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A Study of the Reactivity of a Tetraphosphadeltacyclene*

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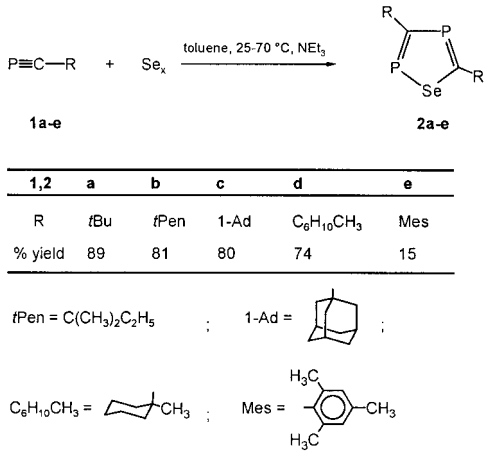
ABSTRACT: *The selective deselenation of the recently described tetraphosphatetracycle* **4a** *leads to the tetraphosphabishomoprismane* **6** *in high yield. Triethylphosphine is used as a deselenating reagent. A further example for a selective decomposition of* **4a** *is performed by mesitylnitrile oxide (***9***), yielding the 1,2,4-oxazaphosphole* **10**. *Bromine and iodine furnish tetracyclic rearrangement products* **13a,b**. *Finally, the applicability of the tetracycle* **4a** *as a ligand in transition metal chemistry is evaluated by complexation with tungsten (***14***) and, respectively, iron (***15***) carbonyl fragments.*

Side aspects of this article are the first synthesis of 3,5-dimesityl-1,2,4-selenadiphosphole **2e** *starting from mesitylphosphaalkyne* **1e**, *as well as the first report on a mixed substitution at a cage compound of type* **4**. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:406–413, 2001

INTRODUCTION

As a part of our superior interest in heterophospholes containing one additional heteroatom [1–5], we recently reported on a convenient, high-yielding synthesis of 1,2,4-selenadiphospholes **2a–d** [6]. In a similar synthetic pathway we also obtained a new class of polycycles, the tetraphosphatetracycles **4a–c**, accessible from the corresponding phosphaalkynes **1a–c** and elemental selenium (Scheme 2).

Comparing the less convenient access to the homologous chalcogenadiphospholes [3,7], the efficiency of the synthesis of the selenadiphospholes **2a–d** (Scheme 1) [6] encouraged us to focus on further derivatives of 1,2,4-selenadiphospholes and to intensify the study of their reactivity. In this context we now report on the synthesis of a previously unknown type of bisaryl-substituted 1,2,4-selenadiphosphole **2e**, as well as on the peculiar features of the tetra-



1,2	a	b	c	d	e
R	*t*Bu	*t*Pen	1-Ad	$C_6H_{10}CH_3$	Mes
% yield	89	81	80	74	15

*t*Pen = $C(CH_3)_2C_2H_5$; 1-Ad = ;

$C_6H_{10}CH_3$ = ; Mes = H_3C, CH_3, H_3C

SCHEME 1

*Dedicated to Professor Naoki Inamoto.

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cyclic cage compounds **4,5**, which we confirm to be accessible from 1,2,4-selenadiphospholes **2a,b,e**.

RESULTS AND DISCUSSION

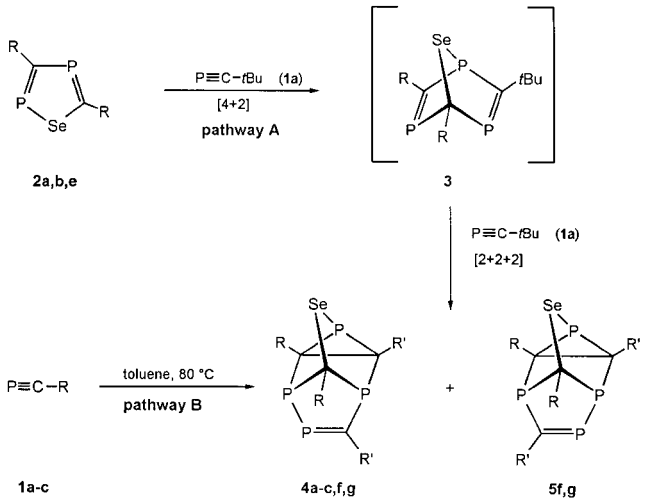
*Synthesis of 3,5-Dimesityl-1,2,4-selenadiphosphole (***2e***)*

With the intention to extend the variety of substituents at 1,2,4-selenadiphospholes **2**, the electronically modified mesitylphosphaalkyne [8] **1e** was applied as a precursor (Scheme 1). The reaction of an excess of elemental selenium (black or gray modification) with the mesitylphosphaalkyne **1e** in toluene at room temperature in the presence of an equimolar amount of triethylamine leads to the 1,2,4-selenadiphosphole **2e**. Due to fast polymerization of the phosphaalkyne, the yield does not exceed 15%. The novel selenadiphosphole shows chemical shifts similar to those of known selenadiphospholes **2a–d** [6]. In particular, the ^{31}P NMR signals with δ = 312.4 and 268.7, and $^{2}J_{P,P}$ = 42, $^{1}J_{P,Se}$ = 429 and $^{2}J_{P,Se}$ = 57.2 Hz identify the compound as a 1,2,4-selenadiphosphole. The slight paramagnetic shift of the P-2 nucleus in comparison to **2a–d** becomes plausible from the electron-withdrawing effect of the mesityl substituents. The formation of **2e** is assumed to follow the earlier suggested mechanism [3,6].

Synthesis of Cage Compounds **4a,f** *and* **5f** *from Selenadiphospholes* **2a,b**

Despite the fact that the most efficient synthetic pathway for the production of the tetracycles **4** starts from an access of phosphaalkyne **1** in the presence of selenium at relatively high temperatures [6], we synthesized the cage compounds **4a,f** from the selenadiphospholes **2a,b** and phosphaalkyne **1a** with the intention to elucidate the mechanism of this reaction (Scheme 2).

The reaction of the bis-*tert*-pentylselenadiphosphole **2b** with *tert*-butylphosphaalkyne **1a** leads to the formation of a pair of regioisomers **4f** and **5f**, which are both characterized by ^{31}P NMR spectroscopy (see Experimental section). The cross experiment shows unambiguously that in a first step, the intermediate selenatriphosphanorbornadiene **3** must be formed regiospecifically. Compound **3f** is unsymmetric in the subsequent homo Diels-Alder cycloaddition of a second equivalent of the phosphaalkyne **1a**; therefore, the two regioisomers **4f** and **5f** are formed in a ratio of 1:1. Since the homo Diels-Alder reaction proceeds much faster than the Diels-Alder reaction of the first step, **3** can neither be isolated nor can it be detected by ^{31}P NMR monitoring of the reaction mixture. Also, according to our expectations, the reaction of bis-*tert*-butylselenadiphosphole **2a** with **1a** yields the cage compound **4a**. Treatment of bis-mesitylselenadiphosphole **2e** with **1a** failed due to the thermal lability of **2e**.



	a	b	c	f	g
R	*t*Bu	*t*Pen	1-Ad	*t*Pen	Mes
R'	*t*Bu	*t*Pen	1-Ad	*t*Bu	*t*Bu
pathway A	72			82	0
pathway B	95	18	49		

SCHEME 2

With the experience from these experiments, we assumed that the formation of the cage compounds **4a–c** starting from an excess of phosphaalkyne **1a–c** and elemental selenium must proceed via the corresponding 1,2,4-selenadiphosphole **2a–c**.

Deselenation of **4a**

The removal of the selenium from the cage structure occurred when **4a** is distilled under reduced pressure above 220°C. In this case, the bishomoprismane **6** was detected in the product mixture, however, only among other decomposition products. A satisfying selectivity is achieved by using triethylphosphine in toluene as a deselenating reagent under severe thermic conditions. For the present experiment, a mixture of the tetraphosphabishomoprismane **6** and the valence isomeric tetraphosphasemibullvalene **7** in a fairly reproducible ratio of approximately 11:3 was obtained. Even so, it is known from the earlier work of our group that the semibullvalene **7** undergoes a slow and thermal isomerization leading to the bishomoprismane **6** [9]. Concerning the mechanism for the formation of **6** and **7**, at first we proposed the generation of the 1,4,6,7-tetraphosphabishomopris-

mane **8**. The thermally induced valence isomerization of this intermediate tetracycle into the products **6** and **7** under the given reaction conditions is also known from our previous work [9,10].

Since the overall yield of the formation of the bishomoprismane **6** is 78% from the starting phosphaalkyne **1a**; this indirect pathway is of a high, previously unrivaled synthetic use.

Decomposition of the Cage Compound **4a** *with Mesitylnitrile Oxide (***9***)*

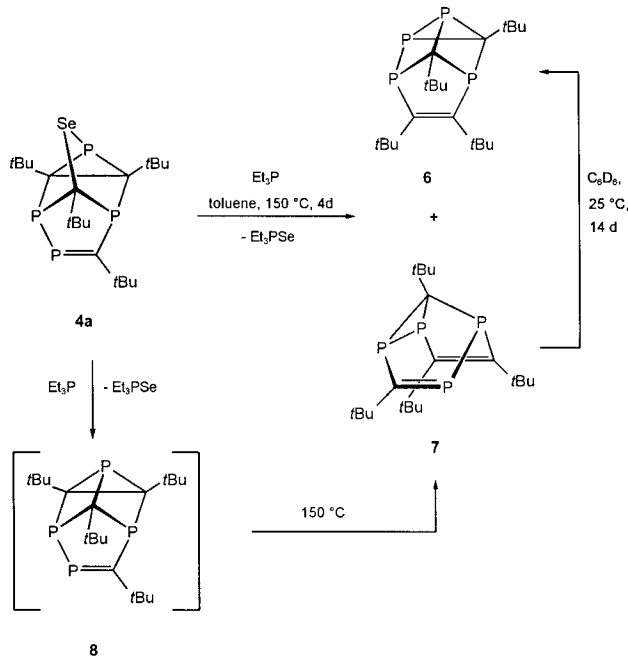
The [3 + 2] cycloaddition of nitrile oxides with phosphaalkynes and phosphaalkenes is well established [11,1b], and even cycloadditions to endo-polycyclic P=C double bonds have been reported by our group [9]. Due to this knowledge, a stable adduct from mesitylnitrile oxide (**9**) and the tetracycle **4a** was expected, and the formation of the 1,2,4-oxazaphosphole **10** is therefore of mechanistic interest. In the first step, the endo-selective [3 + 2] cycloaddition of the mesitylnitrile oxide (**9**) to the phosphaalkene moiety must be assumed since the analogous addition of mesitylnitrile oxide (**9**) to a tetraphosphabishomoprismane was confirmed in a previous example by an X-ray structure analysis [9].

The cycloadduct, however, is unstable and decomposes in a retro-[2 + 2 + 2]-homo Diels-Alder reaction, forming the 1,2,4-oxazaphosphole **10** and also the triphosphaselenanorbornadiene **11**. While the latter compound can neither be isolated nor detected in the reaction mixture by monitoring, it is presumed to decompose further unselectively. The formation of the 1,2,4-oxazaphosphole **10** has been proved unambiguously by spectroscopic analysis and comparison with data reported in the literature [11].

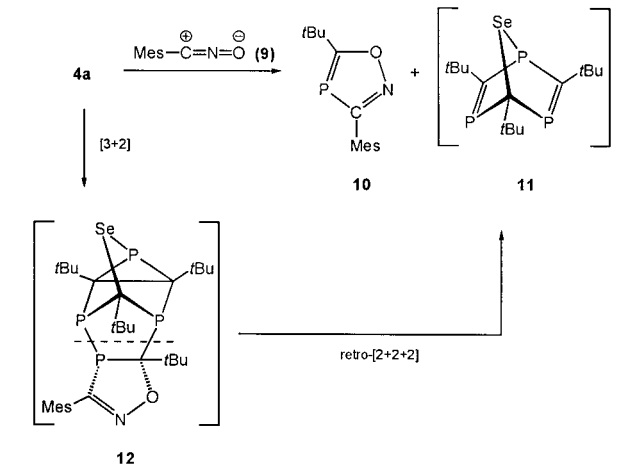
Reaction of Tetracycle **4a** *with Iodine*

Elemental halogens are well known to cleave phosphorus–phosphorus bonds even under mild reaction conditions [12], as found, for example, in the case of tetramers of the *tert*-butylphosphaalkyne [13].

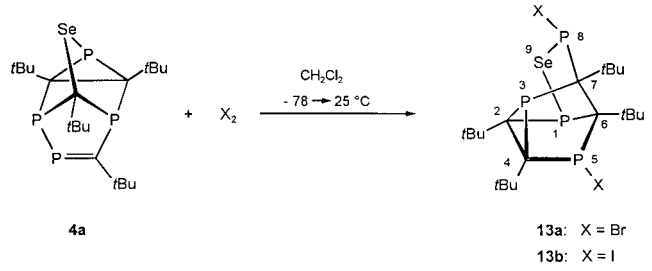
When an equimolar amount of elemental bromine or iodine is slowly added to a solution of **4a** in dichloromethane at −78°C, and the solution is then allowed to thaw with subsequent stirring for 24 hours, a yellow, flaky precipate of **13a** or, respectively, a dark brown precipitate of **3b** is formed (Scheme 5). The pure products were obtained by crystallization from tetrahydrofuran (THF) at −20°C. While the result of the bromination was discussed in the preceding article [6], elemental and mass spectrometric analysis clearly showed that, also in the case of the iodine reaction, two halogen



SCHEME 3



SCHEME 4



SCHEME 5

atoms have been added to the tetracyclic compound **4a**.

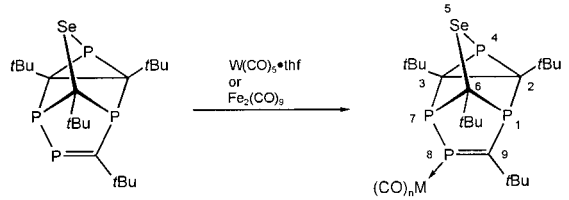
The ^{31}P NMR spectrum of **13b** reveals the presence of four nonequivalent phosphorus atoms. In comparison with the spectrum of **13a**, all resonances are nearly alike; however, the signals of P-5 (δ = 144.3) and P-8 (δ = 213.7) are slightly shifted to higher field, while the signals of P-3 (δ = −101.3) and P-1 (δ = 164.2) are very slightly shifted to lower field. Due to these data and those obtained from the ^{13}C NMR spectra, the cage compounds **13a** and **b** are unambiguously isostructural.

Tetraphosphatetracycle **4a** *as a Ligand in Transition Metal Complexes*

On consideration that the cage compound **4a** may function as an organophosphorus ligand in transition metal chemistry, several possibilities for the regioseletivity of the coordination of the metal would have to be evaluated. In our previous work, alkylation occurred at the P-4 atom, whereas chalcogenation was found to take place at P-7 [6].

Pentacarbonyltungsten Fragment. When a freshly prepared solution of a $W(CO)_5$·THF is caused to react with a pure sample of the deltacyclene **4a** and the mixture is stirred for one day at room temperature, a yellowish solid is obtained after removal of the solvent. Mass spectrometric analysis clearly shows the coordination of the phosphorus cage **4a** to the tungsten.

The ^{31}P NMR spectrum reveals the retention of the cage framework because the coupling pattern is preserved. All signals exhibit a double-double doublet pattern, with the exception of the pseudo triplet structured signal of the phosphirane system in the typical high-field region. However, the phosphaalkene moiety is shifted to higher field by $\Delta\delta$ = −92 to δ = 319.



4a **14, 15**

	14	15
M	W	Fe
n	5	4

SCHEME 6

The regioselectivity of the coordination becomes obvious from the tungsten satellite signals ($^1J_{W,P}$ = 233.6 Hz), confirming the direct adjacency of the tungsten to the phosphaalkene subunit. Concomitantly, the P-7–P-8 coupling increases by a typically small value up to 316 Hz, again indicating that the attack of the tungsten must have occurred at one of these positions.

The ^{13}C NMR data support the deductions from the ^{31}P NMR spectrum (see Experimental section), whereas an X-ray crystallographic analysis (Figure 1) irrevocably confirms the structure of this transition metal complex T [14].

The η^1-coordination of the pentacarbonyl tungsten subunit to P-8 is shown clearly. The W–P bond length of 2.523(2) Å is in the usual range for this bond type [15]. Both the P–C bond length of the phosphaalkene subunit (1.696 Å) and the angular sum at C-9 (Σ = 358.5°) are nearly in congruity with the precursor **4a**.

Tetracarbonyliron Fragment. In the case of treatment of the tetraphosphatetracycle **4a** with nonacarbonyldiiron, an analogous reactivity is observed. Once again, the ^{31}P NMR spectra reveals four magnetically inequivalent phosphorus nuclei. The

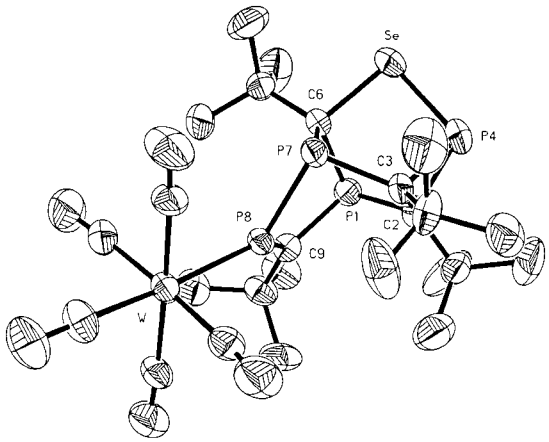


FIGURE 1 Crystal Structure [14] of **14**. Selected bond lengths (Å) and angles (°). Se–C(6) 1.986(7), Se–P(4) 2.232(2), P(1)–C(9) 1.866(7), P(1)–C(6) 1.865(7), P(1)–C(2) 1.875(7), P(8)–C(9) 1.696(7), P(8)–P(7) 2.218(3), P(7)–C(6) 1.862(7), P(7)–C(3) 1.878(7), P(4)–C(3) 1.859(7), P(4)–C(2) 1.878(8), C(2)–C(3) 1.576(11), W–P(8) 2.523(2); C(6)–Se–P(4) 91.0(2), C(9)–P(1)–C(6) 97.4(3), C(9)–P(1)–C(2) 101.7(3), C(6)–P(1)–C(2) 94.4(3), C(9)–P(8)–P(7) 101.1(3), C(6)–P(7)–C(3) 94.5(3), C(6)–P(7)–P(8) 94.(2), C(3)–P(7)–P(8) 98.3(2), C(3)–P(4)–C(2) 49.9(3), C(3)–P(4)–Se 100.3(2), C(2)–P(4)–Se 100.7(2) P(7)–C(6)–P(1) 102.7(3), P(7)–C(6)–Se 105.2(3), P(1)–C(6)–Se 103.9(3), P(8)–C(9)–P(1) 113.5(4), C(3)–C(2)–P(4) 64.4(4), C(3)–C(2)–P(1) 111.8(5), P(4)–C(2)–P(1) 111.5(4), C(2)–C(3)–P(4) 65.7(4), C(2)–C(3)–P(7) 109.8(5), P(4)–C(3)–P(7) 113.6(4).

coupling patterns as well as the chemical shifts are alike with those of the tungsten complex **14**. Especially the double-double doublet structure of the signal in the low-field region (δ = 347.9) rises between the shifts of the precursor **4a** and that of the tungsten complex **14**, thus indicating that the phosphaalkene subunit is preserved.

The coordination of the cage compound to the iron is further illustrated by the ^{13}C NMR spectra. The carbonyl ligands in equatorial and axial positions are allocated to the signals at δ = 214.0 and 215.5. The axial carbonyl ligand reveals furthermore a coupling with P-8 ($^2J_{P,C}$ = 6.4 Hz), whereas the equatorial carbonyls are split into a double doublet ($^2J_{P,C}$ = 15.7 Hz, $^3J_{P,C}$ = 3.6 Hz). Due to the absence of a significant large coupling between P-8 and the carbonyl-C, well known as a trans effect, we assume an equatorial coordination of P-8 in the iron complex **15**.

EXPERIMENTAL

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 **1a–d** [16], **1e** [8], **2a,b, 4a, 13a** [6], and **9** [17] were prepared by published methods. 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 hours in vacuo and then deactivated with 4% water (Brockmann activity II). The bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus (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. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AC 200 and Bruker AMX 400 spectrometers and referenced to the solvent as an internal standard. ^{31}P NMR spectra were measured on a Bruker AC 200 (80.8 MHz) spectrometer with 85% H_3PO_4 as an external standard. Mass spectrometry (MS) and high-resolution mass spectrometry (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.

*3,5-Dimesityl-1,2,4-selenadiphosphole (***2e***)*

A mixture of an excess of selenium (103 mg, 1.3 mmol), Et_3N (0.18 mL, 1.3 mmol), and mesitylphosphaalkyne (175 mg, 1.1 mmol) was stirred at room temperature in toluene (3 mL) in a Schlenk pressure tube. After 14 days (^{31}P NMR monitoring) the insoluble material was removed by filtration through a D3 sinter filled to a depth of 3 cm with Celite. The product was purified by bulb-to-bulb distillation and obtained as a yellowish oil. Yield: 33 mg (15% based on phosphaalkyne); b.p. 205°C/10^{-3} mbar. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 312.4 (d, $^2J_{P,P}$ = 42.0, $^1J_{P,Se}$ = 429.2 Hz; P-2), 268.7 (d, $^2J_{P,P}$ = 42.0, $^2J_{P,Se}$ = 57.2 Hz; P-4); ^1H NMR (C_6D_6): δ = 7.51 (s, 2H, *meta*-H), 7.13 (s, 2H, *meta*-H), 2.31–2.64 (b, 12H, CH_3 (4×)), 1.65 (s, 3H, CH_3), 1.27 (s, 3H, CH_3).

*3,6-Bis(1,1-dimethylpropyl)-2,9-(di-tert-butyl-5-selena-1,4,7,8-tetraphospha-tetracyclo [4.3.0.0.^{2,4}.0^{3,7}]non-8-ene (***4f***) and 2,6-Bis(1,1-dimethylpropyl)-3,9-(di-tert-butyl-5-selena-1,4,7,8-tetraphosphatetracyclo[4.3.0.0.^{2,4}.0^{3,7}] non-8-ene (***5f***)*

To a solution of 1,2,4-*tert*-pentylselenadiphosphole **2b** (215 mg, 0.7 mmol) in toluene, an excess of *tert*-butylphosphaalkyne **1a** (0.23 mL, 1.75 mmol) was added. The reaction mixture was heated for 7 days at 90°C in a Schlenk pressure tube, and an orange solution was obtained. After the solution had been allowed to cool, all volatile components were removed in vacuo, and the orange residue was subjected to column chromatography (silica gel, pentane:ether 2:1). The second, pale orange fraction gave a mixture of pure **4f, 5f**, after removal of the solvent. Yield: 322 mg (90% of the diphosphole); m.p. 145°C. Regioisomer **4f** or **5f**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 410.4 (dd, $^1J_{P,P}$ = 279.0, $^2J_{P,P}$ = 17.4 Hz; P-8); 136.9 (dd, $^1J_{P,P}$ = 279.0, $^2J_{P,P}$ = 34.9 Hz; P-7); 122.9 (dd, $^2J_{P,P}$ = 34.9, $^2J_{P,P}$ = 17.4 Hz; P-1); −98.9 (s, $^1J_{P,Se}$ = 244.1 Hz; P-4); regioisomer **4f** or **5f**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 409.6 (dd, $^1J_{P,P}$ = 279.0, $^2J_{P,P}$ = 17.4 Hz; P-8); 133.8 (dd, $^1J_{P,P}$ = 279.0, $^2J_{P,P}$ = 34.9 Hz; P-7); 121.4 (dd, $^2J_{P,P}$ = 34.9, $^2J_{P,P}$ = 17.4 Hz; P-1); −101.3 (s, $^1J_{P,Se}$ = 244.1 Hz; P-4).

Deselenation of **4a***: 3,5,7,8-Tetra-tert-butyl-1,2,4,6-tetraphosphabishomoprismane (***6***)*

Compound **4a** (90.6 mg, 0.19 mmol) was dissolved in 3 mL of toluene in a Schlenk pressure tube, and triethylphosphine (56 μL, 0.38 mmol) was added. The solution was heated for 4 days (^{31}P NMR reaction monitoring) at 150°C; afterward, the volatile components were removed in vacuo. The residue was dissolved in pentane, and the insoluble material was removed by filtration through a D3 sinter filled to a depth of 2 cm with Celite. Again, the solvent was removed and a mixture of yellow and white crystalls

were obtained. The remaining Et_3PSe was removed by bulb-to-bulb distillation (first fraction, 120°C/10^{-3} mbar), and **6** and **7** were obtained as a second fraction (160°C/10^{-3} mbar). After the product mixture had been left for two weeks in benzene, complete isomerization of the tetraphosphasemibullvalene **7** to the tetraphosphabishomoprismane **6** was observed (^{31}P NMR reaction monitoring), and **6** was isolated as yellow crystals without further purification. Yield: 63 mg (0.16 mmol, 82%; mixture of **6** and **7**, complete isomerizable to **6**); b.p. 160°C/10^{-3} mbar; spectroscopic data for **6**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 91.6 (pt, $^2J_{P,P}$ = 34.1 Hz; P-6), 86.7 (ddd, $^1J_{P,P}$ = 173.2, $^2J_{P,P}$ = 34.1, $^2J_{P,P}$ = 11.8 Hz; P-1), −152.5 (ddd, $^1J_{P,P}$ = 107.3, $^2J_{P,P}$ = 34.1, $^2J_{P,P}$ = 11.8 Hz; P-4), −238.7 (dd, $^1J_{P,P}$ = 168.1, $^1J_{P,P}$ = 107.3 Hz; P-2); ^{1}H NMR (C_6D_6): 1.43 (d, $^4J_{P,H}$ = 2.4 Hz; C(C$\underline{H}_3$)$_3$), 1.40 (s; C(C$\underline{H}_3$)$_3$), 1.12 (s; C(C$\underline{H}_3$)$_3$), 0.80 (s; C(C$\underline{H}_3$)$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 177.9 (ddd, $^1J_{P,C}$ = 43.6, $^2J_{P,C}$ = 4.0, $^2J_{P,C}$ = 1.6 Hz; C-8), 173.5 (dd, $^1J_{P,C}$ = 45.3, $^2J_{P,C}$ = 10.5 Hz; C-7), 55.7 (dpt, $^1J_{P,C}$ = 81.0, $|^1J_{P,C} + {}^1J_{P,C}|$ = 30.7 Hz; C-5), 41.4 (d, $^2J_{P,C}$ = 27.5; C(CH$_3$)$_3$), 38.2 (dd, $^2J_{P,C}$ = 23.7, $^3J_{P,C}$ = 1.2; C(CH$_3$)$_3$), 35.4 (d, $^3J_{P,C}$ = 14.6 Hz; C(C$\underline{H}_3$)$_3$), 34.1 (ptd, $^2J_{P,C}$ = 14.4, $^2J_{P,C}$ = 6.9 Hz; C(CH$_3$)$_3$), 33.4 (m; C(C$\underline{H}_3$)$_3$), 33.4 (d, $^3J_{P,C}$ = 17.4 Hz; C(C$\underline{H}_3$)$_3$), 33.0 (m; C-3); 32.4 (m; C(C$\underline{H}_3$)$_3$), 26.8 (ptd, $|^3J_{P,C} + {}^3J_{P,C}|$ = 7.9, $^3J_{P,C}$ = 5.1 Hz; C(C$\underline{H}_3$)$_3$); EIMS (70 eV): 400 (61, M^+), 262 (100, $[P_4(C^tBu)_2]^+$), 169 (92, $[P(C^tBu)_2]^+$), 57 (45, $[^tBu]^+$), HRMS ($C_{20}H_{36}P_4$): Calcd.: 400.1765; found: 400.1766.

*5,8-Diiodo-2,4,6,7-tetra-tert-butyl-9-selena-1,3,5,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]-nonane (***13b***)*

To a magnetically stirred solution of **4a** (112 mg, 0.25 mmol) in CH_2Cl_2 (3 mL) at −78°C was added slowly an equimolar amount of iodine (2.03 mL of a 0.125 M solution in CH_2Cl_2, 64 mg, 0.25 mmol). The mixture was allowed to warm to room temperature and stirred for 24 hours to complete the reaction. The color of the solution changed to dark brown. After the volatile components had been removed in high vacuum, **13b** was purified by recrystallization at −20°C from THF to give yellow crystals. Yield: 147 mg (80%); m.p.: 75°C (decomp.); $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 213.7 (dd, $^2J_{P,P}$ = 22.9, $^2J_{P,P}$ = 11.4, $^1J_{P,Se}$ = 364.3 Hz; P-8), 164.2 (dpt, $^2J_{t,P}$ = 22.9, $^2J_{P,P}$ = 3.8, $^1J_{P,Se}$ = 223.2 Hz; P-1), 144.3 (dd, $^2J_{P,P}$ = 11.4, $^2J_{P,P}$ = 3.8 Hz; P-5), −101.3 (d, $^2J_{P,P}$ = 3.8 Hz; P-3); ^{1}H NMR ($CDCl_3$): 1.65 (d, 9H, $^4J_{P,H}$ = 2.3 Hz; C(C$\underline{H}_3$)$_3$), 1.52 (d, 9H, $^4J_{P,H}$ = 1.9 Hz; C(C$\underline{H}_3$)$_3$), 1.51 (d, 9H, $^4J_{P,H}$ = 2.1 Hz; C(C$\underline{H}_3$)$_3$), 1.48 (s, 9H; C(C$\underline{H}_3$)$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6): 69.2 (overlapping multiplet, unresolved; frame-C), 68.0 (overlapping multiplet, unresolved; frame-C), 62.8 (overlapping multiplet, unresolved; frame-C), 50.0 (overlapping multiplet, unresolved; frame-C), 49.4 (pt, $|^2J_{P,C} + {}^2J_{P,C}|$ = 8.8 Hz; C(CH$_3$)$_3$), 43.7 (dd, $^2J_{P,C}$ = 28.0, $^2J_{P,C}$ = 15.3 Hz; C(CH$_3$)$_3$), 37.1 (dd, $^2J_{P,C}$ = 14.7, $^2J_{P,C}$ = 9.8 Hz; C(CH$_3$)$_3$), 35.7 (dd, $^2J_{P,C}$ = 15.5, $^2J_{P,C}$ = 10.8 Hz; C(CH$_3$)$_3$), 35.1 (pt, $|^3J_{P,C} + {}^3J_{P,C}|$ = 16.8 Hz; C(C$\underline{H}_3$)$_3$), 34.4 (d, $^3J_{P,C}$ = 4.1 Hz; C(C$\underline{H}_3$)$_3$), 34.2 (d, $^3J_{P,C}$ = 5.7 Hz; C(C$\underline{H}_3$)$_3$), 33.9 (dd, $^3J_{P,C}$ = 5.9, $^3J_{P,C}$ = 3.7 Hz; C(C$\underline{H}_3$)$_3$); IR (CCl_4): 2961 (s, CH), 1717 (w), 1551 (m, *t*-Bu), 1398 (w), 1367 (m), 1260 (s), 1070(s), 752 (vs); EIMS (70 eV): 606 (3, $[M - I]^+$), 479 (16, $[M - 2I]^+$), 400 (4, $[M - 2I - Se]^+$), 231 (5, $[P_3C\text{-}t\text{-}Bu_2]^+$), 169 (100, $[P(C\text{-}t\text{-}Bu)_2]^+$), 131 (19, $[P_2C\text{-}t\text{-}Bu]^+$), 69 (12, $[C\text{-}t\text{-}Bu]^+$), 57 (16, $[t\text{-}Bu]^+$), elemental analysis $C_{20}H_{36}P_4SeI_2$: (733.16 g/mol) calcd.: C, 32.76; H, 4.95; found: C, 32.41; H, 4.85.

*8-η^1-2,3,6,9-Tetra-tert-butyl-5-selena-1,4,7,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-pentacarbonyltungsten (***14***)*

A suspension of hexacarbonyltungsten (129 mg, 0.37 mmol) in 13 mL THF was irradiated for 20 minutes in a water-cooled photoreactor. The yellowish solution of pentacarbonyltetrahydrofuranetungsten was added to a pure sample of **4a** (146 mg, 0.30 mmol), and the mixture was stirred for 24 hours. After removal of the solvent in a high vacuum, the residue was subjected to column chromatography on silica gel. Compound **14** was eluted with pentane as a second, yellowish-orange fraction. After evaporation of the solvent, **14** was obtained as a bright yellow solid. Recrystallization from benzene gave single crystals, which were suitable for X-ray analysis. Yield: 171 mg (70% from **4a**); m.p.: 90°C; $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 318.7 (ddd, $^1J_{P,P}$ = 315.7, $^2J_{P,P}$ = 23.2, $^3J_{P,P}$ = 6.3, $^1J_{P,W}$ = 233.6 Hz; P-8), 153.6 (ddd, $^1J_{P,P}$ = 315.7, $^2J_{P,P}$ = 31.2, $^3J_{P,P}$ = 1.4, $^2J_{P,W}$ = 13.1 Hz; P-7), 127.8 (ddd, $^2J_{P,P}$ = 31.2, $^2J_{P,P}$ = 23.2, $^2J_{P,P}$ = 1.1 Hz; P-1), −101.8 (dd, $^2J_{P,P}$ = 6.3, $^2J_{P,P}$ = 2.1, $^1J_{P,Sc}$ = 216.2 Hz; P-4); ^{1}H NMR (C_6D_6): δ = 1.66 (s, 9H; C(C$\underline{H}_3$)$_3$), 1.39 (s, 9H; C(C$\underline{H}_3$)$_3$), 1.30 (s, 9H; C(C$\underline{H}_3$)$_3$), 1.25 (s, 9H; C(C$\underline{H}_3$)$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6): 226.9 (ddd, $^1J_{P,C}$ = 74.1, $^1J_{P,C}$ = 26.2, $^2J_{P,C}$ = 3.1 Hz; C-9), 198.9 (dd, $^2J_{P,C}$ = 29.3, $^3J_{P,C}$ = 2.1 Hz; C$\underline{O}_{ax.}$), 196.1 (dd, $^2J_{P,C}$ = 7.4, $^3J_{P,C}$ = 2.8 $^1J_{C,W}$ = 125.9 Hz; C$\underline{O}_{eq.}$), 77.5 (overlapping multiplets, unresolved; C-6), 71.7 (overlapping multiplets, unresolved; C-3), 67.8 (overlapping multiplets, unresolved; C-2), 43.2 (d, $^2J_{P,C}$ = 19.5 Hz; C9C(CH$_3$)$_3$), 37.8 (dpt, $|^2J_{P,C} + {}^2J_{P,C}|$ = 23.7, $^3J_{P,C}$ = 2.7 Hz; C(CH$_3$)$_3$), 36.6 (dd, $^3J_{P,C}$ = 11.7, $^3J_{P,C}$ = 7.4 Hz; C(C$\underline{H}_3$)$_3$), 35.8 (dpt, $|^2J_{P,C} + {}^2J_{P,C}|$ = 36.9, $^3J_{P,C}$ = 1.8

Hz; C(CH$_3$)$_3$), 35.3 (ddd, $^2J_{P,C}$ = 19.7, $^2J_{P,C}$ = 9.6, $^3J_{P,C}$ = 1.6 Hz; C(CH$_3$)$_3$), 34.9 (ddd, $^3J_{P,C}$ = 12.5, $^3J_{P,C}$ = 6.8, $^4J_{P,C}$ = 2.4 Hz; C(CH$_3$)$_3$), 34.5 (dpt, $|^3J_{P,C} + {}^3J_{P,C}|$ = 9.23, $^4J_{P,C}$ = 1.2 Hz; C(CH$_3$)$_3$), 33.9 (dd, $^3J_{P,C}$ = 7.6, $^3J_{P,C}$ = 4.0 Hz; C(CH$_3$)$_3$); IR (CCl_4): 2950 (m, CH), 2073(CO), 1954(CO), 1550 (*t*-Bu), 1253 (w) 1006 (w), 790 (vs); EIMS (70eV): *m/z* = 803 (1, $[M]^+$), 664 (1, $[M - 5CO]^+$), 480 (25, $[M - W(CO)_5]^+$), 231 (13, $[P_3C\text{-}t\text{-}Bu_2]^+$), 169 (47, $[P(C\text{-}t\text{-}Bu)_2]^+$), 69 (100, [C-*t*-Bu]$^+$), 57 (18, [*t*-Bu]$^+$); elemental analysis $C_{25}H_{36}O_5P_4SeW$ (803.2 g/mol): calcd.: C, 37.38, H, 4.52; found: C, 37.93; H, 4.79.

*8-η¹-2,3,6,9-Tetra-tert-butyl-5-selena-1,4,7,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-en-tetracarbonyl iron (***15***)*

To a suspension of nonacarbonyldiiron (102 mg, 0.28 mmol) in 5 mL of toluene maintained at room temperature, a solution of the tetracycle **4a** (112 mg, 0.24 mmol) in 3 mL of toluene was added dropwise. After the suspension has been stirred for 5 days, the insoluble material was removed by filtration through a D3 sinter filled to a depth of 2 cm with Celite (eluent: toluene). Pure **15** was obtained as a red oil after removal of the solvent in vacuo. Yield: 129 mg (85%); b.p. 147°C/10^{-3} mbar; $^{31}P\{^1H\}$ NMR (C_6D_6): 347.9 (ddd, $^1J_{P,P}$ = 343.3, $^2J_{P,P}$ = 22.9, $^3J_{P,P}$ = 5.7 Hz; P-8), 151.1 (dd, $^1J_{P,P}$ = 343.3, $^2J_{P,P}$ = 28.6 Hz; P-7), 129.7 (dpt, $|^2J_{P,P} + {}^2J_{P,P}|$ = 53.4, $^2J_{P,P}$ = 3.8 Hz; P-1), −100.5 (dpt, $|^2J_{P,P} + {}^2J_{P,P}|$ = 10.91, $^2J_{P,P}$ = 2.4, $^1J_{P,Se}$ = 213.7 Hz; P-4); ^{1}H NMR (C_6D_6): 1.62 (s, 9H; C(CH$_3$)$_3$), 1.43 (s, 9H; C(CH$_3$)$_3$), 1.31 (s, 18H; C(CH$_3$)$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6): 220.5 (ddd, $^1J_{P,C}$ = 73.8, $^1J_{P,C}$ = 28.4, $^2J_{P,C}$ = 4.4 Hz; C-9), 215.4 (d, $^2J_{P,C}$ = 6.4 Hz; CO$_{ax.}$), 214.0 (dd, $^2J_{P,C}$ = 15.7, $^3J_{P,C}$ = 3.6 Hz; CO$_{eq.}$), 74.8 (overlapping multiplets, unresolved; C-6), 72.3 (overlapping multiplets, unresolved; C-3), 67.5 (overlapping multiplets, unresolved; C-2), 43.4 (d, $^2J_{P,C}$ = 19.5 Hz; C-9-C(CH″$_3$)$_3$), 38.2 (dpt, $|^2J_{P,C} + {}^2J_{P,C}|$ = 20.4, $^3J_{P,C}$ = 2.1 Hz; C(CH$_3$)$_3$), 36.8 (ddd, $^2J_{P,C}$ = 19.7, $^2J_{P,C}$ = 11.7, $^3J_{P,C}$ = 2.4 Hz; C(CH$_3$)$_3$), 36.4 (ddd, $^2J_{P,C}$ = 10.4, $^2J_{P,C}$ = 7.6, $^3J_{P,C}$ = 1.6 Hz; C(CH$_3$)$_3$), 35.1 (dpt, $|^3J_{P,C} + {}^3J_{P,C}|$ = 21.7, $^4J_{P,C}$ = 1.2 Hz; C(CH$_3$)$_3$), 34.5 (pt, $|^3J_{P,C} + {}^3J_{P,C}|$ = 19.5 Hz; C(CH$_3$)$_3$), 33.5 (pt, $|^3J_{P,C} + {}^3J_{P,C}|$ = 8.0 Hz; C(CH$_3$)$_3$), 33.3 (dpt, $|^3J_{P,C} + {}^3J_{P,C}|$ = 7.6, $^4J_{P,C}$ = 1.0 Hz; C(CH$_3$)$_3$); IR (CCl_4): 2963 (s, CH), 2055 (vs, CO), 1985 (vs, CO), 1551 (m, *t*-Bu), 1472 (m, *t*-Bu), 1396 (m), 1366 (m), 1204 (m), 1007 (w), 764 (vs), 613 (s); EIMS (70eV): *m/z* = 647 (1, $[M]^+$), 564 (13, $[M - 3CO]^+$), 536 (9, $[M - 4CO]^+$), 480 (64, $[M - Fe(CO)_4]^+$), 400 (6, $[M - Fe(CO)_4 - Se]^+$), 169 (73, $[P(C\text{-}t\text{-}Bu)_2]^+$), 57 (100, [*t*-Bu]$^+$); elemental analysis: $C_{24}H_{36}O_4P_4SeFe$ (647.25 g/mol): calcd.: C, 44.54; H, 5.61; found: C, 46.13; H, 6.19.

Crystal Structure Analysis of **14**

Crystal Data: $C_{25}H_{36}O_5P_4SeW$, M_r = 803.2, triclinic, space group $P\bar{1}$, a = 1006.7(2), b = 1118.9(2), c = 1680.9(4) pm, α =, β = 74.320(10)°, γ = V = 1.6706(6) nm^3; Z = 2; d_c = 1.597 Mg/m^3.

Data collection: The data collection was performed using an automatic four-circle diffractometer (Siemens P4) at 293(2) K. Crystal dimensions: 0.3 × 0.25 × 0.2. The measurements were made in the range $-1.99 < \theta < 24.02°$, λ = 0.71073 Mo Kα (graphite monochromator), $-1 \le h \le 11$, $-12 \le k \le 12$, $-18 \le 1 \le 19$, a total of 6260 reflections, of which 5343 were independent reflections.

Structure solution and refinement: The structure was solved using direct methods (SHELXS-86) [18] and refined with the full matrix least-squares procedure against F^2 (SHELXL-93) [19]. The anisotropic refinement converged at R^1 = 0.0405 and wR^2 = 0.0977 [$I \ge 2\sigma_{(I)}$] and R^1 = 0.0546, wR^2 = 0.1018 [all data]. The difference Fourier synthesis on the basis of the final structural model showed a maximum of 886 e/nm^3 and a minimum of −1498 e/nm^3 [14].

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[14] Crystallographic data (excluding structure factors) for compound **14** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-153051. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).
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