2C)_2(P^tBu)_4$ (1). A solution of $[H_2C(PCl_2)_2]$ (1.866 g, 8.57 mmol) in 40 mL of THF was cooled to −78 °C prior to the addition of a solution of ^{t}BuMgCl (36.0 mL of a 1.0 M solution in THF) dropwise via syringe. The reaction mixture was stirred for 1 h at −78 °C, 1/2 h at 23 °C, and finally heated for 6 h at 50 °C. The solvent was removed under vacuum, before redissolution in Et_2O and filtration through a PTFE disk. After removal of the solvent, the yellow solid product was extracted with about 80 mL of argon-sparged MeOH; decantation of the methanolic solution left a white powder (1.082 g, 2.84 mmol, 66%, calculated from $[H_2C(PCl_2)_2]$). This product could be further purified by sublimation at 45 °C under dynamic vacuum to give **1** in 53% yield. Crystals suitable for single-crystal diffraction were grown by slow evaporation of a concentrated solution in anhydrous hexanes. Mp 141−142 °C (sealed tube). Elemental analysis calcd (%) for $C_{18}H_{40}P_4$ (380.41): C 56.83, H 10.60; found: C 56.85, H 10.76. $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 23 °C): δ −25.9 (s). ^{1}H NMR (toluene-d_8, 23 °C): δ 1.87 (m, 4H, CH_2), 1.24 (t, 36H, CH_3). $^{1}H\{^{31}P\}$ NMR (toluene-d_8, 23 °C): δ 1.87 (s, 4H, CH_2), 1.24 (s, 36H, CH_3). ^{13}C NMR (toluene-d_8, 23 °C): δ 9.0 (t, 2C, CH_2), 29.9 (t, 12C, CH_3), 30.7 (s, 4C, $\underline{C}CH_3$). MS (CI): *m/z* 381.22 (MH^+, 100). MS (EI): *m/z* 380.22 (M^+, 5), 323.15 (M^+-^{t}Bu, 100), 267.11 (M^+-2^{t}Bu, 32), 211.07 (M^+-3^{t}Bu, 10), 154.97 (M^+-4^{t}Bu, 8).

Synthesis of 1,4-$(H_2C)_2(P^tBu)_4S$ (2a). A solution of **1** (0.150 g, 0.394 mmol) in 7.0 mL of toluene was cooled to −78 °C prior to dropwise addition of a cold solution of elemental sulfur (0.009 g, 0.281 mmol) in toluene (3.0 mL) with vigorous stirring. The reaction mixture was left in the cold bath for 8 h and then the bath was allowed to warm slowly to room temperature (ca. 30 h). A $^{1}P\{^{1}H\}$ NMR spectrum of the crude reaction solution showed a mixture of **2a**, **1**, and **3a**, in a 4:4:1 ratio. $^{31}P\{^{1}H\}$ NMR (toluene, 23 °C): δ 61.2 (dd, 1P, P2, $^{1}J(^{31}P,^{31}P) = -312$ Hz, $^{2}J(^{31}P,^{31}P) = 15$ Hz), −9.9 (dd, 1P, P5, $^{1}J(^{31}P,^{31}P) = -218$ Hz, $^{2}J(^{31}P,^{31}P) = 9$ Hz), −24.0 (ddd, 1P, P6, $^{1}J(^{31}P,^{31}P) = -218$ Hz, $^{2}J(^{31}P,^{31}P) = 15$ Hz, $^{3}J(^{31}P,^{31}P) = -22$ Hz), −31.2 (ddd, 1P, P3, $^{1}J(^{31}P,^{31}P) = -312$ Hz, $^{2}J(^{31}P,^{31}P) = 9$ Hz, $^{3}J(^{31}P,^{31}P) = -22$ Hz).

Synthesis of 1,4-$(H_2C)_2(P^tBu)_4Se$ (2b). A solution of **1** (0.100 g, 0.262 mmol) in 6.0 mL of toluene was cooled to −78 °C prior to transfer by cannula to a cold slurry of elemental selenium (0.019 g, 0.236 mmol) in 4.0 mL of toluene with vigorous stirring. The reaction mixture was left in the dry ice-acetone bath for 48 h and then allowed to reach room temperature slowly. A $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture showed about 90% conversion to **2b**. Upon removal of the solvent, the crude sample was taken up in hexanes. Decantation of the supernatant from insoluble material and removal of solvent under vacuum provided **2b** as a white powder (0.094 g, 0.205 mmol, 78%, calculated from **1**) mp 93−97 °C (sealed tube)]. The presence of <5% of **1** in this powder was evident from the ^{31}P NMR spectrum; this impurity could not be removed by further recrystallization. $^{31}P\{^{1}H\}$ NMR (toluene, 23 °C): δ 45.5 (dd, 1P, P2, $^{1}J(^{31}P,^{31}P) = -321$ Hz, $^{2}J(^{31}P,^{31}P) = 11$ Hz, $^{3}J(^{31}P,^{31}P) = -2$ Hz, $^{1}J(^{31}P,^{77}Se) = 700$ Hz), −9.1 (dd, 1P, P5, $^{1}J(^{31}P,^{31}P) = -216$ Hz, $^{2}J(^{31}P,^{31}P) = 8$ Hz, $^{3}J(^{31}P,^{31}P) = -2$ Hz), −23.7 (ddd, 1P, P6, $^{1}J(^{31}P,^{31}P) = -216$ Hz, $^{2}J(^{31}P,^{31}P) = 11$ Hz, $^{3}J(^{31}P,^{31}P) = -24$ Hz), −28.7 (ddd, 1P, P3, $^{1}J(^{31}P,^{31}P) = -321$ Hz, $^{2}J(^{31}P,^{31}P) = 8$ Hz, $^{3}J(^{31}P,^{31}P) = -24$ Hz). ^{77}Se NMR (toluene-d_8, 23 °C): δ −238.1 (d, 1Se, $^{1}J(^{77}Se,^{31}P) = 700$ Hz). MS (CI): *m/z* 461.3 (MH^+, 5), 381.3 (MH^+-Se, 100). HRMS (CI, %): *m/z* Found: 461.1309 (MH^+, 100) Calculated 461.1324. ^{1}H NMR (toluene-d_8, 23 °C): δ 0.95 (d, 9H, P3C$(C\underline{H}_3)_3$, $^{3}J(^{1}H,^{31}P) = 12$ Hz), 1.36 (d, 9H, P2C$(C\underline{H}_3)_3$, $^{3}J(^{1}H,^{31}P) = 17$ Hz), 1.87 (m, 2H, P5C$\underline{H}_2$), 2.68 (m, 2H, P2C$\underline{H}_2$). A small amount of hexanes, which remained in the sample even after a number of days under dynamic vacuum, partially obscured two of the $C(CH_3)_3$ resonances.

Synthesis of 1,4-$(H_2C)_2(P^tBu)_4S_2$ (3a). A cold solution of **1** (0.098 g, 0.258 mmol) in 5.0 mL of toluene (−78 °C) was transferred by cannula to a flask containing an excess of elemental sulfur (0.021g, 0.639 mmol) in 2.0 mL of toluene. After 1h at low temperature, the reaction mixture was stirred in an ice bath overnight, at which time the reaction mixture was stirred for an additional 30 h at room temperature. A $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture showed complete conversion to **3a**. Upon removal of solvent, the product was isolated as a pale yellow powder, which was purified by fractional sublimation of excess sulfur (yield after sublimation 0.110 g, 0.247 mmol, 96%, calculated from **1**). Crystals suitable for single-crystal X-ray diffraction were isolated from slow diffusion of hexanes into a concentrated solution of **3a** in toluene. Mp 190−195 °C (sealed tube). Spectroscopic data for the powder and crystals were identical. $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 23 °C): δ 63.0 (dd, 2P, P2/P5, $^{1}J(^{31}P,^{31}P) = -296$ Hz, $^{2}J(^{31}P,^{31}P) = 17$ Hz, $^{3}J(^{31}P,^{31}P) = -1$ Hz), −26.7 (dd, 2P, P3/P6, $^{1}J(^{31}P,^{31}P) = -296$ Hz, $^{2}J(^{31}P,^{31}P) = 17$ Hz, $^{3}J(^{31}P,^{31}P) = -42$ Hz). ^{1}H NMR (toluene-d_8, 23 °C): δ 1.15 (d, 18H, P3/P6C$(C\underline{H}_3)_3$, $^{2}J(^{1}H,^{31}P) = 14$ Hz), 1.36 (d, 18H, P2/P5C$(C\underline{H}_3)_3$, $^{2}J(^{1}H,^{31}P) = 16$ Hz), 3.04 (m, 4H, CH_2). ^{13}C NMR (toluene-d_8, 23 °C): δ 26.1 (dd, 2C, P3/P6$\underline{C}CH_3$), 26.2 (dd, 2C, P2/P5$\underline{C}(CH_3)_3$), 27.4 (dd, 6C, P3/P6C$(\underline{C}H_3)_3$), 28.3 (dd, 6C, P2/P5C$\underline{C}H_3$), 30.7 (s, 2C, CH_2). MS (CI): *m/z* 445.3 (MH^+, 100). HRMS (CI, %): *m/z* Found: 445.1608 (MH^+, 90) Calculated 445.1600.

Synthesis of 1,4-$(H_2C)_2(P^tBu)_4Se_2$ (3b). A cold (−78 °C) solution of **1** (0.100 g, 0.263 mmol) in 10 mL of toluene was transferred by cannula to a flask containing a cold slurry of elemental selenium (0.043 g, 0.552 mmol) in 5.0 mL of toluene. After 3 h at low temperature, the reaction mixture was stirred in an ice bath for 1 h and then at room temperature for an additional 6 h. A $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture showed complete conversion to **3b**. Filtration through a PTFE membrane was sufficient to remove unreacted selenium. Upon removal of solvent, the product was isolated as a white powder (0.090 g, 0.167 mmol, 64%, calculated from **1**). Crystals suitable for single-crystal X-ray diffraction were isolated from slow diffusion of hexanes into a concentrated solution of **3b** in toluene. Mp 117−120 °C (sealed tube). Spectroscopic data for the powder and crystals were identical. $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 23 °C): δ 48.3 (dd, 2P, P2/P5, $^{1}J(^{31}P,^{31}P) = -304$ Hz, $^{2}J(^{31}P,^{31}P) = 16$ Hz, $^{3}J(^{31}P,^{31}P) = -3$ Hz, $^{1}J(^{31}P,^{77}Se) = 715$ Hz), −24.5 (dd, 2P, P3/P6, $^{1}J(^{31}P,^{31}P) = -304$ Hz, $^{2}J(^{31}P,^{31}P) = 16$ Hz, $^{3}J(^{31}P,^{31}P) = -43$ Hz). ^{1}H NMR (toluene-d_8, 23 °C): δ 1.13 (d, 18H, P3/P6C$(C\underline{H}_3)_3$), $^{2}J(^{1}H,^{31}P) = 14$ Hz), 1.37 (d, 18H, P2/P5C$(C\underline{H}_3)_3$), $^{2}J(^{1}H,^{31}P) = 17$ Hz), 3.12 (m, 4H, CH_2). ^{13}C NMR (toluene-d_8, 23 °C): δ 26.2 (dd, 2C, P3/P6$\underline{C}(CH_3)_3$), 26.3 (dd, 2C, P2/P5$\underline{C}(CH_3)_3$), 27.8 (dd, 6C, P3/P6C$(\underline{C}H_3)_3$), 28.2 (dd, 6C, P2/P5C$(\underline{C}H_3)_3$), 30.7 (s, 2C, CH_2). ^{77}Se NMR (toluene-d_8, 23 °C): δ −258.1 (d, 1Se, $^{1}J(^{77}Se,^{31}P) = 723$ Hz. MS (CI): *m/z* 541.3 (MH^+, 30), 461.3 (MH^+-Se, 95), 381.3 (MH^+-2Se, 30). HRMS (CI, %): *m/z* Found: 541.0472 (MH^+, 100) Calculated 541.0489.

Synthesis of 1-(H_2C)-2,4-$(P^tBuS)_2$-3-S (4a). To a mixture of **1** (0.060 g, 0.158 mmol) and elemental sulfur (0.036g, 1.123 mmol) was added 6.0 mL of toluene, prior to heating the solution to reflux with stirring. Occasionally, an aliquot was removed and a $^{31}P\{^{1}H\}$ NMR spectrum was recorded to monitor the progress of the reaction. As the reaction proceeded, these aliquots revealed a complex mixture of products in the $^{31}P\{^{1}H\}$ NMR spectrum, which after 111 h gave rise to one intense singlet. At this time the solution was allowed to cool to room temperature, and the solvent was removed under vacuum. The product was isolated as a pale yellow powder, and unreacted sulfur was removed by fractional sublimation (yield after sublimation 0.075 g, 0.262 mmol, 83%, calculated from **1**). Although the complete removal of sulfur was not possible, the NMR spectra showed the product to be free of other impurities. $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 23 °C): δ 63.4 (s, 2P). ^{1}H NMR (toluene-d_8, 23 °C): δ 1.15 (d, 18H, CH_3, $^{2}J(^{1}H,^{31}P) = 21$ Hz), 3.13 (t, 2H, CH_2, $^{2}J(^{1}H,^{31}P) = 11$ Hz). ^{13}C NMR (toluene-d_8, 23 °C): δ 24.3 (s, 2C, C$(\underline{C}H_3)_3$), 30.7 (s, 2C, $\underline{C}(CH_3)_3$), 45.6 (t, 2C, CH_2, $^{2}J(^{13}C,^{31}P) = 31$ Hz). MS (CI): *m/z* 287.0 (MH^+, 100). HRMS (CI, %): *m/z* Found: 286.0195 (MH^+, 100) Calculated 286.0202. Crystals suitable for single-crystal X-ray diffraction were isolated from slow diffusion of hexanes into a concentrated solution of **4a** in toluene.

Spectroscopic Data for 1-(H_2C)-2,5-$(P^tBuS)_2$-3,4-S_2 (5a). Compound **5a** was only observed as a minor product in the synthesis of **4a**. Although the relative concentration of **5a** could be increased by using a large excess of sulfur, the conditions necessary to synthesize **5a** as the major product were not found. $^{31}P\{^{1}H\}$ NMR (toluene-d_8, 23 °C): δ 116.2 (s, 2P). ^{1}H NMR (toluene-d_8, 23 °C): δ 1.15 (d, 18H, CH_3, $^{2}J(^{1}H,^{31}P) = 21$ Hz), 2.89 (t, 2H, CH_2, $^{2}J(^{1}H,^{31}P) = 9$ Hz). MS (CI): *m/z* 319.0 (MH^+, 45).

Synthesis of 1-(H_2C)-2,5-$(P^tBuSe)_2$-3-Se (4b) and 1-(H_2C)-2,5-$(P^tBuS)_2$-3,4-Se_2 (5b). To a mixture of **1** (0.150 g, 0.394 mmol) and elemental selenium (0.186g, 2.356 mmol) was added 16.0 mL of toluene, prior to heating the solution to reflux with stirring. After 26 h the gray slurry had given rise to an opaque brown solution, at which time the solution was cooled to room temperature and the solids were allowed to settle. A $^{31}P\{^{1}H\}$ NMR spectrum of the supernatant showed

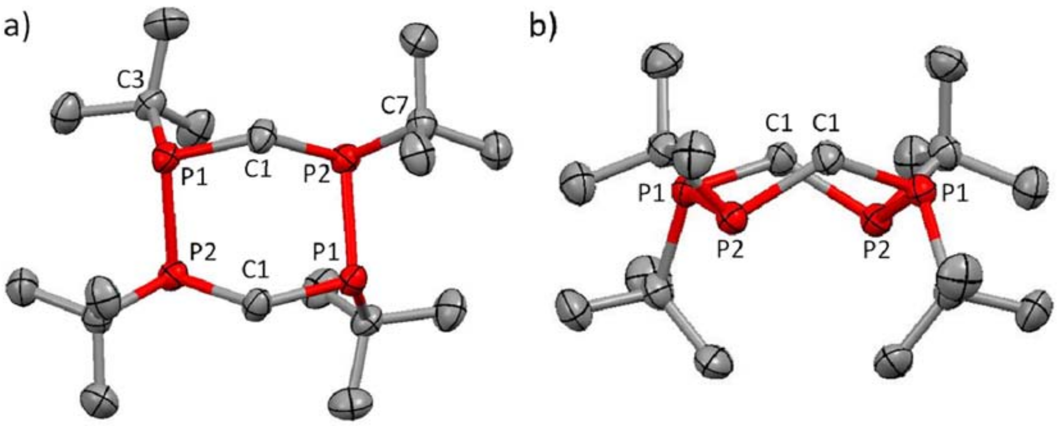


Figure 1. Crystal structure of 1,4-$(H_2C)_2(P^tBu)_4$, **1**, a) as viewed from the top, and b) from the side. Thermal ellipsoids are shown at 50% probability and hydrogen atoms have been omitted for clarity.

a mixture of two products, which were identified as **4b** and **5b**. As the solution cooled, **4b** fractionally crystallized, and the orange supernatant was decanted. In this manner, **4b** was isolated as a yellow crystalline solid (0.077 g, 0.180 mmol, 23%, calculated from **1**). Crystals suitable for single-crystal X-ray diffraction were isolated by slow cooling of a hot solution in toluene. Mp 284−286 °C. Elemental analysis calcd (%) for $C_9H_{20}P_2Se_3$ (427.07): C 25.30, H 4.70; found: C 25.85, H 4.13. $^{31}P\{^1H\}$ NMR (toluene-d_8, 23 °C): δ 36.6 (s, 2P, $^1J(^{31}P, ^{77}Se_{(exo)})$ = 807 Hz, $^1J(^{31}P, ^{77}Se_{(endo)})$ = 225 Hz, $^2J(^{31}P, ^{31}P)$ = 13 Hz)^{1}H NMR (toluene-d_8, 23 °C): δ 1.13 (d, 18H, CH_3, $^2J(^1H,^{31}P)$ = 22 Hz), 3.76 (t, 2H, CH_2, $^2J(^1H,^{31}P)$ = 11 Hz). ^{13}C NMR (toluene-d_8, 23 °C): δ 24.6 (s, 2C, CH_3), 30.0 (s, 2C, $\underline{C}CH_3$), 46.7 (t, 2C, CH_2, $^1J(^{13}C,^{31}P)$ = 22 Hz). ^{77}Se NMR (toluene-d_8, 23 °C): δ −47.6 (d, $Se_{(exo)}$, $^1J(^{77}Se,^{31}P)$ = 807 Hz,), +475.5 (t, $Se_{(endo)}$, $^1J(^{77}Se,^{31}P)$ = 224 Hz,). MS (MALDI, HCCA): *m/z* 428.9 (MH$^+$, 4000 au), 451.7 (M$^+$+Na, 2000 au)

After repeated concentration and decantation of the orange supernatant, **5b** was formed as orange crystals suitable for X-ray diffraction (0.113 g, 0.256 mmol, 32% calculated from **1**).

Mp 246−248 °C. $^{31}P\{^1H\}$ NMR (toluene-d_8, 23 °C): δ 88.7 (s, 2P, $^1J(^{31}P,^{77}Se_{(exo)})$ = 764 Hz, $^1J(^{31}P, ^{77}Se_{(endo)})$ = 372 Hz, $^2J(^{31}P, ^{77}Se_{(endo)})$ = 9 Hz, $^2J(^{31}P, ^{31}P)$ = 41 Hz). ^{1}H NMR (toluene-d_8, 23 °C): δ 1.28 (d, 18H, CH_3, $^2J(^1H,^{31}P)$ = 20 Hz), 3.59 (t, 2H, CH_2, $^2J(^1H,^{31}P)$ = 9 Hz). ^{13}C NMR (toluene-d_8, 23 °C): δ 25.8 (s, 2C, CH_3), 30.4 (s, 2C, $\underline{C}CH_3$), 46.7 (t, 2C, CH_2, $^1J(^{13}C,^{31}P)$ = 9 Hz). mp 284−286 °C. ^{77}Se NMR (toluene-d_8, 23 °C): δ −131.5 (dd, $Se_{(exo)}$, $^1J(^{77}Se,^{31}P)$ = 736 Hz, $^3J(^{77}Se,^{31}P)$ = 9 Hz), +410.5 (dd, $Se_{(endo)}$, $^1J(^{77}Se,^{31}P)$ = 371 Hz, $^2J(^{77}Se,^{31}P)$ = 9 Hz). MS (MALDI, HCCA): *m/z* 508.7 (MH$^+$, 4000 au), 531.7 (MH$^+$+Na, 4000 au). In solution **5b** decomposes to **4b** with the extrusion of elemental selenium. Consequently, a sample with sufficient purity for elemental analysis could not be isolated.

■ RESULTS AND DISCUSSION

Synthesis, Spectroscopic Characterization, and Crystal Structure of 1. The synthetic method used to generate **1** employed modifications of the Grignard method, that is, the reaction of $H_2C(PCl_2)_2$ with ^{t}BuMgCl, which provided an optimum yield of 66%. Although this yield is lower than the literature value of 90%,[12e] these modifications provided a sample of very high purity, which proved to be essential for careful investigation of the chalcogenation reactions. The identity of **1** was first determined through a combination of mass spectrometric (EI and CI) techniques, and NMR (^{31}P and ^{1}H) spectroscopy. The CI mass spectrum shows the molecular ion at 381.23 *m/z*. In the EI mass spectrum the molecular ion as well as four fragment ions appear, each corresponding to a loss of one, two, three, or all four ^{t}Bu groups, respectively. The observed melting point range of 141−142 °C is consistent with the value reported in the literature.[12c] The singlet at −25.9 ppm observed in the $^{31}P\{^1H\}$ NMR spectrum indicates equivalence of the phosphorus atoms.[30] In the $^1H\{^{31}P\}$ NMR two singlets are observed, corresponding to methyl (δ = 1.24 ppm) and methylene (δ = 1.87 ppm) protons (cf. 1.37 and 2.02 ppm, respectively, in benzene-d_6) with the appropriate relative intensities; in a nondecoupled spectrum, apparent peak multiplicities (triplet and quintet, respectively) are indicative of higher-order effects.

X-ray quality crystals of **1** were grown by slowly cooling a concentrated hexanes solution, and the crystal structure is illustrated in Figure 1. Selected bond lengths and angles for **1** are provided in Table 3. The 1,4-C_2P_4 ring, **1**, crystallizes in the monoclinic space group *C*2/*c* with four molecules in the unit cell. The six-membered ring exhibits a twist-boat geometry with the four phosphorus atoms in the *pseudo*-plane which is twisted by 28.6°. The ^{t}Bu groups bound to P1 occupy axial positions, while those on P2 are equatorial. The transannular distances [(P2···P2) = 3.7367(7) and (P1···P1) = 4.0044(9) Å] are longer than the sum of van der Waals radii (3.60 Å).[31]

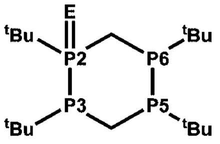
Of the reported C_2P_4 ring systems exhibiting this connectivity only 1,4-$(H_2C)_2(PPh)_4$ has been crystallographically characterized.[12d,32] Unlike **1**, the tetraphenyl derivative of this six-membered ring adopts a highly folded chair conformation in the solid state.[12d] The reported transannular P···P distance of 3.75 Å is on the order of those observed in **1**, and the bond lengths and angles are similar [*d*(P−P) = 2.194(4), *d*(P−C) = 1.915(9), 1.89(1) Å, cf. *d*(P−P) = 2.211(1), *d*(P−C) = 1.857(3), 1.888(2) Å in **1**].

Monochalcogenides 1,4-$(H_2C)_2(P^tBu)_3(PE^tBu)$ (E = S, Se): Synthesis and NMR Spectra. Initial studies of the reactions of **1** with sulfur and selenium were performed by using first 1 equiv and then 2 equiv of chalcogen at low temperatures, to determine the degree to which mono- or disubstitution could be controlled. These experiments involved mixing the reagents as cold solutions or slurries (−78 °C) in toluene with stirring, prior to slowly warming the reaction mixture to room temperature. With selenium, these conditions were effective in achieving control, and resulted in a new species **2b** exhibiting four distinct resonances in the $^{31}P\{^1H\}$ NMR spectrum, together with a small amount of **1**. These four phosphorus resonances have equal integrated intensities and are composed of doublets of doublets centered at 45.6 (P2) and −9.1 (P5) ppm, together with doublets of doublets of doublets at −23.8 (P6) and −28.8 (P3) ppm, respectively.[33] A graphical representation of this spectrum and a spectrum modeled using gNMR are shown in Figure 2.

Although the presence of four separate resonances provides sufficient evidence to suggest monosubstitution, a significant

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 1, 2b, 3a, 3b

	1	3a	3b
Bond Lengths (Å)			
P1−C1	1.844(2)	1.835(2)	1.832(4)
C1−P2	1.857(3)	1.865(2)	1.867(4)
P1−C3	1.879(3)	1.869(2)	1.872(4)
P2−C7	1.888(2)	1.897(2)	1.902(4)
P1−P2	2.2108(8)		
P2−P3		2.2255(7)	2.223(2)
P3−C2		1.832(2)	1.830(4)
C2−P4		1.868(2)	1.870(4)
P4−P1		2.2174(5)	2.216(1)
P3−C11		1.866(2)	1.874(4)
P4−C15		1.898(2)	1.902(4)
P1−E1		1.9619(7)	2.116(1)
P3−E2		1.9621(7)	2.114(1)
Bond Angles (deg)			
P1−C1−P2	122.8(1)	120.27(9)	120.3(2)
C1−P2−P1	100.11(8)		
P2−P1−C1	103.06(8)		
C1−P2−P3		94.70(6)	94.6(1)
P2−P3−C2		100.37(6)	100.3(1)
P3−C2−P4		118.61(9)	118.4(2)
C2−P4−P1		94.32(5)	93.9(1)
C1−P2−C7	100.0(1)	99.60(9)	99.8(2)
C2−P3−C11		105.97(8)	106.0(2)
C2−P3−E2		110.45(6)	110.0(1)
C2−P4−C15		99.84(8)	100.0(2)
C1−P1−C3	106.3(1)	105.23(8)	108.4(1)
C1−P1−E1		109.69(6)	108.7(1)



2 a) E = S
b) E = Se

amount of information lies in the chemical shifts, as well as the observed P−P couplings. The shift in P2 from −25.9 to +45.6 ppm is immediately indicative of a formal oxidation of the phosphorus center, that is, a change from a three-coordinate to a four-coordinate environment. A similar change in the chemical shift (+28 ppm) was reported by Baudler for the addition of sulfur to the phosphorus atoms geminal to the endocyclic carbon of $(PhP)_4CH_2$.[9] The two $^1J_{PP}$ coupling constants in **2b** (−321 and −216 Hz) are consistent with similar couplings reported for adjacent three- and four-coordinate phosphorus atoms or two adjacent three-coordinate phosphorus centers, respectively.[34]

In contrast to these observations, a 1:1 molar ratio of sulfur and **1** consistently resulted in a distribution of three products, which were identified as monosulfide (**2a**), by analogy to **2b**, the starting material **1**, and a compound later identified as the disulfide **3a** (vide infra). This suggests that even at these low temperatures, disubstitution cannot be avoided with sulfur; this lack of selectivity may be due to the higher reactivity of *cyclo*-S_8 compared to that of gray selenium. Although less well-resolved, the $^{31}P\{^1H\}$ NMR spectrum of **2a** resembles that of **2b** with resonances at 61.2 (P2) and −9.9 (P5) together with doublets of doublets of doublets −24.0 (P6) and −31.2 (P3) ppm, respectively; the observed $^1J_{PP}$ couplings are about −312 and −218 Hz (see Supporting Information).[35]

Similar to the low-temperature reactions with sulfur, addition of either sulfur or selenium to **1** at room temperature resulted in a medley of the mono- and dichalcogenated species and unreacted **1**.

Dichalcogenides 1,4-$(H_2C)_2(P^tBu)_2(PE^tBu)_2$ (E = S, Se): Synthesis, NMR Spectra, and X-ray Structures of 3a, 3b.

The strong tendency of reactions with sulfur to yield a disubstituted derivative prompted a series of experiments designed to target the dichalcogenides specifically. In each case the reactions were performed as in monochalcogenation, that is, by using low temperatures and then slowly warming the reaction mixture to room temperature in the presence of 2 equiv of chalcogen. With sulfur, **1** was cleanly converted to the minor product previously observed in the monochalcogenation reactions. The AA′XX′ splitting pattern of the $^{31}P\{^1H\}$ NMR spectrum of the product **3a** appears as two doublets of doublets of equal integration (Figure 3a). The resonances centered at 63.1 and −26.8 ppm correspond to one four-coordinate and one three-coordinate phosphorus environment, respectively, and show significant higher-order effects, evident from the inequivalent peak intensities. In the case of selenium, a similar $^{31}P\{^1H\}$ NMR spectrum was obtained for **3b**, with resonances centered at 48.3 and −24.5 ppm (Figure 3b); the chemical shifts of these resonances are consistent with higher nuclear shielding caused by selenium, and the same higher order effects are visible. For each resonance (in both **3a** and **3b**) the $^1J_{PP}$ coupling constants are large (ca. 300 Hz) and equal, indicating addition of of the two chalcogen atoms on opposite sides of the ring). Reactions performed in the presence of an excess of chalcogen showed no changes in the $^{31}P\{^1H\}$ NMR spectra, suggesting that

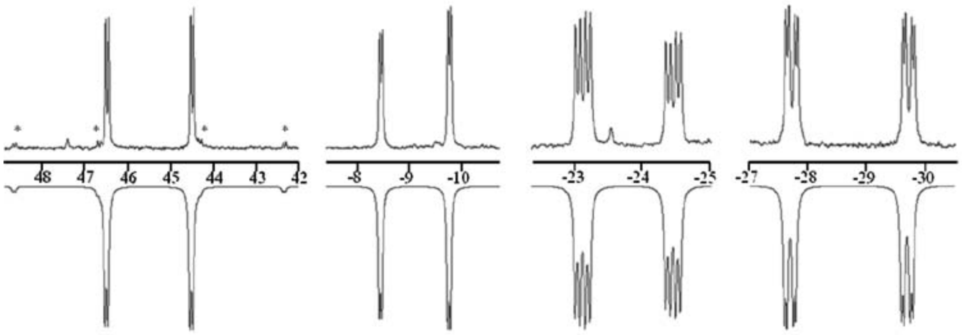


Figure 2. Experimental (upright) and simulated (inverted) expansions of the four resonances observed in the $^{31}P\{^1H\}$ NMR spectrum of **2b** (* denotes ^{77}Se satellites).[33] Parameters for the AGMX spin system are collected in Table 1.

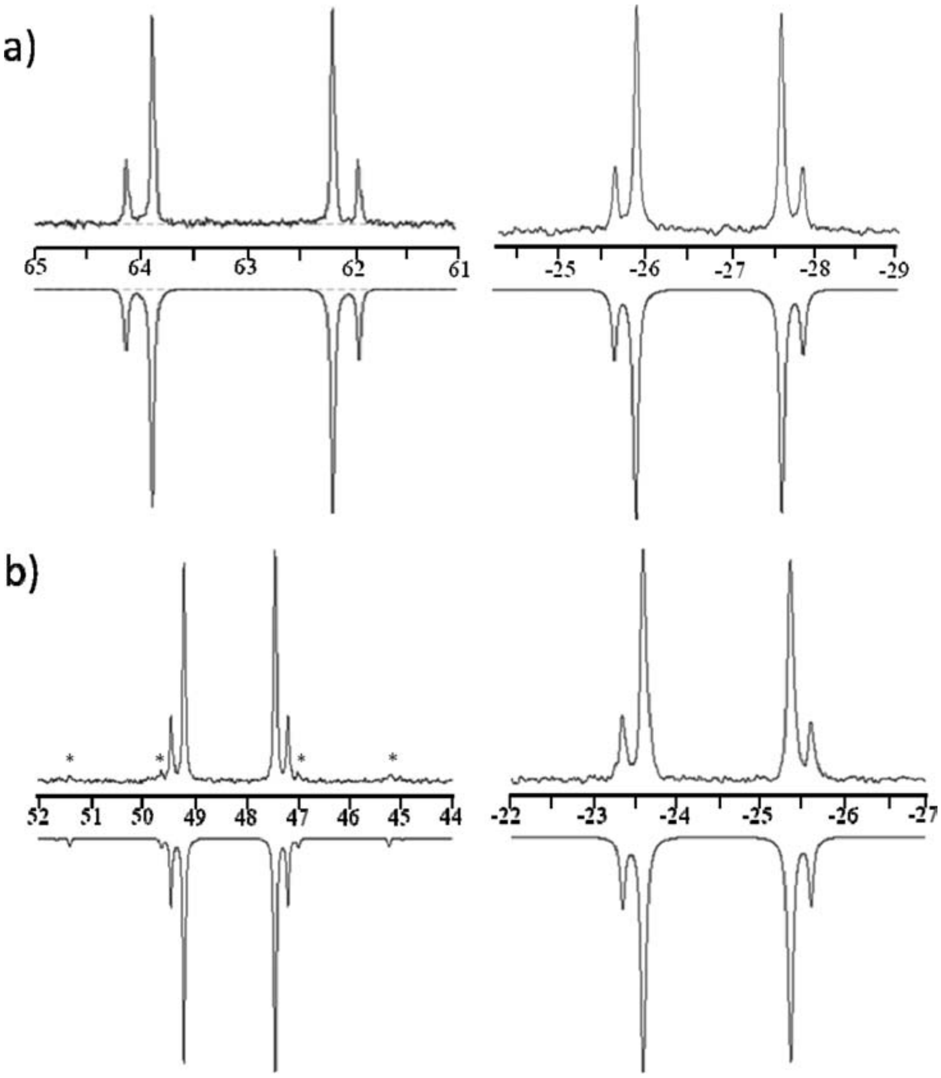


Figure 3. Experimental (upright) and simulated (inverted) expansions of the $^{31}P\{^1H\}$ NMR spectra of (a) **3a** and (b) **3b** (* denotes ^{77}Se satellites). Parameters for the AA′XX′ spin system are collected in Table 1.

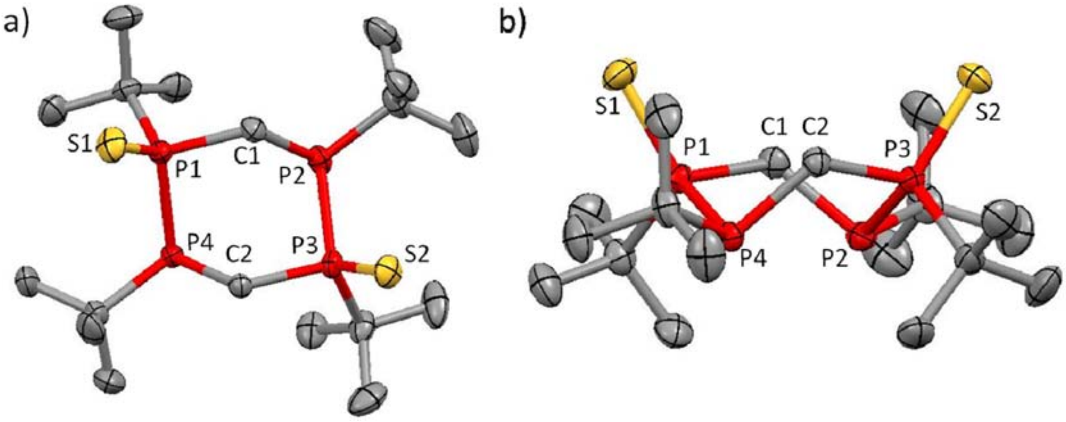


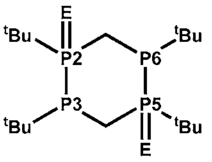
Figure 4. Crystal structure of 1,4-$(H_2C)_2$-2,5-$(P^tBuS)_2$-3,6-$(P^tBu)_2$, **3a**, (a) as viewed from the top, and (b) from the side. Thermal ellipsoids are shown at 50% probability, and hydrogen atoms have been omitted for clarity.

only dichalcogenation is observed and that a single isomer is preferentially formed at ambient temperatures.

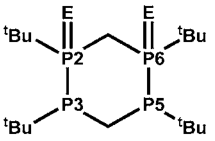
The identities of **3a** and **3b** were revealed to be 2,5-disubstituted isomers by single crystal X-ray diffraction. High-quality crystals were obtained by layering a concentrated toluene solution of **3a** or **3b** with hexanes. The crystals are isostructural and the molecular structure of **3a**, as a representative example, is illustrated in Figure 4. Selected bond lengths and bond angles for **3a** and **3b** are provided in Table 3. The dichalcogenated 1,4-C_2P_4 rings, **3a** and **3b**, crystallize in the orthorhombic space group

Pbca with four and eight molecules in the unit cell, respectively. Similar to **1**, in both cases the six-membered C_2P_4 ring exhibits a twist-boat geometry, but the *pseudo*-plane in both **3a** and **3b** is instead defined by the two four-coordinate phosphorus centers and two carbon atoms (the *pseudo*-planes are twisted by 18.29° and 17.94° for **3a** and **3b**, respectively). All ^{t}Bu groups reside in equatorial positions, and the chalcogens are axial. The terminal P−S bond lengths [1.9619(7), 1.9621(7)] in **3a** are similar to those reported for the disulfide of the $(PPh)_4CH_2$ ring (1.928(6) and 1.935(6) Å),[36] while the *d*(P−Se) values of 2.116(1) and 2.114(1) Å in **3b** are comparable to $^{t}Bu_3PSe$ (2.1326(4) Å).[37] All transannular P···P distances are longer than the sum of van der Waals radii[31] (3.3683(6) Å and 3.356(1) Å for three-coordinate P centers, and 3.9265(6) and 3.917(1) for four-coordinate P centers of **3a** and **3b**, respectively).

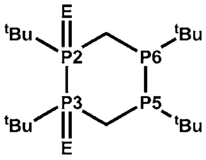
Calculated Structures of Dichalcogenated Isomers. One of the more intriguing results of these studies was the predominant preference for the formation of 2,5-dichalcogenated isomers. To address this selectivity a computational study was undertaken in which the structures of the 2,5-, 2,6-, and 2,3-dichalcogenated isomers (**3**, **3′**, and **3″**) were optimized. With sulfur or selenium, the three isomers are close in energy, with the 2,5-isomer, **3**, being the most stable. However, **3′** has an energy only 12.6 kJ mol^{-1} higher for sulfur (cf. 13.6 kJ mol^{-1} for Se) and **3″** is 20.9 kJ mol^{-1} higher than **3** for sulfur (25.0 kJ mol^{-1} for Se). In view of these relatively small differences in energies, it would be reasonable to expect that at least one of the other isomers could be accessible in solution.



3



3′



3″

To gain a better understanding of the effect of chalcogenation on the electronic structure of the system, a fragment analysis was undertaken in which the changes in the electron density as a result of the substitution were modeled. With a single chalcogen at P2, there is a significant reorganization of electron density in the region surrounding the directly bound phosphorus atom (Figure 5a). As a result of this substitution, there is a notable decrease of electron density at P3, a very small change in P6, and no apparent change in P5.[33] Upon subsequent chalcogenation at P5 (Figure 5b), there is a marked decrease in electron density at P6. These results are also apparent in the calculated charges on the phosphorus atoms (Table 4), where substitution leads to an increased positive charge on all centers. Taken together, these data suggest that chalcogenation leads to an effective deactivation of nearby phosphorus sites toward further oxidation, consistent with the preference for 2,5-substitution and the lack of more highly chalcogenated products. These results also suggested, however, that at least the 2,6-isomers **3′** could be observed experimentally.

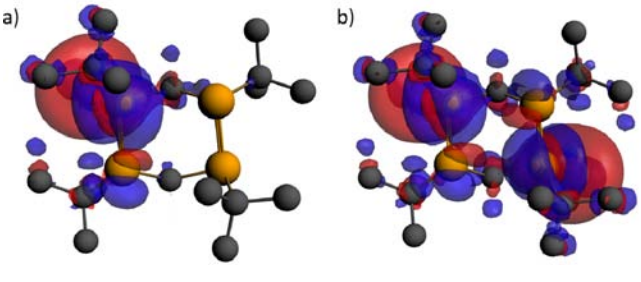


Figure 5. Reorganization of electron density upon (a) monochalcogenation at P2, and (b) dichalcogenation at P2 and P5. Regions in blue denote depletion of electron density, red denotes an increase.

Table 4. Changes in Hirshfeld Atomic Charges on Phosphorus Resulting from Mono- and Di-Chalcogenation at P2 and P5[33]

	S/Se	2S/2Se
P2	0.148/0.139	0.148/0.139
P3	0.018/0.023	0.017/0.022
P5	0.001/0.001	0.148/0.139
P6	0.005/0.004	0.017/0.022

Thermal Isomerism of 3a and 3b. In view of the greater lability of the P−Se bond compared to the P−S bond, the selenium derivative **3b** was chosen for initial investigations of thermal isomerism. Thus, a solution of **3b** in toluene-d$_8$ was heated to 60 °C in an attempt to drive the formation of other disubstituted isomers. In 1 h increments, a sample was removed from the hot solution, cooled rapidly to −78 °C to quench the reaction, and then a ^{31}P{^{1}H} NMR spectrum was recorded. After only 1 h of heating, new resonances centered at 55.3 and −12.0 ppm with equal integration appeared in the ^{31}P{^{1}H} NMR spectrum, which exhibited an AA′XX′ splitting pattern (Figure 6). The chemical shifts of these resonances are consistent with four- and three-coordinate phosphorus centers, respectively, and the observed equivalent $^{1}J_{PP}$ value of 307 Hz on each resonance indicates the formation of the 2,6-diselenide isomer, **3b′**.

Integration of the NMR spectrum showed about 4% conversion of **3b** to **3b′** after 1 h. The amount of **3b′** increases until 10 h reaction time, at which point **3b′** accounts for about 38% of the mixture. An additional 17 h heating resulted in only a slight growth of **3b′** to 40%. The experimental and gNMR-modeled spectra are shown in Figure 7. A small amount of a third species, which was identified as **2b**, became visible after 6 h. The proportion of **2b** increases with long reaction times (ca. 9% after 27 h), suggesting that the isomerism process likely occurs through a dissociative mechanism.

A similar experiment in which a solution of the sulfur analogue **3a** was heated in toluene-d$_8$ at 60 °C revealed no discernible change after 20 h. However, elevation of the temperature to 95 °C initiated the isomerism, yielding results consistent with those for **3b**. The ^{31}P{^{1}H} NMR spectrum of the new isomer **3a′** exhibited an AA′XX′ pattern with two resonances centered at 66.9 and −20.2 ppm, corresponding to the four- and three-coordinate phosphorus centers, respectively, and ^{31}P−^{31}P couplings of 315 and 25 Hz. The isomerism process is much slower with sulfur than with selenium, likely because of the stronger P−S compared to the P−Se bond, and only 12% conversion is observed after heating for 22 h. The experimental and gNMR-modeled spectra of the AA′XX′ spin system are shown in Figure 8. In contrast to the selenium system, monosulfide, **2a**, was not detected under these conditions; this result is not surprising in light of the facile formation of the disulfide in the monochalcogenation experiments.

Reactions of 1 with Chalcogens at Elevated Temperatures: Formation and Spectroscopic Characterization of Four-and Five-membered Rings. In the initial attempts to

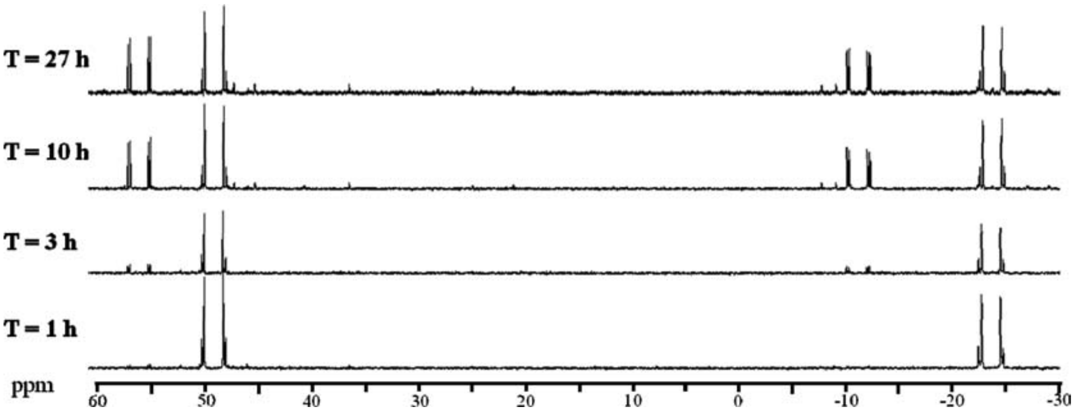


Figure 6. $^{31}P\{^{1}H\}$ NMR Spectra showing thermal isomerism of **3b** in toluene-d_8 at 60 °C.

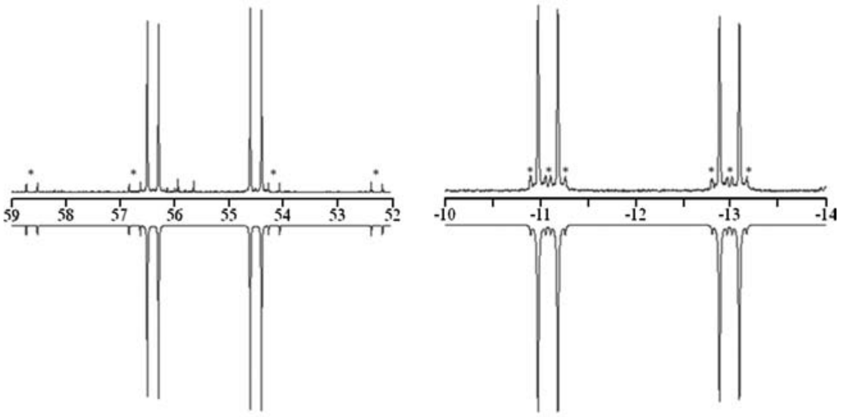


Figure 7. Expansions of the experimental (upright) and simulated (inverted) $^{31}P\{^{1}H\}$ NMR spectrum of **3b**′ (* denotes ^{77}Se satellites). Parameters for the AA′XX′ spin system are collected in Table 1.

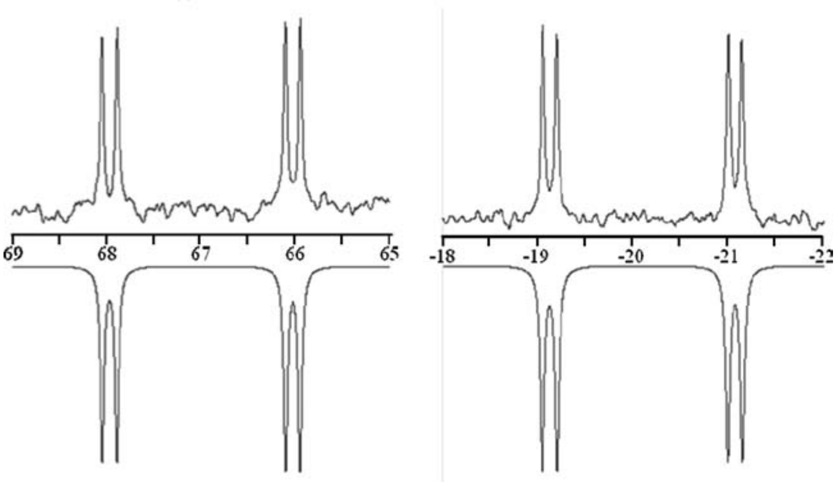
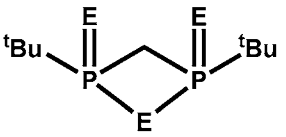


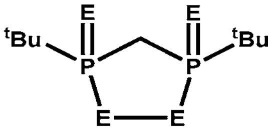
Figure 8. Experimental (upright) and simulated (inverted) expansions of the $^{31}P\{^{1}H\}$ NMR spectrum of **3a**′. Parameters for the AA′XX′ spin system are collected in Table 1.

further elucidate the outcome of reactions of **1** with large amounts of chalcogen, the C_2P_4 ring was treated with an excess of sulfur or selenium in boiling toluene, with the expectation that the elevated temperature would drive the reaction to the thermodynamically favorable products. In the case of selenium the use of 6 equiv of the chalcogen gave a mixture of two compounds after 24 h, as indicated by singlets centered at 88.7 and 38.3 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum in toluene-d_8. The chemical shifts of these resonances suggested four-coordinate phosphorus centers although, based on that criterion, the environments are very different than those found previously in **2b**, **3b**, or **3b**′.

The presence of ^{77}Se satellites on each resonance allowed for a preliminary assignment of the products as the four-membered ring **4b** and the five-membered ring **5b** based on their $^{31}P\{^{1}H\}$ NMR spectra. The resonance centered at 38.3 ppm exhibits only two sets of ^{77}Se satellites with couplings of 809 and 225 Hz; the satellites resulting from the largest coupling are split by 14 Hz, because of magnetically inequivalent phosphorus centers. This resonance is attributed to the four-membered ring **4b**. By contrast, the resonance at 88.7 ppm exhibits three sets of ^{77}Se satellites with couplings of 764, 372, and 9 Hz, respectively, each of which is split into doublets with 40 Hz coupling again because of the magnetically inequivalent phosphorus atoms of the five-membered ring **5b**.



4 a) E = S
b) E = Se



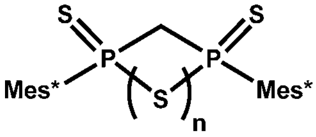
5 a) E = S
b) E = Se

Similar compounds with a phenyl substituent on each phosphorus atom have been previously reported. The five-membered PCPSeSe ring, synthesized in 94% yield from $H_2C(PhP)_4$ with selenium under similar conditions (Scheme 2) exhibits a singlet in the ^{31}P NMR at 43 ppm in $CDCl_3$, with analogous couplings to selenium of 775, 342, and 13 Hz.[38] The four-membered PCPSe analogue, prepared by treatment of the PCPSeSe ring with Me_3SiCN, shows a single resonance at −4.1 ppm in the ^{31}P NMR spectrum with 810 and 221 Hz couplings to ^{77}Se.[10] Although the resonances of the corresponding phenyl derivatives appear at much lower frequencies than those of **4b** and **5b**, the similar magnitudes of the reported coupling constants provide strong support for our identifications.

Reaction of **1** with about 7 equiv of sulfur in boiling toluene for 5 days resulted in a single major product (ca. 94%), which appears as a singlet in the $^{31}P\{^1H\}$ NMR spectrum in toluene-d_8 at 63.4 ppm, and a minor product showing a single resonance at 115 ppm (ca. 6%). The chemical shift of the intense resonance is similar to that of the four-coordinate phosphorus environment in **3a**, while the chemical shift of the minor product is significantly deshielded. The structures were tentatively assigned to the four-membered ring **4a** and the five-membered ring **5a**, based on analogy to the selenium analogues; the positions of these peaks are shifted to much higher frequency because of poor nuclear shielding of the phosphorus by sulfur as compared to selenium.

Similar sulfur-containing heterocycles have also been previously described from the reaction of sulfur with $H_2C(PhP)_4$ (Scheme 2).[10,38] The five-membered ring was reported to exhibit a resonance at 80.3 ppm in the ^{31}P NMR spectrum, measured in $CDCl_3$, while the signal for the four-membered ring appeared at 29.8 ppm. Additional reports of heterocycles containing these structural motifs involved the direct reaction of sulfur with a 1,3-diphosphosphaallene. The five-membered ring synthesized in this manner, **6** (n = 2), was observed in only trace amounts, and exhibits a singlet in the $^{31}P\{^1H\}$ NMR at 87.6 ppm in $CDCl_3$.[39] The *cis*- and *trans*-isomers of the four-membered analogue, **6** (n = 1), (based on the orientation of the S_{exo} atoms) were reported to have $^{31}P\{^1H\}$ NMR chemical shifts of 48.1 and 45.1 ppm, respectively, in $CDCl_3$.[39,40] Again, the reported resonances are shifted significantly from our findings likely because of the different substituents on phosphorus and solvent effects.

Although the minor product from the reaction with sulfur has not been unequivocally identified as **5a**, support for this composition was provided by the observation of an ion in the CI mass spectrum of crude **4a** with m/z = 419, which corresponds to $[M^+ + S]$ (M = **4a**). Additional resonances in the ^{1}H NMR spectrum of crude **4a**, attributable to ^{t}Bu and methylene environments, integrated to 6% relative to the corresponding resonances in **4a**. The relative integrations of these peaks correlate exactly with those observed in the $^{31}P\{^1H\}$ spectrum. Attempts to enhance the formation of **5a** by using a large excess of sulfur resulted in only a slight increase in the concentration of **5a** relative to **4a** (ca. 14% by $^{31}P\{^1H\}$ NMR).



6

Crystal Structures of 4a, 4b, and 5b. The identities of the selenium-containing products were confirmed as **4b** and **5b**, and the major sulfur product was shown to be **4a**, by single crystal X-ray diffraction. High-quality crystals of **4a** were obtained by layering a concentrated toluene solution with hexanes. In the case of selenium, cooling the reaction mixture resulted in the immediate precipitation of **4b** as small yellow-green crystals, which could be isolated by decantation; dissolution of these crystals in hot toluene, followed by slow cooling afforded yellow prisms of good quality. The decanted supernatant was subjected to several concentration and cooling cycles to remove all remaining **4b**, prior to crystallization of a mixture of orange

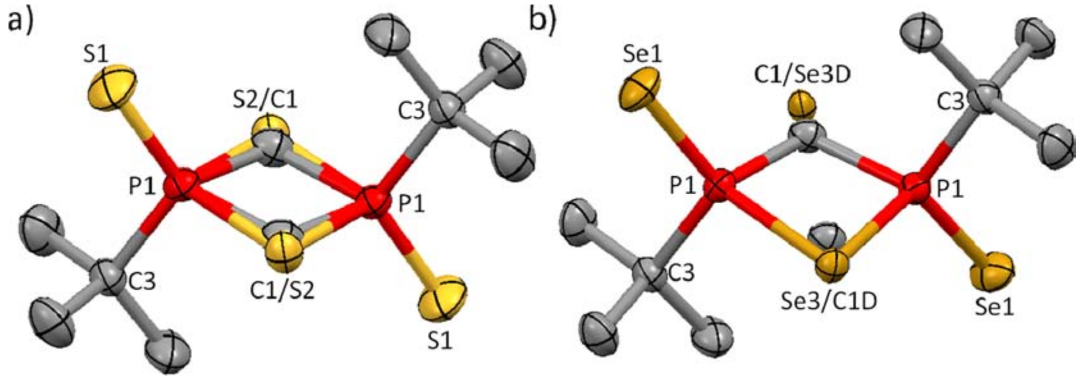


Figure 9. Crystal structures of the PCPE four-membered heterocycles where (a) E = S (**4a**), and (b) E = Se (**4b**). The positions of E_{endo} and C1 are disordered in the lattice. Thermal ellipsoids are shown at 50% probability, and hydrogen atoms have been omitted for clarity.

prisms and red needles, which were identified as **5b** and red selenium, respectively.

The molecular structures of **4a** and **4b** are isostructural, and they are represented graphically in Figure 9. Selected bond lengths and angles are provided in Table 5. In each case, the ^{t}Bu groups exhibit a *trans*- orientation relative to the four-membered ring defined by the PCPE unit. The sulfur derivative, **4a**, crystallizes in the orthorhombic space group *Cmca* with two molecules in the unit cell, while the selenium analogue **4b** adopts the space group *Ibca* with eight molecules in the unit cell. In each case there is substitutional disorder in the ring, based on the positions of the endocyclic chalcogen and carbon atoms (for **4a** this disorder is 46%, while in **4b** it accounts for only 5%).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 4a, 4b, 5b

	4a	4b	5b
	Bond Lengths (Å)		
P1−C1	1.85(1)	1.829(5)	1.831(6)
P1−C3	1.840(3)	1.854(4)	1.852(7)
P1−E1	1.927(1)	2.088(1)	2.097(2)
P1−E2	2.103(4)	2.2738(9)	2.250(2)
E2−E3			2.340(1)
E3−P2			2.226(2)
P2−E4			2.099(2)
P2−C7			1.853(7)
P2−C1			1.852(7)
	Bond Angles (deg)		
C1−P1−C3	109.4(6)	108.9(3)	105.2(6)
C1−P1−E1	117.9(6)	116.2(2)	115.6(2)
C1−P1−E2	91.4(6)	91.7(2)	106.2(2)
P1−E2−P1	81.4(2)	76.30(4)	
P1−C1−P1	95.8(9)	100.3(4)	
P1−E2−E3			97.09(5)
E2−E3−P2			97.02(5)
E3−P2−C1			104.5(2)
C1−P2−E4			113.8(2)
C1−P2−C7			107.5(3)
P1−C1−P2			119.9(4)

The endocyclic P−S and P−C bond distances in **4a** (2.103(4) and 1.85(1) Å, respectively) are within error of those reported for the related structure **6** (n = 1).[41] Similarly, the exocyclic P−S bond length (1.927(1) Å) is similar to the analogous bond distances in **6** (n = 1) (1.923(3), 1926(3) Å).[41] Although **6** (n = 1) exhibits a *cis*-orientation of exocyclic chalcogen atoms, and as a consequence lower symmetry, the structural parameters are directly comparable. The *endo*- and *exo*-cyclic P−Se bond lengths in **4b** (2.2738(9) and 2.088(1) Å, respectively) are also comparable to those reported for the related phenyl derivative (ca. 2.28 and 2.1 Å);[10] the endocyclic P−C bond length of 1.829(5) Å in **4b** is much shorter than those reported for the phenyl derivative (i.e., 2.078(7) and 2.164(7) Å in the independent molecules). The latter P−C bond lengths are substantially longer than typical single-bond values (1.87 Å);[42] this discrepancy may be related to the treatment of the positional disorder for the phenyl derivative.[10]

The molecular structure of **5b** is illustrated in Figure 10. Selected bond lengths and angles are summarized in Table 5. Similar to **4a** and **4b**, the ^{t}Bu groups exhibit a *trans*- orientation relative to the PCPSeSe ring. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The five-membered heterocycle exhibits an envelope shape, with a single selenium atom (Se2) residing 0.935(3) Å out of the plane. The endocyclic selenium atoms display weak contacts to a single exocyclic selenium (Se4) of an adjacent molecule (3.713(1) and 3.686(1) Å), which are only slightly shorter than the sum of van der Waals radii (3.80 Å).[31] All of the endocyclic bond lengths, as well as the exocyclic P−Se bond distances (Table 5), are within error of those reported for the corresponding phenyl derivative.[38]

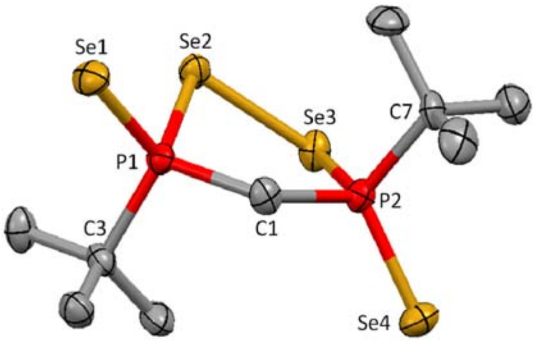


Figure 10. Crystal structure of the PCPSeSe five-membered heterocycle **5b**. Thermal ellipsoids are shown at 50% probability, and hydrogen atoms have been omitted for clarity.

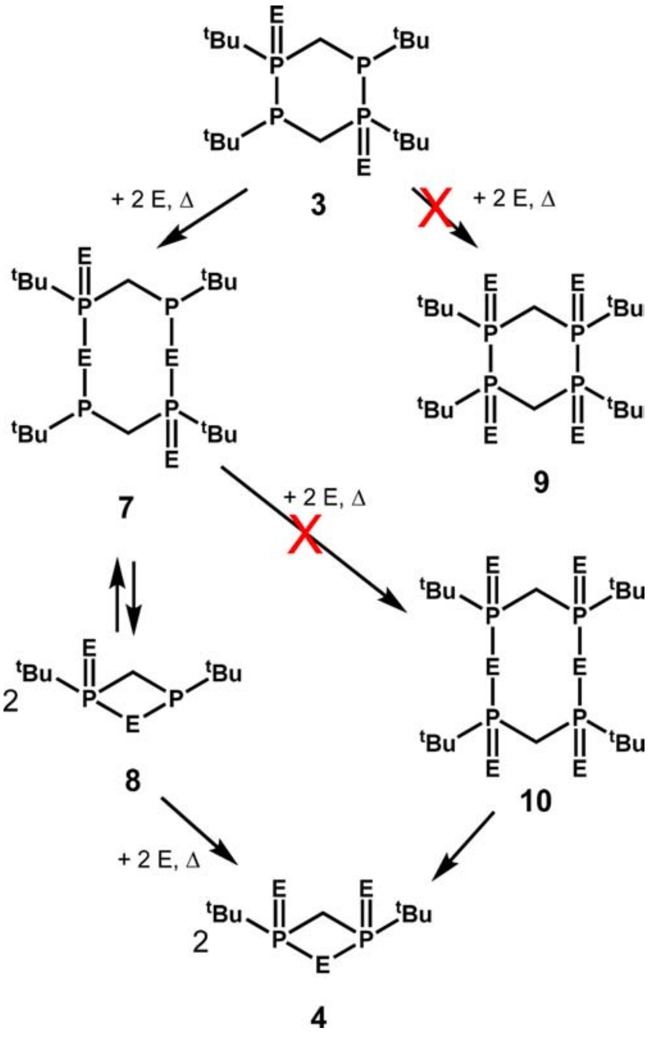
The heterocycle **5b** is unstable in solution over extended periods, and ring contraction to give **4b** with extrusion of red selenium occurs, even under an atmosphere of argon gas. A similar precipitation of elemental selenium was reported to take place for the corresponding phenyl derivative in the presence of oxygen by Woollins et al.;[38] however, the identities of the byproducts of that decomposition were not reported. Compound **4b** exhibits low solubility in organic solvents and crystallizes readily from solution; in toluene this four-membered ring showed no signs of rearrangement or decomposition after many days. By contrast, the analogous phenyl-substituted derivative (synthesized as shown in Scheme 2, followed by deselenation with Me_3SiCN) readily reforms the five-membered ring in solution, simultaneously yielding a mixture of rearranged products.[10] We note, however, that the reaction of the *C*-dimethylated derivative $Me_2C(PPh)_4$ with selenium preferentially forms a four-membered PCPSe ring, which exhibits stability in solution similar to that of **4b**.[38] Attempts to convert a pure sample of **4b** to **5b** by using an excess of elemental selenium in toluene, showed about 22% conversion after 37 h reflux. By contrast, the transformation of **4a** to **5a** under similar reaction conditions proved unsuccessful even after 132 h reflux. This result may be related to the relative lability of the P−Se bond, which allows for selenium insertion to expand the ring. The observation that **4a** and **5a** do not interconvert is surprising however, and suggests that they are each formed from two different intermediate species.

Proposed Scheme for Reactions of 1 with Chalcogens.

The experimental evidence from low and high-temperature reactions, and thermal isomerism experiments, has provided substantial information regarding the identities of the most stable products in the chalcogenation of **1** as a function of stoichiometry. The intermediates which link the dichalcogenated six-membered rings, **3**, to the ring-contracted four- and five-membered heterocycles **4** and **5** are of particular interest.

In an attempt to identify a feasible reaction scheme, DFT calculations of the total bonding energies for minimized geometries were performed on several possible intermediates in the transformation of **3** to the four-membered rings (**4**), for both S and Se derivatives. As the degree of chalcogenation is increased, a significant stabilization of the molecules is observed (ca. 200 kJ mol^{-1} for each equivalent of S and about 175 kJ mol^{-1} for Se). Consequently, only those potential intermediates that exhibit the same number of chalcogen atoms can be compared directly. To minimize computational time, the calculations were limited to species that result from the addition of two chalcogen atoms to the C_2P_4 ring for each step (Scheme 3).

Scheme 3



The first step in the addition of two chalcogen atoms to **3** could occur either via (a) insertion of a chalcogen atom into the two P−P bonds to give the eight-membered ring **7** or (b) oxidation of the three-coordinate phosphorus atoms to four-coordinate centers with retention of the six-membered ring, as in **9**. There is literature precedent for the insertion of sulfur of selenium into the P−P bonds of diphosphanes $R_2P{-}PR_2$.[43] Although the treatment of 1,4-$(CH_2)_2(P^iPr)_4$ with sulfur has been reported to oxidize all four three-coordinate phosphorus centers to give **9** (with ^{t}Bu groups replaced by ^{i}Pr), there is no structural evidence for this product, and the characterization data are very limited.[11]

The experimental observations and computational results from the current comprehensive investigation of the chalcogenation of **1**, as a function of stoichiometry and temperature, indicate that the formation of **9** is unlikely in view of the substantial deactivation of the remaining three-coordinate phosphorus sites upon dichalcogenation. Furthermore, the calculated energies of **7** and **9** show that the insertion products **7** are preferred by 31.6 kJ mol^{-1} for sulfur and by 63.6 kJ mol^{-1} for selenium suggesting that the ring expansion is the most likely initial step in the reaction pathway. The calculations also show that the four-membered rings **8** are only slightly higher in energy, by 1.2 kJ mol^{-1} for sulfur and 13.4 kJ mol^{-1} for selenium, than the corresponding dimers **7**. Thus, a dimer−monomer equilibrium between **7** and **8** in solution is feasible and would account for the formation of the four-membered rings **4**, since the oxidation of the three-coordinate phosphorus center in **8** is exothermic. An alternative pathway to **4** that would involve the formation of **10** by oxidation of the three-coordinate phosphorus centers in **7** followed by monomerization is unlikely in view of our calculations that reveal a marked deactivation (increase in positive charge) of the three-coordinate phosphorus centers remaining after dichalcogenation (cf. formation of **7** in preference to **9**; calculated energies for **10** are given in the SI).

In attempts to gain some evidence for the formation of the intermediates **7**, the reactions of **1** with 4 equiv of chalcogen in hot toluene were monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In these experiments the major products were the four-membered rings (**4a** or **4b**) and the dichalcogenated six-membered rings (**3a**, **3a**′ and **3b**, **3b**′), which accounted for about 90% of the integrated NMR resonances for sulfur and 95% for selenium. Although the presence of other species was evident in the NMR spectra, the low intensity of the resonances precluded definitive identifications.

Although these calculations do not directly address the formation of the five-membered rings **5**, our experimental observations indicate that **5a** is not produced by sulfur insertion into a P−S bond in **4a**, although that route is feasible for the transformation of the selenium system **4b** into **5b** (vide supra). It can be envisaged, however, that the ring-contracted products **5** with dichalcogenated (−E−E−) linkages are generated by a pathway similar to that shown on the left-hand side of Scheme 3, except that the initial step would involve the double insertion of chalcogen atoms into P−P bonds of **3** to give P−E−E−P linkages in a nine- or ten-membered heterocycle.

■ CONCLUSIONS

In the context of the objectives posed in the Introduction, we have shown that by using 1 equiv of chalcogen, the monoselenide **2b** is formed selectively from the six-membered C_2P_4 ring **1**. By contrast, the monosulfide **2a** cannot be obtained as a pure sample; it is always admixed with the dichalcogenated derivative even with carefully controlled chalcogen addition at low temperatures. The reactions of **1** with two or more equiv of chalcogen generate dichalcogenides quantitatively and exclusively as the 2,5-isomers **3a** and **3b**. The preference for the formation of this isomer has been explained with DFT calculations of the redistribution of electronic densities and atomic charges that occurs at the phosphorus centers upon oxidation. At elevated temperatures, the 2,5-isomers **3a** and **3b** are partially transformed into the corresponding 2,6-isomers **3a**′ and **3b**′; the appearance of the monoselenide **2b** in the hot solution suggests that this isomerism occurs through a dissociative mechanism. In the presence of an excess of chalcogen at elevated temperatures, **1** is transformed into the four-membered rings **4a** and **4b**, while with a large excess of selenium, the five-membered ring **5b** is produced in good yield. A possible pathway for the generation of the ring-contracted products **4a** and **4b**, which involves chalcogen insertion into the P−P bonds of the corresponding six-membered rings **3a** and **3b**, has been proposed based on DFT calculations of the relative energies of likely intermediates.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A comparison of the simulated and experimental $^{31}P\{^1H\}$ NMR spectrum of **2a**, tabulated numerical values for the coupling constants of **2a** and **2b**, and the crystallographic information files for compounds **1**, **3a**, **3b**, **4a**, **4b**, **5b**. Cartesian coordinates and bonding energies for all optimized structures are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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