Cycloaddition Behavior of 1,2-Thiaphospholes: Reactions with Diazocumulenes and with Cyclopentadiene

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Dedicated to Professor Gerhard Himbert at the occasion of his 60th birthday

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1,2-Thiaphospholes **3a**,**b** react with (1-diazo-2-oxoalkyl)silanes **1a**–**c** to form [1,2]thiaphospholo[2′,3′:3,4][1,3]diphospholo[1,5-*b*][1,2]thiaphosphole systems **4** with *cis-anti-cis* configuration of the tricyclic framework. They are accompanied by small amounts of compounds **5** that are presumably the *cis-syn-cis* isomers of **4**, and 6-alkylidene-1-phospha-2-thiabicyclo[3.1.0]hex-3-enes **6**. It is likely that these reactions proceed by [3+2] cycloaddition of diazocumulenes, which coexist with diazo compounds as minor equilibrium components, at the P=C bond of the heterophospholes, followed by N_2 elimination and formation of short-lived 2-alkylidene-1,2(λ^5)thiaphospholes. The latter can either add to excess thiaphosphole to form the tricyclic products or undergo electrocyclization to form bicyclic alkylidenephosphiranes. Thiaphosphole **3a** does not seem to react directly with cyclopentadiene in a [4+2] or [2+4] cycloaddition. Reaction with excess cyclopentadiene at 120 °C yields the polycyclic compounds **15** and **16**, which are likely to arise from a Diels–Alder reaction of **3a**, reacting as a heterodiene, with the cyclopentadiene dimer.

Introduction

1,2-Thiaphospholes can be conceived as analogues of thiophenes where one C=C bond has been replaced by a P=C bond. Like all heterophospholes containing a two-coordinate three-valent (σ^2,λ^3) phosphorus atom, the incorporation of a phosphaalkene moiety into a heteroaromatic system stimulates questions about the aromatic character and the reactivity of such compounds. Theoretical calculations of aromaticity indices and photoelectron spectroscopy studies have confirmed the aromatic character of a variety of heterophospholes[1] and their benzo derivatives.[2] The conjugative properties of the P=C and the C=C bond have been found to be very similar in spite of the lower double-bond strength of the P=C bond.[3] Nevertheless, some types of heterophospholes show a remarkably high ability for addition and cycloaddition reactions; for comprehensive reviews of the chemistry of heterophospholes, see refs.[4−7] Concerning cycloaddition reactions, an inspection of the literature suggests that the P=C bond of heterophospholes is more amenable to reactions with 1,3-dipoles than with 1,3-diene systems (although no systematic investigations are available). To date, 1,2,3(λ^3)-2*H*-diazaphospholes represent the most-investigated heterophospholes; they react with diazo, nitrile ylide, nitrile imine, nitrile oxide, and azide dipoles.[6] Diazo dipoles[8] were also found to react with a 1,3,4-thiazaphosphole[9] and with 1,2,3,4-3*H*-triazaphospholes.[10]

Märkl and Hölzl in 1988−89 reported the first preparations of 1,2-thiaphospholes in very low yields.[11,12] The first practical synthesis was published by Saito and co-workers in 1993.[13,14] Regitz et al. have recently reported a novel synthesis of 3,4-bis(acceptor)-substituted 1,2-thiaphospholes.[15] 3,5-Diaryl-1,2-thiaphospholes have been found to be quite unreactive toward common dienophiles; norbornadiene, norbornene, and diethyl azodicarboxylate reacted only well above 100 °C to form 2:1 adducts resulting from a twofold Diels−Alder reaction.[14] With acrylic esters, methyl vinyl ketone, and ethyl propiolate as dienophiles, [4+2] cycloaddition was successful only in the presence of Lewis acids ($AlCl_3$, $EtAlCl_2$), in which case they occur readily at 20 °C.

No reactions of 1,2-thiaphospholes with 1,3-dipoles have been reported so far. Based on the smooth cycloaddition reaction of α-diazo-α-silyl ketones (via their diazocumulene isomers, see Scheme 1) with 2-acyl-1,2,3-diazaphospholes[16] and 1,2,3,4-3*H*-triazaphospholes,[10] we became attracted to 1,2-thiaphospholes as potential dipolarophiles. Furthermore, since no reactions with cyclopentadienes have been reported in the literature, we wondered whether the P=C bond of 1,2-thiaphospholes could also serve as a dienophilic component in Diels−Alder reactions.

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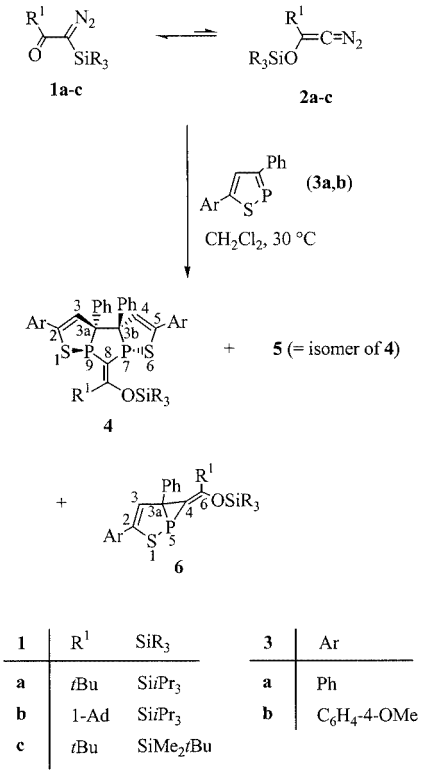


1	R^1	SiR_3
a	*t*Bu	Si*i*Pr$_3$
b	1-Ad	Si*i*Pr$_3$
c	*t*Bu	SiMe$_2$*t*Bu

3	Ar
a	Ph
b	C_6H_4-4-OMe

Scheme 1. Reactions of diazo compounds **1** or **2** with thiaphospholes **3**

Results and Discussion

Reactions with Diazocumulenes

1,2-Thiaphospholes **3a**,**b** were prepared in two steps from the corresponding 1,3-diarylpropenones by the procedures of Motoki[17] and Saito[14]. (1-Diazo-2-oxoalkyl)silanes **1a**−**c** were chosen as reaction partners; they are likely to be in equilibrium with minor amounts of diazocumulenes **2a**−**c**, which are much more reactive 1,3-dipoles than the former.[18] The reaction of equimolar amounts of the two components at 20 °C was complete in ca. 15−28 h and was accompanied by gas evolution (N_2) (Scheme 1, Table 1). In all cases, column chromatography furnished the tricyclic compounds **4** as the major products (36−83%). In the cases of *i*Pr$_3$Si-substituted diazo compounds **1**/**2a**,**b**, the bicyclic alkylidenephosphiranes **6** were also isolated in low yields (4−8%). The ^{31}P NMR spectra of the crude product mixtures indicated the presence of trace amounts of a third component that could be isolated only in one case and to which structure **5a** was tentatively assigned.

Elemental analyses and mass spectra indicated that compounds **4a**−**f** are 2:1 adducts of thiaphosphole and diazo ketone having lost N_2. An X-ray crystal structure analysis of **4a** revealed the novel heterotricyclic structure of a perhydro-1,3-diphosphole that is [*c*,*e*]-annelated with two 2,3-dihydro-1,2-thiaphosphole rings. The molecule plot (Figure 1) shows the *cis-anti-cis* configuration of the tricyclic core, in which both thiaphosphole rings adopt an envelope conformation with their P atom at the tip. The central ring has a half-chair conformation that allows an almost normal staggered arrangement around the C4−C5 bond [e.g., the torsion angle with respect to the phenyl substituents is 60.5(3)°]. Both phosphorus atoms have a tetrahedral environment (sum of bond angles: 289.0° at P1, 287.0° at P2). The steric demand of the bulky *t*Bu and OSi*i*Pr$_3$ groups is likely to account for a torsional twist of 11° at the exocyclic C=C bond. Crystal structures of related heterotricycles, with dihydro-1,2,3-diazaphospholes instead of dihydro-1,2-thiaphospholes as the outer rings, are known.[16,19]

Table 1. Products obtained from diazo compounds **1/2** and thiaphospholes **3**

4−**6**[a]	Precursors	R^1	SiR_3	Ar	**4** [%]	**5** [%]	**6** [%]
a	**1a** + **3a**	*t*Bu	Si*i*Pr$_3$	Ph	40	6	4
b	**1a** + **3b**	*t*Bu	Si*i*Pr$_3$	C_6H_4-4-OMe	52	n.i.	8
c	**1b** + **3a**	1-Ad	Si*i*Pr$_3$	Ph	54	n.i.	6
d	**1b** + **3b**	1-Ad	Si*i*Pr$_3$	C_6H_4-4-OMe	36	n.i.	4
e	**1c** + **3a**	*t*Bu	SiMe$_2$*t*Bu	Ph	80	n.i.	0
f	**1c** + **3b**	*t*Bu	SiMe$_2$*t*Bu	C_6H_4-4-OMe	83	n.i.	0

[a] 1-Ad = 1-adamantyl; n.i. = not isolated, trace amounts according to ^{31}P NMR spectroscopy.

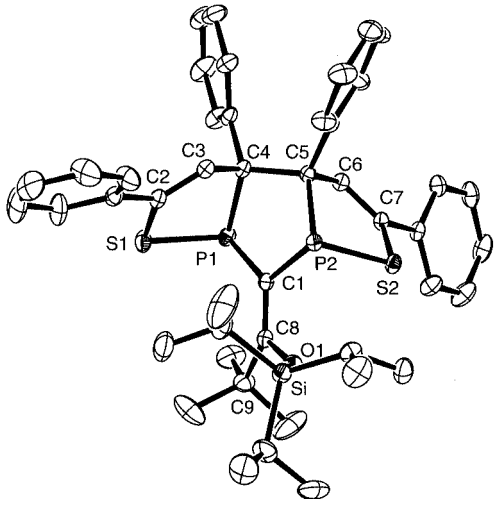


Figure 1. Structure of **4a** in the solid state (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; selected bond lengths [Å], bond angles [°], and torsion angles [°]: C1−P1 1.827(3), C1−P2 1.836(3), C1−C8 1.340(4), P1−S1 2.136(1), P1−C4 1.895(3), C4−C5 1.577(3), P2−S2 2.135(1), P2−C5 1.887(3); P1−C1−P2 113.0(2), P1−S1−C2 94.82(9), P2−S2−C7 94.12(9), C8−O1−Si 138.2(2); P1−C4−C5−P2 −57.2(2), C3−C4−C5−C6 171.9(2), C1−P1−C4−C5 44.4(2), C1−P2−C5−C4 42.4(2), P1−C1−C8−C9 17.7(4), P2−C1−C8−O1 11.1(3)

In the ^{1}H and ^{13}C NMR spectra, corresponding atoms in the two halves of the tricyclic system give rise to signals with slightly different chemical shifts. Similarly, the ^{31}P NMR spectra of **4a**−**f** show signals for two phosphorus atoms at δ = 71.1−72.1 and 84.9−88.2 ppm with $^2J_{P,P}$ coupling constants of 18.3−19.8 Hz. As in structurally related compounds,[16] several remarkably large long-range couplings between the phosphorus nuclei and atoms of the substituents at the exocyclic double bond are observed,

which point to a through-space interaction between the lone pair of electrons at the P atom and nuclei in close proximity. Thus, $^6J_{P,H}$ = 2.8 Hz is found for one of the diastereotopic (Si−)CH_3 groups in **4e**,**f**, while the second one gives rise to a singlet. In the Si*i*Pr_3-substituted compounds **4a**−**d**, the methine carbon atom of the isopropyl groups displays a $^5J_{P,C}$ coupling constant of 6.7−7.2 Hz, and $^6J_{P,H}$ = 2.4 Hz is observed for one of the adjacent diastereotopic methyl groups in **4b** and **4d**. For the two methyl carbon nuclei of the $SiMe_2$*t*Bu group in **4e**,**f**, $^5J_{P,C}$ values of 15.3 and 4.8−5.2 Hz are found. Finally, values ranging from 11.0 to 12.9 Hz are encountered for the ^4J coupling constant between phosphorus and the respective carbon atoms of the *t*Bu or adamantyl substituent at the same side of the exocyclic double bond.

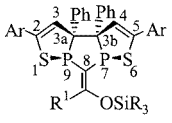
The identity of compound **5a** could not be established beyond doubt, because no crystals suitable for X-ray diffraction analysis could be obtained. According to elemental analysis, this compound is an isomer of **4a** and has almost the same R_f value as the latter in liquid chromatography on silica gel. Diagnostic NMR spectroscopic data of the two compounds are compared in Table 2 under the assumption that the latter have the same constitution. We see that one of the major differences is in the ^{31}P NMR spectroscopic data: in compound **5a**, the chemical shifts of the two phosphorus atoms are almost the same, and the P,P coupling constant is almost twice as large as that in **4a**. Since the chemical shifts of the olefinic protons and the carbon atoms of the tricyclic framework in general do no not differ much and those of the β-carbon atom at the enol ether moiety and of the *t*Bu and Si*i*Pr_3 substituents are almost identical, we assume that **5a** has indeed the same connectivity as **4a** and is a stereoisomer of the latter with a *cis*-*syn*-*cis* configuration of the tricyclic core (**5aA**). It should be noted that in a related investigation, the stereoisomers *cis*-*anti*-*cis*-**7**[20] and *cis*-*syn*-*cis*-**7**[21] have also been isolated and could both be identified by crystal structure analysis.[19]

Table 2. Selected NMR chemical shifts and coupling constants ($J_{P,P}$, $J_{P,H}$, $J_{P,C}$) of compounds **4a** and **5aA** ($CDCl_3$; δ [ppm]; *J* [Hz] in parentheses)

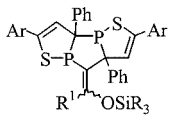
	4a	**5aA**[a]
P-7, P-9	71.9, 87.7 (18.3)	94.48, 94.73 (30.5)
3-H, 4-H	6.64 (5.0, 2.8), 6.79 (5.0, 2.8)	6.77 (11.2, 1.9), 6.89 (6.9)
C-2, C-5	144.2 (3.6, 1.2), 145.9 (3.6, 1.2)	137.7 (s), 143.0 (8.6)
C-3, C-4	124.6 (br. s), 124.9 (br. s)	125.8 (br. pseudo-t), 129.6 (broadened d)
C-3a, C-3b	71.9 (11.9, 7.7), 73.8 (11.0, 7.2)	76.1 (19.1), 79.1 (18.1, 6.7)
C-8	112.8 (59.6, 50.0)	112.2 (60.1, 52.5)
=COSi	174.9 (21.0, 14.3)	181.4 (31.0, 20.5)
$C(CH_3)_3$	41.8 (s)	41.8 (s)
$C(CH_3)_3$	30.7 (12.4)	30.5 (11.4)
SiC	14.4 (7.2)	15.1 (7.6)

[a] P,P,H and P,P,C spin systems in **5aA** are of the ABX type; for multiplets that were not well resolved, exact coupling constants could not be calculated.

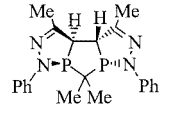
It is also evident from Table 2 that the P,H and P,C coupling constants of corresponding pairs of atoms (e.g., 3-H/4-H, C-3a/C-3b, for numbering see formula in Scheme 1) are very similar in **4a**, but remarkably different in **5aA**. This may at first glance suggest that the correct formula of **5a** is that of the constitutional isomer **5aB** rather than **5aA**. We discard structure **5aB**, however, inter alia because the enol ether moiety in that structure should not have NMR spectroscopic data so similar to those of **4a**. The different coupling patterns can be explained by different symmetry properties of the tricyclic framework of **4a** and **5aA**: The half-chair conformation, found in the solid state structure of **4a** (see above) approximately generates a local C_2 symmetry of the tricyclic core and the atoms directly attached to it (C_2 axis running through C-8 and the midpoint of C-3−C-3b), which also holds for the geometry of coupling pathways (e.g., P-9−C-3a−C-3b−C-4−4-H is formally symmetry-related to P-7−C-3b−C-3a−C-3−3-H). The structural formula of **5aA**, on the other hand, suggests mirror symmetry of the tricyclic core. This structure implies, however, an eclipsed conformation at the C-3a−C-3b bond that, according to a molecular model, would generate severe steric hindrance between the adjacent phenyl groups as well as the thiaphospholine rings. The necessary twist around this bond removes any degree of symmetry from the tricyclic core, and therefore, the "symmetry" of the spin coupling can also be expected to be lower than that in **4a**.



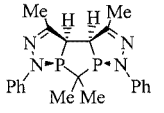
5A



5B



cis, *anti*, *cis*- **7**
δ_P = 63.7 ppm
$J_{P,P}$ = 16.0 Hz

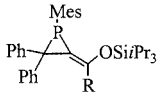


cis, *syn*, *cis*- **7**
δ_P = 99.1 ppm
($J_{P,P}$ not given)

The bicyclic alkylidenephosphiranes **6** were identified by the high-field shifts of their ^{31}P resonance (δ_P = −113.3 to −116.6 ppm), which are characteristic for phosphirane rings.[22] A comparison with the related 2-alkylidenephosphirane[23] **8** can be made, which has a similar ^{31}P chemical shift (R^1 = *t*Bu: δ_P = −134.5 ppm). The signals of the tetracoordinate ring carbon atom in **6a** and **8** differ by only 5 ppm, while that of the olefinic ring carbon atom in **6a** is shifted to higher field by 22 ppm (**6a**: δ_C = 92.8 ppm, $^1J_{P,C}$ = 72.9 Hz; **8**: δ_C = 114.8 ppm, $^1J_{P,C}$ = 47.6 Hz). The configuration at the exocyclic double bond in **6a**−**d** is likely to be the same as in **8**: ^5J(P,Si*C*H) coupling constants in the range 4.1−5.2 Hz indicate the *cis* relationship of the coupling nuclei, i.e., the (*Z*) configuration at this bond.

While a few monocyclic 2-alkylidenephosphiranes besides **8** are known (see, for example, refs.[24−26]), **6a**−**d** ap-

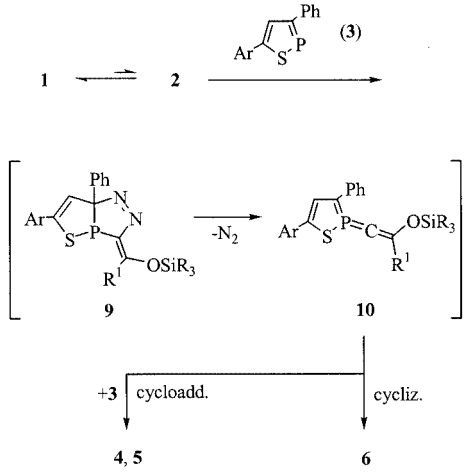
pear to be the first examples that are incorporated in a bicyclic ring system.



Mes = mesityl
R = Ph, 1-Ad

8

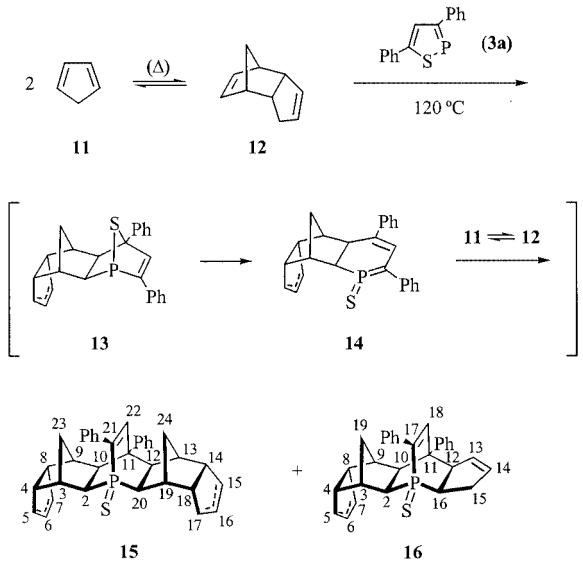
A mechanistic picture is given in Scheme 2. It is likely that diazocumulenes **2**, which coexist with diazo ketones **1** as minor equilibrium components, undergo 1,3-dipolar cycloaddition reactions with thiaphospholes **3** to give bicyclic pyrazolines **9**. These products lose molecular nitrogen under the reaction conditions at 20 °C to form 2-vinylidene-1,2(λ^5)thiaphospholes **10** that are immediately trapped in a [$3_{4\pi}+2_{2\pi}$] cycloaddition with still available thiaphosphole **3** to give the tricyclic systems **4** and **5**. A competing 4π electrocylization reaction of the bis(methylene)phosphorane moiety (ref.[27] and references cited therein) converts intermediates **10** into bicyclic alkylidenephosphiranes **6**. The same diazo dipoles **1** or **2** react with acyclic phosphaalkenes[23,27,28] and with 2-acyl-1,2,3-diazaphospholes[16] to give cycloaddition products analogous to **9** that are stable enough to be isolated and are dediazoniated only at elevated temperature. In the diazaphosphole case, the thermal decomposition of the cycloadducts leads to tricyclic compounds related to **4**.



Scheme 2. Mechanistic steps of the formation of **4**−**6**

Reaction with Cyclopentadiene

In contrast to its high dipolarophilic reactivity towards diazo compounds **1** or **2**, the P=C bond of thiaphospholes **3** is not suited to act as a dienophile in a Diels−Alder reaction with cyclopentadiene. No reaction of **3a** with cyclopentadiene (**11**) was observed at 20−80 °C. When **3a** was heated, however, with a large excess of cyclopentadiene at 120 °C in a sealed tube, two products were formed that could be isolated by column chromatography (Scheme 3). The major product was a high-melting solid that showed a molecular ion peak at m/z = 518 in the EI mass spectrum, corresponding to a 4:1 adduct of cyclopentadiene and **3a**. The major fragment peaks were those corresponding to the loss of one and two dicyclopentadiene units. An X-ray crystal structure analysis was performed on crystals obtained from a *p*-xylene solution and revealed the octacyclic structure **15**, with two molecules of **15** and one *p*-xylene molecule in the asymmetric unit of the crystal. Figure 2 shows that the polycyclic ring system has the *endo-syn-exo-exo-syn-endo* configuration.



Scheme 3. Reaction of thiaphosphole **3a** with cyclopentadiene

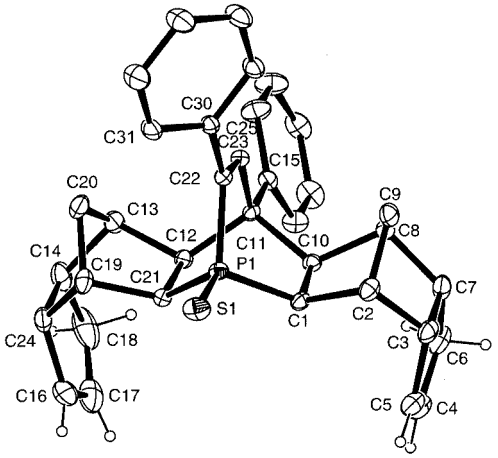


Figure 2. Structure of $\Delta^{5,15}$-**15** in the solid state (ORTEP plot); ellipsoids of thermal vibration are shown at the 20% probability level; only one of the two independent molecules in the unit cell is shown; selected bond lengths [A], bond angles [°], and torsion angles [°] (values for the second independent molecule are given in brackets): P1−S1 1.9466(14) [1.9495(14)], P1−C1 1.828(3) [1.805(4)], P1−C21 1.820(3) [1.826(3)], P1−C22 1.809(3) [1.821(3)], C22−C23 1.340(4) [1.339(4)], C16−C17 1.345(7) [1.337(6)], C17−C18 1.470(8) [1.478(5)], C4−C5 1.345(7) [1.359(7)], C4−C6 1.465(5) [1.447(8)]; endocyclic bond angles at C5 111.5(4) [110.6(5)], C4 113.4(3) [112.6(5)], C6 105.5(3) [106.9(4)], C16 110.5(5) [112.4(4)], C17 112.6(5) [112.7(4)], C18 105.7(4) [105.0(3)]; P1−C22−C30−C31 −48.0(5) [-44.2(4)], C23−C11−C15−C25 −16.2(5) [9.6(5)]

With respect to the double-bond positions in the two outer cyclopentene rings, three constitutional isomers can thus be expected, namely $\Delta^{5,16}$, $\Delta^{6,15}$, and $\Delta^{5,15}$. While the first two isomers are *meso* forms, the third one occurs as an enantiomeric pair (i.e., $\Delta^{5,15}$ and $\Delta^{6,16}$). In line with these symmetry properties and the expectation that all three positional isomers are formed with more or less the same probability (cf. mechanistic scheme), three closely spaced ^{31}P NMR signals are observed (δ = 25.6, 26.6, and 27.5 ppm) that have relative intensities of approximately 1:2:1 and can therefore be assigned to *meso*, *rac*, and *meso* forms, respectively. The ^{1}H and ^{13}C NMR spectra do not readily allow us to distinguish the signal sets of the three isomers because of extensive signal overlap and the mentioned intensity ratio. An effort to take advantage of the ASIS effect (aromatic solvent-induced shift) also failed. Nevertheless, a careful analysis of H,H and C,H correlation spectra gave evidence for the presence of these three isomers. In the crystal structure of **15** (vide supra and Figure 2), both independent molecules represent the *rac*-$\Delta^{5,15}$ isomer according to the bond geometries in the allylic moieties; the major difference between both molecules is found in the orientation of the phenyl ring attached to the central P-containing ring. The C=C and =C−CH_2 bond lengths in both parts of the molecule shown in Figure 2 are very close to the typical values for such bonds. The same is true for one cyclopentene ring in the second molecule, but in the other cyclopentene ring, the C=C bond is somewhat elongated [1.359(7) vs. 1.345(6) Å] and the =C−CH_2 bond is shortened [1.447(8) vs. 1.465(5) Å]. These differences, as well as those for the adjacent bonds in the five-membered ring, could point to the presence of a minor amount of the unsymmetrical diastereoisomer, but the rather high standard deviations suggest that we should not draw a firm conclusion. It is, of course, possible that the values of the estimated standard deviations are just a consequence of the superposition of the two positional isomers in the crystal structure; a further indication for this situation is given by the significantly larger temperature factors of the carbon atoms of the allylic moiety showing the somewhat atypical bond lengths.

The minor product from the reaction of **3a** with cyclopentadiene at 120 °C was obtained as a viscous oil. The molecular-ion peak (EI-MS) was found at *m*/*z* = 452, which suggests a 3:1 adduct of cyclopentadiene and **3a**. The major fragment peaks correspond to the loss of a cyclopentadiene and a dicyclopentadiene unit, respectively. These data and mechanistic reasoning suggested the hexacyclic framework shown in formula **16**, and a ^{31}P NMR spectrum indicated the presence of two isomers (δ = 32.7 and 33.6 ppm) in a 0.9:1.0 ratio. Again, a straightforward interpretation of the 1D ^{1}H and ^{13}C NMR spectra was not possible because of the close superposition of the signal sets of the two components. A thorough analysis, however, using several 2D techniques [H,H-COSY; inverse C,H correlation optimized at 140 Hz (HMQC); inverse long-range C,H correlation (HMBC) optimized at 7 Hz; P,H correlation] resulted in a complete signal assignment (Table 3) and showed unequivocally the presence of the $\Delta^{5,13}$ and $\Delta^{6,13}$ constitutional isomers. The very close agreement of the ^{1}H and ^{13}C chemical shifts of the C-12−C-16 cyclopentene ring indicates that the double bond position and the stereochemistry of this ring is the same in both isomers. The position of this cyclopentene ring as *exo* with respect to the central phosphacyclohexane ring was established by the observation of a cross peak between 10-H and 12-H for both isomers in a NOESY experiment, indicating that these protons are on the same side of the molecular framework.

Table 3. Assignments of ^{1}H and ^{13}C NMR signals, based on 2D correlation spectra, for the mixture of **$\Delta^{5,13}$-16** (**A**) and **$\Delta^{6,13}$-16** (**B**) (δ [ppm], *J* [Hz]); ^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz; $CDCl_3$ as solvent; when no assignment to **A** and **B** is made, the first (second) δ_H value and the first (second) δ_C value are associated

Position	^{1}H	^{13}C ($J_{C,P}$ in parentheses)
1	−	δ_P =32.7 (**A**), 33.6 (**B**)
2	2.30, 2.35	40.72 (49.7), 44.17 (49.3)
3	3.04 **A**, 2.85 **B**	41.43 **A**, 42.64 **B**
4	3.16 **A**, 2.60 **B**	54.87 **A**,[a] **B**
5	5.65 **A**, 2.25−2.41 **B**	131.83 **A**, 31.73 **B**
6	5.80 **A**, 5.82 **B**	132.32 **A**, 132.70 **B**
7	1.95−2.00[b] (1 H) **A**, 2.08−2.17 (1 H) **A**, 5.43 **B**	31.57 **A**, 131.17 **B**
8	2.38 **A**, 2.96 **B**	[a] **A**, 54.78 **B**
9	1.80 ($J_{H,H}$ = 3.9 Hz) **A**, 2.02 **B**	44.36, 43.01
10	2.65 **A**, 2.45 **B**	51.73 (6.5), 48.77 (6.6)
11	−	47.24 (37.2), 47.45 (37.5)
12	3.78, 3.84	61.44 (5.0), 60.93 (4.9)
13	5.59 **A**, **B**	132.23, 132.27
14	5.09 **A**, **B**	130.26, 130.42
15	2.50−2.76 (4 H)	35.25, 35.35
16	2.80−2.91 (2 H)	39.17 (52.1), 39.55 (52.8)
17	−	134.87 (55.3), 135.76 (55.3)
18	7.22, 7.25	145.50, 144.07
19	1.03−1.07 (2 d, 2 H) **A**, **B**, 1.98−2.04 (2 H) **A**, **B**	37.65 **A**, 37.55 **B**
Phenyl	7.08−7.55	125.22−129.31 (CH), 142.73 and 142.84 (C_q)

[a] δ_C = 43.66 or 43.98 ppm ($J_{C,P}$ = 12.2 Hz). [b] Long-range correlation with δ = 1.80 ppm (9-H, **A**).

Obviously, **3a** is unreactive towards cyclopentadiene at ambient temperature,[29] and at elevated temperature it reacts as a heterodiene with the cyclopentadiene dimer **12** (Scheme 2). The expected [4+2] cycloaddition product **13** isomerizes under the reaction conditions to form dihydrophosphinine 1-sulfide derivative **14**, which undergoes another Diels−Alder reaction, either with dicyclopentadiene to form **15** or with cyclopentadiene to form **16**. The formation of **15** is fully analogous to the reaction of **3a** with norbornene.[14]

Conclusions

These investigations have provided several interesting results. After 2-acyl-1,2,3-diazaphospholes and 1,2,3-triazaphospholes, 1,2-thiaphospholes have now been uncovered as another class of heterophospholes with a P=C bond that

is able to undergo 1,3-dipolar cycloaddition with diazo compounds **1** and **2**. At the same time, these are the first reported reactions of 1,2-thiaphospholes with 1,3-dipoles. Although the initial cycloaddition products could not be isolated, known analogies with other compounds their reactions (i.e., isolation and thermally induced transformation of cycloaddition products with phosphaalkenes or 2-acyl-1,2,3-diazaphospholes) leave no doubt about their intermediacy. Among the products, the 1-phospha-2-thiabicyclo[3.1.0]hex-3-ene derivatives **6**, formed in minor amounts, deserve being mentioned because they have a rather strained 2-alkylidenephosphirane ring incorporated in the bicyclic framework. The existence of these compounds may reflect once more the possibility of reducing the angle strain of strained ring systems by incorporating sulfur atoms into them.

While the P=C bond of thiaphospholes **3** is obviously a very good dipolarophile towards diazo compounds **1** and **2**, a cycloaddition with cyclopentadiene, in which **3a** behaves as the dienophile, was not observed in the same temperature range. Rather, the 1,2-thiaphosphole acts as a hetero-1,3-diene toward the cyclopentadiene dimer **12** at elevated temperature, thereby reflecting the known reluctance of these thiophene-like molecules to undergo a Diels–Alder reaction even with activated alkenes. It should be worthwhile to compare the different cycloaddition behavior of 1,2-thiaphospholes towards diazo dipoles and 1,3-dienes by computational studies of the reaction profiles.

After the submission of this manuscript, a contribution by Binger, Regitz, and their co-workers was published in this journal,[30] describing [2+2], [2+3] and [4+2] cycloaddition reactions with 3,4-bis(acceptor)-substituted 1,2-thiaphospholes.

Experimental Section

General Remarks: All reactions were carried out in rigorously dried glassware under argon. Solvents were dried by standard procedures and kept under argon. The petroleum ether used had a boiling point range of 30–60 °C. Column chromatography was performed under hydrostatic conditions (silica gel Si 60, Macherey–Nagel, 0.063–0.02 mm, column size 60 × 4 cm). NMR: Bruker AMX-500 (^{1}H: 500.14 MHz; ^{13}C: 125.77 MHz; ^{31}P: 202.48 MHz) and Bruker AMX-400 (^{1}H: 400.13 MHz; ^{13}C: 100.61 MHz). $CDCl_3$ was used as solvent. The ^{13}C NMR spectra were recorded as proton-decoupled, but phosphorus-coupled; thus, the signal multiplicities reported here indicate P,C coupling; pt = pseudo-triplet. The following references were applied: internal TMS for the proton spectra, the solvent signal for the ^{13}C NMR spectra [δ($CDCl_3$) = 77.0], and external 85% H_3PO_4 for the ^{31}P spectra. IR: Perkin–Elmer IR-1310 and IR-883 as well as Bruker Vector-22 spectrometers; relative intensities are given in parentheses. MS: Varian MAT-711 and Finnigan MAT-SSQ-7000. Microanalyses: Perkin–Elmer EA-240 and EA-2400 (University of Kaiserslautern). Melting points were determined with an apparatus according to Dr. Tottoli (Büchi) and are uncorrected.

Materials: (1-Diazo-2-oxoalkyl)silanes **1a**,[31] **1b**,[32] and **1c**[31] were prepared as published. Yields higher than those reported were achieved when the purification by column chromatography was carried out at −4 °C (silica gel, 0.063–0.2 mm, mixtures of diethyl ether/petroleum ether). 1,2-Thiaphospholes **3a**,**b** were prepared according to refs.[14,17]

***cis-anti-cis*-8-[(2,2-Dimethyl-1-(triisopropylsilyloxy)propylidene)]-2,3a,3b,5-tetraphenyl-3a,3b-dihydro[1,2]thiaphospholo[2′,3′:3,4]-[1,3]diphospholo[1,5-*b*][1,2]thiaphosphole (4a), Isomer 5a (Presumably *cis-syn-cis*-Isomer 5aA), and 4-[(*Z*)-2,2-Dimethyl-1-(triisopropylsilyloxy)propylidene]-2,3a-diphenyl-3a,4-dihydrophosphireno[1,2-*b*][1,2]thiaphosphole (6a):** A solution of thiaphosphole **3a** (0.424 g, 1.67 mmol) and diazo ketone **1a** (0.471 g, 1.67 mmol) in dichloromethane (15 mL) was stirred at 20 °C for 15 h. The solvent was evaporated and the residue was subjected to column chromatography (silica gel, diethyl ether/petroleum ether, 1:14). Workup of three consecutive fractions gave first **6a** (0.034 g, 4% yield), then **4a** (0.253 g, 40%) and **5a** (0.040 g, 6%).

4a: Colorless crystals, m.p. 153 °C (dec.). IR (KBr): ṽ = 1526 (s), 1490 (m), 1444 (m), 1255 (s), 1150 (vs), 755 (vs), 688 (vs) cm^{-1}. ^{31}P NMR: δ = 71.9 (d, $^2J_{P,P}$ = 18.3 Hz), 87.7 (d, $^2J_{P,P}$ = 18.3 Hz) ppm. ^{1}H NMR (500.14 MHz): δ = 1.06 (d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHCH_3), 1.12 (d, $^3J_{H,H}$ = 7.8 Hz, 9 H, CHCH_3), 1.36 [s, 9 H, C(CH_3)$_3$], 1.53 (sept, $^3J_{H,H}$ = 7.5 Hz, 3 H, CHCH$_3$), 6.64 (dd, $^3J_{P,H}$ = 5.0, $^4J_{P,H}$ = 2.8 Hz, 1 H, 3-H or 4-H), 6.79 (dd, $^3J_{P,H}$ = 5.0, $^4J_{P,H}$ = 2.8 Hz, 1 H, 4-H or 3-H), 7.14–7.31 (m, 16 H, *m*- and *p*-H$_{Ph}$), 7.48–7.50 (m, 4 H, *o*-H$_{Ph}$) ppm. ^{13}C NMR (125.77 MHz): δ = 14.4 (d, $^5J_{P,C}$ = 7.2 Hz, SiCH), 18.6 (s, SiCHCH$_3$), 18.7 (s, SiCHCH$_3$), 30.7 [d, $^4J_{P,C}$ = 12.4 Hz, C(CH$_3$)$_3$], 41.8 [d, $^3J_{P,C}$ = 3.8 Hz, C(CH$_3$)$_3$], 71.7 (dd, $^1J_{P,C}$ = 11.9, $^2J_{P,C}$ = 7.7 Hz, C-3a or C-3b), 73.8 (dd, $^1J_{P,C}$ = 11.0, $^2J_{P,C}$ = 7.2 Hz, C-3b or C-3a), 112.8 (dd, $^1J_{P,C}$ = 59.6, 50.0 Hz, C-8), 124.6 (br. pt, C-3 or C-4), 124.9 (br. pt, C-4 or C-3), 127.1 (s, *m*-C$_{Ph}$), 127.3 (s, *m*-C$_{Ph}$), 127.4 (s, *m*-C$_{Ph}$), 127.46 (pt, 2 × *p*-C$_{Ph}$), 127.53 (s, *m*-C$_{Ph}$), 128.2 (s, *o*-C$_{Ph}$), 128.3 (s, *o*-C$_{Ph}$), 128.49 (s, *p*-C$_{Ph}$), 128.52 (s, *p*-C$_{Ph}$), 129.07 (d, $^3J_{P,C}$ = 19.6 Hz, *o*-C$_{Ph}$), 129.13 (d, $^3J_{P,C}$ = 18.6 Hz, *o*-C$_{Ph}$), 135.6 (dd, $J_{P,C}$ = 4.3, 1.0 Hz, *i*-C$_{Ph}$), 136.4 (dd, $J_{P,C}$ = 4.1, 1.2 Hz, *i*-C$_{Ph}$), 138.7 (dd, $^2J_{P,C}$ = 19.6, $^3J_{P,C}$ = 2.4 Hz, *i*-C$_{Ph}$), 139.1 (dd, $^2J_{P,C}$ = 19.6, $^3J_{P,C}$ = 2.9 Hz, *i*-C$_{Ph}$), 144.2 (dd, $J_{P,C}$ = 3.6, 1.2 Hz, C-2 or C-5), 145.9 (dd, $J_{P,C}$ = 3.6, 1.2 Hz, C-5 or C-2), 174.9 (dd, $^2J_{P,C}$ = 21.0, 14.3 Hz, =COSi) ppm. MS (FD, 10.5 kV): *m*/*z* (%) = 762 [M$^+$ − H]. $C_{45}H_{52}OP_2S_2Si$ (763.07): calcd. C 70.83, H 6.89; found C 71.32, H 7.14.

5a (5aA): Light-yellow powder, m.p. 192 °C. ^{31}P NMR: δ = 94.5 (d, $^2J_{P,P}$ = 30.5 Hz), 94.8 (d, $^2J_{P,P}$ = 30.5 Hz) ppm. ^{1}H NMR (500.14 MHz): δ = 1.22 (d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHCH_3), 1.26 (d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHCH_3), 1.34 [s, 9 H, C(CH$_3$)$_3$], 1.66 (sept, $^3J_{H,H}$ = 7.5 Hz, 3 H, CHCH$_3$), 6.77 (dd, $J_{P,H}$ = 11.2, $J_{P,H}$ = 1.9 Hz, 1 H), 6.89 (d, $J_{P,H}$ = 6.9 Hz, 1 H), 7.05–7.07 (m, 6 H, *m*- and *p*-H$_{Ph}$), 7.16–7.26 (m, 7 H, *o*-, *m*- and *p*-H$_{Ph}$), 7.34–7.39 (m, 3 H, *m*- and *p*-H$_{Ph}$), 7.46 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, *o*-H$_{Ph}$), 7.66 (d, $^3J_{H,H}$ = 6.9 Hz, 2 H, *o*-H$_{Ph}$) ppm. ^{13}C NMR (125.77 MHz): δ = 15.1 (d, $J_{P,C}$ = 7.6 Hz, SiCH), 18.68 (s, SiCHCH$_3$), 18.73 (s, SiCHCH$_3$), 30.5 [d, $J_{P,C}$ = 11.4 Hz, C(CH$_3$)$_3$], 41.8 [s, C(CH$_3$)$_3$], 76.1 (d, $J_{P,C}$ = 19.1 Hz), 79.1 (dd, $J_{P,C}$ = 18.1, 6.7 Hz), 112.2 (dd, $J_{P,C}$ = 60.1, 52.5 Hz), 125.8 (pt), 126.5 (d, $J_{P,C}$ = 1.9 Hz), 126.6–128.5 (13 s), 129.6 (broadened d), 136.4 (s, *i*-C$_{Ph}$), 136.9 (d, $J_{P,C}$ = 1.9 Hz, *i*-C$_{Ph}$), 137.7 (s), 140.7 (d, $J_{P,C}$ = 23.8 Hz, *i*-C$_{Ph}$), 142.0 (d, $J_{P,C}$ = 19.1 Hz, *i*-C$_{Ph}$), 143.0 (d, $J_{P,C}$ = 8.6 Hz), 181.4 (dd, $J_{P,C}$ = 31.0, 20.5 Hz, =COSi) ppm. $C_{45}H_{52}OP_2S_2Si$ (763.07): calcd. C 70.83, H 6.89; found C 70.60, H 6.92.

6a: Colorless crystals, m.p. 98 °C. IR (KBr): ṽ = 1646 (s), 1628 (s), 1481 (m), 1457 (m), 1272 (vs), 1217 (s), 1201 (vs), 1144 (s), 1073

(s), 1018 (s), 826 (s), 805 (s), 755 (s), 692 (s) cm^{-1}. ^{31}P NMR: δ = −113.3 ppm. ^{1}H NMR (500.14 MHz): δ = 1.16 [s, 9 H, $C(CH_3)_3$], 1.13−1.25 [m, 18 H, $CH(CH_3)_2$], 1.64 (sept, $^{3}J_{H,H}$ = 7.5 Hz, 3 H, $CHCH_3$), 6.78 (d, $^{3}J_{P,H}$ = 5.5 Hz, 1 H, 3-H), 7.16−7.33 (m, 8 H, H_{Ph}), 7.48−7.50 (m, 2 H, *o*-H_{Ph}) ppm. ^{13}C NMR (125.77 MHz): δ = 14.6 (d, $^{5}J_{P,C}$ = 4.7 Hz, Si*C*H), 18.4 (s, SiCH*C*H_3), 18.5 (s, SiCH*C*H_3), 28.4 [s, $C(CH_3)_3$], 41.0 [s, $C(CH_3)_3$], 57.2 (d, $^{1}J_{P,C}$ = 21.1 Hz, C-3a), 92.8 (d, $^{1}J_{P,C}$ = 72.9 Hz, C-4), 125.9 (s, *o*-C_{Ph}), 126.1 (s, *p*-C_{Ph}), 126.7 (s, *o*-C_{Ph}), 127.6 (s, C-3), 128.1 (s, *p*-C_{Ph}), 128.4 (s, *m*-C_{Ph}), 128.5 (s, *m*-C_{Ph}), 136.7 (d, $^{3}J_{P,C}$ = 4.5 Hz, *i*-C_{Ph}), 141.3 (s, C-2), 142.5 (d,$^{2}J_{P,C}$ = 2.5 Hz, *i*-C_{Ph}), 163.8 (d, $^{2}J_{P,C}$ = 7.2 Hz, =COSi) ppm. $C_{30}H_{41}OPSSi$ (508.78): a correct elemental analysis was not obtained because of an impurity (δ_P = 35.8 ppm).

***cis-anti-cis*-Tricyclic Compound 4b and Alkylidenephosphirane 6b:** A solution of thiaphosphole **3b** (0.336 g, 1.13 mmol) and diazo ketone **1a** (0.338 g, 1.13 mmol) in dichloromethane (15 mL) was stirred at 20 °C for 15 h. The solvent was evaporated and the residue was subjected to column chromatography (silica gel, diethyl ether/petroleum ether, 1:9). The first fraction yielded **6b** (0.052 g, 8%), the second fraction gave **4b** (0.242 g, 52%).

4b: Light-yellow microcrystals, m.p. 153 °C. IR (KBr): ṽ = 1607 (s), 1526 (s), 1506 (vs), 1463 (s), 1442 (m), 1298 (m), 1257 (vs), 1176 (vs), 1148 (s), 1034 (s), 778 (m), 740 (m), 726 (s), 698 (s), 686 (s) cm^{-1}. ^{31}P NMR: δ = 71.5 (d, $^{2}J_{P,P}$ = 18.8 Hz), 87.0 (d, $^{2}J_{P,P}$ = 18.8 Hz) ppm. ^{1}H NMR (500.14 MHz): δ = 1.07 (d, $^{3}J_{H,H}$ = 7.8 Hz, 9 H, $CHCH_3$), 1.13 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.36 [s, 9 H, $C(CH_3)_3$], 1.54 (sept, $^{3}J_{H,H}$ = 7.5 Hz, 3 H, $CHCH_3$), 6.54 (dd, $^{3}J_{P,H}$ = 5.0, $^{4}J_{P,H}$ = 3.1 Hz, 1 H, 3-H or 4-H), 6.66 (dd, $^{3}J_{P,H}$ = 5.3, $^{4}J_{P,H}$ = 2.8 Hz, 1 H, 4-H or 3-H), 6.81 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, *m*-H_{anisyl}), 6.82 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, *m*-H_{anisyl}), 7.13−7.30 (m, 10 H_{Ph}), 7.41 ($^{3}J_{H,H}$ = 8.7 Hz, 2 H, *o*-H_{anisyl}), 7.42 (d, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, *o*-H_{anisyl}) ppm. ^{13}C NMR (125.77 MHz): δ = 14.4 (d, $^{5}J_{P,C}$ = 7.2 Hz, SiCH), 18.6 (d, $^{6}J_{P,C}$ = 2.4 Hz, SiCH*C*H_3), 18.7 (s, SiCH*C*H_3), 30.7 [d, $^{4}J_{P,C}$ = 12.9 Hz, $C(CH_3)_3$], 41.8 [d, $^{3}J_{P,C}$ = 3.3 Hz, $C(CH_3)_3$], 55.3 (s, 2 × OCH_3), 71.6 (dd, $^{1}J_{P,C}$ = 10.4, $^{2}J_{P,C}$ = 7.6 Hz, C-3a or C-3b), 73.8 (dd, $^{1}J_{P,C}$ = 10.5, $^{2}J_{P,C}$ = 7.6 Hz, C-3b or C-3a), 113.5 (s, *m*-C_{anisyl}), 113.7 (s, *m*-C_{anisyl}), 113.1 (dd, $^{1}J_{P,C}$ = 58.7, $^{1}J_{P,C}$ = 48.6 Hz, C-8), 122.8 (m, C-3 or C-4), 123.4 (m, C-4 or C-3), 127.3 (s, *m*- and *p*-C_{Ph}), 127.5 (s, *m*-C_{Ph}), 128.3 (s, *i*-C_{anisyl}), 128.4 (s, *i*-C_{anisyl}), 128.5 (s, *o*-C_{anisyl}), 128.7 (s, *o*-C_{anisyl}), 129.07 (d, $^{3}J_{P,C}$ = 19.1 Hz, *o*-C_{Ph}), 129.14 (d, $^{3}J_{P,C}$ = 18.6 Hz, *o*-C_{Ph}), 139.0 (dd, $^{2}J_{P,C}$ = 19.6, $^{3}J_{P,C}$ = 1.9 Hz, *i*-C_{Ph}), 139.3 (dd, $^{2}J_{P,C}$ = 20.0, $^{3}J_{P,C}$ = 2.9 Hz, *i*-C_{Ph}), 143.7 (dd, $^{2}J_{P,C}$ = 2.9, $^{4}J_{P,C}$ = 1.4 Hz, C-2 or C-5), 145.4 (dd, $^{2}J_{P,C}$ = 2.6, $^{4}J_{P,C}$ = 1.4 Hz, C-5 or C-2), 159.89 (s, *p*-C_{anisyl}), 159.95 (s, *p*-C_{anisyl}), 174.6 (dd, $^{2}J_{P,C}$ = 21.0, $^{2}J_{P,C}$ = 14.3 Hz, =COSi) ppm. $C_{47}H_{56}O_3P_2S_2Si$ (823.12): calcd. C 68.58, H 6.86; found C 67.91, H 7.16.

6b: Light-yellow crystals, m.p. 150 °C (dec.). IR (KBr): ṽ = 1645 (s), 1606 (s), 1503 (s), 1455 (m), 1293 (s), 1271 (s), 1254 (vs), 1233 (s), 1217 (s), 1201 (s), 1171 (s), 1030 (s), 836 (s), 825 (s), 801 (m) cm^{-1}. ^{31}P NMR: δ = −115.4 ppm. ^{1}H NMR (500.14 MHz): δ = 1.16 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.16 [s, 9 H, $C(CH_3)_3$], 1.20 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.63 (sept, $^{3}J_{H,H}$ = 7.5 Hz, $CHCH_3$), 3.79 (s, 3 H, OCH_3), 6.66 (d, $^{3}J_{P,H}$ = 5.6 Hz, 3-H), 6.85 (d, $^{3}J_{H,H}$ = 8.9 Hz, 2 H_{anisyl}), 7.16−7.30 (m, 5 H, H_{Ph}), 7.42 (d, $^{3}J_{H,H}$ = 8.9 Hz, 2 H, *o*-H_{anisyl}) ppm. ^{13}C NMR (125.77 MHz): δ = 14.6 (d, $^{5}J_{P,C}$ = 4.1 Hz, Si*C*H), 18.4 (s, SiCH*C*H_3), 18.5 (s, SiCH*C*H_3), 28.4 [s, $C(CH_3)_3$], 40.9 [s, $C(CH_3)_3$], 55.3 (s, OCH_3), 57.3 (d, $^{1}J_{P,C}$ = 21.0 Hz, C-3a), 93.1 (d, $^{1}J_{P,C}$ = 73.7 Hz, C-4), 113.8 (s, *m*-C_{anisyl}), 125.9 (s, *o*-C_{Ph}), 126.06 (s, *p*-C_{Ph}), 126.13 (s, C-3), 128.0 (s, *o*-C_{anisyl}), 128.5 (s, *m*-C_{Ph}), 129.4 (d, $^{3}J_{P,C}$ = 3.3 Hz, *i*-C_{anisyl}), 140.8 (s, C-2), 142.6 (s, *i*-C_{Ph}), 159.7 (s, *p*-C_{anisyl}), 163.6 (d, $^{2}J_{P,C}$ = 6.7 Hz, =COSi) ppm. $C_{31}H_{43}O_2PSSi$ (538.81): calcd. C 69.10, H 8.04; found 69.11, H 8.26.

***cis-anti-cis*-Tricyclic Compound 4c and Alkylidenephosphirane 6c:** A solution of thiaphosphole **3a** (0.617 g, 2.43 mmol) and diazo ketone **1b** (0.875 g, 2.43 mmol) in dichloromethane (30 mL) was stirred at 20 °C for 26 h. The solvent was evaporated, and the residue was subjected to column chromatography (silica gel, diethyl ether/petroleum ether, 1:19). The first fraction yielded **6c** (0.087 g, 6%), the second fraction gave **4c** (0.550 g, 54%).

4c: Colorless microcrystals, m.p. 194 °C (dec.). IR (KBr): ṽ = 1594 (m), 1573 (m), 1516 (s), 1488 (s), 1444 (s), 1251 (m), 1230 (m), 1201 (s), 1175 (s), 1105 (m), 1084 (m), 1017 (m), 880 (m), 756 (vs), 734 (s), 723 (s), 707 (m), 697 (s), 677 (s) cm^{-1}. ^{31}P NMR: δ = 71.6 (d, $^{2}J_{P,P}$ = 18.8 Hz), 88.2 (d, $^{2}J_{P,P}$ = 18.8 Hz) ppm. ^{1}H NMR (500.14 MHz): δ = 1.07 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.12 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.56 (sept, $^{3}J_{H,H}$ = 7.5 Hz, 3 H, $CHCH_3$), 1.67−1.69 (m, 6 H, Ad), 2.04−2.15 (m, 9 H, Ad), 6.62 (dd, $^{3}J_{P,H}$ = 5.0, $^{4}J_{P,H}$ = 3.1 Hz, 1 H, 3-H or 4-H), 6.78 (dd, $^{3}J_{P,H}$ = 5.1, $^{4}J_{P,H}$ = 3.0 Hz, 1 H, 4-H or 3-H), 7.13−7.31 (m, 16 H, *m*- and *p*- H_{Ph}), 7.48−7.50 (m, 4 H, *o*-H_{Ph}) ppm. ^{13}C NMR (125.77 MHz): δ = 14.4 (d, $^{5}J_{P,C}$ = 6.7 Hz, Si*C*H), 18.7 (s, SiCH*C*H_3), 18.8 (s, SiCH*C*H_3), 28.6 (s, C-3,-5,-7-Ad), 36.6 (s, C-4,-6,-10-Ad), 41.5 (d, $^{4}J_{P,C}$ = 12.4 Hz, C-2,-8,-9-Ad), 44.2 (s, C-1-Ad), 71.5 (pt, $^{1}J_{P,C}$ + $^{2}J_{P,C}$ = 18.2 Hz, C-3a or C-3b), 73.6 (pt, $^{1}J_{P,C}$ + $^{2}J_{P,C}$ = 19.8 Hz, C-3b or C-3a), 113.1 (dd, $^{1}J_{P,C}$ = 59.8, $^{1}J_{P,C}$ = 51.7 Hz, C-8), 124.5 (br. s, C-3 or C-4), 125.0 (br. s, C-4 or C-3), 127.1−128.5 (8 s), 129.1 (d), 135.6 (s), 136.5 (s), 138.7 (d), 139.2 (d), 144.0 (s, C-2 or C-5), 145.9 (s, C-5 or C-2), 175.1 (dd, $^{2}J_{P,C}$ = 19.3, $^{2}J_{P,C}$ = 14.1 Hz, =COSi) ppm. $C_{51}H_{58}OP_2S_2Si$ (841.18): calcd. C 72.82, H 6.95; found C 72.70, H.6.84.

6c: Light-yellow microcrystals, m.p. 165 °C (dec.). IR (KBr): ṽ = 1645 (s), 1490 (m), 1446 (m), 1319 (m), 1264 (s), 1247 (s), 1233 (s), 1184 (m), 1107 (m), 1091 (m), 1068 (m), 1016 (m), 882 (m), 831 (m), 782 (m), 772 (m), 756 (s) cm^{-1}. ^{31}P NMR: δ = −114.3 ppm. ^{1}H NMR (500.14 MHz): δ = 1.17 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.20 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.55−1.66 (m, 6 H, Ad + 3 H, $CHCH_3$), 1.83−1.97 (m, 9 H, Ad), 6.77 (d, $^{3}J_{P,H}$ = 5.6 Hz, 1 H, 3-H), 7.16−7.35 (m, 8 H_{Ph}), 7.48−7.50 (m, 2 H, *o*-H_{Ph}) ppm. ^{13}C NMR (125.77 MHz): δ = 14.6 (d, $^{5}J_{P,C}$ = 5.2 Hz, Si*C*H), 18.4 (s, SiCH*C*H_3), 18.6 (s, SiCH*C*H_3), 28.4 (s, C-3,-5,-7-Ad), 36.8 (s, C-4,-6,-10-Ad), 39.6 (s, C-2,-8,-9-Ad), 43.2 (s, C-1-Ad), 57.2 (d, $^{1}J_{P,C}$ = 21.0 Hz, C-3a), 92.9 (d, $^{1}J_{P,C}$ = 71.5 Hz, C-4), 126.0 (d, $^{3}J_{P,C}$ = 1.5 Hz, *o*-C_{Ph}), 126.1 (s, *p*-C_{Ph}), 126.8 (s, *o*-C_{Ph}), 127.9 (s, C-3), 128.1 (s, *p*-C_{Ph}), 128.5 (s, 2 *m*-C_{Ph}), 136.8 (d, $^{3}J_{P,C}$ = 4.8 Hz, *i*-C_{Ph}), 141.1 (s, C-2), 142.8 (d,$^{2}J_{P,C}$ = 2.9 Hz, *i*-C_{Ph}), 163.8 (d, $^{2}J_{P,C}$ = 7.2 Hz, =COSi) ppm. $C_{36}H_{47}OPSSi$ (586.89): calcd. C 73.68, H 8.07; found C 73.56, H 8.32.

***cis-anti-cis*-Tricyclic Compound 4d and Alkylidenephosphirane 6d:** A solution of thiaphosphole **3b** (0.704 g, 2.48 mmol) and diazo ketone **1b** (0.893 g, 2.48 mmol) in dichloromethane (15 mL) was stirred at 20 °C for 15 h. The solvent was evaporated and the residue was subjected to column chromatography (silica gel, diethyl ether/petroleum ether, 1:9). The first fraction yielded **6d** (0.062 g, 4%), the second fraction gave **4d** (0.401 g, 36%).

4d: Light-yellow microcrystals, m.p. 170 °C. IR (KBr): ṽ = 1607 (s), 1507 (vs), 1463 (m), 1442 (s), 1298 (m), 1255 (vs), 1201 (s), 1176 (vs), 1106 (m), 1035 (s), 881 (m), 832 (m), 779 (s), 734 (s), 698 (s), 678 (s) cm^{-1}. ^{31}P NMR: δ = 71.1 (d, $^{2}J_{P,P}$ = 18.8 Hz), 87.3 (d, $^{2}J_{P,P}$ = 18.8 Hz) ppm. ^{1}H NMR (500.14 MHz): δ = 1.09 (d, $^{3}J_{H,H}$ = 7.5 Hz, 9 H, $CHCH_3$), 1.14 (d, $^{3}J_{H,H}$ = 7.6 Hz, 9 H, $CHCH_3$), 1.58 (sept, $^{3}J_{H,H}$ = 7.6 Hz, 3 H, $CHCH_3$), 1.71 (s, 6 H,

Ad), 2.06−2.08 (m, 6 H, Ad), 2.14−2.16 (m, 3 H, Ad), 3.80 (s, 3 H, OCH_3), 6.54 (dd, $^3J_{P,H}$ = 5.1, $^4J_{P,H}$ = 3.1 Hz, 1 H, 3-H or 4-H), 6.66 (dd, $^3J_{P,H}$ = 5.1, $^4J_{P,H}$ = 3.0 Hz, 1 H, 4-H or 3-H), 6.83 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *m*-H_{anisyl}), 6.85 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *m*-H_{anisyl}), 7.14−7.32 (m, 10 H, Ph), 7.44 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *o*-H_{anisyl}), 7.46 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *o*-H_{anisyl}) ppm. ^{13}C NMR (125.77 MHz): δ = 14.4 (d, $^5J_{P,C}$ = 7.2 Hz, SiCH), 18.7 (d, $^6J_{P,C}$ = 2.4 Hz, SiCH*C*H_3), 18.8 (s, SiCH*C*H_3), 28.6 (d, $^5J_{P,C}$ = 1.4 Hz, C-3,-5,7-Ad), 36.6 (s, C-4,-6,-10-Ad), 41.5 (dd, $^4J_{P,C}$ = 12.7, 1.2 Hz, C-2,-8,-9-Ad), 44.1 (d, $^3J_{P,C}$ = 4.3 Hz, C-1-Ad), 55.28 (s, OCH_3), 55.30 (s, OCH_3), 71.4 (dd, $^1J_{P,C}$ = 11.5, $^2J_{P,C}$ = 8.1 Hz, C-3a or C-3b), 73.6 (dd, $^1J_{P,C}$ = 11.2, $^2J_{P,C}$ = 7.9 Hz, C-3b or C-3a), 113.3 (dd, $^1J_{P,C}$ = 60.8, $^1J_{P,C}$ = 49.8 Hz, C-8), 113.5 (s), 113.6 (s), 122.7 (m, C-3 or C-4), 123.4 (m, C-4 or C-3), 127.3 (s), 127.4 (s), 128.3 (s), 128.38 (s), 128.43 (s), 128.7 (s), 129.08 (d), 129.13 (d), 139.0 (dd), 139.4 (dd), 143.4 (dd, $^2J_{P,C}$ = 3.1, $^4J_{P,C}$ = 1.2 Hz, C-2 or C-5), 145.4 (dd, $^2J_{P,C}$ = 3.6, $^4J_{P,C}$ = 1.2 Hz, C-5 or C-2), 159.8 (s), 159.9 (s), 174.8 (dd, $^2J_{P,C}$ = 20.5, $^2J_{P,C}$ = 14.8 Hz, =COSi) ppm. $C_{53}H_{62}O_3P_2S_2Si$ (901.24): calcd. C 70.63, H 6.93; found C 70.45, H 7.33.

6d: Yellow powder, m.p. 174 °C. IR (KBr): ṽ = 1644 (s), 1607 (s), 1507 (s), 1452 (m), 1300 (m), 1263 (m), 1251 (vs), 1231 (vs), 1175 (s), 827 (s) cm^{-1}. ^{31}P NMR: δ = −116.6 ppm. ^{1}H NMR (500.14 MHz): δ = 1.16 (d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHCH_3), 1.20 (d, $^3J_{H,H}$ = 7.5 Hz, 9 H, CHCH_3), 1.55−1.64 (m, 6 H, Ad + 3 H, CHCH$_3$), 1.83−1.97 (m, 9 H, Ad), 3.81 (s, 3 H, OCH_3), 6.65 (d, $^3J_{P,H}$ = 5.1 Hz, 1 H, 3-H), 6.87 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, *m*-H_{anisyl}), 7.16−7.31 (m, 5 H, H_{Ph}), 7.43 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, *o*-H_{anisyl}) ppm. ^{13}C NMR (125.77 MHz): δ = 14.6 (d, $^5J_{P,C}$ = 4.3 Hz, Si*C*H), 18.4 (s, SiCH*C*H_3), 18.6 (s, SiCH*C*H_3), 28.4 (s, C-3,-5,-7-Ad), 36.8 (s, C-4,-6,-10-Ad), 39.6 (s, C-2,-8,-9-Ad), 43.1 (s, C-1-Ad), 55.3 (s, OCH_3), 57.3 (d, $^1J_{P,C}$ = 21.0 Hz, C-3a), 93.2 (d, $^1J_{P,C}$ = 72.5 Hz, C-4), 113.8 (s), 126.0 (s), 126.4 (s *p*-C_{Ph} and C-3), 128.0 (s), 128.4 (s), 129.5 (d), 140.6 (s, C-2), 142.8 (s), 159.7 (s), 163.5 (d, $^2J_{P,C}$ = 5.7 Hz, =COSi) ppm. $C_{37}H_{49}O_2PSSi$ (616.92): calcd. C 72.04, H 8.01; found C 71.68, H 7.96.

***cis-anti-cis*-8-[{2,2-Dimethyl-1-[(1,1-dimethylethyl)dimethylsilyloxy]-propylidene}]-2,3a,3b,5-tetraphenyl-3a,3b-dihydro[1,2]thiaphospholo[2′,3′:3,4][1,3]diphospholo[1,5-*b*][1,2]thiaphosphole (4e):** A solution of thiaphosphole **3a** (0.865 g, 3.40 mmol) and diazo ketone **1c** (0.818 g, 3.40 mmol) in dichloromethane (30 mL) was allowd to react at 20 °C for 18 h. The solvent was evaporated at 0.01 mbar, and the residue was treated with pentane. A colorless powder formed which was separated by centrifugation and washed with pentane; yield: 0.976 g (80%), m.p. 203 °C (dec.). IR (KBr): ṽ = 1594 (w), 1573 (w), 1529 (s), 1490 (m), 1443 (m), 1258 (s), 1159 (s), 822 (s), 810 (s), 755 (vs), 689 (s) cm^{-1}. ^{1}P NMR: δ = 72.1 (d, $^2J_{P,P}$ = 19.8 Hz), 85.7 (d, $^2J_{P,P}$ = 19.8 Hz) ppm. ^{1}H NMR (500.14 MHz): δ = 0.28 (s, 3 H, $SiCH_3$), 0.28 (d, $^6J_{P,H}$ = 2.8 Hz, 3 H, $SiCH_3$), 1.00 [s, 9 H, $SiC(CH_3)_3$], 1.35 [s, 9 H, $CC(CH_3)_3$], 6.65 (dd, $^3J_{P,H}$ = 4.8, $^4J_{P,H}$ = 2.9 Hz, 1 H, 3-H or 4-H), 6.69 (dd, $^3J_{P,H}$ = 5.1, $^4J_{P,H}$ = 3.5 Hz, 1 H, 4-H or 3-H), 7.17−7.33 (m, 16 H, *m*- and *p*-H_{Ph}), 7.47−7.49 (m, 4 H, *o*-H_{Ph}) ppm. ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = −2.5 (d, $^5J_{P,C}$ = 15.3 Hz, $SiCH_3$), −1.6 (d, $^5J_{P,C}$ = 4.8 Hz, $SiCH_3$), 19.6 [s, Si*C*$(CH_3)_3$], 27.1 [d, $^6J_{P,C}$ = 3.8 Hz, SiC(*C*$H_3)_3$], 30.1 [dd, $^4J_{P,C}$ = 11.0, $^4J_{P,C}$ = 1.4 Hz, CC(*C*$H_3)_3$], 41.1 [d, $^3J_{P,C}$ = 3.8 Hz, C*C*$(CH_3)_3$], 71.1 (dd, $^1J_{P,C}$ = 11.7, $^2J_{P,C}$ = 7.9 Hz, C-3a or C-3b), 74.1 (dd, $^1J_{P,C}$ = 11.0, $^2J_{P,C}$ = 7.6 Hz, C-3b or C-3a), 114.5 (dd, $^1J_{P,C}$ = 58.7, $^1J_{P,C}$ = 49.6 Hz, C-8), 124.9 (br. s, C-3 or C-4), 125.1 (br. s, C-4 or C-3), 127.3 (s), 127.4 (s, *m*- and *p*-C_{Ph}), 127.5 (s, *m*- and *p*-C_{Ph}), 128.2 (s), 128.3 (s), 128.51 (s), 128.54 (s), 129.1 (d), 135.7 (d), 136.5 (d), 138.6 (dd), 139.0 (dd), 144.7 (dd, $^4J_{P,C}$ = 1.9 Hz, C-2 or C-5), 146.2 (d, $^2J_{P,C}$ = 3.3 Hz, C-5 or C-2), 174.0 (dd, $^2J_{P,C}$ = 21.0, $^2J_{P,C}$ = 13.8 Hz, =COSi) ppm. $C_{42}H_{46}OP_2S_2Si$ (720.99): calcd. C 69.97, H 6.43; found C 69.43, H 6.32.

***cis-anti-cis*-Tricyclic Compound 4f:** The compound was prepared from thiaphosphole **3b** (0.392 g, 1.38 mmol) and diazo ketone **1c** (0.331 g, 1.38 mmol) as described for **4e** and was obtained as a colorless powder; yield: 0.449 g (83%); m.p. 184 °C (dec.). IR (KBr): ṽ = 1608 (s), 1546 (s), 1505 (vs), 1260 (vs), 1252 (vs), 1176 (vs), 1138 (s), 1030 (s), 827 (s), 779 (s), 726 (m), 720 (m) cm^{-1}. ^{31}P NMR: δ = 71.4 (d, $^2J_{P,P}$ = 19.8 Hz), 84.9 (d, $^2J_{P,P}$ = 19.8 Hz) ppm. ^{1}H NMR (500.14 MHz): δ = 0.28 (s, 3 H, $SiCH_3$), 0.29 (d, $^6J_{P,H}$ = 2.8 Hz, 3 H, $SiCH_3$), 1.00 [s, 9 H, $SiC(CH_3)_3$], 1.35 [s, 9 H, $CC(CH_3)_3$], 3.79 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 6.55 (dd, $^3J_{P,H}$ = 4.9, $^4J_{P,H}$ = 3.0 Hz, 1 H, 3-H or 4-H), 6.58 (dd, $^3J_{P,H}$ = 5.2, $^4J_{P,H}$ = 3.5 Hz, 1 H, 4-H or 3-H), 6.82 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *m*-H_{anisyl}), 6.83 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, *m*-H_{anisyl}), 7.16−7.29 (m, 10 H, Ph), 7.42 (d, $^3J_{H,H}$ = 8.7 Hz, 4 H, *o*-H_{anisyl}) ppm. ^{13}C NMR (125.77 MHz): δ = −2.5 (d, $^5J_{P,C}$ = 15.3 Hz, $SiCH_3$), −1.6 (d, $^5J_{P,C}$ = 5.2 Hz, $SiCH_3$), 19.6 [s, Si*C*$(CH_3)_3$], 27.1 [s, SiC(*C*$H_3)_3$], 30.1 [d, $^4J_{P,C}$ = 11.0 Hz, CC(*C*$H_3)_3$], 41.1 [s, C*C*$(CH_3)_3$], 55.3 (s, 2 OCH_3), 71.0 (pt, C-3a or C-3b), 74.0 (pt, C-3b or C-3a), 113.5 (s), 113.6 (s), 114.8 (dd, $^1J_{P,C}$ = 57.7, 50.4 Hz, C-8), 123.4 (m, C-3 or C-4), 127.3 (s), 127.36 (s, *m*- and *p*-C_{Ph}), 127.42 (s), 128.46 (s), 128.47 (s), 128.58 (s), 128.62 (s), 129.1 (d), 138.8 (d), 139.2 (d), 144.2 (s, C-2 or C-5), 145.7 (s, C-5 or C-2), 159.9 (s), 173.6 (dd, $^2J_{P,C}$ = 21.5, 13.8 Hz, =COSi) ppm. $C_{44}H_{50}O_3P_2S_2Si$ (781.04): calcd. C 67.66, H 6.45; found C 67.55, H 6.61.

Cycloaddition Products 15 and 16: A mixture of **3a** (0.254 g, 1.00 mmol) and cyclopentadiene (**11**, 3.0 mL, 36.5 mmol) was placed in a closed thick-walled glass tube and heated at 120 °C for 2 h. The excess of cyclopentadiene was evaporated at 0.01 mbar. The residue was purified by chromatography on silica gel (eluent: toluene) to give **15** (0.263 g, 51%) and **16** (0.129 g, 29%). Product **15** was recrystallized form *p*-xylene to give colorless prisms that started to soften at 244 °C and melted in the range 256−262 °C. Product **16** was a obtained as a viscous oil that became resinous on storing; a satisfactory elemental analysis could not be obtained.

11,21-Diphenyl-1-phosphaoctacyclo[9.9.2.1^{3,9}.1^{13,19}.0^{4,8}.0^{2,10}.-0^{12,20}.0^{14,18}]tetraicosa-5,15,21-triene 1-Sulfide and Isomers (15): A mixture of the $\Delta^{5,15}$, $\Delta^{5,16}$, and $\Delta^{6,15}$ isomers (hereafter called **A**, **B**, and **C**) in an approximate 2:1:1 ratio (see ^{31}P NMR) was obtained. IR (KBr): ṽ = 1597 (m), 1494 (m), 1442 (m), 909 (m), 755 (s), 722 (s), 690 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500.14 MHz): δ = 0.93−1.02 (m, 8 H, 23-H^1 and 24-H^1 in **A**, **B**, **C**), 1.73, 1.79 (2 d, each 2 H, J = 3.9/3.9 Hz, 9-H in **A**, 9-H + 13-H in **B**), 1.88−1.94 (m, 8 H, 23-H^2, 24-H^2 in **A**, **B**, **C**), 1.94−2.36 (several m, 32 H), 2.39 (dd, J = 9.0, 11.4 Hz, 2 H), 2.50 (dd, J = 11.4, 9.0 Hz, 2 H), 2.52−2.58 (m, 4 H), 2.62 (t, J = 9.5 Hz, 2 H), 2.67 (t, J = 9.5 Hz, 2 H), 2.70−2.78 (m, 4 H), 2.88−2.98 (m, 8 H, 3-H in **A**, 3-H and 19-H in **B**, 14-H in **A**, 8-H and 14-H in **C**), 3.06−3.16 (m, 4 H, 4-H in **A**, 4-H and 18-H in **B**), 5.43−5.48 (m, 4 H, 15-H in **A**, 7-H and 15-H in **C**), 5.62−5.64 (m, 4 H, 5-H in **A**, 5-H and 17-H in **B**), 5.81−5.85 (m, 8 H, 6-H and 16-H in **A**, **B**, **C**), 7.25−7.67 (m, 22-H and H_{Ph} in **A**, **B**, **C**) ppm. ^{13}C NMR ($CDCl_3$, 125.77 MHz): δ = 31.56/31.67 (CH_2-allyl), 37.95/37.98/38.03 (C-23, C-24), 41.37−47.15 (C-3,-8,-9,-10,-11,-12,-13,-18,-19,-20), 50.08 ($J_{C,P}$ = 7.3 Hz)/50.61 ($J_{C,P}$ = 7.0 Hz)/53.07 ($J_{C,P}$ = 7.2 Hz)/53.51 ($J_{C,P}$ = 7.1 Hz) (C-10 and C-12 in **A**, **B**, **C**), 55.00−55.31 (C-4, C-14), 131.14 (=CH, C-15 in **A**, C-7,-15 in **C**), 131.87/131.91 (=CH, C-5 in **A**, C-5,-17 in **B**), 132.38/132.93 (C-6, C-16 in **A**, **B**, **C**), 125.65, 126.46, 127.73, 127.93, 127.98, 128.17, 128.27 and 128.31 (CH_{Ph}),

Table 4. Crystal data and details of structure refinement for [**4a**−diethyl ether solvate] and [$\Delta^{5,15}$-**15**−*p*-xylene solvate]

	4a	**15** ($\Delta^{5,15}$ isomer)
Empirical formula	$C_{45}H_{52}OP_2S_2Si \times (C_2H_5O)_2$	$(C_{35}H_{35}PS)_2 \times (C_8H_{10})$
Formula mass	837.14	1143.48
Temperature [K]	293(2)	295(2)
Wavelength [Å]	0.71073	0.71073
Crystal size [mm]	0.38 × 0.35 × 0.15	0.38 × 0.27 × 0.15
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	12.101(1)	9.552(2)
b [Å]	13.455(1)	9.672(2)
c [Å]	16.686(2)	33.614(6)
α [°]	81.24(1)	90.66(2)
β [°]	75.95(1)	94.77(2)
γ [°]	66.35(1)	100.26(2)
Volume [Å^3]	2409.5(4)	3044.2(9)
Z	2	2
$\rho_{calcd.}$ [g·cm^{-3}]	1.154	1.248
μ(Mo-K_α) [cm^{-1}]	2.37	1.86
θ range [°]	1.88−25.96	2.14−25.91
Index ranges	$-14 \le h \le 14$	$-11 \le h \le 10$
	$-15 \le k \le 15$	$-11 \le k \le 11$
	$-20 \le l \le 20$	$-39 \le l \le 41$
Reflections collected	20809	22949
Independent reflections (R_{int})	8762 (0.0460)	10963 (0.0486)
Completeness of data set [%]	92.8	92.6
Data/restraints/parameters	8762/6/516	10963/0/741
Goodness-of-fit on F^2	0.693	0.799
Final *R* indices [$I > 2\sigma(I)$]; R_1, wR_2	0.0457, 0.1141	0.0445, 0.1115
R indices (all data); R_1, wR_2	0.0920, 0.1369	0.1101, 0.1289
largest diff. peak, hole [e·Å^{-3}]	0.35, −0.21	0.24, −0.20

136.82 (C_{Ph}), 136.88 ($J_{C,P}$ = 53.6 Hz, C-21), 143.17 (C_{Ph}), 144.80 (C-22) ppm. ^{31}P NMR ($CDCl_3$, 202.46 MHz): δ = 25.6, 26.6, 27.5 (rel. intensities = 1.00:2.06:0.83) ppm. MS (EI, 70 eV): *m*/*z* (%) = 518 (9) [M$^+$], 386 (64) [M$^+$ − dicyclopentadiene], 354 (4), 287 (8), 254 (100) [M$^+$ − 2 dicyclopentadiene], 191 (8), 165 (6), 115 (8), 91 (28). $C_{35}H_{35}PS$ (518.69): calcd. C 81.05, H 6.80; found C 80.95, H 6.80.

11,17-Diphenyl-1-phosphahexacyclo[9.5.2.1^{3,9}.0^{2,10}.0^{4,8}.0^{12,16}]-nonadeca-5,13,17-triene 1-Sulfide and $\Delta^{6,13,17}$ Isomer (16): A mixture of the two isomers in a 0.9:1.0 ratio was obtained. IR (KBr): $\tilde{\nu}$ = 1599 (m), 1493 (m), 1445 (m), 811 (m), 758 (s), 735 (m), 696 (s) cm^{-1}. ^{1}H NMR (500.14 MHz, $CDCl_3$) (for the intensities given here, the composition of the mixture is approximated as 1:1; see Table 3 for assignment of signals): δ = 1.03−1.07 (2d, 2 H), 1.80 (d, *J* = 3.9 Hz, 1 H), 1.30−2.04 (m, 4 H), 2.08−2.17 (m, 1 H), 2.25−2.41 (m, 5 H), 2.42−2.49 (dd, 1 H), 2.50−2.76 (m, 6 H), 2.80−2.91 (m, 3 H), 2.92−3.00 (unstructured m, 1 H), 3.03−3.05 (dd, 1 H), 3.12−3.20 (unstructured m, 1 H), 3.76−3.80 (t, 1 H), 3.83−3.86 (t, 1 H), 5.04−5.13 (ddd, 2 H), 5.40−5.45 (dd, 1 H), 5.55−5.63 (m, 2 H), 5.63−5.67 (dd, 1 H), 5.75−5.85 (m, 2 H), 7.10−7.60 (m, 22 H) ppm. ^{31}P NMR ($CDCl_3$): δ = 32.7, 33.6 (rel. intensities = 0.9:1.0) ppm. MS (EI, 70 eV): *m*/*z* (%) = 452 (6) [M$^+$], 386 (41) [M$^+$ − C_5H_6], 319 (2), 287 (5), 254 (100) [M$^+$ − 3C_5H_6], 191 (10), 165 (7), 115 (7), 91 (11), 77 (7), 66 (41). $C_{30}H_{29}PS$ (452.59).

X-ray Crystallographic Study: Single crystals of **4a** were grown from diethyl ether at −30 °C; they contained one diethyl ether molecule per formula unit. Crystals of **15** were obtained by slow concentration of a solution in *p*-xylene. Data collection was carried out with a Stoe IPDS instrument. The structures were solved with direct methods and refined by a full-matrix least-squares method (SHELX-97[33]). Hydrogen atoms were calculated geometrically and treated as riding on their bond neighbors in the refinement procedure. The diethyl ether molecules in the crystal structure of **4a** are somewhat disordered according to the very large ellipsoids of thermal vibration. Some geometrical restraints (keywords DFIX and FLAT) were applied to stabilize the refinement. Molecule plots: ORTEP-3.[34] Crystallographic data and details of the refinement for the two structures are given in Table 4. CCDC-195551 (**4a**) and -195552 (**15**) 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].

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