Organophosphorus Compounds; 142:[1] A Simple Approach to 1,2,4-Selena- and Telluradiphospholes from Phosphaalkynes and the Chalcogen Elements and a First Study of their Reactivity

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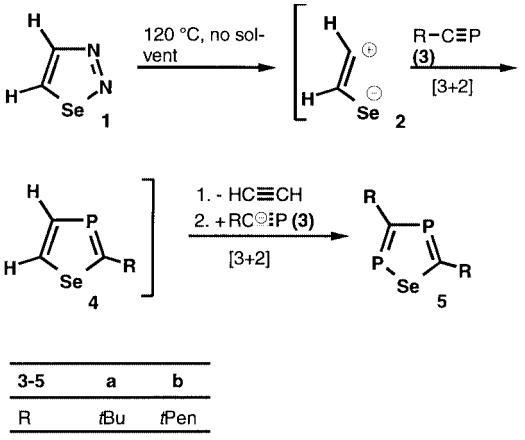
Dedicated to Professor José Elguero on the occasion of his 65th birthday.

Abstract: Phosphaalkynes **3** react with elemental selenium or tellurium to furnish the 1,2,4-selena- (**5**) or 1,2,4-telluradiphospholes (**15**), respectively. Although the telluradiphospholes **15** do not exhibit any selective cycloaddition reactivity, two equivalents of the phosphaalkyne **3** do undergo cycloaddition to the selenadiphospholes **5** through a [4+2]/[2+2+2] sequence to afford the tetracyclic products **8**. The crystal structure of compound **8a** has been determined. This cage compound is alkylated at P-4 on reaction with methyl trifluoromethanesulfonate to give **10** while selenium and sulfur react at P-7 of **8** to afford **11a,b**. Compound **8a** reacts with bromine by way of P/P bond cleavage and an unexpected rearrangement to furnish another tetracyclic compound **12** with a novel structure that has been confirmed by X-ray crystallography.

Key words: phosphaacetylenes, chalcogenes, heterophospholes, Diels–Alder reaction, cage compounds



3-5	a	b
R	*t*Bu	*t*Pen

Scheme 1

Introduction

Two major aspects of current research in the field of low-coordinated phosphorus compounds are the synthesis of phospholes with additional heteroatoms[2–5] and the construction of phosphorus-containing cage compounds.[6] A further as yet neglected aspect is the reactivity of kinetically stabilized phosphaalkynes **3** towards the elements selenium and tellurium.

1,2,4-Selenadiphospholes **5** were previously only accessible by thermolysis of 1,2,3-selenadiazole (**1**) in the presence of phosphaalkynes with yields not exceeding 17%. Probable intermediates in this process are the 1,3-dipole **2** and the 1,3-selenadiphospholes **4**[4] (Scheme 1). There is also a report that the reaction of a 1,2,4-triphosphole with elemental selenium furnishes the 1,2,4-selenadiphosphole **5a**, again only in modest yield.[7]

We now report on a higher-yielding synthesis of the 1,2,4-selenadiphosphole **5** and their tellurium analogues **15** as well as the results of a first investigation of their reactivities.

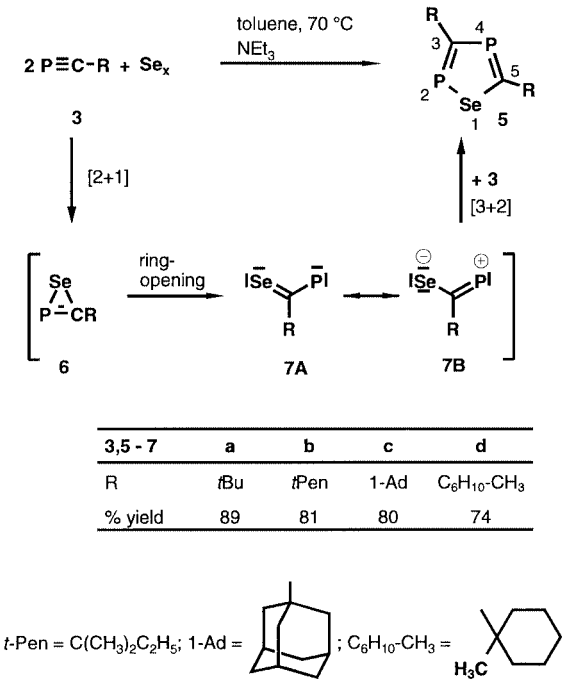
A New Approach to 1,2,4-Selenadiphospholes 5

The reaction of an excess of elemental selenium (black or gray modification) with the phosphaalkynes **3a–d** in toluene at 70°C in the presence of an equimolar amount of triethylamine leads to the 1,2,4-selenadiphospholes **5** (Scheme 2). The simple and economic workup involves merely filtration from excess selenium with subsequent bulb-to-bulb distillation and furnishes the products in yields of up to 89%. The analytical data of **5a,b** agree with those reported in the literature. The novel products **5c,d** show comparable chemical shift values in their NMR spectra: in particular the ^{31}P NMR signals with shifts of δ = 255.8 (263.9) and 287.2 (292.9) and couplings of $^{2}J(P,P)$ = 49 (48) Hz and $^{1}J(P,Se)$ = 449 (379) Hz identify the compounds as 1,2,4-selenadiphospholes. In addition, the MS and HRMS data confirm the elemental composition and constitution of **5c,d**.

A plausible mechanism for the formation of the selenadiphospholes **5** involves the intermediate formation of the selenoxophosphinidenes **7**, generated in turn by ring opening of the selenaphosphirenes **6**. The 1,3-dipoles **7A** ↔ **7B** then undergo regioselective [3+2] cycloaddition to a second equivalent of the respective phosphaalkyne **3** (Scheme 2).

[4+2] Cycloadditions of 5 with Phosphaacetylenes 3

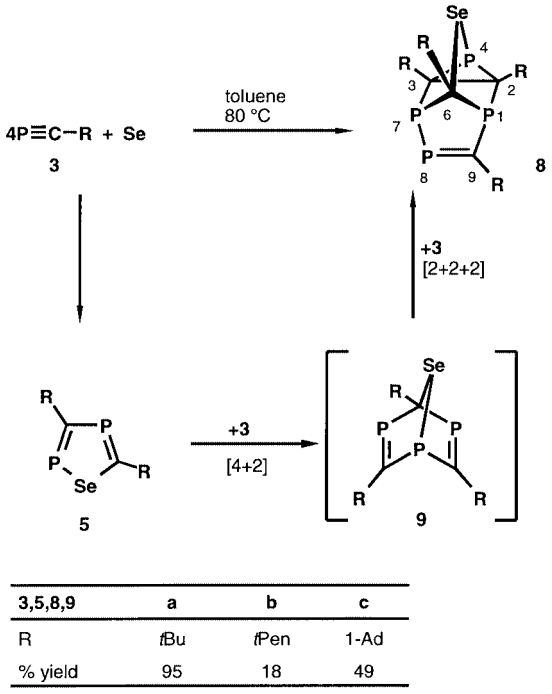
Use of a deficit of selenium in the reactions with the phosphaalkynes **3a,c** resulted in the formation of the tetracyclic products **8a,c** in very good yields; in the case of **3b**,



3,5 - 7	a	b	c	d
R	*t*Bu	*t*Pen	1-Ad	C_6H_{10}-CH_3
% yield	89	81	80	74

Scheme 2

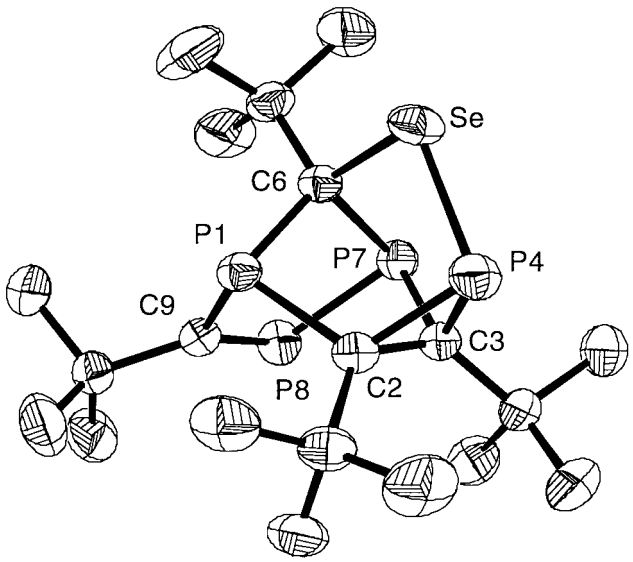
which can only be used as a solution in hexamethyldisiloxane, the corresponding reaction furnished **8b** in only 18% yield (Scheme 3).



3,5,8,9	a	b	c
R	*t*Bu	*t*Pen	1-Ad
% yield	95	18	49

Scheme 3

Elemental analysis as well as the HR and EI mass spectra confirm the compositions of compounds **8a–c**. The structures were elucidated mainly on the basis of the ^{31}P NMR spectra as discussed below for the example of product **8a**. The ^{31}P NMR spectrum of **8a** contains a pseudo-triplet signal at $\delta = -100.5$, i.e. in the high-field region typical for a phosphirane system. The pseudo-triplet structure due to selenium satellite signals [^1J(P,Se) = 223 Hz] confirms the direct adjacency of the selenium nucleus and thus the unambiguous assignment of this signal to P-4. A second signal at $\delta = 123.5$, indicative of a $\lambda^3\sigma^3$-phosphorus atom (P-1), exhibits a double double doublet structure. In addition to the coupling with P-4, ^2J(P,P) couplings to P-8 (16.7 Hz) and P-7 (38.5 Hz) are also observed. Phosphorus P-7 is assigned to the double double doublet signal at $\delta = 136.6$ which, with its significantly large coupling of ^1J(P,P) = 282.0 Hz, confirms the existence of the P–P increment. The AMNX spin system at $\delta = 411.1$ is unequivocally due to a $\lambda^3\sigma^2$-phosphorus atom (P-8) on account of its extreme low-field position. The ^{13}C NMR data support the deductions from the ^{31}P NMR spectrum (see experimental section) while an X-ray crystallographic analysis (Figure 1) irrevocably confirms the structure of this novel cage compound.



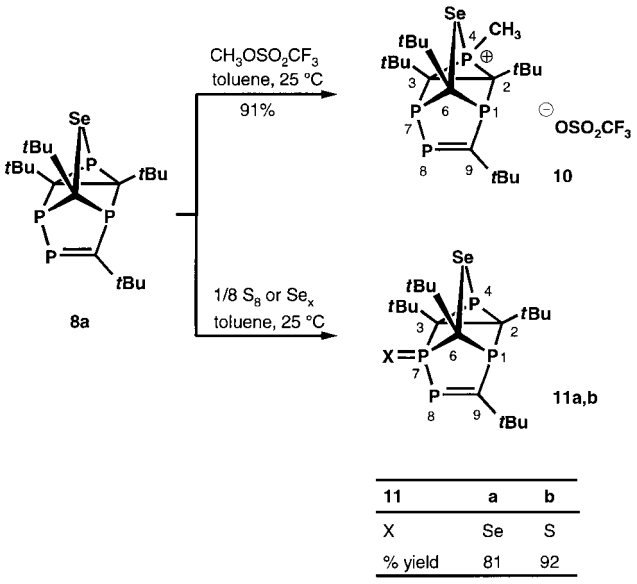
Selected bond length [Å] and angles [°]: Se–C(6) 1.989(2), Se–P(4) 2.2390(7), P(1)–C(9) 1.856(2), P(1)–C(6) 1.884(2), P(1)–C(2) 1.916(2), P(8)–C(9) 1.690(2), P(8)–P(7) 2.2267(9), P(7)–C(6) 1.864(2), P(7)–C(3) 1.886(2), P(4)–C(3) 1.863(2), P(4)–C(2) 1.864(2), C(2)–C(3) 1.574(3); C(6)–Se–P(4) 91.33(6), C(9)–P(1)–C(6) 97.09(9), C(9)–P(1)–C(2) 99.53(9), C(6)–P(1)–C(2) 94.02(9), C(9)–P(8)–P(7) 98.25(7), C(6)–P(7)–C(3) 94.86(10), C(6)–P(7)–P(8) 95.82(7), C(3)–P(7)–P(8) 97.45(7), C(3)–P(4)–C(2) 49.94(9), C(3)–P(4)–Se 100.81(7), C(2)–P(4)–Se 100.86(7), P(7)–C(6)–P(1) 102.39(9), P(7)–C(6)–Se 105.25(10), P(1)–C(6)–Se 103.89(10), P(8)–C(9)–P(1) 117.47(11), C(3)–C(2)–P(4) 64.99(10), C(3)–C(2)–P(1) 110.42(14), P(4)–C(2)–P(1) 112.13(10), C(2)–C(3)–P(4) 65.07(10), C(2)–C(3)–P(7) 111.06(14), P(4)–C(3)–P(7) 112.82(10)[17]

Figure 1 Crystal Structure of **8a**

The phosphaalkene unit in the structure is characterized by the typical P/C double bond length[8] of 1.690(2) Å as well as the planar geometry at C-9 (angular sum = 359.7°). In addition, the C-9/C-*t*-Bu bond length of 1.557(3) Å is somewhat shorter than the analogous bond lengths of the sp^3-hybridized skeletal carbon atoms to the respective *t*-butyl groups of around 1.582(3) Å. The P/P bond length between P-8 and P-7 is 2.2267(9) Å. The P/C bond lengths lie between 1.856(2) and 1.886(2) Å and are thus in the usual range for P/C single bonds.[9] The three-membered ring contains two almost identical bond lengths of 1.863(2) Å (P-4/C-3) and 1.864(2) Å (P-4/C-2) which are somewhat longer than the published average value of 1.835 Å for phosphiranes. Accordingly the C-2/C-3 bond length of 1.574(3) Å is markedly longer while the internal angle at P4 of 49.9° is only slightly larger than the average literature values (1.525 Å and 49°) for this class of compounds.[10]

For a reasonable discussion of the mechanism of formation of the tetracyclic compounds **8a–c** we must assume that the 1,2,4-selenadiphospholes **5a–c** are intermediates. They then undergo a [4+2] cycloaddition with one equivalent of the phosphaalkyne **3a−c** to furnish the 7-selena-1,3,5-triphosphabicyclo[2.2.1]hepta-2,5-dienes **9a–c** which react in a homo Diels–Alder process with another equivalent of the phosphaalkyne **3a–c** to afford the products **8a–c**. The intermediates **9a–c** cannot be isolated or even detected in the reaction mixture by NMR spectroscopy.

In contrast, the phospholes **5a–c** can be observed in the reaction mixture by ^{31}P NMR spectroscopy. Furthermore, it was found in an independent experiment that compound **5a** does react with 2 equivalents of **3a** to furnish **8a** in comparable yield.



11	a	b
X	Se	S
% yield	81	92

Scheme 4

Alkylation and Oxidation of Selenatetraphosphatetracyclononene 8a

a) Alkylation with Methyl Trifluoromethanesulfonate

Treatment of the tetraphosphatetracyclononene **8a** with methyl trifluoromethanesulfonate in toluene at 25°C furnishes the sulfonate **10** in a surprising selectivity (Scheme 4). In the ^{31}P NMR spectrum of **10** the signal for P-8 (δ = 412.7) remains more or less unchanged while those for P-7 (δ = 46.6) and P-1 (δ = 80.5) experience pronounced shifts to higher field. The signal for P-4 is shifted by Δδ = +10 ppm to a value observed previously for the alkylated phosphorus atom in a comparable cage structure.[11] In the ^{13}C NMR spectrum, the typical coupling of the signal at δ = 17.8 for the methyl group with the phosphorus atom P-4 [^1J(C,P) = 26.9 Hz] confirms the postulated structure.

b) Reaction with Selenium

Gray selenium reacts with **8a** in the presence of a catalytic amount of triethylamine even at room temperature to furnish the cage compound **11a** oxidized at P-7 (Scheme 4). The composition of the product is confirmed by mass spectrometry and oxidation at the P-7 position is clearly demonstrated by the NMR data.[12] All signals in the ^{31}P NMR spectrum experience a slight shift to higher field. Retention of the P-7/P-8 bond with concomitant conversion of P-7 to a λ^5-phosphorus atom is demonstrated by the significant increase in the ^1J(P,P) coupling to 339.5 Hz. At the same time, ^{77}Se-satellite splitting of the P-7 signal with the typically large ^1J(P,Se) coupling of 740 Hz is seen. The low field position of the ^{31}P NMR signal for P-8 at δ = 343.8 unambiguously demonstrates retention of the λ^3-phosphaalkene unit so that an attack of selenium at P-8 can be excluded with certainty.

The ^{13}C NMR data of **11a** differ only marginally from those of the starting material; the only conspicuous feature is the untypical breakdown of the coupling between C-6 and the neighboring, selenium-substituted phosphorus atom P-7.

c) Reaction with Sulfur

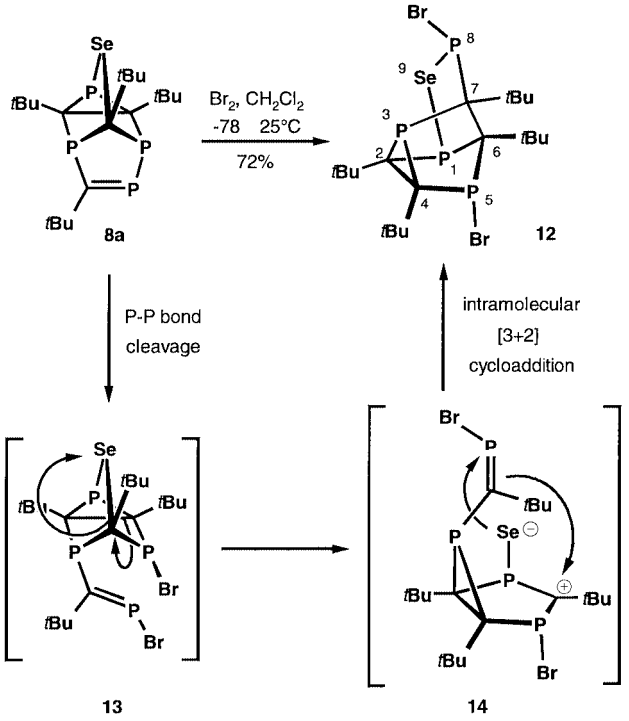
The reaction of **8a** with S_8 in the presence of 15 mol% Et_3N is complete within 24 h and affords the cage compound **11b** with a sulfur substituent at P-7. The retention of the cage structure is apparent from the ^{31}P and ^{13}C NMR spectra.

The increase in the P-7/P-8 coupling to ^1J(P,P) = 417.8 Hz again indicates that the sulfur substitution must have occurred at one of these positions. Since the P-8/C-9 coupling decreases to ^1J(P,C) = 60 Hz, the formation of a methylenethioxophosphorane unit can be discounted as such a structure would require a value of more than 100 Hz.[13] At the same time, high field shifts are experienced not only by the ^{31}P NMR signal of P8 (to δ = 239) but also

by the ^{13}C NMR signal of C-9 (to $\delta = 162.2$); these observations are attributed to the formation of the unusual conjugated S=P−P=C system.

Reaction of the Tetracyclic Compound 8a with Bromine

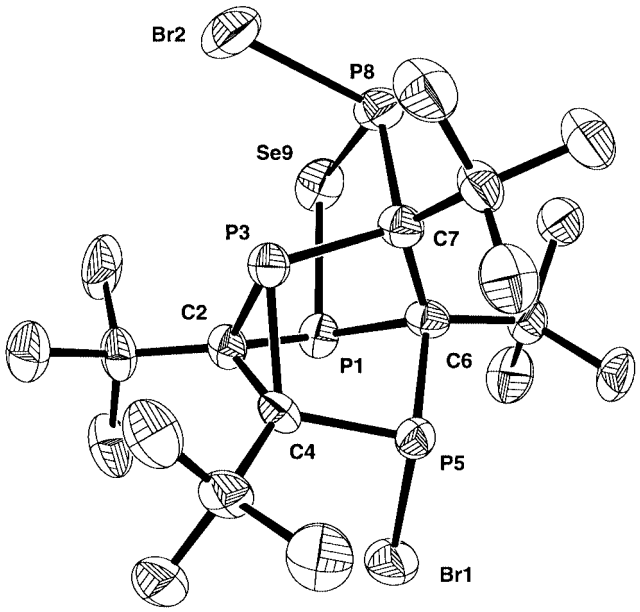
When an equimolar amount of elemental bromine is slowly added to a solution of **8a** in dichloromethane at −78°C and the solution is allowed to thaw and is then stirred for 24 hours a yellow flaky precipitate of **12** is formed (Scheme 5). The pure product is obtained by crystallization from THF at −20°C. Mass spectrometric analysis clearly shows that two bromine atoms have been added to the tetracyclic compound **8a**.



Scheme 5

The ^{31}P NMR spectrum reveals the presence of four nonequivalent phosphorus atoms. On comparison with the spectrum of **8a** it is apparent that (a) the phosphaalkene unit is no longer intact since the signal at lowest shift is now found at $\delta = 221.7$, (b) there is no P/P bond because large P/P coupling constants are absent, and (c) a phosphirane unit is present as by a signal at $\delta = -126.3$. Two of the phosphorus signals ($\delta = 149.5$ and. 221.7) exhibit ^1J(P,Se) couplings of between 216.8 and 339.8 Hz, indicative of a rearrangement of the tetracyclic skeleton.

An X-ray crystallographic analysis demonstrated the structure of compound **12**. The rearrangement of the skeleton is first obvious from the fact that the selenium atom is now bonded to two phosphorus substituents as shown by the typical bond lengths of 2.271(2) Å (Se/P1) and 2.231(3) Å (Se/P8), respectively, similar in length to the one P/Se bond in **8a**.



Selected bond length [Å] and angles [°]: Br(2)−P(8) 2.312(2), Br(1)−P(5) 2.286(2), Se(9)−P(8) 2.231(3), Se(9)−P(1) 2.271(2), P(3)−C(2) 1.846(8), P(3)−C(4) 1.874(7), P(3)−C(7) 1.902(8), P(1)−C(6) 1.871(7), P(1)−C(2) 1.878(7), P(8)−C(7) 1.930(7), P(5)−C(4) 1.817(7), P(5)−C(6) 1.885(7), C(2)−C(4) 1.580(9), C(7)−C(6) 1.604(10); P(8)−Se(9)−P(1) 95.67(8), C(2)−P(3)−C(4) 50.3(3), C(2)−P(3)−C(7) 99.1(3), C(4)−P(3)−C(7) 99.1(3), C(6)−P(1)−C(2) 92.9(3), C(6)−P(1)−Se(9) 94.7(2), C(2)−P(1)−Se(9) 108.9(2), C(7)−P(8)−Se(9) 99.1(2), C(7)−P(8)−Br(2) 104.5(2), Se(9)−P(8)−Br(2) 99.32(10), C(4)−P(5)−C(6) 93.8(3), C(4)−P(5)−Br(1) 99.7(2), C(6)−P(5)−Br(1) 106.4(2), C(4)−C(2)−P(3) 65.8(4), C(4)−C(2)−P(1) 107.3(4), P(3)−C(2)−P(1) 109.6(4), C(2)−C(4)−P(5) 112.9(5), C(2)−C(4)−P(3) 63.9(4), P(5)−C(4)−P(3) 106.6(4), C(6)−C(7)−P(3) 104.2(5), C(6)−C(7)−P(8) 108.7(5), P(3)−C(7)−P(8) 107.6(3), C(7)−C(6)−P(1) 106.3(5), C(7)−C(6)−P(5) 102.6(5), P(1)−C(6)−P(5) 98.9(3)[17]

Figure 2 Crystal Structure of **12**

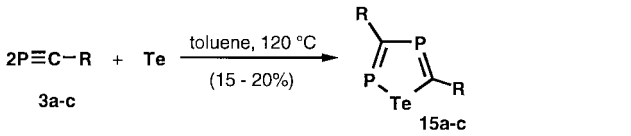
The angle at selenium is now expanded to 95.7°. The phosphirane unit (C-2/P-3/C-4) shows a slight deviation from the symmetry since the bond lengths P-3/C-2 (1.846(8)) and P-3/C-4 (1.874(7)) differ and both exceed the reported average bond length of 1.835 Å for phosphacyclopropanes. Similarly, the C-2/C-4 bond length of 1.580(9) Å varies markedly and the internal angle at P-3 of 50.3(3)° also varies, albeit only slightly, from the published average values (1.525 Å and 49°) for phosphiranes.[10]

Most of the P-C bond lengths are between 1.817(7) and 1.885(7) Å and thus in the usual range for P-C single bonds.[9] Exceptions are the P-3/C-7 bond length of 1.902(8) Å and the P-8/C-7 bond length of 1.930(7) Å which are stretched somewhat on account of the steric situation.

In analogy to the well-known P/P bond cleavage by halogens[18] the initial step in the mechanism is assumed to be the diastereoselective[19] formation of the intermediate **13** which, however, cannot be detected by spectroscopy. Then, the tetracyclic product **12** is generated in a two-step process involving rearrangement (**13** → **14**) and subsequent intramolecularer 1,3-dipolar cycloaddition (→ **12**). Accordingly, the reaction is diastereoselective with regard to the newly generated stereocenters P-5 and P-8, as is confirmed by the NMR spectroscopic data.

1,2,4-Telluradiphospholes 15

Under harsher conditions (120°C in toluene in a Schlenk pressure tube) the phosphaalkynes **3a–c** exhibit an analogous reactivity towards elemental tellurium. In addition to oligomers of the phosphaalkyne, the previously unknown 1,2,4-telluradiphospholes **15a–c** are formed (Scheme 6), albeit in modest yields, through the postulated intermediacy of a telluroxophosphinidene and subsequent [3+2] cycloaddition with one equivalent of the phosphaalkyne. The yellowish oils obtained tend to form amorphous crystals, they are thermally labile and decompose unselectively on exposure to light with deposition of elemental tellurium.



3,15	a	b	c
R	*t*Bu	*t*Pen	1-Ad

Scheme 6

The compositions and constitutions of these novel heterocyclic compounds were confirmed by high resolution mass spectrometry and by their characteristic NMR spectra. A conspicuous feature is the close positioning of the two ^{31}P NMR signals at (for **15a**) δ = 299.6 and 302.5 with a ^{2}J(P,P) coupling of 49 Hz. The ^{13}C NMR spectrum of **15a** reveals drastic downfield shifts for the ring carbon atom signals which appear as double doublets at δ = 212.3 and 227.0. Attempts to realize cycloaddition reactions with the telluradiphospholes gave unselective results and, in particular, did not lead to the formation of cage compounds analogous to **8** (^{31}P NMR monitoring).

All reactions were performed under argon (purity >99.998%) atmosphere using Schlenk techniques. The solvents were dried by standard procedures, distilled, and stored under argon. Compounds **3a–c** were prepared by published methods.[14] Column chromatography was performed in water-cooled glass tubes under argon. The eluate was monitored with a UV absorbance detector (λ = 254 nm). Silica gel was heated for 3 h in vacuo and then deactivated with 4% H_2O (Brockmann activity II). The bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus, the temperatures stated are oven temperatures. Melting points were determined on a Mettler FP61 apparatus (heating rate 2°C/min) and are uncorrected. Microanalyses were performed with a Perkin-Elmer Analyzer 2400. ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker AC 200 and Bruker AMX 400 spectrometers and referenced to the solvent as internal standard. ^{31}P NMR spectra were measured on a Bruker AC 200 (80.8 MHz) spectrometer with 85% H_3PO_4 as external standard. MS and HRMS were recorded on a Finnigan MAT 90 spectrometer at 70 eV ionization voltage. IR spectra were measured on a Perkin-Elmer 16 PC FT-IR spectrophotometer.

1,2,4-Selenadiphospholes 5a–c; General Procedure

An excess of selenium, Et_3N, and the corresponding phosphaacetylene were heated in toluene (4 mL) in a Schlenk pressure tube at 70°C. After the reaction was over (ca. 24 h, ^{31}P NMR monitoring), the residue was taken up in pentane (10 mL) and the insoluble material was removed by filtration through a D3 sinter filled to a depth of 2 cm with Celite. The products were purified by bulb-to-bulb distillation.

3,5-Di-*tert*-butyl-1,2,4-selenadiphosphole (5a)

From *tert*-butylphosphaacetylene (**3a**; 0.6 mL, 4.4 mmol), Et_3N (0.6 mL, 4.4 mmol), and selenium (Se_{grey}, 345 mg, 4.4 mmol); yield: 548 mg (89%); bp 140°C/=0.001 mbar. Analytical data are identical to those reported in the literature.[4]

3,5-Di-*tert*-pentyl -1,2,4-selenadiphosphole (5b)

From *tert*-pentylphosphaacetylene (**3b**; 110.1 mg, 0.96 mmol as a 26% solution in hexamethyldisiloxane), Et_3N (130 µL, 0.96 mmol), and selenium (Se_{grey}, 76 mg, 0.96 mmol); yield: 116.7 mg (81% based on the phosphaacetylene); bp 140°C/0.001 mbar. Analytical data are identical to those reported in the literature.[4]

3,5-Diadamant-1-yl-1,2,4-selenadiphosphole (5c)

From adamant-1-ylphosphaacetylene (**3c**; 90 mg, 0.51 mmol), Et_3N (70 µL, 0.51 mmol), and selenium (49 mg, 0.62 mmol); yield: 88.8 mg (80%); mp 163°C.

^{1}H NMR ($CDCl_3$): δ = 1.45–1.75 (m, 15 H, 1-Ad), 1.85–2.20 (m, 15 H, 1-Ad).

^{13}C NMR ($CDCl_3$): δ = 29.4 [d, ^{4}J(C,P) = 2.3 Hz, CH], 29.5 [d, ^{4}J(C,P) = 1.5 Hz, CH], 36.3 (s, CH_2), 36.4 (s, CH_2), 45.2 [dd, ^{2}J(C,P) = 19.1, ^{2}J(C,P) = 16.8 Hz, *i*-C], 45.6 [dd, ^{2}J(C,P) = 15.3, ^{3}J(C,P) = 5.3 Hz, *i*-C], 48.2 [dd, ^{3}J(C,P) = 14.5, ^{3}J(C,P) = 9.9 Hz, CH_2], 48.5 [d, ^{3}J(C,P) = 12.2 Hz, CH_2], 216.2 [dd, ^{1}J(C,P) = 66.8, ^{2}J(C,P) = 5.5 Hz, C-5], 223.5 [dd, ^{1}J(C,P) = 85.4, ^{1}J(C,P) = 73.2 Hz, C-3].

^{31}P NMR (C_6D_6): δ = 255.8 [d, ^{2}J(P,P) = 49.3, ^{2}J(P,Se) = 79 Hz, P-4], 287.2 [d, ^{2}J(P,P) = 49.3 Hz, ^{1}J(P,Se) = 449 Hz, P-2].

MS (EI, 70 eV): *m*/*z* (%) = 436 (40, M^+), 325 (100, M^+ – SeP), 294 (12, 1-AdC≡C-1-Ad^+), 147 (8, 1-AdC^+), 135 (57, Ad^+).

HRMS: *m*/*z* calcd for $C_{22}H_{30}P_2Se$ 436.0988, found 436.0988.

3,5-Bis(1-methylcyclohex-1-yl)-1,2,4-selenadiphosphole (5d)

From 1-methylcyclohex-1-ylphosphaacetylene (**3d**; 104 mg, 0.74 mmol as a 17% solution in hexamethyldisiloxane), Et_3N (70 µL NEt_3, 0.51 mmol), and selenium (68 mg, 0.86 mmol); yield: 98.6 mg (74%); bp 190°C/0.008 mbar.

^{1}H NMR (C_6D_6): δ = 1.28–2.27 (m, 20 H, CH_2), 1.42 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3).

^{13}C NMR (C_6D_6): δ = 22.8 [dd, ^{4}J(C,P) = 3.0, ^{4}J(C,P) = 1.0 Hz, CH_2], 22.9 [d, ^{4}J(C,P) = 4.4 Hz, CH_2], 25.9 (s, CH_2), 25.9 (s, CH_2), 26.0 (s, CH_2), 35.1 (s, CH_3), 35.2 (s, CH_3), 42.5 [dd, ^{3}J(C,P) = 14.9, ^{3}J(C,P) = 10.4 Hz, CH_2], 42.8 [d, ^{3}J(C,P) = 12.8 Hz, CH_2], 46.3 [dd, ^{2}J(C,P) = 18.5, ^{2}J(C,P) = 16.1 Hz, *i*-C], 46.9 [dd, ^{2}J(C,P) = 14.4,

^3J(C,P) = 5.9 Hz, *i*-C], 215.7 [dd, ^1J(C,P) = 64.7, ^2J(C,P) = 5.2 Hz, C-5], 223.3 [dd, ^1J(C,P) = 83.5, ^1J(C,P) = 68.1 Hz, C-3].

^{31}P NMR (C_6D_6): δ = 263.9 [d, ^2J(P,P) = 48.4, ^2J(P,Se) = 63 Hz, P-4], 292.9 [d, ^2J(P,P) = 48.4 Hz, ^1J(P,Se) = 379 Hz, P-2].

MS (EI, 70 eV): *m*/*z* (%) = 360 (66, M^+), 345 (8, $M^+ - CH_3$), 279 (79, $M^+ - SeH$), 249 [27, $P(CC_7H_{13})_2^+$], 220 (13, $SeP{\equiv}CC_7H_{13}^+$), 171 (9, $P_2CC_7H_{13}^+$), 109 (100, $CC_7H_{13}^+$), 97 (60, $C_7H_{13}^+$).

HRMS: *m*/*z* calcd for $C_{16}H_{26}P_2Se$ 360.0674, found 360.0674.

5,1,4,7,8-Selenatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enes (8), General Procedure

Compounds **8** are best prepared by heating a mixture of an excess of phosphaacetylenes **3a–c** and selenium in toluene (5 mL) at 90°C for 48 h in a Schlenk pressure tube. After cooling the reaction mixture to 25°C, the excess of phosphaacetylene is removed at 25°C/0.001 mbar. The orange residue is taken up in pentane/Et_2O (1:2) and subjected to column chromatography on silica gel (0.063 − 0.2 mm) with the same solvent mixture. After elution of a yellow fraction containing the corresponding 1,2,4-selenadiphospholes **5a–c**, a second pale orange fraction was obtained that gave pure **8a-c** after evaporation of the solvent.

2,3,6,9-Tetra-*tert*-butyl-5,1,4,7,8-selenatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (8a)

From *tert*-butylphosphaacetylene (**3a**; 0.26 mL, 2 mmol) and selenium (Se_{grey}, 32 mg, 0.4 mmol); yield: 167.1 mg (95%); mp 138°C.

^{1}H NMR (C_6D_6): δ = 1.24 [s, 9 H, $C(CH_3)_3$], 1.33 [d, ^4J(H,P) = 2.1 Hz, 9 H, $C(CH_3)_3$], 1.34 [s, 9 H, $C(CH_3)_3$], 1.56 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (C_6D_6): δ = 34.6 [dpt, ^3J(C,P) + ^3J(C,P) = 4.2, ^4J(C,P) = 2.1 Hz, $C(CH_3)_3$], 35.1 [ddd, ^2J(C,P) = 26.7, ^2J(C,P) = 9.6, ^3J(C,P) = 1.9 Hz, $C(CH_3)_3$], 35.9 [pt, ^3J(C,P)+^3J(C,P) = 12.4 Hz, $C(CH_3)_3$], 36.0 [dd, ^3J(C,P) = 12.4, ^3J(C,P) = 6.7 Hz, $C(CH_3)_3$], 36.7 [ddd, ^3J(C,P) = 9.9, ^3J(C,P) = 6.6, ^4J(C,P) = 3.3 Hz, $C(CH_3)_3$], 37.1 [ddd, ^2J(C,P) = 18.1, ^2J(C,P) = 12.4, ^3J(C,P) = 2.9 Hz, $C(CH_3)_3$], 37.8 [ddd, ^2J(C,P) = 11.9, ^2J(C,P) = 9.5, ^3J(C,P) = 2.9 Hz, $C(CH_3)_3$], 44.6 [dd, ^2J(C,P) = 20.0, ^2J(C,P) = 12.4 Hz, CMe_3 at C-9], 66.4 [ptpt, ^1J(C,P) + ^1J(C,P) = 46.7, ^3J(C,P) + ^2J(C,P) = 4.5 Hz, C-2], 75.8 [ddpt, ^1J(C,P) + ^1J(C,P) = 46.3, ^2J(C,P) = 12.4, ^2J(C,P) = 6.2 Hz, C-3], 78.4 [ddd, ^1J(C,P) = 41.0, ^1J(C,P) = 32.4, ^2J(C,P) = 2.9 Hz, C-6], 245.1 [dd, ^1J(C,P) = 79.6 Hz, ^1J(C,P) = 67.2 Hz, C-9].

^{31}P NMR (C_6D_6): δ = –100.5 [pt, ^3J(P,P) + ^2J(P,P) = 6.9 Hz, ^1J(P,Se) = 223 Hz, P-4], 123.5 [ddd, ^2J(P,P) = 38.5, ^2J(P,P) = 16.7, ^2J(P,P) = 6.9 Hz, P-1], 136.6 [ddd, ^1J(P,P) = 282.0, ^2J(P,P) = 38.5, ^2J(P,P) = 4.2 Hz, P-7], 411.1 [ddd, ^1J(P,P) = 282.0, ^2J(P,P) = 16.7, ^3J(P,P) = 6.9 Hz, P-8].

^{77}Se NMR (C_6D_6): δ = 59.2 [dd, ^1J(Se,P) = 209 Hz, ^2J(Se,P) = 22 Hz]

MS (EI, 70 eV): *m*/*z* (%) = 480 (51, M^+), 369 (6, $M^+ - SeP$), 349 (6, $M^+ - P_2C$-*t*-Bu), 231 (39, P_3C-*t*-Bu_2^+), 169 [100, P(C-*t*-$Bu)_2^+$], 131 (20, P_2C-*t*-Bu^+), 69 (20, C-*t*-Bu^+), 57 (15, $C_4H_9^+$).

$C_{20}H_{36}P_4Se$	calcd	C	50.11	H	7.57
(479.4)	found		50.22		7.71

2,3,6,9-Tetrakis-*tert*-pentyl-5,1,4,7,8-selenatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (8b)

From *tert*-pentylphosphaacetylene (**3b**; 2.7 mL, 5 mmol as a 26% solution in hexamethyldisiloxane) and selenium (Se_{grey}, 87 mg, 1.1 mmol); yield: 106 mg (18%); mp 151°C.

^{31}P NMR (C_6D_6): δ = –99.8 [s, ^1J(P,Se) = 246 Hz, P-4], 122.7 [dd, ^2J(P,P) = 32.3, ^2J(P,P) = 18.4 Hz, P-1], 133.9 [dd, ^1J(P,P) = 281.2, ^2J(P,P) = 32.3 Hz, P-7], 410.3 [dd, ^1J(P,P) = 281.2, ^2J(P,P) = 18.4 Hz, P-8].

MS (EI, 70 eV): *m*/*z* (%) = 536 (7, M^+), 308 (42, P_2C_2-*t*-Pen_2Se^+), 259 (11, P_3C_2-*t*-Pen_2^+), 197 [45, P(C-*t*-$Pen)_2^+$], 145 (23, P_2C-*t*-Pen^+), 83 (82, C-*t*-Pen^+), 71 (40, $C_5H_{11}^+$), 44 (100, $C_3H_8^+$).

HRMS: m/z calcd for $C_{24}H_{44}P_4Se$ 536.1558, found 536.1558.

2,3,6,9-Tetraadamant-1-yl-5,1,4,7,8-selenatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (8c)

From adamant-1-ylphosphaacetylene (**3c**; 897 mg, 5 mmol) and selenium (78 mg, 1 mmol); yield: 396 mg (49% based on selenium); mp 236°C.

^{1}H NMR ($CDCl_3$): δ = 1.2 − 2.9 (unresolved signals).

^{13}C NMR (C_6D_6): δ = 29.1 (s, C_c), 29.3 (s, C_c), 29.5 (s, C_c), 29.7 (s, C_c), 36.3 (s, C_d), 36.4 (s, C_d), 36.5 (s, C_d), 36.6 (s, C_d), 39.1 − 48.7 (unresolved signals, C_a and C_b), 66.9 [ptpt, ^1J(C,P) = ^1J(C,P) = 44.4, ^2J(C,P)+^3J(C,P) = 1.9 Hz, C-2], 74.1 [ddpt, ^1J(C,P) = ^1J(C,P) = 47.5, ^2J(C,P) = 11.0, ^2J(C,P) = 4.7 Hz, C-3], 76.8 [ddd, ^1J(C,P) = 38.7, ^1J(C,P) = 30.8, ^2J(C,P) = 1.9 Hz, C-6], 243.0 [dd, ^1J(C,P) = 78.6, ^1J(C,P) = 67.5 Hz, C-9].

^{31}P NMR ($CDCl_3$): δ = –104.0 [s, ^1J(P,Se) = 218 Hz, P-4], 112.1 [d, ^2J(P,P) = 34.9 Hz, P-1], 121.7 [dd, ^1J(P,P) = 279.0, ^2J(P,P) = 34.9, P-7], 403.7 [d, ^1J(P,P) = 279.0 Hz, P-8].

^{77}Se NMR ($CDCl_3$): δ = 67.2 [dd, ^1J(Se,P) = 206 Hz, ^2J(Se,P) = 23 Hz].

MS (EI, 70 eV): *m*/*z* (%) = 792 (6, M^+), 712 (10, $M^+ - Se$), 356 (4, PC≡1-Ad^+), 325 [33, P(C-1-$Ad)_2^+$], 294 (46, 1-AdC≡C-1-Ad^+), 135 (100, 1-Ad^+).

HRMS: *m*/*z* calcd for $C_{44}H_{60}P_4Se$ 792.2811, found 792.2811.

2,3,6,9-Tetra-*tert*-butyl-4-methyl-5,1,4,7,8-selenatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene Trifluoromethanesulfonate (10)

To a magnetically stirred solution of **8a** (119.1 mg, 0.24 mmol) in toluene (3 mL) at 25°C was added methyl triflate (28 μL, 0.24 mmol). After 4 h, the solution turned yellow and the volatile components were removed at 25°C/0.001 mbar. The yellow residue was taken up in CH_2Cl_2 and **10** was obtained as yellow needles by crystallization at −78°C; yield: 141 mg (91%); mp 141°C.

^{1}H NMR ($CDCl_3$): δ = 1.20 [s, 9 H, $C(CH_3)_3$], 1.33 [d, ^4J(H,P) = 2.5 Hz, 9 H, $C(CH_3)_3$], 1.38 [d, ^4J(H,P) = 2.5 Hz, 9 H, $C(CH_3)_3$], 1.56 [s, 9 H, $C(CH_3)_3$], 2.62 [d, ^2J(H,P) = 11.2 Hz, 3 H, CH_3].

^{13}C NMR ($CDCl_3$): δ = 17.8 [d, ^1J(C,P) = 26.9 Hz, CH_3 at P-4], 34.1 [s, $C(CH_3)_3$], 34.2 [pt, ^3J(C,P) + ^3J(C,P) = 2.7 Hz, $C(CH_3)_3$], 34.8 [pt, ^3J(C,P) + ^3J(C,P) = 1.9 Hz, $C(CH_3)_3$], 35.4 [dpt, ^2J(C,P) + ^2J(C,P) = 8.5, ^3J(C,P) = 1.9 Hz, $C(CH_3)_3$], 35.8 [ptd, ^3J(C,P) = 9.4, ^3J(C,P) + ^4J(C,P) = 1.9 Hz, $C(CH_3)_3$], 37.2 [dd, ^2J(C,P) = 19.6, ^2J(C,P) = 14.2 Hz, $C(CH_3)_3$], 38.8 [dd, ^2J(C,P) = 11.7, ^2J(C,P) = 3.1 Hz, $C(CH_3)_3$], 45.8 [dd, ^2J(C,P) = 7.5, ^2J(C,P) = 6.8 Hz, $C(CH_3)_3$ at C-9], 61.9 [pt, ^1J(C,P) + ^1J(C,P) = 48.3 Hz, C-2], 66.0 [ddd, ^1J(C,P) = 76.3, ^1J(C,P) = 52.5, ^2J(C,P) = 6.2 Hz, C-6], 69.2 [ddd, ^1J(C,P) = 43.6, ^1J(C,P) = 42.0, ^2J(C,P) = 1.6 Hz, C-3], 120.5 [q, ^1J(C,F) = 320.4 Hz, CF_3], 203.1 [dd, ^1J(C,P) = 85.7 Hz, ^1J(C,P) = 25.2 Hz, C-9].

^{31}P NMR (C_6D_6): δ = –91.5 [s, ^1J(P,Se) = 219.9 Hz, P-4], 46.6 [d, ^1J(P,P) = 263.9 Hz, P-7], 80.5 [d, ^2J(P,P) = 22.3 Hz, P-1], 412.7 [dd, ^1J(P,P) = 263.9, ^2J(P,P) = 22.3 Hz, P-8].

MS (EI, 70 eV): *m*/*z* (%) = 495 (52, M^+), 417 (100, $M^+ - P_2CH_3$), 231 [28, P_3(C-*t*-$Bu)_2^+$], 169 [78, P(C-*t*-$Bu)_2^+$], 131 (41, P_2C-*t*-Bu^+), 69 (38, C-*t*-Bu^+), 57 (45, $C_4H_9^+$).

HRMS: *m*/*z* calcd for $C_{21}H_{39}P_4Se$ 495.1167, found 495.1166.

2,3,6,9-Tetra-*tert*-butyl-7-selenoxo-5,1,4,7,8-selenatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (11a)

To a magnetically stirred solution of **8a** (216 mg, 0.45 mmol) in toluene (3 mL) at 25°C were added selenium (Se_{grey}, 35 mg, 0.45 mmol) and Et_3N (10 μL, 0.07 mmol). After 6 d the volatile components were removed at 25°C/0.001 mbar. The orange residue was taken up in pentane/Et_2O (100:1) and subjected to column chromatography on silica gel (0.063 − 0.2 mm) with the same solvent mixture. The first pale orange fraction was collected to give pure **11a** after evaporation of the solvent; yield: 203 mg (81%); mp 158°C.

^{1}H NMR (C_6D_6): δ = 1.26 [s, br, 9 H, $C(CH_3)_3$], 1.39 [s, 9 H, $C(CH_3)_3$], 1.49 [s, 9 H, $C(CH_3)_3$], 1.72 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR (C_6D_6): δ = 33.5 [pt, ^3J(C,P) + ^3J(C,P) = 2.9 Hz, $C(CH_3)_3$], 34.4 [dd, ^2J(C,P) = 12.6, ^2J(C,P) = 6.5 Hz, $C(CH_3)_3$], 35.3 [s, br, $C(CH_3)_3$], 36.0 [dd, ^3J(C,P) = 16.8, ^3J(C,P) = 11.2 Hz, $C(CH_3)_3$], 36.6 [dd, ^2J(C,P) = 9.5, ^2J(C,P) = 6.8 Hz, $C(CH_3)_3$], 37.8 [dpt, ^2J(C,P) = 12.9, ^2J(C,P) + ^3J(C,P) = 2.4 Hz, $C(CH_3)_3$], 38.9 [ptd, ^2J(C,P) = 8.8, ^2J(C,P) + ^3J(C,P) = 2.3 Hz, $C(CH_3)_3$], 44.4 [ddd, ^2J(C,P) = 20.9, ^2J(C,P) = 11.3, ^3J(C,P) = 8.9 Hz, CMe_3 at C-9], 53.5 [ddd, ^1J(C,P) = 43.3, ^1J(C,P) = 27.7, ^2J(C,P) = 4.8 Hz, C-2], 72.3 [ddd, ^1J(C,P) = 59.1, ^1J(C,P) = 42.9, ^2J(C,P) = 4.8 Hz, C-3], 76.2 [dd, ^1J(C,P) = 41.4, ^1J(C,P) = 2.9 Hz, C-6], 243.3 [ddd, ^1J(C,P) = 74.6, ^1J(C,P) = 69.6, ^2J(C,P) = 3.4 Hz, C-9].

^{31}P NMR (C_6D_6): δ = −123.3 [s, br, ^1J(P,Se) = 209 Hz, P-4], 43.3 [d, ^2J(P,P) = 34.9, P-1], 99.0 [dd, ^1J(P,P) = 339.5, ^2J(P,P) = 34.9, ^1J(P,Se) = 744 Hz, P-7], 343.8 [d, ^1J(P,P) = 339.5 Hz, P-8].

IR (C_7H_8): ν = 3059 (C–H), 3031 (C–H), 3017 (C–H), 2919 (C–H), 1492, 1456, 1077, 729, 794 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 560 (10, M^+), 480 (37, M^+ − Se), 369 (6, M^+ − Se_2P), 349 (6, M^+ − Se − P_2C-*t*-Bu), 280 [4, Se(C-*t*-Bu)$_2P_2^+$], 231 [39, P_3(C-*t*-Bu)$_2^+$], 169 [100, P(C-*t*-Bu)$_2^+$], 131 (17, P_2C-*t*-Bu$^+$), 69 (20, C-*t*-Bu$^+$), 57 (15, $C_4H_9^+$).

HRMS: *m*/*z* calcd for $C_{20}H_{36}P_4Se_2$ 560.0098, found 560.0098.

2,3,6,9-Tetra-*tert*-butyl-7-thioxo-5,1,4,7,8-selenatetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (11b)

To a magnetically stirred solution of **8a** (214 mg, 0.45 mmol) in toluene (3 mL) at r.t. were added sulfur (S_8, 14 mg, 0.45 mmol) and Et_3N (10 μL, 0.07 mmol). The color of the solution changed slowly to bright yellow. After 24 h the volatile components were removed at 25°C/0.001 mbar and **11b** was purified by recrystallization from CH_2Cl_2 to give yellow needles; yield: 212 mg (92%); mp 150°C.

^{1}H NMR (C_6D_6): δ = 1.34 [s, 9 H, $C(CH_3)_3$], 1.39 [s, 9 H, $C(CH_3)_3$], 1.45 [s, 9 H, $C(CH_3)_3$], 1.65 [d, ^4J(H,P) = 1.0 Hz, 9 H, $C(CH_3)_3$].

^{13}C NMR (C_6D_6): δ = 32.8 [dd, ^3J(C,P) = 11.0, ^3J(C,P) = 6.6 Hz, $C(CH_3)_3$], 33.4 [pt, ^3J(C,P) + ^3J(C,P) = 4.7 Hz, $C(CH_3)_3$], 35.2 [dd, ^2J(C,P) = 12.9, ^2J(C,P) = 1.7 Hz, $C(CH_3)_3$], 35.5 [dd, ^3J(C,P) = 11.9, ^3J(C,P) = 10.2 Hz, $C(CH_3)_3$], 36.5 [dd, ^3J(C,P) = 12.3, ^3J(C,P) = 7.2 Hz, $C(CH_3)_3$], 36.8 [ddd, ^2J(C,P) = 15.8, ^2J(C,P) = 9.3, ^3J(C,P) = 1.8 Hz, $C(CH_3)_3$], 38.4 [ddd, ^2J(C,P) = 12.3, ^2J(C,P) = 8.7, ^3J(C,P) = 2.6 Hz, $C(CH_3)_3$], 40.2 [dd, ^2J(C,P) = 17.7, ^2J(C,P) = 5.9 Hz, $C(CH_3)_3$ at C-9], 66.9 [m, ^1J(C,P) = 45.2, ^1J(C,P) = 42.4, ^2J(C,P) = 10.7, ^3J(C,P) = 6.8 Hz, C-2], 69.6 [ddpt, ^1J(C,P) + ^1J(C,P) = 47.6, ^2J(C,P) = 27.2, ^2J(C,P) = 5.6 Hz, C-3], 72.1 [dddd, ^1J(C,P) = 37.3, ^1J(C,P) = 29.6, ^2J(C,P) = 11.8, ^3J(C,P) = 3.4 Hz, C-6], 162.2 [ddd, ^1J(C,P) = 61.0, ^1J(C,P) = 11.8, ^2J(C,P) = 3.4 Hz, C-9].

^{31}P NMR (C_6D_6): δ = −91.8 [pt, ^2J(P,P)+^3J(P,P) = 6.3, ^1J(P,Se) = 207 Hz, P-4], 107.6 [ddd, ^1J(P,P) = 417.8, ^2J(P,P) = 24.1, ^2J(P,P) = 6.3 Hz, P-7], 118.3 [pt, ^2J(P,P) + ^2J(P,P) = 26.0 Hz, P-1], 239.4 [ddd, ^1J(P,P) = 417.8, ^2J(P,P) = 26.0, ^3J(P,P) = 6.3 Hz, P-8].

MS (EI, 70 eV): *m*/*z* (%) = 512 (47, M^+), 480 (13, M^+ − S), 280 [5, P_2(C-*t*-Bu)$_2$Se$^+$], 231 (20, P_3C-*t*-Bu$_2^+$), 169 [100, P(C-*t*-Bu)$_2^+$], 131 (19, P_2C-*t*-Bu$^+$), 69 (42, C-*t*-Bu$^+$), 57 (41, *t*-Bu$^+$).

HRMS: *m*/*z* calcd for $C_{20}H_{36}P_4SSe$ 512.0597, found 512.0597.

5,8-Dibromo-2,4,6,7-tetra-*tert*-butyl-9-selena-1,3,5,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]-nonane (12)

To a magnetically stirred solution of **8a** (55 mg, 0.12 mmol) in CH_2Cl_2 (3 mL) at −78°C was added slowly Br_2 (18.3 mg, 0.12 mmol). The mixture was allowed to warm to r.t. and stirred for 24 h to complete the reaction. The color of the solution changed slowly to bright yellow. After the volatile components were removed at 25 °C/0.001 mbar **12** was purified by recrystallization from THF to give yellow crystals; yield: 55.2 mg (72%); mp 152°C.

^{1}H NMR ($CDCl_3$): δ = 1.50 [s, 9 H, $C(CH_3)_3$], 1.52 [dd, ^4J(H,P) = 3.7, ^4J(H,P) = 2.0 Hz, 9 H, $C(CH_3)_3$], 1.54 [dd, ^4J(H,P) = 3.4, ^4J(H,P) = 1.7 Hz, 9 H, $C(CH_3)_3$], 1.71 [d, ^4J(H,P) = 2.5 Hz, 9 H, $C(CH_3)_3$].

^{31}P NMR ($CDCl_3$): δ = −126.3 [d, ^2J(P,P) = 8.1, P-4], 149.5 [dd, ^2J(P,P) = 28.5, ^2J(P,P) = 8.1, ^1J(P,Se) = 216.8 Hz, P-1], 159.5 [d, ^2J(P,P) = 8.1 Hz, P-5], 221.7 [dd, ^2J(P,P) = 28.5, ^2J(P,P) = 8.1, ^1J(P,Se) = 339.8 Hz, P-8].

MS (EI, 70 eV): *m*/*z* (%) = 640 (4, M^+), 559 (16, M^+ − Br), 480 [19, M^+ − 2Br], 400 (4, M^+ − 2Br − Se), 231 [99, P_3C-*t*-Bu$^+$], 169 (100, P(C-*t*-Bu)$_2^+$), 131 (12, P_2C-*t*-Bu$^+$), 69 (7, C-*t*-Bu$^+$), 57 (9, *t*-Bu$^+$).

HRMS: *m*/*z* calcd for $C_{20}H_{36}Br_2P_4Se$ 637.9301, found 637.9302.

$C_{20}H_{36}Br_2P_4Se$	calcd	C	37.58	H	5.68
(479.4)	found		37.31		5.43

1,2,4-Telluradiphospholes 15a-c, General Procedure

An excess of Te and the corresponding phosphaacetylene were heated in toluene (4 mL) in a Schlenk pressure tube at 120°C. After the reaction was over (^{31}P NMR monitoring), the residue was taken up in pentane (10 mL) and the insoluble material was removed by filtration through a D3 sinter filled to a depth of 3 cm with Celite. The products were purified by bulb-to-bulb distillation.

3,5-Di-*tert*-butyl-1,2,4-telluradiphosphole (15a)

From *tert*-butylphosphaacetylene (**3a**; 0.13 mL, 1.0 mmol) and tellurium (128 mg, 1.0 mmol); yield: 25 mg (15% based on phosphaacetylene); bp 105°C/0.001 mbar.

^{1}H NMR (C_6D_6): δ = 1.47 [d, ^4J(H,P) = 1.27 Hz, 9 H, $C(CH_3)_3$], 1.66 [d, ^4J(H,P) = 2.04 Hz, 9 H, $C(CH_3)_3$].

^{13}C NMR ($CDCl_3$): δ = 33.8 [dd, ^3J(C,P) = 10.5, ^3J(C,P) = 8.7 Hz, 3-C$(CH_3)_3$], 35.1 [d, ^3J(C,P) = 11.3 Hz, 5-C$(CH_3)_3$], 42.3 [pt, ^2J(C,P) = ^2J(C,P) = 19.9 Hz, 3-$C(CH_3)_3$], 43.5 [d, ^2J(C,P) = 20.8 Hz, 5-$C(CH_3)_3$], 212.3 [dd, ^1J(C,P) = 61.0, ^2J(C,P) = 9.2 Hz, C-5], 227.0 [dd, ^1J(C,P) = 82.7, ^1J(C,P) = 65.8 Hz, C-3].

^{31}P NMR (C_6D_6): δ = 299.6 [d, ^2J(P,P) = 49.1 Hz, P-4], 302.5 [d, ^2J(P,P) = 49.1 Hz, P-2].

MS (EI, 70 eV): *m*/*z* (%) = 330 (23, M^+), 230 (15, M^+ − P≡C-*t*-Bu), 199 (2, M^+ − TeH), 169 (66, [(*t*-BuC)$_2$P]$^+$), 161 (9, [Te–P]$^+$), 99 (87, M^+ − P≡C-*t*-Bu − TeH), 69 (74, [C-*t*-Bu]$^+$), 57 (12, [*t*-Bu]$^+$).

HRMS: *m*/*z* calcd for $C_{10}H_{18}P_2Te$ 329.9951, found 329.9951.

3,5-Di-*tert*-pentyl-1,2,4-telluradiphosphole (15b)

From *tert*-pentylphosphaacetylene (**3b**; 114.1 mg, 1.0 mmol as a 26% solution in hexamethyldisiloxane) and Te (128 mg, 1.0 mmol); yield: 36 mg (20% based on the phosphaacetylene); bp 110°C/0.001 mbar.

^{1}H NMR (C_6D_6): δ = 0.79 [t, ^3J(H,H) = 7.48 Hz, 3 H, CH_2CH_3], 0.83 [t, ^3J(H,H) = 7.38 Hz, 3 H, CH_2CH_3], 1.46 [d, ^4J(H,P) = 1.79 Hz, 6 H, 5-C$(CH_3)_2$], 1.63 [d, ^4J(H,P) = 2.69 Hz, 6 H, 3-C$(CH_3)_2$],

1.69 [q, 2 H, ^3J(H,H) = 7.48 Hz, CH_2CH$_3$], 2.03 [q, 2 H, ^3J(H,H) = 7.38 Hz, CH$_2$CH$_3$].

^{13}C NMR ($CDCl_3$): δ = 9.2 [d, ^4J(C,P) = 1.0 Hz, 3-/5-CH$_2$*C*H$_3$], 9.3 [d, ^4J(C,P) = 2.1 Hz, 3-/5-CH$_2$*C*H$_3$], 31.9 [dd, ^3J(C,P) = 17.9, ^3J(C,P) = 10.5 Hz, 3-C(*C*H$_3$)$_2$], 33.7 [d, ^3J(C,P) = 14.7 Hz, 5-C(*C*H$_3$)$_2$], 40.7 [dd, ^3J(C,P) = 10.5, ^3J(C,P) = 7.4 Hz, 3-C*C*H$_2$], 42.2 [d, ^3J(C,P) = 6.8 Hz, 5-C*C*H$_2$], 48.4 [pt, ^2J(C,P) + ^2J(C,P) = 17.9 Hz, 3-*C*(CH$_3$)$_2$], 49.3 [d, ^2J(C,P) = 21.0 Hz, 5-*C*(CH$_3$)$_2$], 208.5 [dd, ^1J(C,P) = 66.1, ^2J(C,P) = 7.6 Hz, C-5], 226.9 [dd, ^1J(C,P) = 86.5, ^1J(C,P) = 76.3 Hz, C-3].

^{31}P NMR (C_6D_6): δ = 301.9 [d, ^2J(P,P) = 52.5 Hz, P-4], 305.6 [d, ^2J(P,P) = 52.5 Hz, P-2].

MS (EI, 70 eV): *m*/*z* (%) = 358 (78, M^+), 329 (62, $M^+ - CH_2CH_3$), 244 (17, M^+ – P≡C-*t*-Pen), 227 (8, M^+ – TeH), 197 (55, M^+ – TeP), 113 (100, M^+ – P≡C-*t*-Pen – TeH), 83 (60, C-*t*-Pen$^+$).

HRMS: *m*/*z* calcd for $C_{12}H_{22}P_2Te$ 358.0265, found 358.0265.

3,5-Diadamant-1-yl-1,2,4-telluradiphosphole (15c)
From adamant-1-ylphosphaacetylene (**3c**; 205 mg, 1.15 mmol) and Te (190 mg, 1.5 mmol), yield: 42 mg (15% based on the phosphaacetylene), bp 215 °C/0.001 mbar.

^{1}H NMR ($CDCl_3$): δ = 1.56–1.97 (m, 15 H, 1-Ad), 2.00–2.42 (m, 15 H, 1-Ad).

^{13}C NMR ($CDCl_3$): δ = 28.9 (s, CH), 29.1 (s, CH), 36.2 (s, CH_2), 36.5 (s, CH_2), 47.1 [dd, ^2J(C,P) = 21.1, ^2J(C,P) = 14.7 Hz, *i*-C], 47.4 [dd, ^2J(C,P) = 19.7, ^3J(C,P) = 7.2 Hz, *i*-C], 49.0 [d, ^3J(C,P) = 11.1 Hz, CH_2], 49.2 [d, ^3J(C,P) = 9.8 Hz, CH_2], 213.7 [dd, ^1J(C,P) = 60.7, ^2J(C,P) = 8.1 Hz, C-5], 229.1 [dd, ^1J(C,P) = 83.4, ^1J(C,P) = 66.7 Hz, C-3].

^{31}P NMR (C_6D_6): δ = 292.7 [d, ^2J(P,P) = 51.0 Hz, P-4], 295.7 [d, ^2J(P,P) = 51.0 Hz, P-2].

MS (EI, 70 eV): *m*/*z* (%) = 486 (8, M^+), 325 [100, P(C-1-Ad)$_2^+$], 294 (27, 1-AdC≡C-1-Ad$^+$), 147 (4, 1-AdC$^+$), 135 (21, 1-Ad$^+$).

HRMS: *m*/*z* calcd for $C_{22}H_{30}P_2Te$ 486.0892, found 486.0891.

Crystal Structure Analysis of 8a
Crystal Data: $C_{20}H_{36}P_4Se$, M_r = 479.33, monoclinic, space group $P2_1/c$, a = 1627.7(3), b = 974.5(2), c = 1619.9(3) pm, β = 114.80(3)°, V = 2.3325(8) nm^3, Z = 4, d_c = 1.365 Mg/m^3.

Data collection: The data collection was performed using an Imaging Plate Diffraction System (STOE-IPDS) at r.t. Crystal dimensions:0.40 × 0.30 × 0.15 mm. The measurements were made in the range 2.51<θ<25.97°, λ = 0.71073 MoKα (graphite monochromator), $-20 \le h \le 19$, $-11 \le k \le 11$, $-19 \le l \le 19$, a total of 19595 reflections, of which 4425 (3632 with $I>2\sigma_{(I)}$) were independent reflections.

Structure solution and refinement: The structure was solved using direct methods (SHELXS-86)[15] and refined with the full matrix least squares procedure against F^2 (SHELXL-93).[16] The anisotropic refinement converged at R1 = 0.0305 and wR2 = 0.0664 [$I>2\sigma_{(I)}$] and R1 = 0.0392, wR2 = 0.0680 (all data). The difference Fourier synthesis on the basis of the final structural model showed a maximum of 476 e/nm^3 and a minimum of −279 e/nm^3.[17]

Crystal Structure Analysis of 12
Crystal Data: $C_{20}H_{36}Br_2P_4Se$, M_r = 639.15, monoclinic, space group $P2_1/n$, a = 907.1(2), b = 2723.3(5), c = 1008.7(2) pm, β = 90.10(3)°, V = 2.4918(9) nm^3, Z = 4, d_c = 1.704 Mg/m^3.

Data collection: The data collection was performed using an Imaging Plate Diffraction System (STOE-IPDS) at r.t. Crystal dimensions:0.30 × 0.20 × 0.15 mm. The measurements were made in the range 2.15<θ<25.10°, λ = 0.71073 MoKα (graphite monochromator), $-10 \le h \le 10$, $-32 \le k \le 32$, $-11 \le l \le 10$, a total of 16688 reflections, of which 4232 (2873 with $I>2\sigma_{(I)}$) were independent reflections.

Structure solution and refinement: The structure was solved using direct methods (SHELX*S*-86)[15] and refined with the full matrix least squares procedure against F^2 (SHELXL-93).[16] The anisotropic refinement converged at R1 = 0.0698 and wR2 = 0.1626 [$I>2\sigma_{(I)}$] and R1 = 0.0954, wR2 = 0.1755 (all data). The difference Fourier synthesis on the basis of the final structural model showed a maximum of 1324 e/nm^3 and a minimum of −1021 e/nm^3.[17]

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