A Novel Approach to 1,2,4-Thiadiphospholes and Functionalized 1,2-Thiaphospholes[‡]

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Phosphaalkynes **1** react regiospecifically in the presence of the thiotantalum(V) compound **2** to afford the 1,2,4-thiadiphospholes **3**. These compounds can function both as η^1 and as η^5 ligands in complexes with group-6 metals. [4+2] Cycloaddition reactions only occur with phosphaalkynes or highly reactive acetylenes as reaction partners. These reactions afford on the one hand the functionalized 1,2-thiaphospholes **17** and, on the other hand, the deltacyclenes **23** and **11**; the latter undergo noteworthy subsequent reactions. In the course of syntheses of the 1,2-thiaphospholes **17**, traces of the tetracyclic cage compounds **18** and **19** can also be isolated.

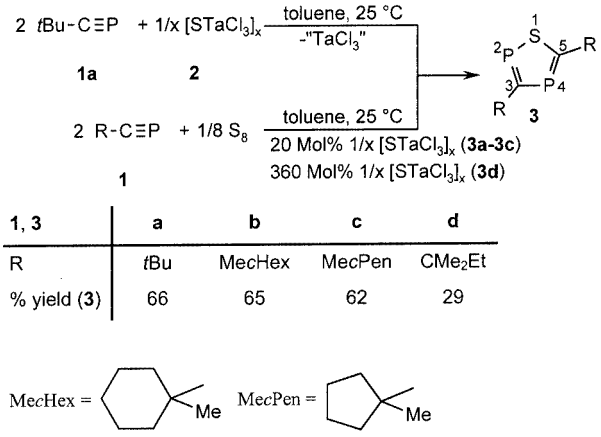
Introduction

Phospholes containing a group-16 heteroatom are attracting increasing interest in the chemistry of low-coordinate phosphorus compounds.[2−7] However, they are still prepared by methods that are of a complex nature or are not generally applicable, and that often furnish only poor yields. Two-component cyclizations involving 2 equiv. of a phosphaalkyne and the elements oxygen, sulfur, selenium, or tellurium represent an interesting alternative; such reactions have already been accomplished with the elements selenium and tellurium,[8] but all attempts so far to use oxygen and sulfur have failed. We now report on a generally applicable synthesis of 1,2,4-thiadiphospholes **3** from kinetically stabilized phosphaalkynes **1** and elemental sulfur, catalyzed by the trichlorothiotantalum complex **2**. In addition, we have found that reactions between **3** and electron-poor acetylenes proceed through a Diels−Alder/retro-Diels−Alder sequence to furnish the 1,2-thiaphospholes **17**, previously only accessible with difficulty.[9,10]

Results and Discussion

Synthesis of 1,2,4-Thiadiphospholes

Phosphaalkynes **1** react with the polymeric trichlorotantalum sulfide **2** at room temperature in a heterogeneous reaction to form the 1,2,4-thiadiphospholes **3** (Scheme 1).[11] As we have demonstrated with the example of the *tert*-butyl derivative **3a**, the efficiency of this synthesis depends strongly on the history of the tantalum complex **2**. When compound **2** was prepared from tantalum(V) chloride and antimony(III) sulfide,[12] the reaction was incomplete and had to be driven to conclusion by the addition of elemental sulfur. In contrast, compound **2** prepared from tantalum(V) chloride and hexamethyldisilathiane[13] reacted smoothly and completely with **1a**. The latter tantalum complex was also able to serve as a catalyst for the synthesis of **3a−c** from **1a−c** and elemental sulfur, provided that pure, hexamethyldisiloxane-free phosphaalkynes **1a−c** were used. The thiadiphosphole **3d** was only obtained in satisfactory yield when an excess of the tantalum complex **2** was employed. The reason for this is that the phosphaalkyne **1d** cannot be prepared free of hexamethyldisiloxane. The by-product



1, 3	a	b	c	d
R	*t*Bu	MecHex	MecPen	CMe_2Et
% yield (**3**)	66	65	62	29

Scheme 1. Synthesis of the 1,2,4-thiadiphospholes **3**

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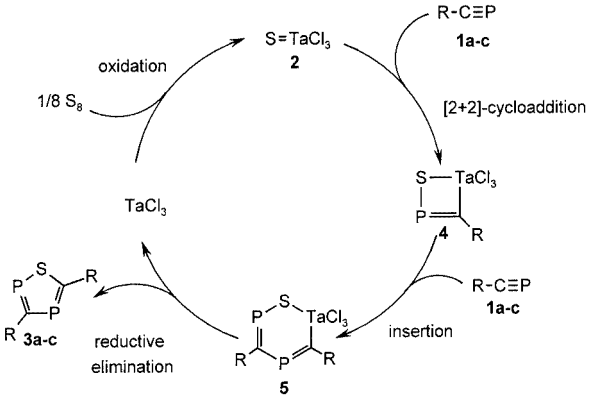
introduced into the reaction mixture by this means apparently reacts irreversibly with **2**, as is also known for niobium(V) chloride and tungsten hexachloride.[14]

For the catalytic formation of the 1,2,4-thiadiphospholes **3a−c** we propose the following reaction mechanism (Scheme 2). The first step involves a [2+2] cycloaddition between **1a−c** and **2** with formation of the metallacyclic species **4**.[15] Insertion of a further molecule of **1a−c** into the metal−carbon bond affords the six-membered metallacycle **5**. This intermediate undergoes a reductive elimination to form the 1,2,4-thiadiphospholes **3a−c**, and the resulting tantalum compound is reoxidized with elemental sulfur to the catalyst **2**.

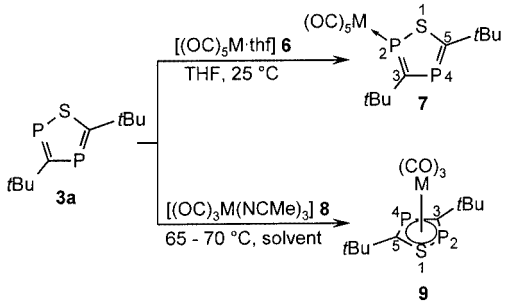


Scheme 2. Proposed reaction mechanism for the catalytic formation of **3a−c**

The molecular compositions of the heterodiphospholes **3** can be derived directly from their elemental analysis data and their high-resolution mass spectra. Furthermore, the ^{31}P and ^{13}C NMR spectra provide valuable diagnostic information. The ^{31}P NMR spectra of all thiadiphospholes **3** contained two doublets ($\delta \approx 267, 255$) in the region typical for a heterodiphosphole. The magnitude of the coupling constants, of 50 Hz on average, was typical for $^{2}J_{P,P}$ couplings. In the ^{13}C NMR spectra the ring carbon atoms gave rise to double doublet signals at low field. The signal for the carbon atom C(5) exhibited a chemical shift of $\delta \approx 209$ with an average $^{1}J_{C,P}$ coupling constant of 67 Hz and an appreciably smaller $^{2}J_{C,P}$ coupling of about 4 Hz. In contrast, the signal for C(3) ($\delta \approx 221$) exhibited two comparably large coupling constants of 70 and 78 Hz on average, on account of its direct adjacency to the two phosphorus atoms. Thus, the regiochemistry of the thiadiphospholes can be unequivocally confirmed as that of the 1,2,4 isomers on the basis of the obtained NMR spectroscopic data.

Group-6 Metal Complexes of 1,2,4-Thiadiphospholes

The thiadiphospholes **3** should theoretically be able to form η^1 or η^5 complexes with transition metals. We have examined the behavior of **3a** towards carbonyl complexes of group-6 metals. Thus, when the 1,2,4-thiadiphosphole **3a** was allowed to react with the pentacarbonyl(tetrahydrofuran)metal complexes **6** (M = Cr, W), the η^1 complexes **7**



6, 7	a	b	8, 9	a	b
M	Cr	W	M	Mo	W
% yield (**7**)	51	22	% yield (**9**)	33	40
			solvent	THF	toluene

Scheme 3. Group-6 metal complexes of 1,2,4-thiadiphospholes

were obtained even at room temperature, by selective coordination of the phosphorus atom P(2) (Scheme 3).[16]

The 1:1 addition of the pentacarbonylmetal fragment to the heterocyclic compound **3a** was unambiguously confirmed by the elemental analysis and mass spectroscopic data. The EI mass spectra revealed the respective molecular ion peaks at m/z = 424 (**7a**) and 556 (**7b**). The observed isotope patterns agreed with those of simulations. The typical cleavage pattern for carbonyl complexes − of first two, then four, and finally five carbonyl ligands − was also observed. The IR spectrum of **7a** contained four carbonyl bands in the region of $\tilde{\nu}$ = 1929 to 2072 cm^{-1}. The ^{31}P and ^{13}C NMR spectra provided information on the site and type of the complexation. In the case of the tungsten complex **7b** there was a marked shielding of the phosphorus atom P(2), as demonstrated by the high-field shift of the ^{31}P NMR signal from δ = 266.8 in the uncomplexed thiadiphosphole **3a** to δ = 208.2 in **7b**. Furthermore, this signal exhibited tungsten satellites with a typical $^{1}J_{P,W}$ coupling constant of 247 Hz. A similar tendency was observed for an analogous tungsten complex of a 1,2,4-selenadiphosphole, the constitution of which was confirmed by X-ray crystallography.[17] Practically no change in the chemical shift of the P(2) signal of **7a** was observed. In comparison to **7b**, however, the signal of phosphorus atom P(4) experienced a larger shift to lower field of around 10 ppm. The analogous chromium complex of a 1,2,4-selenadiphosphole, the structure of which was also confirmed by X-ray crystallography, showed comparable changes in its ^{31}P NMR signals.[17] The $^{2}J_{P,C}$ coupling constants of the signals of the carbonyl ligand carbon atoms at δ = 215 (**7a**) or 199 (**7b**) (CO_{ax}) and at δ = 221 (**7a**) or 195 (**7b**) (CO_{eq}) were characteristic for the η^1 complexation. In accord with literature data, the axial carbonyl ligands gave rise to appreciably larger $^{2}J_{P,C}$ couplings [13.3 (**7a**) or 34.5 Hz (**7b**)] than the equatorial carbonyl ligands (2.4 Hz for **7a**, 8.0 Hz for **7b**).[18]

The η^5 complexes **9** of the 1,2,4-thiadiphosphole **3a** were obtained by treatment of **3a** with the tris(acetonitrile) complexes **8**. The half-sandwich complexes **9** were isolated as a

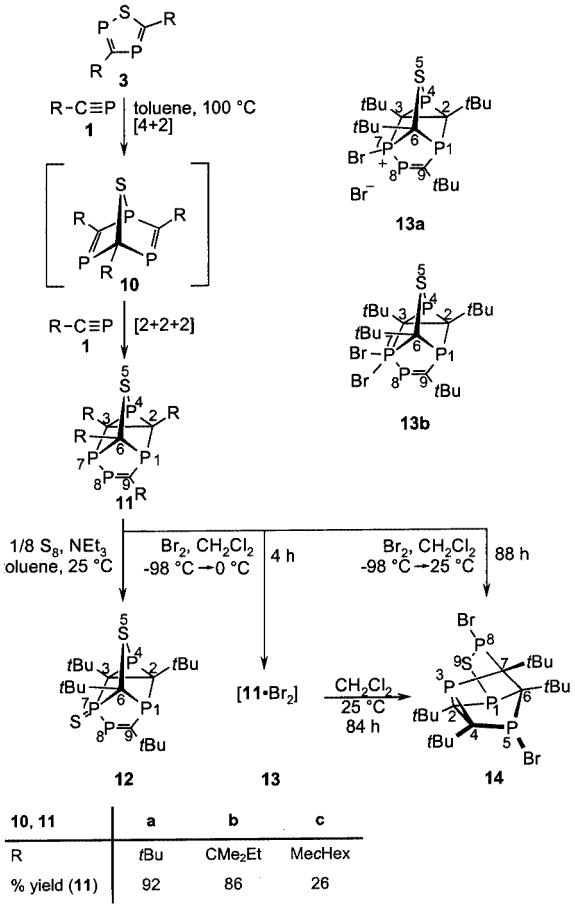
red oil (**9a**)[16] or as a red solid (**9b**), in 33 and 40% yields after prolonged heating at 65 and 70 °C. The molecular compositions of the complexes **9** were confirmed by elemental analysis and mass spectroscopic data (molecular ion peaks, isotope patterns). Again, the successive cleavage of individual carbonyl ligands typical of carbonyl complexes was observed. Information about the nature of the complexation was provided by the ^{31}P and ^{13}C NMR spectra. The η^5 complexation was reflected in a strong shift of the signals of the two phosphorus atoms to higher field. Those for P(2) experienced a shift from δ = 266.8 for **3a** to δ = 83.1 for **9a** and to δ = 51.6 for **9b**. The changes in the chemical shifts of the signals for P(4) were analogous. In addition, the ^{31}P NMR spectrum of **9b** showed tungsten satellite signals with a $^1J_{P,W}$ coupling constant of 7.8 Hz for P(4) and of 6.9 Hz for P(2), thus unambiguously confirming coordination of both phosphorus atoms to the metal center, while *end-on* coordination could be ruled out on the basis of the sizes of the couplings. The complexation of the ring carbon atoms was also clearly apparent from the ^{13}C NMR spectroscopic data. Thus, the signals for carbon atoms C(3) and C(5) in compound **9b** experienced a marked shift to higher field, to δ = 141.8 for C(3) and to δ = 138.7 for C(5). The complexation was also reflected in an increase of the $^1J_{C,P}$ coupling constants of the ring carbon atoms of up to 104.7 Hz. Similar trends have also been observed for an η^5-tricarbonylchromium complex of 3,5-di-*tert*-butyl-1,2,4-selenadiphosphole.[19]

[4+2] Cycloadditions with Phosphaacetylenes

Initial exploratory results on the [4+2] cycloaddition potential of the hetero-1,3-diene system of **3** were provided by the reactions between the heterocyclic compounds **3** and the corresponding, identically substituted, kinetically stabilized phosphaalkynes **1** (Scheme 4). Analogously to the homologous 1,2,4-oxadiphospholes[20] and 1,2,4-selenadiphospholes,[8] formation of the air- and water-stable thiatetraphosphadeltacyclenes **11** in moderate (**11c**) to very good yields (**11a**, **11b**) was observed.[16] In order to achieve this reaction, however, more drastic conditions (5−8 d at 100 °C) were required than for the 1,2,4-oxadiphospholes and the corresponding selenadiphospholes, on account of the aromatic character of **3** (NICS value comparable with that of furan[21]).

Here, again, a primary [4+2] cycloaddition step of a phosphaalkyne molecule to the heterodiene system may be assumed. However, the 7-thia-1,3,5-triphosphanorbornadiene **10**, probably formed initially, could not be isolated or even detected by NMR spectroscopy. This step is followed immediately by a homo-Diels−Alder reaction between a second molecule of the phosphaalkyne and the 1,4-diene system of the bicyclic system **10**, as often found in organophosphorus chemistry.[8,20,22]

The molecular composition of the tetracyclic species **11** formed from 1 equiv. of the thiadiphosphole and 2 equiv. of the phosphaalkyne **1** was clearly demonstrated by the elemental analysis and mass spectroscopic data. The ^1H, ^{13}C, and ^{31}P NMR spectroscopic data were entirely consistent with the tetracyclic structure. Final confirmation was obtained from an X-ray crystallographic analysis (Figure 1).



10, 11	a	b	c
R	*t*Bu	CMe$_2$Et	MecHex
% yield (**11**)	92	86	26

Scheme 4. Synthesis and oxidation of the tetracyclic compound **11**

In the phosphirane unit, two almost identical P−C bond lengths of 1.854(2) Å and 1.856(2) Å are found, and these are only insignificantly longer than those of other P−C single bonds. In addition, the C(2)−C(3) bond length of 1.566(2) Å and the internal angle at P(4) of 49.94(7)° only slightly exceed the average values. The phosphaalkene unit P(8)−C(9) has a typical P−C double bond length of 1.688(2) Å. The angular sum of 359.7° at the skeletal carbon atom C(9) indicates a planar geometry for the P−C double bond. The separation between the phosphorus atom P(8) and the directly adjacent atom P(7) of 2.2091(7) Å is in the typical range for known P−P single bonds.

Oxidation Reactions of 11a

Treatment of the tetracyclic compound **11a** with elemental sulfur in the presence of a catalytic amount of triethylamine resulted in a selective transformation of the cage compound after only 6 h at room temperature. Column chromatographic workup furnished the thiatetraphosphadeltacyclene **12**, sulfurized at P(7), in good yield (Scheme 4). The homologous selenatetraphosphadeltacyclene was also sulfurized at the same position.[8a] Multiple sulfurization of

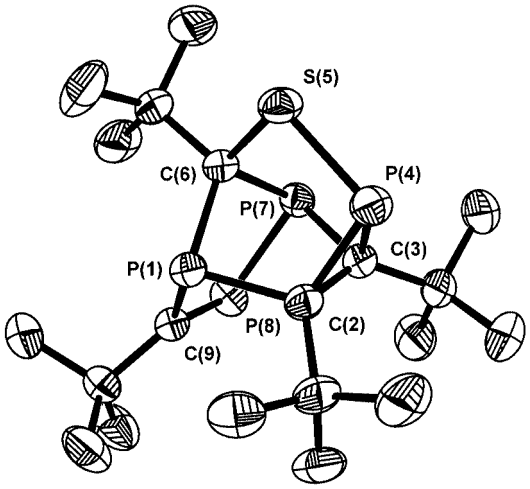


Figure 1. Molecular structure of **11a**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity, displacement ellipsoids at 50% probability: S(5)−C(6) 1.830(2), S(5)−P(4) 2.0898(9), P(1)−C(9) 1.848(2), P(1)−C(6) 1.880(2), P(1)−C(2) 1.906(2), P(8)−C(9) 1.688(2), P(8)−P(7) 2.2091(7), P(7)−C(6) 1.868(2), P(7)−C(3) 1.877(2), P(4)−C(2) 1.854(2), P(4)−C(3) 1.856(2), C(3)−C(2) 1.566(2); C(6)−S(5)−P(4) 95.82(5), C(9)−P(1)−C(6) 97.97(7), C(9)−P(1)−C(2) 100.06(7), C(6)−P(1)−C(2) 92.51(7), C(9)−P(8)−P(7) 98.33(6), C(6)−P(7)−C(3) 93.59(7), C(6)−P(7)−C(8) 96.81(5), C(3)−P(7)−P(8) 98.26(6), C(2)−P(4)−C(3) 49.94(7), C(2)−P(4)−S(5) 100.41(5), C(3)−P(4)−S(5) 100.46(5), S(5)−C(6)−P(7) 105.33(8), S(5)−C(6)−P(1) 104.61(8), P(7)−C(6)−P(1) 102.15(7), P(8)−C(9)−P(1) 117.54(9), C(2)−C(3)−P(4) 64.95(8), C(2)−C(3)−P(7) 110.81(10), P(4)−C(3)−P(7) 111.04(8), C(3)−C(2)−C(41) 128.91(13), C(3)−C(2)−P(4) 65.10(8), C(3)−C(2)−P(1) 110.98(10), P(4)−C(2)−P(1) 110.75(8)

11a did not occur even when a large excess of sulfur was used under analogous conditions.

The 1:1 composition of **12**, formed from the starting material and one atom of sulfur, was evident from its mass spectral and elemental analysis data. The site of sulfurization could be deduced from the measured ^{31}P NMR spectrum. A characteristic feature for a reaction at P(7) is the marked increase of the $^{1}J_{P,P}$ coupling constant from 284.8 Hz to 417.7 Hz. Although the signal for P(8) at δ = 234.8 had experienced an appreciable shift to higher field, it remained in the range typical for a $\lambda^3\sigma^2$-phosphorus atom. Additional indications of the site of sulfurization could be found in the ^{13}C NMR spectrum. Analogously with P(8), the signal for C(9) was also shifted to higher field (δ = 162.7) and was split into a double doublet with $^{1}J_{C,P}$ coupling constants of 73.5 Hz and 11.2 Hz. For a thioxophosphorane increment, however, a $^{1}J_{C,P}$ coupling constant of more than 100 Hz would be expected.[23] Thus, the question of the site of sulfurization was unequivocally answered in favor of phosphorus atom P(7).

A regioselective oxidation reaction with elemental bromine could be achieved at a reaction temperature of −98 °C (Scheme 4). After the reaction mixture had been allowed to warm to 0 °C, the dibromo derivative **13** was isolated in quantitative yield. The P−P single bond in the framework of the thiaphosphadeltacyclene was retained.

The EI mass spectrum (*m*/*z* = 592) confirmed that the tetracyclic compound **13** contained both bromine atoms. However, no definitive statement could be made as to whether it was a bromophosphonium bromide structure **13a** or a dibromophosphorane structure **13b**. The NMR spectroscopic data confirmed that the skeleton of **11a** had been retained in the product **13**. Although the ^{31}P NMR signals of all phosphorus atoms showed shifts to higher field to a greater or lesser extent, the $^{1}J_{P,P}$ coupling constant of 282.3 Hz showed that the P−P single bond increment had remained intact. An electrophilic addition of bromine to the P−C double bond of the tetracyclic system **11a** could be ruled out by the low-field position of the signal for the phosphorus atom P(8) (δ = 253.8). Of the two remaining phosphorus atoms of the dihydrotriphosphole increment, that for P(7) at δ = −18.2 was the most prominent (Δδ = 145.9). The phosphorus atom P(1) gave a signal at δ = 33.3. Only a slight shift to higher field was observed for the phosphorus atom of the phosphirane increment (δ = −106.8). These data all clearly support an increase in coordination at the phosphorus atom P(7), even though the barely appreciable decrease in the $^{1}J_{P,P}$ coupling constant must be viewed as atypical in relation to previous observations in cases of an increase in coordination at P(7).[8a,20]

The tetraphosphadeltacyclene **13** underwent a rearrangement in dichloromethane at room temperature to furnish the tetracyclic product **14** (Scheme 4). Direct treatment of **11** with bromine also furnished the same product when the reaction mixture was allowed to warm from −98 °C to 25 °C and stirred for 88 h. After recrystallization from tetrahydrofuran, **14** was obtained in 42% yield. Compound **14** possesses a structure analogous to that observed for the products of the reactions between the homologous selenaphosphadeltacyclene and elemental bromine and iodine.[8]

The equimolar composition of the cage compound **14**, formed from 1 equiv. of **11a** and 1 equiv. of bromine, was confirmed by its EI mass spectrum and by HRMS. The constitution of the tetracyclic product **14** could not be deduced unambiguously from its NMR spectroscopic data. However, the ^{1}H, ^{13}C, and ^{31}P NMR spectra were consistent with the proposed structure, which was also confirmed by X-ray crystallographic analysis (Figure 2). The results obtained revealed that, in contrast to the previously reported P−P bond cleavage reactions with bromine,[24] no direct cleavage of the P−P bond by the halogen had occurred in this case. The primary step involves an increase in coordination at P(7), followed by a bromine shift with concomitant P−P bond breakage, which then results in product **14**, probably via the intermediates already postulated for the homologous selenatetraphosphadeltacyclene.[8a]

The crystal structure analysis shows two slightly stretched bond lengths of 1.841(3) [P(3)−C(2)] and 1.867(3) Å [P(3)−C(4)] for the phosphirane unit. The angle at P(3), of 50.06(12)°, and the C−C bond length [C(2)−C(4) of 1.569(4) Å], slightly exceed the average literature values. Most of the remaining P−C single bonds with lengths in the range 1.822(3)−1.892(3) Å are close to the average of 1.855 Å. Only the P−C bond lengths at the bridgehead of **14**, with values of 1.916(3) [P(3)−C(7)] and 1.918(3) Å

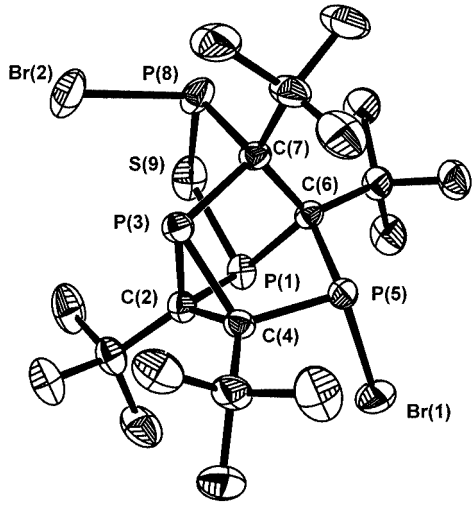
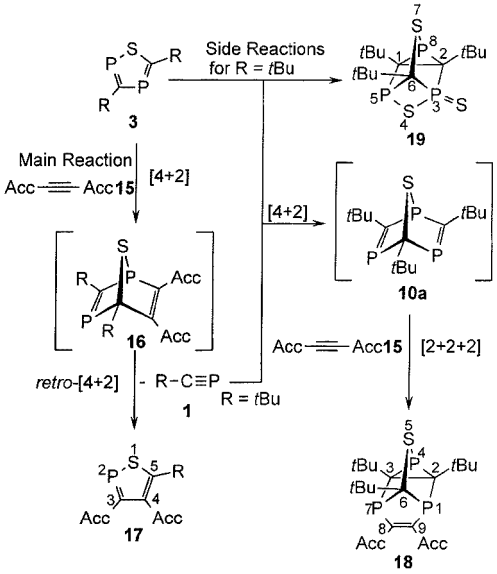


Figure 2. Molecular structure of **14**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity, displacement ellipsoids at 50% probability: S(9)−P(8) 2.079(2), S(9)−P(1) 2.1382(13), Br(1)−P(5) 2.2871(10), Br(2)−P(8) 2.3129(10), P(1)−C(6) 1.855(3), P(1)−C(2) 1.873(3), P(3)−C(2) 1.841(3), P(3)−C(4) 1.867(3), P(3)−C(7) 1.916(3), P(5)−C(4) 1.822(3), P(5)−C(6) 1.892(3), P(8)−C(7) 1.918(3), C(2)−C(4) 1.569(4), C(6)−C(7) 1.615(4); P(8)−S(9)−P(1) 100.55(5), C(6)−P(1)−C(2) 93.30(12), C(6)−P(1)−S(9) 94.53(10), C(2)−P(1)−S(9) 107.96(10), C(2)−P(3)−C(4) 50.06(12), C(2)−P(3)−C(7) 98.39(13), C(4)−P(3)−C(7) 99.04(12), C(4)−P(5)−C(6) 93.69(12), C(4)−P(5)−Br(1) 100.01(10), C(6)−P(5)−Br(1) 105.92(9), C(7)−P(8)−S(9) 98.31(10), C(7)−P(8)−Br(2) 105.37(9), S(9)−P(8)−Br(2) 100.05(5), C(4)−C(2)−P(3) 65.8(2), C(4)−C(2)−P(1) 108.3(2), P(3)−C(2)−P(1) 109.5(2), C(2)−C(4)−P(5) 112.7(2), C(2)−C(4)−P(3) 64.1(2), P(5)−C(4)−P(3) 107.1(2), C(7)−C(6)−P(1) 105.0(2), C(7)−C(6)−P(5) 102.6(2), P(1)−C(6)−P(5) 99.73(14), C(6)−C(7)−P(3) 104.2(2), C(6)−C(7)−P(8), 108.0(2), P(3)−C(7)−P(8) 106.49(14)



16, 17	a	b	c	d	e	f	g	h
R	*t*Bu	CMe_2Et	MecHex	MecPen	*t*Bu	MecPen	MecHex	*t*Bu
Acc	CN	CN	CN	CN	CF_3	CF_3	CF_3	CO_2Me
solvent	Et_2O	Et_2O	Et_2O	Et_2O	toluene	toluene	toluene	toluene
% yield	81	77	63	66	35	59	78	38

16, 17	i	j	k	l	15, 18	a	b	c	d
R	CMe_2Et	MecPen	MecHex	*t*Bu	Acc	CN	CF_3	CO_2Me	CO_2Et
Acc	CO_2Me	CO_2Me	CO_2Me	CO_2Et	% yield	< 1	8	12	–
solvent	toluene	toluene	toluene	toluene					
% yield	47	53	84	35					

Scheme 5. Synthesis of the 1,2-thiaphospholes **17** and the cage compounds **18** and **19**

[P(8)−C(7)], markedly exceed this average value. This is probably due to the strained steric relationships around C(7), since the C−C bond length at C(6)−C(7) of 1.615(4) Å is also stretched somewhat. The newly introduced structural unit of the phosphorus−sulfur bridge exhibits P−S single bond lengths of 2.079(2) and 2.1382(13) Å. The internal angle at the sulfur atom S(9) is 100.55(5)°.

Synthesis of 1,2-Thiaphospholes

The heterocyclic species **3** also underwent primary Diels−Alder reactions with activated acetylenes to afford the norbornadiene system **16**. However, this was not followed by a homo-Diels−Alder reaction; instead a retro-Diels−Alder reaction with cleavage of **1** took place. The 1,2-thiaphospholes **17** were formed in moderate to good yields (Scheme 5). When dicyanoacetylene (**15a**) was employed as the substrate, the reaction took place even at room temperature, while slightly elevated temperatures of 50 or 60 °C were required for the other acetylenes tested (**15b−d**). The heterocyclic products **17** were obtained by removal of the solvent and subsequent distillation.

An appreciable excess of the employed acetylene was required for all of the reactions; this may be due to the polymerization behavior potential of the alkyne on the one hand, or to kinetic reasons on the other. In the reaction of **3a**, a side reaction furnishing the tetracyclic species **18** was observed, due to reaction of **3a** with liberated **1a**. The thus formed norbornadiene system **10a** was trapped by the acetylene **15** in a homo-Diels−Alder reaction to afford the triphosphatetracyclene **18**. Since only small amounts of starting materials were used in the syntheses of the other 1,2-thiaphospholes **17b−d**,**f**,**g**,**i−l**, analogous heterocyclic products could not be isolated in these reactions because of their low yields.

Dimethyl acetylenedicarboxylate (**15c**) reacted with **3a** at 100 °C to furnish numerous, inseparable products, among which the 1,2-thiaphosphole **17h** and the isomeric 1,3-thiaphosphole could be identified by ^{31}P NMR spectroscopy. This indicates that, under these reaction conditions, cleavage of **3a** to **1a** and a thioxophosphinidene 1,3-dipole may also occur, as has also been observed in the reaction between the selenium homologue of **3a** and **15c**.[25]

The molecular compositions of the 1,2-thiaphospholes **17** were confirmed by their mass spectral and elemental analysis data. The IR spectra indicated that the functional groups of the alkyne were retained. Thus, the spectra of **17a−d** contained characteristic bands for nitriles in the range $\tilde{\nu}$ = 2209−2228 cm^{-1}, those of **17e−g** bands for C−F stretching at $\tilde{\nu}$ = 1168 cm^{-1}, and those of **17h−l** characteristic carbonyl bands. As examples for structure elucidation, the three *tert*-butyl-substituted derivatives **17a**, **17e**, and **17h** are discussed below. The ^{31}P NMR signals for the three compounds were observed at δ = 241.4, 208.1,

and 226.1, in the typical range for $\lambda^3\sigma^2$-phosphorus atoms incorporated into aromatic or heteroaromatic systems. The $^{13}C\{^1H\}$ spectra furnished additional information about the constitutions. Thus, as expected, the signals for the ring carbon atoms C(5) experienced the largest shifts to lower field (δ = 181.7, 177.6, and 170.3) and were split by $^2J_{C,P}$ couplings of 4.0−9.4 Hz. The carbon atoms C(3) gave rise to signals at δ = 146.7, 167.4, and 167.2, split by a characteristic $^1J_{C,P}$ coupling constant of about 57 Hz. The other signals, and especially the complex ^{13}C NMR splitting patterns due to the two trifluoromethyl groups of **17e**, were in agreement with the proposed structures.

According to the results of the mass spectral and elemental analyses, the cage compounds **18** were composed of 3 equiv. of phosphaalkyne **1a**, 1 sulfur atom, and 1 equiv. of the respective acetylene **15**. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra provided important diagnostic information about the symmetry of the tetracyclic products **18**. Nevertheless, the constitution of the cage compounds **18** could unequivocally only be determined by an X-ray crystallographic analysis (Figure 3).

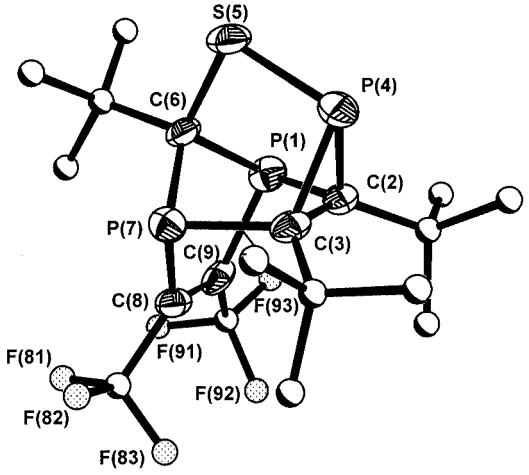


Figure 3. Molecular structure of **18b**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity, displacement ellipsoids at 50% probability: P(7)−C(8) 1.848(5), P(7)−C(6) 1.872(4), P(7)−C(3) 1.887(4), P(1)−C(9) 1.853(5), P(1)−C(6) 1.866(4), P(1)−C(2) 1.885(4), P(4)−C(3) 1.855(4), P(4)−C(2) 1.865(5), P(4)−S(5) 2.097(2), S(5)−C(6) 1.813(4), C(8)−C(9) 1.341(6), C(3)−C(2) 1.571(6); C(8)−P(7)−C(6) 92.5(2), C(8)−P(7)−C(3) 97.4(2), C(6)−P(7)−C(3) 92.9(2), C(9)−P(1)−C(6) 92.6(2), C(9)−P(1)−C(2) 96.4(2), C(6)−P(1)−C(2) 93.6(2), C(3)−P(4)−C(2) 50.0(2), C(3)−P(4)−S(5) 100.25(14), C(2)−P(4)−S(5) 101.0(2), C(6)−S(5)−P(4) 95.36(14), C(9)−C(8)−P(7) 114.6(3), S(5)−C(6)−P(1) 106.0(2), S(5)−C(6)−P(7) 106.3(2), P(1)−C(6)−P(7) 100.8(2), C(2)−C(3)−P(4) 65.4(2), C(2)−C(3)−P(7) 110.2(3), P(4)−C(3)−P(7) 111.6(2), C(3)−C(2)−P(4) 64.7(2), C(3)−C(2)−P(1) 110.5(3), P(4)−C(2)−P(1) 110.0(2), C(8)−C(9)−P(1) 114.5(3)

Except for the C−C double bond with a length of 1.341(6) Å as a newly introduced structural unit, all bond lengths and angles in the skeleton are in the same range as those of the deltacyclene **11a**. The angular sums of the two olefinic carbon atoms C(8) and C(9) are both 360°, thus indicating a planar geometry for the double bond system.

On treatment of **3a** with dimethyl acetylenedicarboxylate (**15c**), the formation of a second by-product **19** was observed (Scheme 5).[26] It was obtained in the same distillate fraction as the cage compound **18c** and subsequently separated from **18c** by column chromatography.

The molecular composition of the cage compound **19**, formed from 3 equiv. of *tert*-butylphosphaacetylene (**1a**) and 3 sulfur atoms, was confirmed by its EI mass spectrum and elemental analysis data. The ^1H, ^{13}C, and ^{31}P NMR spectroscopic data were consistent with the proposed structure, which was unequivocally confirmed by an X-ray crystallographic study (Figure 4).

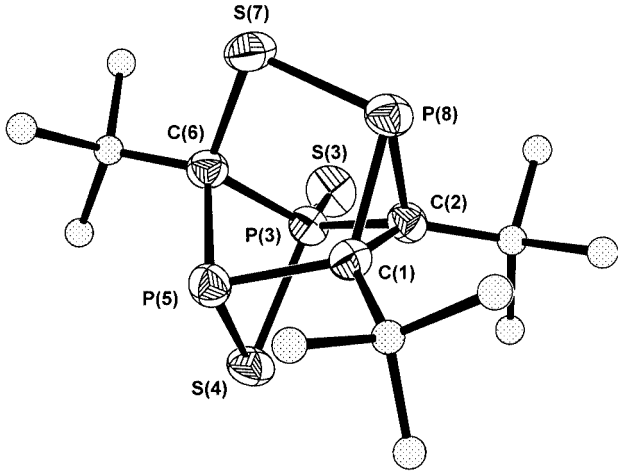
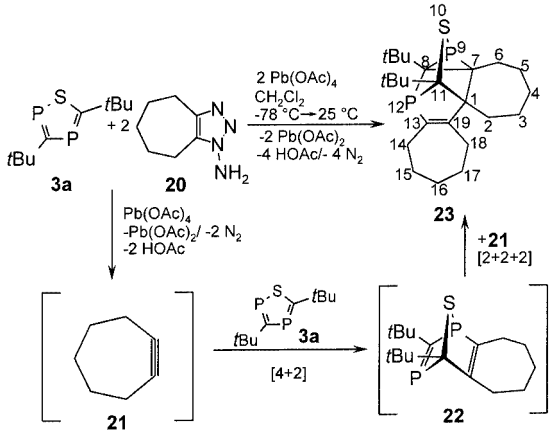


Figure 4. Molecular structure of **19**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity, displacement ellipsoids at 50% probability: P(3)−C(6) 1.841(3), P(3)−C(2) 1.872(2), P(3)−S(3) 1.9206(9), P(3)−S(4) 2.1068(9), S(4)−P(5) 2.1379(12), P(5)−C(1) 1.878(2), P(5)−C(6) 1.899(2), P(8)−C(2) 1.843(3), P(8)−C(1) 1.848(2), P(8)−S(7) 2.0965(9), S(7)−C(6) 1.809(3), C(1)−C(2) 1.569(3); C(6)−P(3)−C(2) 97.01(11), C(6)−P(3)−S(3) 121.95(8), C(2)−P(3)−S(3) 123.25(8), C(6)−P(3)−S(4) 89.60(8), C(2)−P(3)−S(4) 98.23(8), S(3)−P(3)−S(4) 119.41(5), C(6)−P(3)−P(5) 47.03(7), P(3)−S(4)−P(5) 75.32(4), C(1)−P(5)−C(6) 93.66(10), C(1)−P(5)−S(4) 95.36(8), C(6)−P(5)−S(4) 87.16(8), C(2)−P(8)−C(1) 50.30(10), C(2)−P(8)−S(7) 101.56(8), C(1)−P(8)−S(7) 100.82(8), C(6)−S(7)−P(8) 96.19(8), C(2)−C(1)−P(8) 64.70(12), C(2)−C(1)−P(5) 108.50(14), P(8)−C(1)−P(5) 114.23(11), C(1)−C(2)−P(8) 65.00(13), C(1)−C(2)−P(3) 103.2(2), P(8)−C(2)−P(3) 112.51(12), S(7)−C(6)−P(3) 110.43(13), S(7)−C(6)−P(5) 109.83(12), P(3)−C(6)−P(5) 87.80(10)

Again, most bond length and angles are similar to those in the deltacyclene **11a**. The P(3)−C(6) bond is, at 1.841(3) Å, slightly shortened, in contrast to the analogous bond in **11a** or **18b**, whereas the P(5)−C(6) bond is, at 1.899(2) Å, slightly lengthened in comparison to those in **11a** and **18b**. The P−S single bonds, at 2.0965(9) [P(8)−S(7)], 2.1379(12) [P(5)−S(4)] and 2.1068(9) Å [P(3)−S(4)] as well as the P(3)−S(3) double bond at 1.9206(9) Å, are in a typical range.

Treatment of the 1,2,4-thiadiphosphole **3a** with 2 equiv. of cycloheptyne (**21**), generated in situ, afforded the cage compound **23** (Scheme 6), but no analogous reaction took place with higher cyclic acetylenes such as cyclooctyne. ^{31}P NMR monitoring already indicated that a reaction course different from that in the case of the thiadiphospholes **3** and the acetylenes **15** had taken place, because no signal was found for the *tert*-butylphosphaalkyne **1a**. The required cycloheptyne (**21**) was generated oxidatively at −78 °C from



Scheme 6. Reaction between **3a** and cycloheptyne (**21**)

the amino-1*H*-triazole **20**. The [4+2] cycloaddition between **21** and **3a** to afford the heteronorbornadiene system **22** is directly followed by a homo-Diels–Alder reaction with an additional equivalent of cycloheptyne (**21**) to furnish the tetracyclic cage compound **23**.

According to the results of the mass spectrum and elemental analysis, the cage compound **23** was composed of 1 equiv. of thiadiphosphole **3a** and 2 equiv. of cycloheptyne (**21**). The $^{31}P\{^1H\}$ NMR spectrum contained two signals split into doublets by a $^2J_{P,P}$ coupling of 1.5 Hz, which indicated that both phosphorous atoms of the heterocycle **3a** were incorporated in the molecular framework of **23**. The resonance at $\delta = -121.3$ was in the typical region for phosphiranes. However, the regiochemistry of the homo-Diels–Alder reaction could not be deduced unambiguously from the ^{31}P or ^{13}C NMR spectra, and so the analogous reaction with 3,5-di-*tert*-butyl-1,2,4-selenadiphosphole was carried out for structural elucidation. Although the homologous selena cage compound was only formed in traces, the regiochemistry of the [2+2+2] cycloaddtion could be unequivocally deduced from the ^{31}P NMR spectrum of the reaction mixture. The introduction of a further NMR-active nucleus showed that the phosphorus atom in the phosphirane system had to be directly bonded to the chalcogen atom in **23**. This was due to the characteristic ^{77}Se satellites with a $^1J_{P,Se}$ coupling constant of 215 Hz at the high-field signal ($\delta = -135.5$). At the other resonance ($\delta = 64.4$), satellites with a typical $^2J_{P,Se}$ coupling constant of about 52 Hz were found. This showed that there was no direct contact between P(12) and the sulfur atom in **23**. In the $^{13}C\{^1H\}$ NMR spectrum, the expected ten signals for the methylene carbon atoms were found between $\delta = 23.0$ and $\delta = 33.7$. The skeletal carbon atoms gave rise to doublets of doublets or pseudo triplets at $\delta = 58.2$ [C(11)], 63.4 [C(8)], 79.4 [C(1)], and 91.3 [C(7)]. For C(13) a doublet with a $^1J_{C,P}$ coupling constant of 27.6 Hz was found at $\delta = 145.0$ in the region typical for C–C double bonds, whereas C(19) appeared as a singlet in the same area.

Experimental Section

General Remarks: All reactions were performed under argon (purity > 99.998%) by Schlenk techniques. The solvents were dried by standard procedures, distilled, and stored under argon. Compounds **1a**,[27] **1b** and **1c**,[28] **1d**,[29] **2**,[13b] **8**,[30] **15a**,[31] and **20**[32] were prepared according to published methods. When the reaction mixture had to be heated above the boiling point of one compound, special pressure Schlenk tubes (3 × 15 cm, wall thickness 2 mm) with screw-threaded Teflon stoppers and Teflon stopcocks were used. Column chromatography was performed under argon in water-cooled glass tubes. The eluate was monitored with a UV absorbance detector ($\lambda = 254$ nm). Silica gel was heated (160 °C) for 24 h under vacuum (10^{-3} mbar) and then deactivated with 4% H_2O (Brockmann activity II). Bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus (temperatures given refer to the heating mantle). Melting points were determined with a Mettler FP61 apparatus (heating rate 2 °C/min) and are uncorrected. Microanalyses were performed with Perkin–Elmer EA 240 and 2400 CHN Analysers and with a Leco CHNS 932. ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded with Bruker WP 200, Bruker AMX 400, and Bruker DPX 400 spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to the solvent as internal standard. ^{31}P shifts are expressed relative to external 85% orthophosphoric acid. Higher order NMR spin systems were resolved by simulation. MS and HRMS were recorded with a Finnigan MAT 90 spectrometer. IR spectra were measured with a Perkin–Elmer 16 PC FT-IR spectrophotometer.

General Procedure for the Synthesis of the 1,2,4-Thiadiphospholes 3: The required amount of the respective phosphaalkyne **1** was added by pipette to a suspension of elemental sulfur and the tantalum complex **2** in toluene. The mixture was stirred for 10 h, all volatile materials were removed under vacuum (25 °C/10^{-3} mbar), *n*-pentane and triphenylphosphane were added, and stirring was continued for a further 10 h at room temperature. The mixture was then filtered through silica gel, and the crude product was eluted through silica gel with *n*-pentane. The respective 1,2,4-thiadiphosphole **3** was obtained as the first fraction.

3,5-Di-*tert*-butyl-1,2,4-thiadiphosphole (3a): This compound was synthesized by use of S_8 (755 mg, 23.5 mmol), trichlorothiotantalum(V) (**2**, 824 mg, 2.58 mmol), toluene (25 mL), *tert*-butylphosphaacetylene (**1a**, 97%, 7.17 M in hexamethyldisiloxane, 3.60 mL, 25.8 mmol), triphenylphosphane (5.00 g, 19.1 mmol), and *n*-pentane (25 mL). Yield: 1966 mg (66%); colorless oil; m.p. 10 °C. ^1H NMR (C_6D_6): $\delta = 1.50$ [d, $^4J_{H,P} = 1.4$ Hz, 9 H, $C(CH_3)_3$], 1.57 [dd, $^4J_{H,P} = 2.1$, $^4J_{H,P} = 0.5$ Hz, 9 H, $C(CH_3)_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 34.9$ [d, $^3J_{C,P} = 11.2$ Hz, $C(CH_3)_3$], 35.9 [dd, $^3J_{C,P} = 13.0$, $^3J_{C,P} = 9.0$ Hz, $C(CH_3)_3$], 41.2 [pt, $^2J_{C,P} = {}^2J_{C,P} = 19.3$ Hz, $C(CH_3)_3$], 41.9 [dd, $^2J_{C,P} = 17.3$, $^3J_{C,P} = 5.6$ Hz, $C(CH_3)_3$], 209.8 [dd, $^1J_{C,P} = 67.5$, $^2J_{C,P} = 4.2$ Hz, C(5)], 221.1 [dd, $^1J_{C,P} = 79.7$, $^1J_{C,P} = 70.2$ Hz, C(3)]. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 254.7$ [d, $^2J_{P,P} = 49.5$ Hz, P(4)], 266.8 [d, $^2J_{P,P} = 49.5$ Hz, P(2)]. MS (EI, 70 eV): *m/z* (%) = 232 (87) [M^+], 217 (81) [$M^+ - CH_3$], 199 (8) [$M^+ - SH$], 169 (41) [$P(CtBu)_2^+$], 131 (29) [P_2CtBu^+], 69 (60) [$CtBu^+$], 57 (100) [tBu^+]. $C_{10}H_{18}P_2S$ (232.25): calcd. C 51.71, H 7.81, S 13.81; found C 51.31, H 7.75, S 13.78.

3,5-Bis(1-methylcyclohex-1-yl)-1,2,4-thiadiphosphole (3b): This compound was synthesized by use of S_8 (1120 mg, 34.9 mmol), trichlorothiotantalum(V) (**2**, 1230 mg, 3.85 mmol), toluene (50 mL), (1-methylcyclohex-1-yl)phosphaacetylene (**1b**, 6.00 mL, 5380 mg, 38.4 mmol), triphenylphosphane (7.61 g, 29.0 mmol), and *n*-pentane (50 mL). Yield: 3910 mg (65%); colorless oil. ^1H NMR

(C_6D_6): δ = 1.41 [s, 3 H, CH_3], 1.50 [d, $^3J_{H,P}$ = 1.2 Hz, 3 H, CH_3], 1.22−1.64 [m, 12 H, CH_2], 1.75−1.83 [m, 2 H, CH_2], 1.86−1.94 [m, 2 H, CH_2], 2.22−2.33 [m, 4 H, CH_2]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.1 [d, $^4J_{C,P}$ = 2.2 Hz, *C*H_2], 23.2 [s, *C*H_2], 26.2 [s, *C*H_2], 26.4 [s, *C*H_2], 33.2 [br s, *C*H_3], 33.8 [br s, *C*H_3], 42.1 [d, $^3J_{C,P}$ = 11.3 Hz, *C*H_2], 43.1 [dd, $^3J_{C,P}$ = 13.7, $^3J_{C,P}$ = 10.4 Hz, *C*H_2], 44.8 [pt, $^2J_{C,P}$ = $^2J_{C,P}$ = 16.5 Hz, C_q], 45.7 [dd, $^2J_{C,P}$ = 14.9, $^3J_{C,P}$ = 5.6 Hz, C_q], 209.4 [d, $^1J_{C,P}$ = 68.3 Hz, C(5)], 221.9 [dd, $^1J_{C,P}$ = 77.9, $^1J_{C,P}$ = 71.9 Hz, C(3)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 254.4 [d, $^2J_{P,P}$ = 49.3 Hz, P(4)], 267.0 [d, $^2J_{P,P}$ = 49.3 Hz, P(2)]. MS (EI, 70 eV): *m*/*z* (%) = 312 (85) [M^+], 297 (18) [$M^+ - CH_3$], 279 (24) [M^+ − SH], 249 (9) [P(CM*ec*Hex)$_2^+$], 172 (17) [SPCM*ec*Hex$^+$] 109 (35) [CM*ec*Hex$^+$], 97 (92) [M*ec*Hex$^+$]. HRMS: *m*/*z*: calcd. for $C_{16}H_{26}P_2S$ 312.1231; found 312.1231.

3,5-Bis(1-methylcyclopent-1-yl)-1,2,4-thiadiphosphole (3c): This compound was synthesized by use of S_8 (359 mg, 11.2 mmol), trichlorothiotantalum(V) (**2**, 320 mg, 1.00 mmol), toluene (25 mL), (1-methylcyclopent-1-yl)phosphaacetylene (**1c**, 2.40 mL, 1920 mg, 10.2 mmol), triphenylphosphane (3.33 g, 12.8 mmol), and *n*-pentane (50 mL). Yield: 900 mg (62%); colorless oil. ^1H NMR (C_6D_6): δ = 1.45 [s, 3 H, CH_3], 1.50 [d, $^3J_{H,P}$ = 1.2 Hz, 3 H, CH_3], 1.55−1.73 [m, 8 H, CH_2], 1.81−1.88 [m, 2 H, CH_2], 1.91−1.98 [m, 2 H, CH_2], 2.20−2.30 [m, 4 H, CH_2]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 24.3 [pt, $^4J_{C,P}$ = $^4J_{C,P}$ = 1.4 Hz, *C*H_2], 24.5 [d, $^4J_{C,P}$ = 1.2 Hz, *C*H_2], 32.5 [dd, $^3J_{C,P}$ = 8.6, $^4J_{C,P}$ = 1.4 Hz, *C*H_3], 33.8 [dd, $^3J_{C,P}$ = 9.8, $^3J_{C,P}$ = 8.6 Hz, *C*H_3], 44.4 [d, $^3J_{C,P}$ = 10.8 Hz, *C*H_2], 44.8 [dd, $^3J_{C,P}$ = 13.3, $^3J_{C,P}$ = 8.8 Hz, *C*H_2], 52.1 [dd, $^2J_{C,P}$ = 18.7, $^2J_{C,P}$ = 17.8 Hz, C_q], 53.1 [dd, $^2J_{C,P}$ = 16.1, $^3J_{C,P}$ = 5.6 Hz, C_q], 209.4 [dd, $^1J_{C,P}$ = 65.1, $^2J_{C,P}$ = 4.4 Hz, C(5)], 220.2 [dd, $^1J_{C,P}$ = 76.9, $^1J_{C,P}$ = 69.3 Hz, C(3)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 253.5 [d, $^2J_{P,P}$ = 51.3 Hz, P(4)], 265.6 [d, $^2J_{P,P}$ = 51.3 Hz, P(2)]. MS (EI, 70 eV): *m*/*z* (%) = 284 (100) [M^+], 269 (13) [$M^+ - CH_3$], 251 (36) [M^+ − SH], 221 (55) [P(CM*ec*Pen)$_2^+$], 95 (53) [CM*ec*Pen$^+$], 83 (20) [M*ec*Pen$^+$]. HRMS: *m*/*z*: calcd. for $C_{14}H_{22}P_2S$ 284.0918; found 284.0918.

3,5-Bis(1,1-dimethylpropyl)-1,2,4-thiadiphosphole (3d): This compound was synthesized by use of S_8 (121 mg, 3.50 mmol), trichlorothiotantalum(V) (**2**, 1725 mg, 5.40 mmol), toluene (5 mL), *tert*-pentylphosphaacetylene (**1d**, 1.76 M in hexamethyldisiloxane, 1.71 mL, 3.00 mmol), triphenylphosphane (2.52 g, 9.60 mmol), and *n*-pentane (20 mL). Yield: 112 mg (29%); colorless oil. ^1H NMR (C_6D_6): δ = 0.74 [t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_2CH_3], 0.79 [t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH_2CH_3], 1.48 [d, $^4J_{H,P}$ = 1.6 Hz, 6 H, C(CH_3)$_2$], 1.53 [dd, $^4J_{H,P}$ = 2.4, $^4J_{H,P}$ = 0.8 Hz, 6 H, C(CH_3)$_2$], 1.77 [q, $^3J_{H,H}$ = 7.5 Hz, 2 H, CH_2CH$_3$], 1.88 [q, $^3J_{H,H}$ = 7.4 Hz, 2 H, CH_2CH$_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 9.4 [d, $^4J_{C,P}$ = 1.7 Hz, CH_2CH_3], 9.5 [pt, $^4J_{C,P}$ = $^4J_{C,P}$ = 1.3 Hz, CH_2CH_3], 32.3 [d, $^3J_{C,P}$ = 12.7 Hz, C(*C*H$_3$)$_2$], 33.0 [dd, $^3J_{C,P}$ = 15.7, $^3J_{C,P}$ = 8.9 Hz, C(*C*H$_3$)$_2$], 39.9 [dd, $^3J_{C,P}$ = 6.4, $^4J_{C,P}$ = 1.3 Hz, *C*H$_2$CH$_3$], 40.9 [dd, $^3J_{C,P}$ = 8.7, $^3J_{C,P}$ = 7.4 Hz, *C*H$_2$CH$_3$], 44.5 [dd, $^2J_{C,P}$ = 17.8, $^2J_{C,P}$ = 17.0 Hz, *C*(CH$_3$)$_2$], 45.3 [dd, $^2J_{C,P}$ = 15.5, $^3J_{C,P}$ = 5.7 Hz, *C*(CH$_3$)$_2$], 208.1 [dd, $^1J_{C,P}$ = 66.6, $^2J_{C,P}$ = 4.2 Hz, C(5)], 219.3 [dd, $^1J_{C,P}$ = 78.4, $^1J_{C,P}$ = 70.4 Hz, C(3)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 258.0 [d, $^2J_{P,P}$ = 49.0 Hz, P(4)], 269.5 [d, $^2J_{P,P}$ = 49.0 Hz, P(2)]. MS (EI, 70 eV): *m*/*z* (%) = 260 (32) [M^+], 245 (3) [$M^+ - CH_3$], 231 (100) [$M^+ - CH_2CH_3$], 145 (4) [P$_2$C*t*Pen$^+$], 71 (22) [*t*Pen$^+$]. HRMS: *m*/*z*: calcd. for $C_{12}H_{22}P_2S$ 260.0918; found 260.0917.

General Procedure for the Synthesis of the η^1 Complexes 7: In an irradiation apparatus, the required amount of the hexacarbonylmetal was dissolved in THF (50 mL), and the solution was irradiated with water cooling for about 25 min (HPK 125 W Philips). After cessation of CO evolution, the 1,2,4-thiadiphosphole **3a** in THF (5 mL) was added, and the mixture was stirred for 24 h at room temperature. After removal of all volatile materials, the residue, in the case of **7a**, was placed in a sublimation apparatus. Excess hexacarbonylchromium was removed at 40 °C/2.4·10^{-2} mbar, and the product sublimed at 85−105 °C/2.4·10^{-2} mbar. For the corresponding tungsten complex **7b**, the residue was subjected to column chromatographic workup with *n*-pentane as eluent.

Pentacarbonyl[2-η^1-(3,5-di-*tert*-butyl-1,2,4-thiadiphosphole)]-chromium(0) (7a): This compound was synthesized by use of hexacarbonylchromium(0) (71 mg, 0.32 mmol) and 1,2,4-thiadiphosphole **3a** (44 mg, 0.19 mmol). Yield: 41 mg (51%); yellow solid; m.p. 127 °C (dec.). ^1H NMR (C_6D_6): δ = 1.29 [d, $^4J_{H,P}$ = 1.2 Hz, 9 H, C(CH_3)$_3$], 1.50 [s, 9 H, C(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 34.1 [dd, $^3J_{C,P}$ = 11.2, $^4J_{C,P}$ = 1.6 Hz, C(*C*H$_3$)$_3$], 35.8 [dd, $^3J_{C,P}$ = 10.8, $^3J_{C,P}$ = 10.0 Hz, C(*C*H$_3$)$_3$], 41.0 [dd, $^2J_{C,P}$ = 19.7, $^2J_{C,P}$ = 11.7 Hz, *C*(CH$_3$)$_3$], 42.1 [dd, $^2J_{C,P}$ = 16.7, $^3J_{C,P}$ = 2.6 Hz, *C*(CH$_3$)$_3$], 204.4 [dd, $^1J_{C,P}$ = 63.4, $^2J_{C,P}$ = 8.0 Hz, C(5)], 214.8 [d, $^2J_{C,P}$ = 13.3 Hz, *CO*$_{ax}$], 215.1 [dd, $^1J_{C,P}$ = 75.3, $^1J_{C,P}$ = 33.1 Hz, C(3)], 221.1 [d, $^2J_{C,P}$ = 2.4 Hz, *CO*$_{eq}$]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 264.7 [d, $^2J_{P,P}$ = 56.1 Hz, P(2) or P(4)], 266.0 [d, $^2J_{P,P}$ = 56.1 Hz, P(2) or P(4)]. IR (KBr): $\tilde{\nu}$ = 2965 (CH), 2072 (CO), 1993 (CO), 1980 (CO), 1929 (CO). MS (EI, 70 eV): *m*/*z* (%) = 424 (17) [M^+], 368 (15) [M^+ − 2 CO], 312 (32) [M^+ − 4 CO], 284 (95) [M^+ − 5 CO], 169 (43) [P(C*t*Bu)$_2^+$], 131 (33) [P$_2$C*t*Bu$^+$], 69 (64) [C*t*Bu$^+$], 57 (100) [*t*Bu$^+$]. $C_{15}H_{18}CrO_5P_2S$ (424.31): calcd. C 42.46, H 4.28; found C 42.84, H 4.23.

Pentacarbonyl[2-η^1-(3,5-di-*tert*-butyl-1,2,4-thiadiphosphole)]-tungsten(0) (7b): This compound was synthesized by use of hexacarbonyltungsten(0) (370 mg, 1.05 mmol) and 1,2,4-thiadiphosphole **3a** (109 mg, 0.47 mmol). Yield: 56 mg (22%); yellow solid. ^1H NMR (C_6D_6): δ = 1.29 [s, 9 H, C(CH_3)$_3$], 1.52 [d, $^4J_{H,P}$ = 1.1 Hz, 9 H, C(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 34.1 [dd, $^3J_{C,P}$ = 11.2, $^4J_{C,P}$ = 1.6 Hz, C(*C*H$_3$)$_3$], 35.8 [pt, $^3J_{C,P}$ = $^3J_{C,P}$ = 10.8 Hz, C(*C*H$_3$)$_3$], 40.9 [dd, $^2J_{C,P}$ = 19.3, $^2J_{C,P}$ = 10.4 Hz, *C*(CH$_3$)$_3$], 42.1 [dd, $^2J_{C,P}$ = 16.9, $^3J_{C,P}$ = 2.8 Hz, *C*(CH$_3$)$_3$], 195.2 [d, $^2J_{C,P}$ = 8.0, $^1J_{C,W}$ = 126.1 Hz, *CO*$_{eq}$], 198.6 [d, $^2J_{C,P}$ = 34.5 Hz, *CO*$_{ax}$], 205.0 [dd, $^1J_{C,P}$ = 66.3, $^2J_{C,P}$ = 10.8 Hz, C(5)], 207.4 [dd, $^1J_{C,P}$ = 77.1, $^1J_{C,P}$ = 23.3 Hz, C(3)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 208.2 [d, $^2J_{P,P}$ = 61.0, $^1J_{P,W}$ = 247.4 Hz, P(2)], 259.8 [d, $^2J_{P,P}$ = 61.0 Hz, P(4)]. MS (EI, 70 eV): *m*/*z* (%) = 556 (23) [M^+], 500 (19) [M^+ − 2 CO], 444 (17) [M^+ − 4 CO], 416 (46) [M^+ − 5 CO], 232 (31) [M^+ − W(CO)$_5$], 169 (15) [P(C*t*Bu)$_2^+$], 131 (12) [P$_2$C*t*Bu$^+$], 69 (38) [C*t*Bu$^+$], 57 (100) [*t*Bu$^+$]. $C_{15}H_{18}O_5P_2SW$ (556.16).

Tricarbonyl[η^5-(3,5-di-*tert*-butyl-1,2,4-thiadiphosphole)]-molybdenum(0) (9a): In a pressure Schlenk tube, the molybdenum complex **8a** (344 mg, 1.14 mmol) was suspended in THF (7 mL) and the heterocyclic compound **3a** (103 mg, 0.44 mmol) was added. The mixture was then stirred for 16 h at 65 °C, during which the color changed to deep red. After removal of all volatile materials, the residue was dissolved in a small amount of *n*-pentane and filtered through Celite. After concentration of the solution under vacuum, the material was transferred to a sublimation apparatus for purification. A white impurity was obtained first at 45 °C/1.6·10^{-2} mbar, followed by the product **9a** at 75−85 °C/1.6·10^{-2} mbar. Yield: 59 mg (33%); red oil. ^1H NMR (C_6D_6): δ = 1.06−1.10 [m, C(CH_3)$_3$]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 53.3 [d, $^2J_{P,P}$ = 33.1 Hz, P(4)], 83.1 [d, $^2J_{P,P}$ = 33.1 Hz, P(2)]. MS (EI, 70 eV): *m*/*z* (%) = 414 (38) [M^+], 386 (20) [M^+ − CO], 358 (13) [M^+ − 2 CO], 330 (100) [M^+ − 3 CO], 232 (32) [M^+ − Mo(CO)$_3$], 169 (10) [P(C*t*Bu)$_2^+$], 69 (8) [C*t*Bu$^+$], 57 (18) [*t*Bu$^+$]. $C_{13}H_{18}MoO_3P_2S$ (412.23).

Tricarbonyl[η^5-(3,5-di-*tert*-butyl-1,2,4-thiadiphosphole)]tungsten(0) (9b): In a pressure Schlenk tube, the tungsten complex **8b** (222 mg, 0.57 mmol) was suspended in toluene (4 mL), and the 1,2,4-thiadiphosphole **3a** (37 mg, 0.16 mmol) was added. The mixture was stirred at 70 °C for 165 h. After completion of the reaction, all volatile materials were removed under vacuum, and the residue was dissolved in a small amount of *n*-pentane and filtered through Celite. The material was then eluted through silica gel with *n*-pentane to provide product **9b** as the third fraction. Yield: 32 mg (40%); red solid. ^{1}H NMR (C_6D_6): δ = 1.11 [d, $^4J_{H,P}$ = 0.7 Hz, 9 H, C(CH_3)$_3$], 1.13 [pt, $^4J_{H,P}$ = $^4J_{H,P}$ = 1.3 Hz, 9 H, C(CH_3)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 35.1 [d, $^3J_{C,P}$ = 8.0 Hz, C(*C*H$_3$)$_3$], 36.6 [pt, $^3J_{C,P}$ = $^3J_{C,P}$ = 9.2 Hz, C(*C*H$_3$)$_3$], 38.5 [pt, $^2J_{C,P}$ = $^2J_{C,P}$ = 16.1 Hz, *C*(CH$_3$)$_3$], 39.2 [dd, $^2J_{C,P}$ = 12.9, $^3J_{C,P}$ = 2.4 Hz, *C*(CH$_3$)$_3$], 138.7 [dd, $^1J_{C,P}$ = 99.4, $^2J_{C,P}$ = 3.4 Hz, C(5)], 141.8 [dd, $^1J_{C,P}$ = 104.8, $^1J_{C,P}$ = 83.9 Hz, C(3)], 210.5 [s, $^1J_{C,W}$ = 177.1 Hz, *C*O]. ^{31}P{^{1}H} NMR (C_6D_6): δ = 33.8 [d, $^2J_{P,P}$ =33.8, $^1J_{P,W}$ = 7.8 Hz, P(4)], 51.6 [d, $^2J_{P,P}$ = 33.8, $^1J_{P,W}$ = 6.9 Hz, P(2)]. IR (KBr): ṽ = 2963 (CH), 2856 (CH), 1993 (CO), 1933 (CO), 1906 (CO). MS (EI, 70 eV): *m*/*z* (%) = 500 (56) [M$^+$], 444 (19) [M$^+$ − 2 CO], 416 (79) [M$^+$ − 3 CO], 57 (86) [*t*Bu$^+$]. $C_{13}H_{18}O_3P_2SW$ (500.14): calcd. C 31.22, H 3.63; found C 32.25, H 3.12.

General Procedure for the Synthesis of the Cage Compounds 11: In a pressure Schlenk tube, the 1,2,4-thiadiphosphole **3** and the respective phosphaalkyne **1** were dissolved in toluene and placed under 4 bar excess pressure of argon. The mixture was stirred for 6−9 d (^{31}P NMR monitoring, incomplete conversion in the case of **11b**) at 105 °C. After completion of the reaction, all volatile materials were removed under vacuum and the residue was eluted through silica gel with *n*-pentane as eluent. The deltacyclene products **11** are obtained as the first (**11a**, **11c**) or second (**11b**) fractions.

2,3,6,9-Tetra-*tert*-butyl-5-thia-1,4,7,8-tetraphosphatetracyclo-[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (11a): This compound was synthesized by use of **3a** (700 mg, 3.01 mmol), *tert*-butylphosphaacetylene (**1a**, 97%, 7.17 M in hexamethyldisiloxane, 967 μL, 6.93 mmol), and toluene (10 mL). Yield: 1204 mg (92%); orange-yellow solid; m.p. 138 °C. ^{1}H NMR (C_6D_6): δ = 1.28 [s, 9 H, C(CH_3)$_3$], 1.31 [d, $^4J_{H,P}$ = 2.2 Hz, 9 H, C(CH_3)$_3$], 1.33 [s, 9 H, C(CH_3)$_3$], 1.55 [s, 9 H, C(CH_3)$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 33.3 [dpt, $^3J_{C,P}$ = $^3J_{C,P}$ = 4.4, $^4J_{C,P}$ = 2.1 Hz, C(*C*H$_3$)$_3$], 34.8 [ddd, $^2J_{C,P}$ = 16.4 Hz, $J_{C,P}$ = 10.7 Hz, $J_{C,P}$ = 1.8 Hz, C(*C*H$_3$)$_3$], 35.8 [dd, $^3J_{C,P}$ = 12.7, $^3J_{C,P}$ = 7.2 Hz, C(*C*H$_3$)$_3$], 36.0 [m, *C*(CH$_3$)$_3$], 36.5 [ddd, $^2J_{C,P}$ = 20.3, $^2J_{C,P}$ = 11.9, $^4J_{C,P}$ = 3.4 Hz, *C*(CH$_3$)$_3$], 37.0 [ddd, $^3J_{C,P}$ = 10.2, $^3J_{C,P}$ = 5.9, $^4J_{C,P}$ = 3.4 Hz, C(*C*H$_3$)$_3$], 37.2 [m, *C*(CH$_3$)$_3$], 44.9 [dd, $^2J_{C,P}$ = 20.1, $^2J_{C,P}$ = 12.1 Hz, *C*(CH$_3$)$_3$], 67.8 [m, C(2)], 76.7 [m, C(3)], 82.3 [ddd, $^1J_{C,P}$ = 36.6, $^1J_{C,P}$ = 27.5 Hz, $J_{C,P}$ = 2.4 Hz, C(6)], 244.9 [ddd, $^1J_{C,P}$ = 79.7, $^1J_{C,P}$ = 66.1, $^2J_{C,P}$ = 1.3 Hz, C(9)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = −96.8 [ptd, $^2J_{P,P}$ = $^3J_{P,P}$ = 7.7, $^2J_{P,P}$ = 1.4 Hz, P(4)], 116.9 [ddd, $^2J_{P,P}$ = 34.4, $^2J_{P,P}$ = 17.1, $^2J_{P,P}$ = 7.7 Hz, P(1)], 127.7 [ddd, $^1J_{P,P}$ = 284.8, $^2J_{P,P}$ = 34.4, $^2J_{P,P}$ = 1.4 Hz, P(7)], 408.3 [ddd, $^1J_{P,P}$ = 284.8, $^2J_{P,P}$ = 17.1, $^3J_{P,P}$ = 7.7 Hz, P(8)]. MS (EI, 70 eV): *m*/*z* (%) = 432 (100) [M$^+$], 369 (4) [M$^+$ − SP], 231 (24) [P$_3$(C*t*Bu)$_2^+$], 169 (67) [P(C*t*Bu)$_2^+$], 131 (27) [P$_2$C*t*Bu$^+$], 69 (24) [C*t*Bu$^+$], 57 (28) [*t*Bu$^+$]. $C_{20}H_{36}P_4S$ (432.45): calcd. C 55.55, H 8.39; found C 55.53, H 8.59.

2,3,6,9-Tetrakis(1,1-dimethylpropyl)-5-thia-1,4,7,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (11b): This compound was synthesized by use of **3b** (55 mg, 0.21 mmol), *tert*-pentylphosphaacetylene (**1b**, 1.76 M in hexamethyldisiloxane, 350 μL, 0.62 mmol), and toluene (3 mL); first fraction: 12 mg (0.05 mmol) of **3b**. Yield: 69 mg (86%); orange-yellow oil. ^{1}H NMR (C_6D_6): δ = 0.73 [t, $^3J_{H,H}$ = 7.5 Hz, 3 H, CH$_2$CH_3], 0.87−0.98 [m, 9 H, CH$_2$CH_3], 1.17−1.55 [m, 24 H, C(CH_3)$_2$], 1.68−2.06 [m, 8 H, CH_2CH$_3$]. ^{31}P{^{1}H} NMR (C_6D_6): δ = −96.6 [pt, $^2J_{P,P}$ = $^3J_{P,P}$ = 6.1 Hz, P(4)], 116.0 [ddd, $^2J_{P,P}$ = 33.4, $^2J_{P,P}$ = 16.1, $^2J_{P,P}$ = 6.1 Hz, P(1)], 125.1 [dd, $^1J_{P,P}$ = 285.6, $^2J_{P,P}$ = 33.4 Hz, P(7)], 407.6 [ddd, $^1J_{P,P}$ = 285.6, $^2J_{P,P}$ = 16.1, $^3J_{P,P}$ = 6.1 Hz, P(8)]. MS (EI, 70 eV): *m*/*z* (%) = 488 (100) [M$^+$], 459 (18) [M$^+$ − Et], 259 (16) [P$_3$(C*t*Pen)$_2^+$], 197 (45) [P(C*t*Pen)$_2^+$], 145 (26) [P$_2$C*t*Pen$^+$], 83 (33) [C*t*Pen$^+$], 71 (30) [*t*Pen$^+$]. HRMS: *m*/*z*: calcd. for $C_{24}H_{44}P_4S$ 488.2114; found 488.2114.

2,3,6,9-Tetrakis(1-methylcyclohex-1-yl)-5-thia-1,4,7,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (11c): This compound was synthesized by use of **3c** (92 mg, 0.30 mmol), (1-methylcyclohex-1-yl)phosphaacetylene (**1b**, 1.01 M in hexamethyldisiloxane, 671 μL, 0.68 mmol), and toluene (2 mL). Yield: 45 mg (26%); orange-yellow solid. ^{1}H NMR (C_6D_6): δ = 0.80−2.40 [m, 40 H, CH_2CH$_3$], 1.22 [s, 3 H, CH_3], 1.35 [s, 3 H, CH_3], 1.43 [s, 3 H, CH_3], 1.68 [s, 3 H, CH_3]. ^{31}P{^{1}H} NMR (C_6D_6): δ = −97.0 [pt, $^2J_{P,P}$ = $^3J_{P,P}$ = 6.4 Hz, P(4)], 109.3 [ddd, $^2J_{P,P}$ = 34.1, $^2J_{P,P}$ = 16.3, $^2J_{P,P}$ = 6.4 Hz, P(1)], 117.6 [dd, $^1J_{P,P}$ = 286.1, $^2J_{P,P}$ = 34.1 Hz, P(7)], 407.6 [ddd, $^1J_{P,P}$ = 286.1, $^2J_{P,P}$ = 16.3, $^3J_{P,P}$ = 6.4 Hz, P(8)]. MS (EI, 70 eV): *m*/*z* (%) = 592 (100) [M$^+$], 280 (17) [P$_2$(CMe*c*Hex)$_2^+$], 249 (29) [P(CMe*c*Hex)$_2^+$], 109 (34) [CMe*c*Hex$^+$], 97 (33) [Me*c*Hex$^+$]. $C_{32}H_{52}P_4S$ (592.71): calcd. C 64.85, H 8.84; found C 64.57, H 8.84.

2,3,6,9-Tetra-*tert*-butyl-5-thia-1,4,7,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene 7-Sulfide (12): The thiatetraphosphadeltacyclene **11a** (85 mg, 0.20 mmol) was dissolved in toluene (2 mL), and triethylamine (15 μL, 0.11 mmol) and sulfur (6.9 mg, 0.20 mmol) were then added. The mixture was stirred at room temperature for 6 h, all volatile materials were removed under vacuum, and the residue was eluted through silica gel with *n*-pentane. The cage compound **12** was obtained as the third fraction. Yield: 74 mg (81%); yellow solid; m.p. 105 °C. ^{1}H NMR (C_6D_6): δ = 1.27 [pt, $^4J_{H,P}$ = $^4J_{H,P}$ = 1.6 Hz, 9 H, C(CH_3)$_3$], 1.31 [s, 9 H, C(CH_3)$_3$], 1.39 [br s, 9 H, C(CH_3)$_3$], 1.62 [d, $^4J_{H,P}$ = 1.6 Hz, 9 H, C(CH_3)$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 32.1 [pt, $^3J_{C,P}$ = $^3J_{C,P}$ = 4.4 Hz, C(*C*H$_3$)$_3$], 32.6 [dd, $^3J_{C,P}$ = 11.2, $^3J_{C,P}$ = 8.0 Hz, C(*C*H$_3$)$_3$], 34.9 [ddd, $^2J_{C,P}$ = 16.3, $^2J_{C,P}$ = 11.5, $^3J_{C,P}$ = 1.3 Hz, *C*(CH$_3$)$_3$], 35.4 [dd, $^3J_{C,P}$ = 11.2, $^3J_{C,P}$ = 8.8 Hz, C(*C*H$_3$)$_3$], 36.3 [ddd, $^2J_{C,P}$ = 18.1, $^2J_{C,P}$ = 10.4, $^3J_{C,P}$ = 2.0 Hz, *C*(CH$_3$)$_3$], 36.6 [dd, $^3J_{C,P}$ = 11.6, $^3J_{C,P}$ = 6.4 Hz, C(*C*H$_3$)$_3$], 37.8 [m, *C*(CH$_3$)$_3$], 40.3 [ddd, $^2J_{C,P}$ = 17.8, $^2J_{C,P}$ = 5.9, $^3J_{C,P}$ = 1.1 Hz, *C*(CH$_3$)$_3$], 68.5 [m, C(2) or C(3)], 70.1 [m, C(3) or C(2)], 75.2 [m, C(6)], 162.7 [dd, $^1J_{C,P}$ = 73.5, $^1J_{C,P}$ = 11.2 Hz, C(9)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = −88.4 [s, P(4)], 97.0 [dd, $^1J_{P,P}$ = 417.7, $^2J_{P,P}$ = 23.8 Hz, P(7)], 109.0 [dd, $^2J_{P,P}$ = 29.6, $^2J_{P,P}$ = 23.8 Hz, P(1)], 234.8 [dd, $^1J_{P,P}$ = 417.7, $^2J_{P,P}$ = 29.6 Hz, P(8)]. MS (EI, 70 eV): *m*/*z* (%) = 464 (41) [M$^+$], 432 (27) [M$^+$ − S], 232 (23) [P$_2$(C*t*Bu)$_2$S$^+$], 169 (100) [P(C*t*Bu)$_2^+$], 131 (32) [P$_2$C*t*Bu$^+$], 69 (43) [C*t*Bu$^+$], 57 (49) [*t*Bu$^+$]. $C_{20}H_{36}P_4S_2$ (464.51): calcd. C 51.71, H 7.81; found C 51.55, H 7.72.

Bromine Adduct 13: The deltacyclene **11a** (84 mg, 0.19 mmol) was dissolved in dichloromethane (2 mL), the solution was cooled to −98 °C in an ether/liquid nitrogen bath, and elemental bromine (9.9 μL, 0.19 mmol) was added from a pipette. The mixture was allowed to thaw and was stirred at 0 °C for 4 h. Removal of all volatile materials under vacuum provided the bromine adduct **13**. Yield: 114 mg (100%); orange-red solid. ^{1}H NMR (CD_2Cl_2): δ = 1.44 [d, $^4J_{H,P}$ = 2.1 Hz, 9 H, C(CH_3)$_3$], 1.49 [s, 9 H, C(CH_3)$_3$], 1.51 [s, 9 H, C(CH_3)$_3$], 1.58 [d, $^4J_{H,P}$ = 2.1 Hz, 9 H, C(CH_3)$_3$]. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = −106.8 [s, P(4)], −18.2 [d, $^1J_{P,P}$ = 282.3 Hz, P(7)], 33.3 [d, $^2J_{P,P}$ = 95.4 Hz, P(1)], 253.8 [dd, $^1J_{P,P}$ = 282.3, $^2J_{P,P}$ = 95.4 Hz, P(8)]. MS (EI, 70 eV): *m*/*z* (%) = 592 (1) [M$^+$], 512 (12) [M$^+$ − Br], 432 (27) [M$^+$ − 2Br], 232 (50) [P$_2$(C*t*Bu)$_2$S$^+$],

169 (100) [P(C*t*Bu)$_2^+$], 131 (31) [P$_2$C*t*Bu$^+$], 69 (22) [C*t*Bu$^+$], 57 (30) [*t*Bu$^+$]. $C_{20}H_{36}Br_2P_4S$ (592.27).

5,8-Dibromo-2,4,6,7-tetra-*tert*-butyl-9-thia-1,3,5,8-tetraphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (14): Elemental bromine (14.7 μL, 0.29 mmol) was added slowly from a pipette to a solution of the thiatetraphosphadeltacyclene **11a** (124 mg, 0.29 mmol) in dichloromethane (4 mL), cooled to −98 °C in an ether/liquid nitrogen bath. After thawing to 25 °C, the solution was stirred for further 88 h at 25 °C. All volatile materials were then removed under vacuum, and the crude product was worked up by recrystallization from tetrahydrofuran at −28 °C. Yield: 71 mg (42%); bright yellow needles; m.p. 148 °C. ^{1}H NMR (CD_2Cl_2): δ = 1.39 [s, 9 H, C(CH_3)$_3$], 1.43−1.45 [m, 18 H, C(CH_3)$_3$], 1.61 [d, $^4J_{H,P}$ = 2.3 Hz, 9 H, C(CH_3)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 34.3 [dd, $^3J_{C,P}$ = 6.9, $^3J_{C,P}$ = 3.5 Hz, C(*C*H$_3$)$_3$], 34.4−35.0 [m, C(*C*H$_3$)$_3$], 35.5 [ddd, $^2J_{C,P}$ = 17.3, $^2J_{C,P}$ = 12.3, $^3J_{C,P}$ = 1.5 Hz, *C*(CH$_3$)$_3$], 35.9 [dd, $^2J_{C,P}$ = 15.7, $^2J_{C,P}$ = 11.1 Hz, *C*(CH$_3$)$_3$], 36.6 [dd, $^2J_{C,P}$ = 14.4, $^2J_{C,P}$ = 9.8 Hz, *C*(CH$_3$)$_3$], 42.1 [dd, $^2J_{C,P}$ = 27.8, $^2J_{C,P}$ = 14.4 Hz, *C*(CH$_3$)$_3$], 51.0 [pt, $^1J_{C,P}$ = $^1J_{C,P}$ = 54.8 Hz, C_q], 66.8−68.0 [m, C_q], 75.7 [m, C_q]. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ = −128.2 [d, $^2J_{P,P}$ = 5.8 Hz, P(3)], 150.6 [dpt, $^2J_{P,P}$ = 31.0, $^2J_{P,P}$ = $^2J_{P,P}$ = 5.8 Hz, P(1)], 160.2 [dd, $^2J_{P,P}$ = 12.6, $^2J_{P,P}$ = 5.8 Hz, P(5)], 223.5 [dd, $^2J_{P,P}$ = 31.0, $^2J_{P,P}$ = 12.6 Hz, P(8)]. MS (EI, 70 eV): *m*/*z* (%) = 592 (10) [M$^+$], 512 (37) [M$^+$ − Br], 432 (15) [M$^+$ − 2Br], 231 (72) [P$_3$(C*t*Bu)$_2^+$], 169 (100) [P(C*t*Bu)$_2^+$], 131 (17) [P$_2$C*t*Bu$^+$], 69 (16) [C*t*Bu$^+$], 57 (38) [*t*Bu$^+$]. HRMS: *m*/*z*: calcd. for $C_{20}H_{36}Br_2P_4S$ 591.9813; found 591.9813.

General Procedure for the Synthesis of the 1,2-Thiaphospholes 17a−17d and the Cage Compound 18a: The respective 1,2,4-thiadiphosphole **3** was dissolved in diethyl ether and an excess of dicyanoacetylene (**15a**) was added from a pipette. This procedure was repeated after 80 h of stirring at 25 °C. The reaction was terminated after a reaction time of 160 h. All volatile materials were then removed under vacuum, and the residue was filtered through Celite with diethyl ether. The 1,2-thiaphospholes **17** and, in the case of **3a**, also a second fraction were obtained after workup by fractional bulb-to-bulb distillation. The latter compound was extracted with *n*-pentane/diethyl ether (5:1), filtered through silica gel, and recrystallized from *n*-pentane/diethyl ether (1:1) at −78 °C.

1,2-Thiaphosphole 17a and the Cage Compound 18a: This compound was synthesized by use of 1,2,4-thiadiphosphole **3a** (903 mg, 3.89 mmol) and diethyl ether (30 mL).

5-*tert*-Butyl-1,2-thiaphosphole-3,4-dicarbonitrile (17a): Yield: 656 mg (81%); colorless solid; b.p. 115 °C/10^{-3} mbar. ^{1}H NMR ($CDCl_3$): δ = 1.52 [s, 9 H, C(CH_3)$_3$]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 30.8 [d, $^4J_{C,P}$ = 0.8 Hz, C(*C*H$_3$)$_3$], 39.8 [d, $^3J_{C,P}$ = 6.4 Hz, *C*(CH$_3$)$_3$], 112.7 [d, $^3J_{C,P}$ = 2.0 Hz, *C*N], 114.0 [d, $^2J_{C,P}$ = 27.7 Hz, *C*N], 118.6 [d, $^2J_{C,P}$ = 7.6 Hz, C(4)], 146.7 [d, $^1J_{C,P}$ = 55.0 Hz, C(3)], 181.7 [d, $^2J_{C,P}$ = 4.0 Hz, C(5)]. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 241.4 [s, P(2)]. IR (KBr): ṽ = 2227 (CN), 2210 (CN). MS (EI, 70 eV): *m*/*z* (%) = 208 (28) [M$^+$], 193 (100) [M$^+$ − CH$_3$], 165 (18) [M$^+$ − PC], 63 (28) [PS$^+$]. HRMS: *m*/*z*: calcd. for $C_9H_9N_2PS$ 208.0224; found 208.0224.

2,3,6-Tri-*tert*-butyl-5-thia-1,4,7-triphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8,9-dicarbonitrile (18a): Yield: 5 mg (< 1%); yellow solid; b.p. 120 °C/10^{-3} mbar. ^{1}H NMR (C_6D_6): δ = 1.01 [br s, 18 H, C(CH_3)$_3$], 1.18 [s, 9 H, C(CH_3)$_3$]. ^{31}P{^{1}H} NMR (C_6D_6): δ = −70.6 [t, $^2J_{P,P}$ = 2.0 Hz, P(4)], 100.7 [d, $^2J_{P,P}$ = 2.0 Hz, P(1) and P(7)]. IR (CCl_4): ṽ = 2204 (CN). MS (EI, 70 eV): *m*/*z* (%) = 408 (30) [M$^+$], 393 (9) [M$^+$ − CH$_3$], 163 (91) [SP$_2$C*t*Bu$^+$], 131 (100) [P$_2$C*t*Bu$^+$], 69 (42) [C*t*Bu$^+$], 63 (11) [PS$^+$], 57 (46) [*t*Bu$^+$]. $C_{19}H_{27}N_2P_3S$ (408.42): calcd. C 55.88, H 6.66, N 6.86; found C 55.76, H 6.85, N 6.61.

5-(1,1-Dimethylpropyl)-1,2-thiaphosphole-3,4-dicarbonitrile (17b): This compound was synthesized by use of **3b** (35 mg, 0.13 mmol) and diethyl ether (2 mL). Yield: 23 mg (77%); colorless solid; b.p. 115 °C/10^{-3} mbar. ^{1}H NMR (C_6D_6): δ = 0.40 [t, $^3J_{H,H}$ = 7.5 Hz, CH_2CH_3], 1.06 [s, 6 H, C(CH_3)$_2$], 1.58 [q, $^3J_{H,H}$ = 7.5 Hz, CH_2CH_3]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 9.1 [s, CH_2CH_3], 28.6 [s, C(*C*H$_3$)$_2$], 35.8 [s, *C*H$_2$CH$_3$], 43.5 [d, $^3J_{C,P}$ = 6.1 Hz, *C*(CH$_3$)$_2$], 112.7 [s, *C*N], 114.0 [d, $^2J_{C,P}$ = 27.6 Hz, *C*N], 118.5 [d, $^2J_{C,P}$ = 7.7 Hz, C(4)], 146.6 [d, $^1J_{C,P}$ = 55.2 Hz, C(3)], 181.1 [d, $^2J_{C,P}$ = 3.1 Hz, C(5)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = 242.1 [s, P(2)]. IR (KBr): ṽ = 2228 (CN), 2213 (CN). MS (EI, 70 eV): *m*/*z* (%) = 222 (20) [M$^+$], 207 (4) [M$^+$ − CH$_3$], 193 (100) [M$^+$ − CH$_2$CH$_3$], 179 (2) [M$^+$ − PC], 63 (15) [PS$^+$]. HRMS: *m*/*z*: calcd. for $C_{10}H_{11}N_2PS$ 222.0381; found 222.0380.

5-(1-Methylcyclohex-1-yl)-1,2-thiaphosphole-3,4-dicarbonitrile (17c): This compound was synthesized by use of **3c** (106 mg, 0.34 mmol) and diethyl ether (3 mL). Yield: 53 mg (63%); colorless solid; b.p. 135 °C/10^{-3} mbar. ^{1}H NMR ($CDCl_3$): δ = 1.37−1.47 [m, 2 H, CH_2], 1.51 [s, 3 H, CH_3], 1.53−1.69 [m, 4 H, CH_2], 1.91−1.99 [m, 2 H, CH_2], 2.17−2.26 [m, 2 H, CH_2]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 22.7 [s, *C*H$_2$], 25.7 [s, *C*H$_2$], 27.3 [br s, *C*H$_3$], 38.6 [s, *C*H$_2$], 43.9 [d, $^3J_{C,P}$ = 6.0 Hz, C_q], 113.2 [d, $^3J_{C,P}$ = 2.0 Hz, *C*N], 114.4 [d, $^2J_{C,P}$ = 27.7 Hz, *C*N], 118.7 [d, $^2J_{C,P}$ = 7.6 Hz, C(4)], 147.0 [d, $^1J_{C,P}$ = 54.6 Hz, C(3)], 182.7 [d, $^2J_{C,P}$ = 3.6 Hz, C(5)]. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 242.3 [s, P(2)]. IR (KBr): ṽ = 2222 (CN), 2209 (CN). MS (EI, 70 eV): *m*/*z* (%) = 248 (45) [M$^+$], 233 (44) [M$^+$ − CH$_3$], 205 (10) [M$^+$ − PC], 63 (49) [PS$^+$]. HRMS: *m*/*z*: calcd. for $C_{12}H_{13}N_2PS$ 248.0537; found 248.0537.

5-(1-Methylcyclopent-1-yl)-1,2-thiaphosphole-3,4-dicarbonitrile (17d): This compound was synthesized by use of **3d** (54 mg, 0.19 mmol) and diethyl ether (3 mL). Yield: 30 mg (66%); colorless solid; b.p. 125 °C/10^{-3} mbar. ^{1}H NMR (C_6D_6): δ = 0.99 [s, 3 H, CH_3], 1.33−1.39 [m, 4 H, CH_2], 1.64−1.71 [m, 4 H, CH_2]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.9 [s, *C*H$_2$], 28.0 [d, $^4J_{C,P}$ = 1.5 Hz, *C*H$_3$], 40.8 [s, *C*H$_2$], 50.2 [d, $^3J_{C,P}$ = 6.1 Hz, C_q], 112.6 [s, *C*N], 114.0 [d, $^2J_{C,P}$ = 27.6 Hz, *C*N], 118.9 [d, $^2J_{C,P}$ = 7.7 Hz, C(4)], 146.3 [d, $^1J_{C,P}$ = 56.0 Hz, C(3)], 182.2 [d, $^2J_{C,P}$ = 3.8 Hz, C(5)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = 241.7 [s, P(2)]. IR (KBr): ṽ = 2226 (CN), 2212 (CN). MS (EI, 70 eV): *m*/*z* (%) = 234 (52) [M$^+$], 219 (64) [M$^+$ − CH$_3$], 192 (100) [M$^+$ − C$_3$H$_6$], 63 (38) [PS$^+$]. HRMS: *m*/*z*: calcd. for $C_{11}H_{11}N_2PS$ 234.0381; found 234.0381.

1,2-Thiaphospholes 17e−g and the Cage Compound 18b: Hexafluorobutyne **15b** (3 mL) was condensed in a pressure Schlenk tube at −78 °C, and treated with a cooled (−78 °C) solution of the thiadiphosphole **3** in toluene. The mixture was allowed to warm to room temperature and was then heated for about two weeks (^{31}P NMR monitoring) at 50 °C (safety shield!). After blowing off excess acetylene at 0 °C and removal of the solvent under vacuum, the residue was subjected to fractional bulb-to-bulb distillation. The first fraction contained the 1,2-thiaphospholes **17e−g** as yellow oils. In the treatment of **3a**, a second fraction containing the tetracyclic species **18b** (150 °C/10^{-3} mbar) was obtained. This was filtered through silica gel with *n*-pentane and the resultant crude product was recrystallized from 1 mL of *n*-pentane at −20 °C.

5-*tert*-Butyl-3,4-bis(trifluoromethyl)-1,2-thiaphosphole (17e): This compound was synthesized by use of **3a** (471 mg, 2.03 mmol) and toluene (7 mL). Yield: 207 mg (35%); yellow oil; b.p. 65 °C/10^{-3} mbar. ^{1}H NMR (C_6D_6): δ = 1.43 [s, 9 H, C(CH_3)$_3$]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 32.1 [q, $^5J_{C,F}$ = 3.3 Hz, C(*C*H$_3$)$_3$], 41.0 [d, $^3J_{C,P}$ =

5.9 Hz, $C(CH_3)_3$], 122.3 [qd, $^1J_{C,F}$ = 274.7, $^3J_{C,P}$ = 2.0 Hz, CF_3], 124.4 [qd, $^1J_{C,F}$ = 272.7, $^2J_{C,P}$ = 24.6 Hz, CF_3], 132.9 [qdq, $^2J_{C,F}$ = 35.6, $^3J_{C,F}$ = 2.0, $^2J_{C,P}$ = 11.8 Hz, C(4)], 167.4 [dq, $^2J_{C,F}$ = 32.5, $^1J_{C,P}$ = 57.8 Hz, C(3)], 177.6 [dq, $^3J_{C,F}$ = 3.0, $^2J_{C,P}$ = 9.4 Hz, C(5)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 208.1 [q, $^3J_{P,F}$ = 57.0 Hz, P(2)]. IR (CCl_4): ṽ = 1161 (CF). MS (EI, 70 eV): *m/z* (%) = 294 (92) [M^+], 279 (100) [$M^+ - CH_3$], 275 (17) [$M^+ - F$], 274 (15) [$M^+ - HF$], 259 (39) [$M^+ - CH_3 - HF$], 251 (19) [$M^+ - PC$], 225 (12) [$M^+ - CF_3$ and $M^+ - C$*t*Bu], 127 (25) [$M^+ -$ *t*Bu $- CF_3$], 101 (5) [*t*BuCS$^+$], 69 (12) [CF_3^+ and C*t*Bu$^+$], 63 (29) [PS^+], 57 (23) [*t*Bu$^+$], 45 (7) [CHS^+], 32 (42) [S^+]. $C_9H_9F_6PS$ (294.20): calcd. C 36.74, H 3.08; found C 36.66, H 3.11.

2,3,6-Tri-*tert*-butyl-8,9-bis(trifluoromethyl)-5-thia-1,4,7-triphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (18b): Yield: 40 mg (8%); yellow crystals; b.p. 150 °C/10^{-3} mbar; m.p. 105 °C. ^1H NMR (C_6D_6): δ = 1.29 [s, 9 H, 6-C(CH_3)$_3$], 1.34 [s, 18 H, 2-C(CH_3)$_3$ and 3-C(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.6 [t, $^3J_{C,P}$ = 5.0 Hz, 6-C(CH_3)$_3$], 35.4 [dd, $^2J_{C,P}$ = 8.1, $^2J_{C,P}$ = 3.5 Hz, 2-*C*(CH_3)$_3$ and 3-*C*(CH_3)$_3$], 35.6 [dd, $^3J_{C,P}$ = 11.9, $^3J_{C,P}$ = 6.5 Hz, 2-*C*(CH_3)$_3$ and 3-C(CH_3)$_3$], 37.5 [td, $^2J_{C,P}$ = 11.5, $^3J_{C,P}$ = 3.8 Hz, 6-*C*(CH_3)$_3$], 73.4 [A part of an AXX′Y spin system, $^1J_{C,P}$ = 47.2, $^1J_{C,P}$ = 44.1, $^2J_{C,P}$ = 3.4 Hz, C(2) and C(3)], 78.5 [td, $^1J_{C,P}$ = 21.5, $^2J_{C,P}$ = 1.5 Hz, C(6)], 122.5 [m, not resolved, $^1J_{C,F} \approx$ 278 Hz, CF_3], 162.4 [m, not resolved, C(8) and C(9)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −83.6 [M part of an AA′MX_3X′$_3$ spin system, $^2J_{P,P}$ = 1.4 Hz, P(4)], 111.6 [AA′ part of an AA′MX_3X′$_3$ spin system, $^2J_{P,P}$ = 1.4, $^3J_{P,F}$ = 12.5, $^4J_{P,F}$ = 6.3, $^2J_{P,P}$ = 12.1, $^5J_{F,F}$ = 2.0 Hz, P(1) and P(7)]. IR (CCl_4): ṽ = 1168 (CF). MS (EI, 70 eV): *m/z* (%) = 494 (100) [M^+], 479 (52) [$M^+ - CH_3$], 475 (8) [$M^+ - F$], 437 (30) [$M^+ -$ *t*Bu], 394 (36) [$M^+ -$ *t*BuCP], 169 (28) [P(C*t*Bu)$_2^+$ and PC*t*BuCF_3^+], 131 (14) [P_2C*t*Bu$^+$], 32 (40) [S^+]. $C_{19}H_{27}F_6P_3S$ (494.40): calcd. C 46.16, H 5.50; found C 47.08, H 5.65.

5-(1-Methylcyclopent-1-yl)-3,4-bis(trifluoromethyl)-1,2-thiaphosphole (17f): This compound was synthesized by use of **3c** (254 mg, 0.89 mmol) and toluene (7 mL). Yield: 169 mg (59%); yellow oil; b.p. 100 °C/10^{-3} mbar. ^1H NMR (C_6D_6): δ = 1.19 [s, 3 H, CH_3], 1.49−1.59 [m, 4 H, CH_2], 1.78−1.92 [m, 2 H, CH_2], 1.94−2.04 [m, 2 H, CH_2]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.9 [s, CH_2], 28.2 [dq, $^5J_{C,F}$ = 3.1, $^4J_{C,P}$ = 3.3 Hz, CH_3], 41.8 [s, CH_2], 51.7 [d, $^3J_{C,P}$ = 5.4 Hz, C_q], 122.2 [q, $^1J_{C,F}$ = 272.8 Hz, CF_3], 124.5 [dq, $^1J_{C,F}$ = 272.3, $^2J_{C,P}$ = 23.7 Hz, CF_3], 132.5 [dq, $^2J_{C,F}$ = 35.4, $^2J_{C,P}$ = 10.7 Hz, C(4)], 166.8 [dq, $^2J_{C,F}$ = 31.4, $^1J_{C,P}$ = 59.5 Hz, C(3)], 177.6 [dq, $^3J_{C,F}$ = 2.4, $^2J_{C,P}$ = 5.7 Hz, C(5)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 210.8 [q, $^3J_{P,F}$ = 54.6 Hz, P(2)]. IR (CCl_4): ṽ = 1160 (CF). $C_{11}H_{11}F_6PS$ (320.34): calcd. C 41.24, H 3.46; found C 41.49, H 3.32.

5-(1-Methylcyclohex-1-yl)-3,4-bis(trifluoromethyl)-1,2-thiaphosphole (17g): This compound was synthesized by use of **3b** (710 mg, 2.27 mmol) and toluene (8 mL). Yield: 591 mg (78%); yellow oil; b.p. 100 °C/10^{-3} mbar. ^1H NMR (C_6D_6): δ = 1.33 [d, $^4J_{H,P}$ = 0.8 Hz, 3 H, CH_3], 1.30−1.35 [m, 2 H, CH_2], 1.35−1.45 [m, 2 H, CH_2], 1.45−1.56 [m, 2 H, CH_2], 1.68−1.76 [m, 2 H, CH_2], 2.11−2.20 [m, 2 H, CH_2]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.1 [s, CH_2], 26.0 [s, CH_2], 27.9 [s, CH_3], 40.2 [s, CH_2], 45.2 [d, $^3J_{C,P}$ = 5.4 Hz, C_q], 122.2 [q, $^1J_{C,F}$ = 274.6 Hz, CF_3], 124.3 [dq, $^1J_{C,F}$ = 272.5, $^2J_{C,P}$ = 24.9 Hz, CF_3], 133.1 [dq, $^2J_{C,F}$ = 35.7, $^2J_{C,P}$ = 11.5 Hz, C(4)], 167.5 [dq, $^2J_{C,F}$ = 32.5, $^1J_{C,P}$ = 57.9 Hz, C(3)], 177.8 [s, C(5)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 209.3 [q, $^3J_{P,F}$ = 57.2 Hz, P(2)]. IR (CCl_4): ṽ = 1160 (CF). MS (EI, 70 eV): *m/z* (%) = 334 (52) [M^+], 319 (15) [$M^+ - CH_3$], 265 (11) [$M^+ - CF_3$], 96 (19) [(Me-*c*Hex − H)$^+$], 82 (100) [(Me*c*Hex − CH_3)$^+$], 69 (16) [CF_3^+]. $C_{12}H_{13}F_6PS$ (334.27): calcd. C 43.12, H 3.92; found C 43.68, H 3.80.

1,2-Thiaphospholes 17h−l and the Cage Compounds 18c and 19: A solution of the respective 1,2,4-thiadiphosphole **3** and a sevenfold excess of the appropriate acetylenedicarboxylate in toluene was heated at 60 °C in a pressure Schlenk tube for 2 d (^{31}P NMR monitoring). After removal of all volatile materials under vacuum, the black residue was subjected to bulb-to-bulb distillation at 10^{-3} mbar. The first fraction (up to 100 °C) consisted of the excess acetylene, while the second fractions − at 115 °C (**17h**), 120 °C (**17l**), 140 °C (**17i**), or 175 °C (**17j**, **17k**) − contained the respective 1,2-thiaphospholes. In the treatment of **3a** with **15c**, a third fraction was obtained (130 °C/10^{-3} mbar); this was subjected to chromatography on silica gel with *n*-pentane/diethyl ether (5:1). The first, colorless fraction contained the cage compound **19**, the second, pale yellow fraction contained the tetracyclic system **18c**.

Dimethyl (5-*tert*-Butyl-1,2-thiaphosphole-3,4-dicarboxylate) (17h): This compound was synthesized by use of **3a** (2870 mg, 12.4 mmol), dimethyl acetylenedicarboxylate (**15c**, 10.5 mL, 84.0 mmol), and toluene (15 mL). Yield: 1400 mg (38%); yellow oil; b.p. 115 °C/10^{-3} mbar. ^1H NMR (C_6D_6): δ = 1.43 [s, 9 H, C(CH_3)$_3$], 3.57 [s, 3 H, CO_2CH_3], 3.82 [s, 3 H, CO_2CH_3]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.9 [s, C(CH_3)$_3$], 39.3 [d, $^3J_{C,P}$ = 6.1 Hz, $C(CH_3)_3$], 52.2 [s, CO_2CH_3], 52.7 [s, CO_2CH_3], 141.4 [d, $^2J_{C,P}$ = 12.3 Hz, C(4)], 163.7 [d, $^2J_{C,P}$ = 22.2 Hz, CO_2CH_3], 167.2 [d, $^1J_{C,P}$ = 58.3 Hz, C(3)], 167.8 [d, $^3J_{C,P}$ = 2.3 Hz, CO_2CH_3], 170.3 [d, $^2J_{C,P}$ = 6.1 Hz, C(5)]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 226.1 [s, P(2)]. IR (CCl_4): ṽ = 1741 (CO), 1725 (CO). MS (EI, 70 eV): *m/z* (%) = 274 (3) [M^+], 191 (28) [$M^+ - C_2CO_2Me$], 69 (79) [C*t*Bu$^+$], 59 (92) [CO_2Me^+], 53 (100) [CH_3PSCO^{2+}], 39 (89) [CH_3PS^{2+}]. $C_{11}H_{15}O_4PS$ (274.28): calcd. C 48.17, H 5.51; found C 48.26, H 5.61.

Dimethyl 2,3,6-Tri-*tert*-butyl-5-thia-1,4,7-triphosphatetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8,9-dicarboxylate (18c): Yield: 355 mg (12%); yellow powder; b.p. 130 °C/10^{-3} mbar; m.p. 118 °C. ^1H NMR (C_6D_6): δ = 1.47 [s, 9 H, 6-C(CH_3)$_3$], 1.49 [s, 18 H, 2-C(CH_3)$_3$ and 3-C(CH_3)$_3$], 3.53 [s, 6 H, CO_2CH_3]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.8 [t, $^3J_{C,P}$ = 5.0 Hz, 6-C(CH_3)$_3$], 35.6 [dd, $^2J_{C,P}$ = 11.1, $^2J_{C,P}$ = 8.1 Hz, 2-*C*(CH_3)$_3$ and 3-*C*(CH_3)$_3$], 35.8 [dd, $^3J_{C,P}$ = 13.0, $^3J_{C,P}$ = 6.1 Hz, 2-C(CH_3)$_3$ and 3-C(CH_3)$_3$], 37.5 [td, $^2J_{C,P}$ = 11.5, $^3J_{C,P}$ = 3.8 Hz, 6-*C*(CH_3)$_3$], 52.4 [s, CO_2CH_3], 72.6 [A part of an AXX′Y spin system, $^1J_{C,P}$ = 44.5, $^1J_{C,P}$ = 39.7, $^2J_{C,P}$ = 6.2 Hz, C(2) and C(3)], 79.6 [td, $^1J_{C,P}$ = 22.6, $^2J_{C,P}$ = 2.3 Hz, C(6)], 164.4 [m, not resolved, C(8) and C(9)], 166.2 [pt, $^2J_{C,P}$ = $^3J_{C,P}$ = 12.3 Hz, CO_2CH_3]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −84.1 [t, $^2J_{P,P}$ = 1.6 Hz, P(4)], 103.2 [d, $^2J_{P,P}$ = 1.6, $^2J_{P,P}$ = 15.7 Hz, P(1) and P(7)]. IR (CCl_4): ṽ = 1724 (CO). $C_{21}H_{33}O_4P_3S$ (474.47): calcd. C 53.61, H 7.01; found C 52.71, H 6.97.

1,2,6-Tri-*tert*-butyl-4,7-dithia-3,5,8-triphosphatetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane 3-Sulfide (19): Yield: 35 mg (2%); colorless crystals; b.p. 130 °C/10^{-3} mbar; m.p. 127 °C. ^1H NMR (C_6D_6): δ = 1.29 [ddd, $J_{H,P}$ = 2.7 Hz, $J_{H,P}$ = 1.5 Hz, $J_{H,P}$ = 0.5 Hz, 9 H, C(CH_3)$_3$], 1.60 [s, 9 H, C(CH_3)$_3$], 1.67 [s, 9 H, C(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.3 [pt, $^3J_{C,P}$ = $^3J_{C,P}$ = 3.8 Hz, C(CH_3)$_3$], 32.9 [pt, $^3J_{C,P}$ = $^3J_{C,P}$ = 4.6 Hz, C(CH_3)$_3$], 34.6 [dd, $^3J_{C,P}$ = 14.5, $^3J_{C,P}$ = 7.6 Hz, C(CH_3)$_3$], 35.7 [pt, $^2J_{C,P}$ = $^2J_{C,P}$ = 11.9 Hz, $C(CH_3)_3$], 36.0 [dd, $^2J_{C,P}$ = 19.5, $^2J_{C,P}$ = 11.1 Hz, $C(CH_3)_3$], 37.4 [dd, $^2J_{C,P}$ = 11.5, $^2J_{C,P}$ = 3.1 Hz, $C(CH_3)_3$], 63.0 [m, not resolved, skeletal C], 71.7 [m, not resolved, skeletal C], 82.2 [m, not resolved, skeletal C]. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −51.4 [dd, $^2J_{P,P}$ = 48.9, $^2J_{P,P}$ = 5.9 Hz, P(8)], 43.2 [dd, $^2J_{P,P}$ = 48.9, $^2J_{P,P}$ = 2.6 Hz, P(3)],

112.4 [dd, $^2J_{P,P}$ = 5.9, $^2J_{P,P}$ = 2.6 Hz, P(5)]. MS (EI, 35 eV): *m*/*z* (%) = 396 (67) [M$^+$], 363 (4) [M$^+$ − S], 301 (5) [M$^+$ − 3 S], 270 (24) [M$^+$ − 3 S − P], 233 (75) [M$^+$ − PC*t*Bu − 2 S], 169 (65) [PC$_2$*t*Bu$_2^+$], 164 (71) [S$_2$PC*t*Bu$^+$], 101 (100) [PC*t*Bu$^+$], 69 (40) [C*t*Bu$^+$], 57 (51) [*t*Bu$^+$]. $C_{15}H_{27}P_3S_3$ (396.47): calcd. C 45.44, H 6.86; found C 46.33, H 6.93.

Dimethyl [5-(1,1-Dimethylpropyl)-1,2-thiaphosphole-3,4-dicarboxylate] (17i): This compound was synthesized by use of **3d** (211 mg, 0.81 mmol), dimethyl acetylenedicarboxylate (**15c**, 1000 µL, 8.10 mmol), and toluene (15 mL). Yield: 110 mg (47%); yellow oil; b.p. 140 °C/10^{-3} mbar. ^{1}H NMR (C_6D_6): δ = 0.81 [t, $^3J_{H,H}$ = 7.4 Hz, CH_2CH_3], 1.42 [s, 6 H, $C(CH_3)_2$], 1.80 [q, $^3J_{H,H}$ = 7.4 Hz, CH_2CH_3], 3.46 [s, 3 H, CO_2CH_3], 3.81 [s, 3 H, CO_2CH_3]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.6 [s, CH_2CH_3], 29.5 [s, $C(CH_3)_2$], 37.5 [s, CH_2CH_3], 43.1 [d, $^3J_{C,P}$ = 6.1 Hz, $C(CH_3)_2$], 52.0 [s, CO_2CH_3], 52.7 [s, CO_2CH_3], 141.9 [d, $^2J_{C,P}$ = 12.2 Hz, C(4)], 163.8 [d, $^2J_{C,P}$ = 22.2 Hz, CO_2CH_3], 167.1 [d, $^1J_{C,P}$ = 58.1 Hz, C(3)], 167.9 [d, $^3J_{C,P}$ = 2.3 Hz, CO_2CH_3], 169.1 [d, $^2J_{C,P}$ = 5.4 Hz, C(5)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = 227.5 [s, P(2)]. IR (CCl_4): ṽ = 1741 (CO), 1725 (CO). MS (EI, 70 eV): *m*/*z* (%) = 288 (14) [M$^+$], 259 (13) [M$^+$ − Et], 227 (100) [M$^+$ − Et − S], 71 (3) [CMe$_2$Et$^+$], 63 (5) [PS$^+$]. $C_{12}H_{17}O_4PS$ (288.30): calcd. C 49.99, H 5.94; found C 49.27, H 6.03.

Dimethyl [(1-Methylcyclopent-1-yl)-1,2-thiaphosphole-3,4-dicarboxylate] (17j): This compound was synthesized by use of **3c** (273 mg, 0.96 mmol), dimethyl acetylenedicarboxylate (**15c**, 825 µL, 6.72 mmol), and toluene (5 mL). Yield: 94 mg (33%); yellow crystals; b.p. 175 °C/10^{-3} mbar; m.p. 58 °C. ^{1}H NMR (C_6D_6): δ = 1.41 [s, 3 H, CH_3], 1.57−1.68 [m, 4 H, CH_2], 1.88−1.98 [m, 2 H, CH_2], 1.98−2.12 [m, 2 H, CH_2], 3.47 [s, 3 H, CO_2CH_3], 3.81 [s, 3 H, CO_2CH_3]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 23.7 [s, CH_2], 28.6 [d, $^4J_{C,P}$ = 2.3 Hz, CH_3], 40.6 [s, CH_2], 50.3 [d, $^3J_{C,P}$ = 5.4 Hz, C_q], 52.0 [s, CO_2CH_3], 52.7 [s, CO_2CH_3], 141.6 [d, $^2J_{C,P}$ = 12.2 Hz, C(4)], 163.9 [d, $^2J_{C,P}$ = 22.9 Hz, CO_2CH_3], 167.2 [d, $^1J_{C,P}$ = 59.7 Hz, C(3)], 167.2 [d, $^3J_{C,P}$ = 2.3 Hz, CO_2CH_3], 170.6 [d, $^2J_{C,P}$ = 6.1 Hz, C(5)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = 227.7 [s, P(2)]. IR (CCl_4): ṽ = 1742 (CO), 1725 (CO). $C_{13}H_{17}O_4PS$ (300.31): calcd. C 51.99, H 5.71; found C 52.17, H 5.65.

Dimethyl [(1-Methylcyclohex-1-yl)-1,2-thiaphosphole-3,4-dicarboxylate] (17k): This compound was synthesized by use of **3b** (1100 mg, 3.55 mmol), dimethyl acetylenedicarboxylate (**15c**, 3.05 mL, 25.0 mmol) and toluene (5 mL). Yield: 935 mg (84%); yellow oil; b.p. 175 °C/10^{-3} mbar. ^{1}H NMR (C_6D_6): δ = 1.38 [s, 3 H, CH_3], 1.47−1.72 [m, 6 H, CH_2], 1.82−2.02 [m, 1 H, CH_2], 2.12−2.22 [m, 2 H, CH_2], 2.24−2.36 [m, 1 H, CH_2], 3.60 [s, 3 H, CO_2CH_3], 3.82 [s, 3 H, CO_2CH_3]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 23.3 [s, CH_2], 26.3 [s, CH_2], 29.8 [s, CH_3], 39.5 [s, CH_2], 43.5 [d, $^3J_{C,P}$ = 5.4 Hz, C_q], 52.2 [s, CO_2CH_3], 52.7 [s, CO_2CH_3], 141.6 [d, $^2J_{C,P}$ = 12.2 Hz, C(4)], 163.6 [d, $^2J_{C,P}$ = 22.2 Hz, CO_2CH_3], 167.0 [d, $^1J_{C,P}$ = 58.1 Hz, C(3)], 167.8 [d, $^3J_{C,P}$ = 2.3 Hz, CO_2CH_3], 169.6 [d, $^2J_{C,P}$ = 5.4 Hz, C(5)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = 227.8 [s, P(2)]. IR (CCl_4): ṽ = 1738 (CO), 1726 (CO). MS (EI, 70 eV): *m*/*z* (%) = 314 (61) [M$^+$], 299 (12) [M$^+$ − CH$_3$], 283 (63) [M$^+$ − P], 282 (58) [M$^+$ − S], 267 (75) [M$^+$ − S − CH$_3$], 251 (11) [M$^+$ − PS], 97 (16) [Me*c*Hex$^+$], 59 (60) [CO$_2$Me$^+$], 31 (100) [P$^+$]. $C_{14}H_{19}O_4PS$ (314.34): calcd. C 53.49, H 6.09; found C 53.83, H 6.61.

Diethyl (5-*tert*-Butyl-1,2-thiaphosphole-3,4-dicarboxylate) (17l): This compound was synthesized by use of **3a** (163 mg, 0.70 mmol), diethyl acetylenedicarboxylate (**15d**, 785 µL, 4.91 mmol), and toluene (10 mL). Yield: 73 mg (35%); yellow oil; b.p. 120 °C/10^{-3} mbar. ^{1}H NMR (C_6D_6): δ = 1.02 [t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3], 1.23 [t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_2CH_3], 1.46 [s, 9 H, $C(CH_3)_3$], 4.07 [q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2CH_3], 4.44 [q, $^3J_{H,H}$ = 7.1 Hz, 2 H, CH_2CH_3]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 14.1 [s, CH_2CH_3], 14.2 [s, CH_2CH_3], 31.9 [s, $C(CH_3)_3$], 39.4 [d, $^3J_{C,P}$ = 5.4 Hz, $C(CH_3)_3$], 61.4 [s, CO_2CH_2], 62.1 [s, CO_2CH_2], 141.9 [d, $^2J_{C,P}$ = 12.3 Hz, C(4)], 163.5 [d, $^2J_{C,P}$ = 22.2 Hz, CO_2CH_2], 167.5 [d, $^3J_{C,P}$ = 2.3 Hz, CO_2CH_2], 168.2 [d, $^1J_{C,P}$ = 58.3 Hz, C(3)], 170.1 [d, $^2J_{C,P}$ = 6.1 Hz, C(5)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = 224.7 [s, P(2)]. IR (CCl_4): ṽ = 1736 (CO), 1731 (CO). MS (EI, 70 eV): *m*/*z* (%) = 302 (21) [M$^+$], 287 (3) [M$^+$ − CH$_3$], 257 (6) [M$^+$ − OEt], 56 (37) [$C_4H_8^+$], 39 (45) [CH_3PS^{2+}]. $C_{13}H_{19}O_4PS$ (302.33): calcd. C 51.65, H 6.33; found C 51.55, H 6.22.

Synthesis of the Hexacyclic Cage Compound 23: Lead(IV) acetate (770 mg, 1.74 mmol) was added in portions to a solution of the thiadiphosphole **3a** (261 mg, 1.12 mmol), the aminotriazole **20** (257 mg, 1.69 mmol), and pyridine (290 µL, 3.60 mmol) in dichloromethane (10 mL). A spontaneous gas evolution took place, and the suspension was stirred at −78 °C for 4 h. The mixture was allowed to thaw, and all insoluble materials were removed by filtration through Celite. The obtained solution was concentrated and eluted through silica gel with *n*-pentane, and the hexacyclic compound **23** was obtained in a colorless fraction (R_f = 0.52). For further purification the crude product was recrystallized from *n*-pentane at −20 °C.

8,11-Di-*tert*-butyl-10-thia-9,12-diphosphahexacyclo-[9.8.0.0^{1,7}.0^{7,9}.0^{8,12}.0^{13,19}]nonadec-13(19)-ene (23): Yield: 38 mg (11%); colorless crystals; m.p. 156 °C. ^{1}H NMR (C_6D_6): δ = 1.30 [s, 9 H, $C(CH_3)_3$], 1.31 [s, 9 H, $C(CH_3)_3$], 1.40−1.62 [m, 3 H, CH_2], 1.67−1.94 [m, 13 H, CH_2], 2.18−2.30 [m, 1 H, CH_2], 2.44−2.56 [m, 2 H, CH_2], 2.61−2.72 [m, 1 H, CH_2]. ^{13}C{^{1}H} NMR (C_6D_6): δ = 23.0 [s, CH_2], 25.6 [s, CH_2], 26.7 [d, $J_{C,P}$ = 10.0 Hz, CH_2], 27.0 [s, CH_2], 27.8 [d, $J_{C,P}$ = 6.1 Hz, CH_2], 31.5 [s, CH_2], 31.6 [d, $J_{C,P}$ = 1.5 Hz, CH_2], 32.4 [s, CH_2], 32.7 [s, CH_2], 33.3 [pt, $J_{C,P}$ = $J_{C,P}$ = 6.1 Hz, $C(CH_3)_3$], 33.3 [pt, $J_{C,P}$ = $J_{C,P}$ = 3.8 Hz, $C(CH_3)_3$], 33.7 [s, CH_2], 34.4 [dd, $^2J_{C,P}$ = 13.4, $^2J_{C,P}$ = 11.9 Hz, $C(CH_3)_3$], 37.7 [dd, $^2J_{C,P}$ = 10.4, $^3J_{C,P}$ = 2.7 Hz, $C(CH_3)_3$], 58.2 [dd, $^1J_{C,P}$ = 43.3, $^2J_{C,P}$ = 4.2 Hz, C(11)], 63.4 [dd, $^1J_{C,P}$ = 43.3, $^1J_{C,P}$ = 35.7 Hz, C(8)], 79.4 [pt, $^2J_{C,P}$ = $^2J_{C,P}$ = 3.4 Hz, C(1)], 91.3 [dd, $^1J_{C,P}$ = 6.1, $^3J_{C,P}$ = 1.5 Hz, C(7)], 145.0 [d, $^1J_{C,P}$ = 27.6 Hz, C(18)], 155.8 [s, C(19)]. ^{31}P{^{1}H} NMR (C_6D_6): δ = −121.3 [d, $^2J_{P,P}$ = 1.5 Hz, P(9)], 32.0 [d, $^2J_{P,P}$ = 1.5 Hz, P(12)]. MS (EI, 35 eV): *m*/*z* (%) =420 (15) [M$^+$], 405 (7) [M$^+$ − CH$_3$], 363 (100) [M$^+$ − *t*Bu], 357 (44) [M$^+$ − PS], 257 (46) [M$^+$ − PS − PC*t*Bu], 256 (96) [M$^+$ − PS − HPC*t*Bu], 57 (11) [*t*Bu$^+$]. $C_{24}H_{38}P_2S$ (420.57): calcd. C 68.54, H 9.11; found C 68.40, H 9.17.

Diffraction Measurements: STOE Imaging Plate Diffraction System, graphite monochromator, Mo-K_α radiation (λ = 0.71073 Å, cell determination and refinement by STOE programs Version 2.75, structure solution by direct methods (SHELXS-86[33]), and structure refinement by SHELXL-93,[34] hydrogen atoms were included in the refinement by use of riding models. CCDC-178098 (**11a**), -178099 (**14**), -178100 (**18b**), and -178101 (**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Crystal Structure Analysis of 11a: $C_{20}H_{36}P_4S$; M = 432.43 g·mol^{-1}; monoclinic; space group $P2_1/c$ (no. 14); lattice constants a = 16.541(3), b = 9.850(2), c = 16.018(3) Å, β = 118.60(3)°, V = 2291.4(8) Å^3; Z = 4; $D_{calcd.}$ = 1.254 Mg/m^3; µ = 0.423 mm^{-1}; T = 293(2) K; crystal size 0.80 × 0.50 × 0.30 mm; 2.53° ≤ Θ ≤ 24.18°;

25946 reflections collected, 3471 independent reflections ($R_{int.}$ = 0.0287); 238 parameters; $w^{-1} = [\sigma^2(F_o^2) + (0.0406P)^2 + 0.6735P]$, $P = [(F_o^2) + 2F_c^2]/3$; $R^1 = 0.0258$, $wR^2 = 0.0692$ [$I > 2\sigma(I)$]; R^1 = 0.0286, $wR^2 = 0.0806$ [all data]; residual electron density 0.224 and −0.147 e/Å^3, $S = GOF$ (on F^2) = 1.045.

Crystal Structure Analysis of 14: $C_{20}H_{36}Br_2P_4S$; M = 592.25 g·mol^{-1}; monoclinic; space group $P2_1/n$ (no. 14); lattice constants a = 9.042(2), b = 27.246(5), c = 10.094(2) Å, β = 90.04(3)°, V = 2486.7(9) Å^3; Z = 4; $D_{calcd.}$ = 1.582 Mg/m^3; μ = 3.607 mm^{-1}; T = 293(2) K; crystal size 0.40 × 0.20 × 0.15 mm; 2.15° ≤ Θ ≤ 26.07°; 33431 reflections collected, 4646 independent reflections ($R_{int.}$ = 0.0742); 244 parameters; $w^{-1} = [\sigma^2(F_o^2) + (0.0295P)^2 + 0.9015P]$, $P = [(F_o^2) + 2F_c^2]/3$; $R^1 = 0.0369$, $wR^2 = 0.0759$ [$I > 2\sigma(I)$]; R^1 = 0.0533, $wR^2 = 0.0792$ [all data]; residual electron density 0.877 and −0.501 e/Å^3, $S = GOF$ (on F^2) = 1.176.

Crystal Structure Analysis of 18b: $C_{19}H_{27}F_6P_3S$; M = 494.38 g·mol^{-1}; monoclinic; space group $P2_1/c$ (no. 14); lattice constants a = 10.014(2), b = 16.174(3), c = 28.378(6) Å, β = 90.06(3)°, V = 4596(2) Å^3; Z = 8; $D_{calcd.}$ = 1.429 Mg/m^3; μ = 0.401 mm^{-1}; T = 293(2) K; crystal size 0.50 × 0.20 × 0.20 mm; 1.91° ≤ Θ ≤ 25.05°; 32172 reflections collected, 7698 independent reflections ($R_{int.}$ = 0.0917); 523 parameters; $w^{-1} = [\sigma^2(F_o^2) + (0.1000P)^2]$, $P = [(F_o^2) + 2F_c^2]/3$; $R^1 = 0.0655$, $wR^2 = 0.1713$ [$I > 2\sigma(I)$]; $R^1 = 0.0953$, $wR^2 = 0.1832$ [all data]; residual electron density 0.632 and −0.483 e/Å^3, $S = GOF$ (on F^2) = 1.090.

Crystal Structure Analysis of 19: $C_{15}H_{27}P_3S_3$; M = 396.46 g·mol^{-1}; monoclinic; space group $P2_1/n$ (no. 14); lattice constants a = 10.521(2), b = 16.315(3), c = 11.486(2) Å, β = 101.90(3)°, V = 1929(7) Å^3; Z = 4; $D_{calcd.}$ = 1.365 Mg/m^3; μ = 0.625 mm^{-1}; T = 293(2) K; crystal size 0.40 × 0.20 × 0.20 mm; 2.20° ≤ Θ ≤ 25.96°; 14946 reflections collected, 3536 independent reflections ($R_{int.}$ = 0.1172); 190 parameters; $w^{-1} = [\sigma^2(F_o^2) + (0.0010P)^2]$, $P = [(F_o^2) + 2F_c^2]/3$; $R^1 = 0.0322$, $wR^2 = 0.0684$ [$I > 2\sigma(I)$]; $R^1 = 0.0552$, $wR^2 = 0.0728$ [all data]; residual electron density 0.282 and −0.244 e/Å^3, $S = GOF$ (on F^2) = 0.869.

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