Cycloaddition Behavior of Electron-Poor 1,2-Thiaphospholes[‡]

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Keywords: Alkynes / Cycloaddition / Phosphorus heterocycles / Sulfur heterocycles / Thiaphospholes

The acceptor-substituted 1,2-thiaphospholes **1** react regioselectively with the electron-rich acetylenes **2** at –78 °C by [2+2] cycloaddition to afford the novel heterobicyclic compounds **4**. As demonstrated by the examples of their reactions with nonacarbonyldiiron(0) and the pentacarbonyltungsten fragment, compounds **4** are able to function as ligands in complex compounds. In addition, the electron-rich double bond in the bicyclic compound **4a** is amenable to further reactions. Hence, treatment with mesitylenecarbonitrile oxide (**7**) proceeds through a chemo-, regio-, and stereoselective [3+2] cycloaddition to afford the novel heterocyclic system **8**. On the other hand, the heterocyclic compounds **1a**, **1d**, **1e**, and **1i** react with 2 equiv. of cyclooctyne (**9**) only at 100 °C, to afford the sulfur-containing phosphabarrelenes **10**, together with the tricyclic compounds **11**.

Introduction

Like the homologous 1,2-oxa- and 1,2-selenaphospholes, 1,2-thiaphospholes exhibit aromatic character, with the aromaticity increasing in the order O < S < Se.[2,3] Because of this, [4+2] cycloadditions between, for example, electron-poor acetylenes and 1,2-oxaphospholes proceed smoothly,[4] while the analogous reactions with 1,2-thia- and 1,2-selenaphospholes do not occur. The previously reported behavior of diaryl-substituted 1,2-thiaphospholes in cycloaddition processes confirms this trend: reactions can only be accomplished by use of harsh reaction conditions or with catalysis by Lewis acids.[5,6]

We now report that acceptor-substituted 1,2-thiaphospholes **1** can participate in [4+2] cycloadditions with cyclooctyne (**9**) while, with electron-rich ynamines **2**, [2+2] cycloadditions with the P=C double bond occur under mild conditions to afford the 2-thia-1-phosphabicyclo[3.2.0]hepta-3,5-dienes **4**.

Results and Discussion

[2+2] Cycloadditions between Acceptor-Substituted 1,2-Thiaphospholes and Ynamines

Donor substitution in ynamines (**2b**–**d**) and especially ynediamines (**2a**), with the resultant increased electron density at the C≡C triple bond, makes these classes of compounds useful building blocks in organic synthesis.[7,8] Thus, in the past decades, the reaction potential of these classes of compounds, in particular with regard to the C≡C triple bond, in [2+1], [2+2], [3+2], and [4+2] cycloadditions has been investigated intensively. The main reactivity was identified as [4+2] cycloaddition towards 1,3-diene and hetero-1,3-diene systems. However, some examples in which a [2+2] cycloaddition occurred at only one double bond of the diene system, with formation of a vinylcyclobutene, were also found.[9–11]

Acceptor-substituted 1,2-thiaphospholes **1** also react with the electron-rich triple bond systems **2** (Scheme 1). Thus, when an diethyl ether solution of the 1,2-thiaphosphole **1** is treated at −78 °C with a 1.5- to 2-fold excess of the appropriate acetylene **2**, [2+2] cycloaddition with the P=C double bond occurs exclusively. In no case did ^{31}P NMR monitoring of the reaction reveal a signal for, for example, a putative [4+2] cycloadduct. Hence, the reaction proceeds with high chemo- and regioselectivities. Acceptor substitution of the P=C double bond appears to be essential, since 3,5-diphenyl-1,2-thiaphosphole does not react with **2a** under analogous conditions.

The [2+2] cycloadducts **4** are easily isolated in analytical purity after filtration of the crude mixtures through silica gel with *n*-pentane/diethyl ether (1:1). They are obtained after removal of the solvent as pale yellow solids or pale yellow to red oils, easily susceptible to polymerization. The yields are in the acceptable range of 55 to 92%, except for those of the bicyclic products **4c**, **4f**, and **4k**, obtained in poorer yields of 34%, 15%, and 39%, respectively.

For the mechanism, we assume a two-step reaction via the betaine intermediate **3**, since here both the positive and the negative charge should be optimally stabilized through substituent effects. An analogous mechanism has been discussed for the reactions between cycloalkenones and ynam-

[‡] Organophosphorus Compounds, 167. Part 166: Ref.[1]

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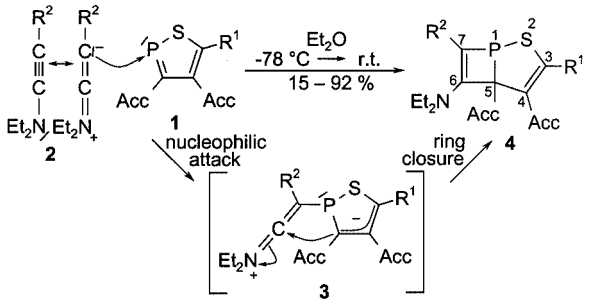


3,4	a	b	c	d	e	f	g
1	a	a	a	b	c	d	e
R^1	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	CMe_2Et	Me^cPen
Acc	CO_2Me	CO_2Me	CO_2Me	CF_3	CN	CO_2Me	CO_2Me
R^2	NEt_2	Me	Et	NEt_2	NEt_2	NEt_2	NEt_2

3,4	h	i	j	k	l	m	n
1	f	g	h	h	h	i	j
R^1	Me^cPen	Me^cPen	Me^cHex	Me^cHex	Me^cHex	Me^cHex	Me^cHex
Acc	CN	CF_3	CN	CN	CN	CO_2Me	CF_3
R^2	NEt_2	NEt_2	NEt_2	Et	$SiMe_3$	NEt_2	NEt_2

2	a	b	c	d
R^2	NEt_2	Me	Et	$SiMe_3$

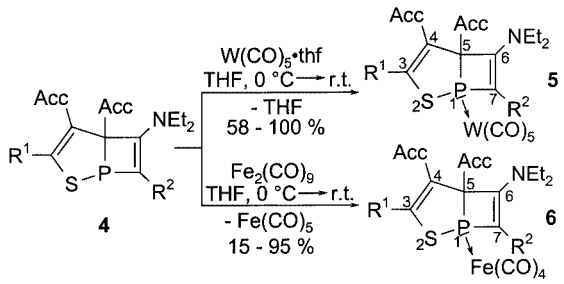
Scheme 1. Synthesis and proposed mechanism for the formation of the [2+2] cycloadducts **4**

ines.[12] The zwitterionic intermediate **3** believed to be formed in the reaction can, however, not be detected by low-temperature ^{31}P NMR spectroscopy.

The constitutions of the bicyclic products were elucidated with the help of their analytical and spectroscopic data. Their compositions, made up of 1 equiv. each of the employed acetylene **2** and of the corresponding 1,2-thiaphosphole **1**, are given unequivocally by the elemental analysis and mass spectral results. Structure elucidation on the basis of NMR spectroscopic data is described for the example of product **4d**. All signals found in the $^{13}C\{^1H\}$ NMR spectrum are compatible both with the bicyclic system **4d** and with a feasible [4+2] cycloadduct. The bicyclo[3.2.0]-heptadiene structure of **4d** can be identified solely through the splitting pattern of the signal for the quaternary carbon atom C-5 at $\delta = 71.3$ ppm. Although no characteristically large $^1J_{C,P}$ coupling to the neighboring phosphorus atom can be detected, a quadruplet splitting with a C,F coupling constant of 31.4 Hz − typical for a $^2J_{C,F}$ coupling − is observed.

The regiochemistry of the addition of the unsymmetrical ynamines **2b**−**c** to the P=C double bond can be deduced by analysis of the ^1H NMR spectrum of the methyl derivative **4b**. The methyl group at C-7 gives a doublet signal at $\delta = 1.76$ ppm, with a $^3J_{H,P}$ coupling of 10.6 Hz. If the methyl group were at C-6, one would observe a $^4J_{H,P}$ coupling, usually with a magnitude of less than 4 Hz.[13] Thus, the respective R^2 substituents must be at C-7 and the diethylamino group at C-6.

The structure of the bicyclic system **4** as deduced from the spectroscopic data was confirmed by an X-ray crystallographic analysis of the derivative **4a** (Figure 1). Suitable crystals were grown from a solution of **4a** in a small amount of diethyl ether at −20 °C.



5	a	b	c	d	e
R^1	*t*Bu	*t*Bu	*t*Bu	Me^cPen	Me^cPen
Acc	CO_2Me	CO_2Me	CF_3	CO_2Me	CF_3
R^2	NEt_2	Me	NEt_2	NEt_2	NEt_2

6	a	b	c	d	e	f	g
R^1	*t*Bu	*t*Bu	*t*Bu	*t*Bu	Me^cPen	Me^cPen	Me^cHex
Acc	CO_2Me	CO_2Me	CN	CF_3	CO_2Me	CF_3	CN
R^2	NEt_2	Me	NEt_2	NEt_2	NEt_2	NEt_2	NEt_2

Scheme 2. Behavior of the heterobicycloheptadienes **4** as ligands

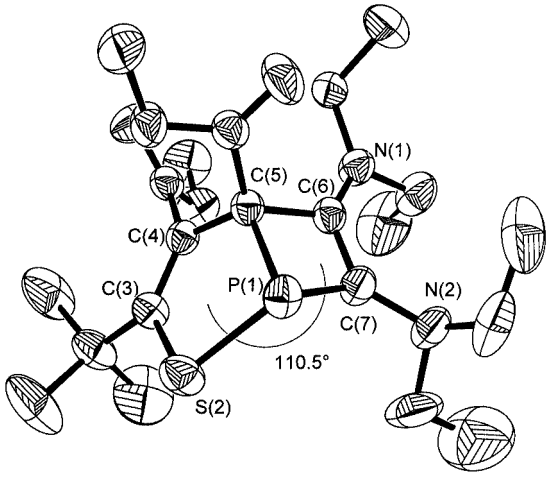


Figure 1. Molecular structure of **4a**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity, displacement ellipsoids at 50% probability: P(1)−C(7) 1.802(3), P(1)−C(5) 1.910(3), P(1)−S(2) 2.1348(13), S(2)−C(3) 1.783(3), N(1)−C(6) 1.347(3), N(2)−C(7) 1.426(4), C(3)−C(4) 1.346(4), C(4)−C(5) 1.513(4), C(5)−C(6) 1.539(3); C(7)−P(1)−C(5) 74.02(12), C(7)−P(1)−S(2) 112.10(11), C(5)−P(1)−S(2) 93.20(9), C(3)−S(2)−P(1) 97.53(10), C(4)−C(3)−S(2) 116.0(2), C(3)−C(4)−C(5) 121.7(2), C(4)−C(5)−C(6) 111.3(2), C(4)−C(5)−P(1) 110.2(2), C(6)−C(5)−P(1) 86.6(2), N(1)−C(6)−C(7) 133.3(2), N(1)−C(6)−C(5) 125.9(2), C(7)−C(6)−C(5) 100.7(2), C(6)−C(7)−N(2) 130.5(3), C(6)−C(7)−P(1) 96.7(2), N(2)−C(7)−P(1) 131.6(2)

The P−S single bond between P(1) and S(2) has a length of 2.1348(13) Å, in the expected range for P−S bonds not incorporated in a heteroaromatic system.[14,15] In contrast, the separation between S(2) and C(3) of 1.783(3) Å is slightly larger than the average of those previously found in vinyl sulfide systems,[16] due on the one hand to the phosphorus substitution and on the other hand to the ring strain in the bicyclic system. The lengthening of the bond between P(1) and C(5) can be explained similarly; its length of

1.910(3) Å is about 3% more than the average of 1.855 Å for reported values. In spite of the threefold heteroatom substitution, the C=C double bond length between C(6) and C(7), of 1.361(4) Å, is not appreciably longer than the C=C double bond lengths in tetra-substituted olefins.

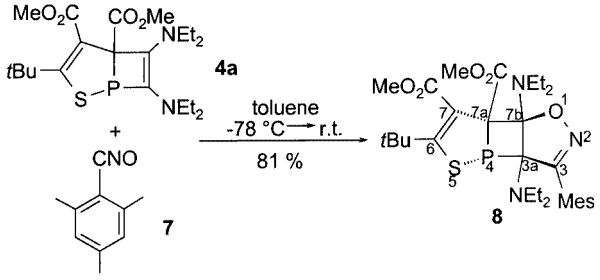
One conspicuous feature is that the lengths of the two C−N bonds differ significantly, 1.347(3) Å [C(6)−N(1)] and 1.426(4) Å [C(7)−N(2)]. The angular sums at the two heteroatoms are also markedly different; the value of exactly 360° at N(1) is suggestive of a planar environment [N(2): 337.7°]. These two observations confirm an interaction between the free electron pair of N(1) and the π-system of the neighboring C=C double bond.

The two least-squares planes through the four- and five-membered ring systems intersect at an angle of 110.5°, which is of the same order of magnitude as the interplanar angles in similar bicycloheptadiene systems.[17,18]

Behavior of the Heterocyclic Compounds 4 as Ligands

Tertiary phosphanes are used as versatile ligands in organometallic chemistry,[19] and so it was of interest to examine whether the bicyclic system **4** could also be coordinated to transition metal fragments. As an example, we investigated treatment with nonacarbonyldiiron(o) and coordination to the pentacarbonyltungsten fragment.

Treatment of the heterobicyclic compounds **4** with pentacarbonyl(tetrahydrofuran)tungsten, generated by photolysis of hexacarbonyltungsten(o) in THF, resulted in expulsion of the weakly bound tetrahydrofuran and formation of the η^1-tungsten complexes **5** in good to quantitative yields (Scheme 2). The metal complexes were obtained in analytical purity as pale yellow solids simply by filtering the crude product through silica gel. Again, no further signals were observed on ^{31}P NMR monitoring of the reaction, and so the complexation reaction proceeds with high chemoselectivity. Synthesis of the analogous tungsten complex of the bicyclic compound **4e** was not possible under these conditions.



Scheme 3. [3+2] Cycloaddition between the heterocyclic compound **4a** and mesitylenecarbonitrile oxide

The 1:1 addition of a pentacarbonyltungsten fragment to the bicyclic system **4** was demonstrated unambiguously by the elemental analysis and mass spectroscopic results.

The η^1-coordination at the phosphorus atom can be deduced from the spectroscopic data. Compound **5a**, for example, exhibits a ^{31}P NMR signal at δ = 68.7; the ^{183}W satellites show a $^1J_{P,W}$ coupling constant of 255.1 Hz, as is typical for an η^1-coordinated system. The ^{13}C NMR spectrum is also in agreement with this interpretation.

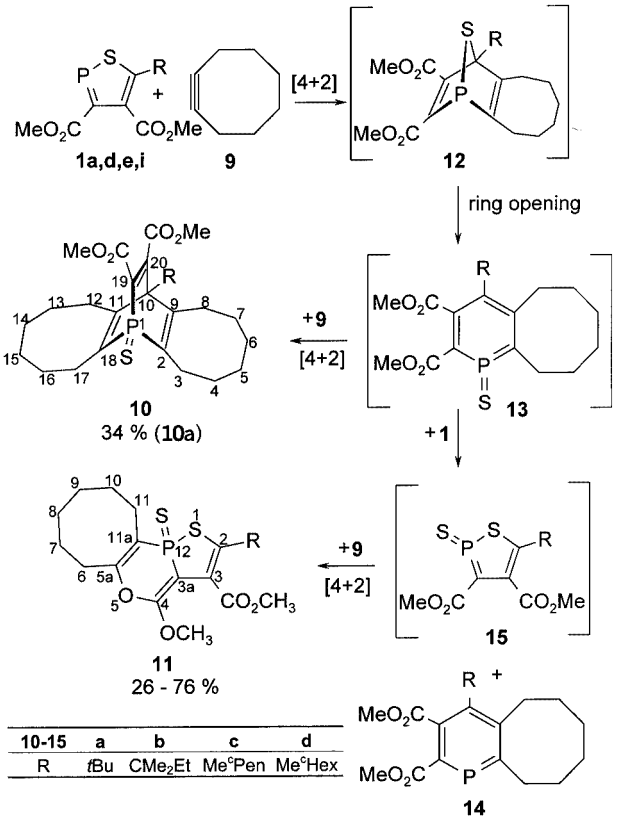
Treatment of the bicyclic compounds **4** with equimolar amounts of nonacarbonyldiiron(o) afforded the η^1-complexes **6** in moderate to very good yields and as yellowish-brown to dark brown oils or solids after a reaction time of about 12 h (Scheme 2).

As in the case of the tungsten complexes **5**, ^{31}P NMR monitoring of the reaction showed the formation of one product, again demonstrating the high chemoselectivity of the reactions. In this case, however, the reaction principle can also be extended to the dicarbonitriles **4e** and **4j**.

Both elemental analysis and mass spectrometric results confirmed the compositions of the complex compounds **6**, each made up of 1 equiv. of the relevant heterobicyclic species **4** and one tetracarbonyliron fragment. The EI mass spectra each contain the respective molecular ion peak at low intensity. Because of the pronounced shift of the ^{31}P NMR signal to lower field (Δδ = 87 ppm on average) we can conclude that complexation has again occurred directly at the phosphorus atom.

[3+2] Cycloaddition between 4a and Mesitylenecarbonitrile Oxide

The electron-rich C=C double bond between C-6 and C-7 in the heterobicyclic compound **4a** is also amenable to further reactions. Thus, treatment with a stoichiometric



Scheme 4. Thermolysis of the heterocyclic compounds **1a**, **1d**, **1e**, and **1i** in the presence of excess cyclooctyne

amount of mesitylenecarbonitrile oxide (**7**) afforded the tricyclic compound **8** in 81% yield after chromatographic separation on silica gel (Scheme 3). This [3+2] cycloaddition proceeds with complete chemo-, regio-, and stereoselectivities. In the product **8**, the two five-membered rings annelated to the phosphetane system are in a *trans* arrangement.

The 1:1 composition of the adduct produced from **4a** and mesitylenecarbonitrile oxide (**7**) was unambiguously demonstrated by its elemental analysis.

The constitution of the product was elucidated by a careful analysis of its NMR spectroscopic data. From the ^{1}H NMR spectrum we can deduce that a [3+2] cycloaddition with the bond between C-6 and C-7 in the starting material **4a** has occurred. The diastereotopic methylene protons of a diethylamino group give rise to two broad, unresolved signals in the correct integration ratios with regard to the other signals, indicating that rotation of this substituent is hindered at room temperature. The regiochemistry of the [3+2] cycloaddition is derived from the ^{13}C NMR spectrum. The signal for the oxime carbon atom C-3 at δ = 157.9 ppm is split into a doublet with a coupling constant of 54.6 Hz, unequivocally indicative of a $^{2}J_{C,P}$ coupling. The magnitude of this coupling also demonstrates the *syn* orientation between C-3 and the free electron pair on the phosphorus atom and, accordingly, the *trans* arrangement of the annelated rings.

Thermolysis of the 1,2-Thiaphospholes 1a, 1d, 1e, and 1i in the Presence of Excess Cyclooctyne

When a solution of the thiaphosphole **1a** in toluene was heated at 100 °C for 20 h with a twofold excess of cyclooctyne (**9**), formation of the polycyclic compounds **10a** and **11a** was observed (Scheme 4). In addition, ^{31}P NMR monitoring of the reaction revealed the presence of an additional signal at δ = 195 ppm in the region typical of phosphinines, attributable to compound **14** on the basis of mechanistic considerations. After separation of the reaction mixture by column chromatography and subsequent recrystallization from *n*-pentane/diethyl ether (3:1), however, only products **10a** and **11a** were obtained, in the form of pale yellow and colorless crystals, respectively.

The reaction principle can also be transferred without difficulty to the 1,2-thiaphospholes **1d**, **1e**, and **1i**; however, in these cases the barrelenes **10b**−**d** were formed to much smaller extents and could not be isolated as pure substances.

Analogous reactions with the heterocyclic compounds **1c** and **1j** did occur, but inseparable product mixtures were obtained, due to numerous subsequent reactions.

Hindered rotation of the alkyl substituent R is observed at room temperature for all four barrelene derivatives **10**; this is indicative of steric interactions with the two adjacent annelated cyclooctane rings. Variable-temperature NMR measurements on compound **10a** (400.1 MHz, [D_8]toluene) showed that the coalescence temperature for this dynamic process had not been reached at 378 K and that the enthalpy of activation $\Delta G^{\ddagger}$ was thus higher than 78 kJ/mol.

The composition of the polycyclic compound **10a**, of 1 equiv. of the thiaphosphole **1a** and 2 equiv. of cyclooctyne (**9**), is demonstrated by the elemental analysis and mass spectrometric results. The compositions of the tricyclic compounds **11**, of 1 equiv. each of cyclooctyne and of the respective 1,2-thiaphosphole **1a**, **1d**, **1e**, and **1i**, together with an additional sulfur atom, can also be deduced from the mass spectrometric and elemental analysis results.

The constitution of the phosphabarrelene **10a** was determined by an X-ray crystallographic analysis. As can be seen from Figure 2, the C_s symmetry observed in solution is no longer present in the crystal. The exocyclic phosphorus−sulfur bond length of 1.9400(13) Å is in the range of previously reported P=S double bond lengths.[20] In addition, the three C=C double bond lengths in the barrelene skeleton of 1.335 Å on average are as expected for tetrasubstituted double bonds.[16]

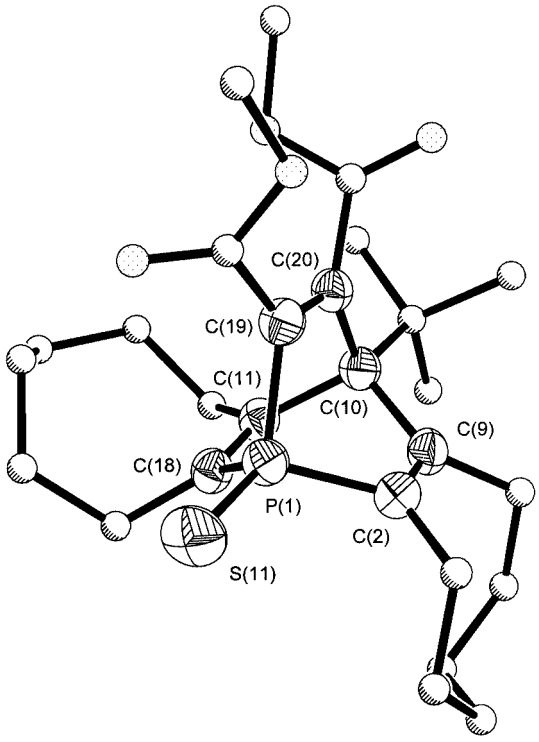


Figure 2. Molecular structure of **10a**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity, displacement ellipsoids at 50% probability: P(1)−C(2) 1.805(3), P(1)−C(18) 1.809(3), P(1)−C(19) 1.811(3), P(1)−S(11) 1.9400(13), C(11)−C(18) 1.333(4), C(11)−C(10) 1.605(4), C(19)−C(20) 1.338(4), C(20)−C(10) 1.578(4), C(10)−C(9) 1.601(4), C(2)−C(9) 1.333(5); C(2)−P(1)−C(18) 100.6(2), C(2)−P(1)−C(19) 97.67(14), C(18)−P(1)−C(19) 97.5(2), C(2)−P(1)−S(11) 118.11(12), C(18)−P(1)−S(11) 118.86(11), C(19)−P(1)−S(11) 119.77(11), C(18)−C(11)−C(12) 118.4(3), C(18)−C(11)−C(10) 117.3(3), C(20)−C(19)−P(1) 113.2(2), C(19)−C(20)−C(10) 118.8(3), C(20)−C(10)−C(9) 106.2(2), C(20)−C(10)−C(11) 103.6(2), C(9)−C(10)−C(11) 106.3(2), C(11)−C(18)−P(1) 114.4(2), C(9)−C(2)−P(1) 113.2(2), C(2)−C(9)−C(10) 118.4(3)

An X-ray crystallographic analysis was necessary to elucidate the structure of the unexpected product **11**. Colorless crystals of **11a** suitable for analysis were obtained from a *n*-pentane/toluene (2:1) solution at −20 °C (Figure 3).

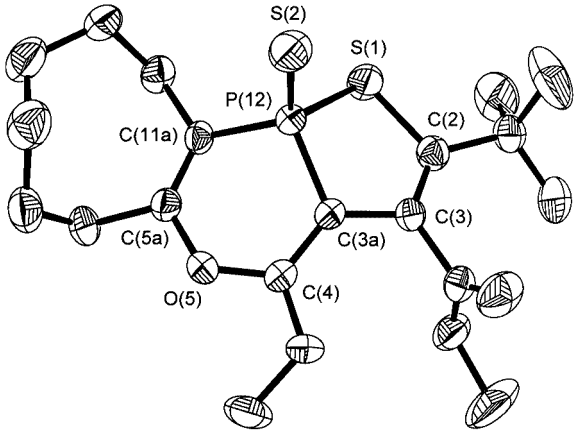


Figure 3. Molecular structure of **11a**; selected bond lengths [Å] and angles [°]; H atoms omitted for clarity, displacement ellipsoids at 50% probability: P(12)−C(3a) 1.760(3), P(12)−C(11a) 1.773(3), P(12)−S(2) 1.9307(12), P(12)−S(1) 2.0960(11), S(1)−C(2) 1.795(3), O(5)−C(4) 1.344(3), O(5)−C(5a) 1.407(3), C(3a)−C(4) 1.361(4), C(3a)−C(3) 1.468(4), C(3)−C(2) 1.353(3), C(5a)−C(11a) 1.332(3); C(3a)−P(12)−C(11a) 101.49(13), C(3a)−P(12)−S(2) 120.19(10), C(11a)−P(12)−S(2) 113.58(10), C(3a)−P(12)−S(1) 93.56(9), C(11a)−P(12)−S(1) 112.83(9), S(2)−P(12)−S(1) 113.30(5), C(2)−S(1)−P(12) 92.83(9), C(4)−O(5)−C(5a) 122.6(2), C(4)−C(3a)−C(3) 129.0(2), C(4)−C(3a)−P(12) 117.6(2), C(3)−C(3a)−P(12) 113.1(2), C(2)−C(3)−C(3a) 116.1(2), C(11a)−C(5a)−O(5) 123.8(3), C(3)−C(2)−S(1) 116.7(2), C(5a)−C(11a)−P(12) 116.6(2), C(3a)−C(4)−O(5) 122.9(2)

The entire structure is dominated by the tetrahedrally coordinated phosphorus atom P(12) (Figure 4).

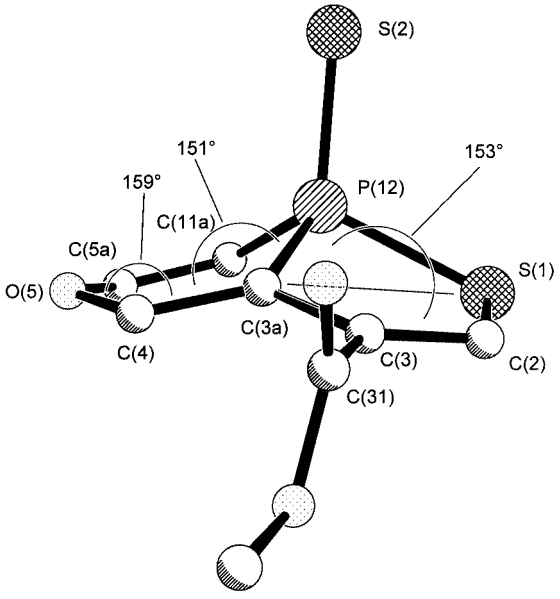


Figure 4. Bicyclic skeleton of compound **11a** with complementary interplanar angles

In the dihydrothiaphosphole system, this atom protrudes in an envelope conformation with an angle of 27° from the plane defined by the carbon atoms C(2), C(3), C(3a), and the sulfur atom S(1). This idealized plane deviates from planarity by an average of only 0.0031 Å. Similarly, the atoms C(3a), C(4), C(5a), and C(11a) lie almost exactly in a plane (mean deviation: 0.0007 Å). Not only the phosphorus atom P(12) but also the oxygen atom O(5) protrude at angles of about 25° in the same spatial direction from this plane, giving rise to a boat-like distortion of the six-membered ring.

The spectroscopic data obtained for the heterocyclic species **11** are in agreement with the tricyclic structure determined by X-ray crystallography.

Our proposed mechanism of formation of the polycyclic products **10** and **11** comprises an initial Diels−Alder reaction between a cyclooctyne molecule and the respective 1,2-thiaphosphole **1** (Scheme 4). The thus formed heteronorbornadiene **12** then reacts by ring-opening to afford the phosphinine 1-sulfide **13**. This species is stabilized either through a [4+2] cycloaddition, resulting in the formation of the barrelenes **10**, or through transfer of sulfur to a further 1,2-thiaphosphole molecule (**1a**, **1d**, **1e**, or **1i**). The thus formed $\lambda^5\sigma^3$-thiaphospholes **15** then react in a hetero-[4+2] cycloaddition to furnish the tricyclic products **11**. Thiaphosphole *P*-sulfide systems of this type, as well as the phosphinine 1-sulfides **13**, have been postulated as reactive intermediates previously.[20,21] There is spectroscopic evidence in support of the phosphinine **14** liberated upon transfer of sulfur from **13** to **15**, as already mentioned, ^{31}P NMR monitoring of the reactions in each case revealed a signal at δ = 195 ppm, in the typical region for phosphabenzenes.

When the thermolysis was performed in the presence of 2.5 equiv. of tri-*n*-butylphosphane, the formation of a product showing a signal at δ = 195 ppm was observed exclusively, together with tri-*n*-butylphosphane sulfide. This is in agreement with the postulated mechanism. The phosphinine **14** could not be isolated in pure form and so could not be characterized further. According to this mechanism, the yields of **10** and **11** (calculated on **1** employed) given in Scheme 4 are satisfactory (26%) to good (76%).

Experimental Section

General Remarks: All reactions were performed under argon (purity > 99.9998%) by use of Schlenk techniques. The solvents were dried by standard procedures, distilled, and stored under argon. Compounds **1**,[22] **2**,[23] **7**,[24] and **9**[25] were prepared by published methods. When the reaction mixture had to be heated, special pressure Schlenk tubes (3 × 8 cm, wall thickness 2 mm) with screw-threaded Teflon stoppers and Teflon stopcocks were used. Column chromatography was performed in water-cooled glass tubes under argon. The eluate was monitored with a UV absorbance detector (λ = 254 nm). Silica gel was heated (160 °C) for 24 h under vacuum (10^{-3} mbar) and then deactivated with 4% H_2O (Brockmann activity II). Melting points were determined with a Mettler FP61 apparatus (heating rate 2 °C/min) and are uncorrected. Microanalyses were performed with a Perkin−Elmer 2400 CHN Analyzer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a Bruker DPX 400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the solvent as internal standard. ^{31}P NMR shifts are expressed relative to external 85% orthophosphoric acid. Higher order NMR spin systems were resolved by simulation. Mass spectra were recorded with Finnigan MAT 90 and MAT 95 spec-

trometers. IR spectra were measured with a Perkin−Elmer Spectrum 1000 FT-IR spectrophotometer.

General Procedure for the Synthesis of the [2+2] Cycloadducts 4: An excess of the appropriate electron-rich acetylene **2** in 10 mL of diethyl ether was slowly added dropwise at −78 °C to a solution of the respective 1,2-thiaphosphole **1** in 10 mL of diethyl ether, the reaction solution immediately turning red. The mixture was allowed to warm to room temp. in the cooling bath overnight, all volatile materials were removed under vacuum (10^{-3} mbar), and the residue was taken up in *n*-pentane/diethyl ether (1:1). This solution was filtered through silica gel (D3 glass sinter, Ø 3.5 cm, filled to a height of 2 cm). After removal of the solvent under vacuum, the bicyclic products **4** were obtained in analytical purity.

Dimethyl 3-*tert*-Butyl-6,7-bis(diethylamino)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarboxylate (4a): This compound was produced from 1,2-thiaphosphole **1a** (142 mg, 0.52 mmol) and ynamine **2a** (200 μL, 174 mg, 1.04 mmol). Yield: 179 mg (78%); bright yellow solid, m.p. 65 °C. ^{1}H NMR (C_6D_6): δ = 1.13 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 6.97, $^3J_{H,H}$ = 6.96 Hz, $N(CH_AH_BCH_3)_2$], 1.21 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.71, $^3J_{H,H}$ = 6.55 Hz, $N(CH_AH_BCH_3)_2$], 1.46 [s, 9 H, $C(CH_3)_3$], 2.82 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.74, $^3J_{H,H}$ = 7.71 Hz, $N(CH_AH_BCH_3)_2$], 2.82 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.74, $^3J_{H,H}$ = 6.55 Hz, $N(CH_AH_BCH_3)_2$], 3.07 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.86, $^3J_{H,H}$ = 6.96 Hz, $N(CH_AH_BCH_3)_2$], 3.51 (s, 3 H, CO_2CH_3), 3.51 (s, 3 H, CO_2CH_3), 3.62 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.86, $^3J_{H,H}$ = 6.97 Hz, $N(CH_AH_BCH_3)_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.1 [s, $N(CH_2CH_3)_2$], 13.7 [s, $N(CH_2CH_3)_2$], 30.7 [s, $C(CH_3)_3$], 38.7 [d, $^3J_{C,P}$ = 6.1 Hz, $C(CH_3)_3$], 42.4 [s, 6-$N(CH_2CH_3)_2$], 49.7 [d, $^3J_{C,P}$ = 6.1 Hz, 7-$N(CH_2CH_3)_2$], 51.4 (s, CO_2CH_3), 52.0 (s, CO_2CH_3), 67.5 (s, C-5), 117.8 (d, $^1J_{C,P}$ = 28.4 Hz, C-7), 126.1 (s, C-4), 148.1 (d, $^2J_{C,P}$ = 19.2 Hz, C-6), 160.9 (s, 4-CO_2Me), 169.1 (d, $^2J_{C,P}$ = 3.8 Hz, 5-CO_2Me), 171.6 (d, $^2J_{C,P}$ = 2.3 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 54.3 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2968 (w, C−H), 1735 (s, C=O), 1725 (vs, C=O), 1599 (m, C=C), 1432 (w), 1220 (m). MS (EI, 35 eV): *m*/*z* (%) = 442 (7) [M^+], 168 (100) [$Et_2NCCNEt_2^+$], 139 (21) [$Et_2NCCNEt^+$], 56 (24) [$C_4H_8^+$]. $C_{21}H_{35}N_2O_4PS$ (442.56): calcd. C 56.99, H 7.97, N 6.33; found C 56.81, H 7.90, N 6.23.

Dimethyl 3-*tert*-Butyl-6-(diethylamino)-7-methyl-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarboxylate (4b): This compound was produced from 1,2-thiaphosphole **1a** (110 mg, 0.40 mmol) and ynamine **2b** (89 mg, 0.80 mmol). Yield: 86 mg (56%); bright yellow oil. ^{1}H NMR (C_6D_6): δ = 1.07 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.04, $^3J_{H,H}$ = 7.00 Hz, 6-$N(CH_AH_BCH_3)_2$], 1.44 [s, 9 H, $C(CH_3)_3$], 1.76 (d, $^3J_{H,P}$ = 10.6 Hz, 3 H, 7-CH_3), 2.82 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.06, $^3J_{H,H}$ = 7.00 Hz, 6-$N(CH_AH_BCH_3)_2$], 3.26 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.06, $^3J_{H,H}$ = 7.04 Hz, 6-$N(CH_AH_BCH_3)_2$], 3.50 (d, 3 H, $^5J_{H,P}$ = 0.8 Hz, 5-CO_2CH_3), 3.51 (s, 3 H, 4-CO_2CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.6 [s, 6-$N(CH_2CH_3)_2$], 14.1 [d, $^2J_{C,P}$ = 16.1 Hz, 7-CH_3], 30.7 [s, $C(CH_3)_3$], 38.7 [d, $^3J_{C,P}$ = 5.4 Hz, $C(CH_3)_3$], 43.1 [s, 6-$N(CH_2CH_3)_2$], 51.4 (s, CO_2CH_3), 52.0 (s, CO_2CH_3), 70.9 (s, C-5), 103.8 (d, $^1J_{C,P}$ = 19.9 Hz, C-7), 125.7 (s, C-4), 151.1 (d, $^2J_{C,P}$ = 12.2 Hz, C-6), 162.2 (d, $^3J_{C,P}$ = 1.5 Hz, 4-CO_2Me), 168.8 (d, $^2J_{C,P}$ = 3.8 Hz, 5-CO_2Me), 171.3 (d, $^2J_{C,P}$ = 2.3 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 52.3 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2970 (w, C−H), 1738 (s, C=O), 1726 (vs, C=O), 1433 (w), 1275 (w). $C_{18}H_{28}NO_4PS$ (385.46): calcd. C 56.09, H 7.32, N 3.63; found C 55.33, H 7.45, N 3.43.

Dimethyl 3-*tert*-Butyl-6-(diethylamino)-7-ethyl-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarboxylate (4c): This compound was produced from 1,2-thiaphosphole **1a** (20 mg, 0.07 mmol) and ynamine **2c** (19 mg, 0.15 mmol). Yield: 10 mg (34%); bright yellow oil. ^{1}H NMR (C_6D_6): δ = 1.09 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.02, $^3J_{H,H}$ = 7.01 Hz, 6-$N(CH_AH_BCH_3)_2$], 1.21 [M part of an ABM_3X spin system, 3 H, $^3J_{H,H}$ = 7.60, $^3J_{H,H}$ = 7.57, $^4J_{H,P}$ = 0.59 Hz, 7-$CH_AH_BCH_3$], 1.46 [s, 9 H, $C(CH_3)_3$], 2.20 (B part of an ABM_3X spin system, 1 H, $^2J_{H,H}$ = 14.64, $^3J_{H,H}$ = 7.57, $^3J_{H,P}$ = 9.60 Hz, 7-$CH_AH_BCH_3$), 2.29 (A part of an ABM_3X spin system, 1 H, $^2J_{H,H}$ = 14.64, $^3J_{H,H}$ = 7.60, $^3J_{H,P}$ = 10.34 Hz, 7-$CH_AH_BCH_3$), 2.85 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.13, $^3J_{H,H}$ = 7.02 Hz, 6-$N(CH_AH_BCH_3)_2$], 3.27 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.13, $^3J_{H,H}$ = 7.01 Hz, 6-$N(CH_AH_BCH_3)_2$], 3.50 (d, 3 H, $^5J_{H,P}$ = 0.7 Hz, 5-CO_2CH_3), 3.51 (s, 3 H, 4-CO_2CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.4 [s, 6-$N(CH_2CH_3)_2$], 14.6 (d, $^3J_{C,P}$ = 9.2 Hz, 7-CH_2CH_3), 22.2 (d, $^2J_{C,P}$ = 13.0 Hz, 7-CH_2CH_3), 30.7 [s, $C(CH_3)_3$], 38.6 [d, $^3J_{C,P}$ = 5.4 Hz, $C(CH_3)_3$], 43.3 [s, 6-$N(CH_2CH_3)_2$], 51.4 (s, CO_2CH_3), 52.0 (s, CO_2CH_3), 69.5 (s, C-5), 110.8 (d, $^1J_{C,P}$ = 22.2 Hz, C-7), 125.7 (s, C-4), 149.7 (d, $^2J_{C,P}$ = 13.0 Hz, C-6), 161.8 (s, 4-CO_2Me), 168.9 (d, $^2J_{C,P}$ = 3.8 Hz, 5-CO_2Me), 171.4 (d, $^2J_{C,P}$ = 2.3 Hz, C-3) ppm. ^{31}P NMR (C_6D_6): δ = 47.7 (X part of an ABM_3X spin system, $^3J_{P,H}$ = 9.60, $^3J_{P,H}$ = 10.34, $^4J_{P,H}$ = 0.59 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2966 (w, C−H), 1738 (vs, C=O), 1726 (vs, C=O), 1433 (w), 1366 (w), 1224 (m).

3-*tert*-Butyl-6,7-bis(diethylamino)-4,5-bis(trifluoromethyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene (4d): This compound was produced from 1,2-thiaphosphole **1b** (140 mg, 0.47 mmol) and ynamine **2a** (185 μL, 160 mg, 0.95 mmol). Yield: 200 mg (92%); bright yellow crystals, m.p. 56 °C. ^{1}H NMR (C_6D_6): δ = 1.04 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 6.98, $^3J_{H,H}$ = 6.96 Hz, 6-$N(CH_AH_BCH_3)_2$], 1.05 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.05, $^3J_{H,H}$ = 6.76 Hz, 7-$N(CH_AH_BCH_3)_2$], 1.41 [s, 9 H, $C(CH_3)_3$], 2.79 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.44, $^3J_{H,H}$ = 6.76, $^4J_{H,P}$ = 2.00 Hz, 7-$N(CH_AH_BCH_3)_2$], 2.83 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.44, $^3J_{H,H}$ = 7.05 Hz, 7-$N(CH_AH_BCH_3)_2$], 2.93 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.69, $^3J_{H,H}$ = 6.96 Hz, 6-$N(CH_AH_BCH_3)_2$], 3.41 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.69, $^3J_{H,H}$ = 6.98 Hz, 6-$N(CH_AH_BCH_3)_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.3 [d, $^4J_{C,P}$ = 1.4 Hz, 7-$N(CH_2CH_3)_2$], 13.7 [s, 6-$N(CH_2CH_3)_2$], 31.3 [q, $^5J_{C,F}$ = 3.6 Hz, $C(CH_3)_3$], 40.3 [d, $^3J_{C,P}$ = 5.6 Hz, $C(CH_3)_3$], 44.7 [s, 6-$N(CH_2CH_3)_2$], 47.1 [d, $^3J_{C,P}$ = 6.2 Hz, 7-$N(CH_2CH_3)_2$], 71.3 (q, $^2J_{C,F}$ = 31.4 Hz, C-5), 120.7 (q, $^2J_{C,F}$ = 34.0 Hz, C-4), 124.4 (qd, $^1J_{C,F}$ = 275.6, $^3J_{C,P}$ = 3.3 Hz, 4-CF_3), 126.9 (qd, $^1J_{C,F}$ = 279.9, $^2J_{C,P}$ = 6.8 Hz, 5-CF_3), 132.9 (d, $^1J_{C,P}$ = 24.6 Hz, C-7), 135.4 (d, $^2J_{C,P}$ = 19.3 Hz, C-6), 167.9 (d, $^2J_{C,P}$ = 3.1 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 25.5 (q, $^3J_{P,F}$ = 36.4 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2973 (m, C−H), 2932 (w, C−H), 2872 (w, C−H), 1594 (m), 1378 (m), 1274 (vs, C−F), 1169 (s), 1121 (m). MS (EI, 35 eV): *m*/*z* (%) = 462 (20) [M^+], 168 (100) [$Et_2NCCNEt_2^+$], 139 (17) [$Et_2NCCNEt^+$], 56 (13) [$C_4H_8^+$]. $C_{19}H_{29}F_6N_2PS$ (462.49): calcd. C 49.34, H 6.32, N 6.06; found C 49.28, H 6.29, N 6.10.

3-*tert*-Butyl-6,7-bis(diethylamino)-2-thia-1-phosphabicyclo[3.2.0]-hepta-3,6-diene-4,5-dicarbonitrile (4e): This compound was produced from 1,2-thiaphosphole **1c** (75 mg, 0.36 mmol) and ynamine **2a** (140 μL, 121 mg, 0.72 mmol). Yield: 75 mg (55%); red oil. ^{1}H NMR (C_6D_6): δ = 0.95 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.33, $^3J_{H,H}$ = 7.22 Hz, $N(CH_AH_BCH_3)_2$], 1.03 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.14, $^3J_{H,H}$ = 7.08 Hz, $N(CH_AH_BCH_3)_2$], 1.33 [s, 9 H, $C(CH_3)_3$], 2.57 [B part of an ABX_3

spin system, 2 H, $^2J_{H,H}$ = 12.74, $^3J_{H,H}$ = 7.08 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 2.63 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.74, $^3J_{H,H}$ = 7.14 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.38 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.34, $^3J_{H,H}$ = 7.33 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.72 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.34, $^3J_{H,H}$ = 7.22 Hz, N(CH$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.5 [d, $^4J_{C,P}$ = 2.3 Hz, 7-N(CH$_2$CH$_3$)$_2$], 13.6 [s, 6-N(CH$_2$CH$_3$)$_2$], 30.0 [s, C(CH$_3$)$_3$], 39.0 [d, $^3J_{C,P}$ = 6.1 Hz, C(CH$_3$)$_3$], 43.6 [s, 6-N(CH$_2$CH$_3$)$_2$], 48.7 [d, $^3J_{C,P}$ = 5.4 Hz, 7-N(CH$_2$CH$_3$)$_2$], 66.0 (s, C-5), 103.5 (d, $^3J_{C,P}$ = 1.5 Hz, 4-CN), 116.9 (d, $^2J_{C,P}$ = 4.6 Hz, 5-CN), 117.1 (d, $^2J_{C,P}$ = 4.6 Hz, C-4), 121.9 (d, $^1J_{C,P}$ = 26.1 Hz, C-7), 144.6 (d, $^2J_{C,P}$ = 21.5 Hz, C-6), 177.9 (d, $^2J_{C,P}$ = 2.3 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 56.1 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2972 (s, C−H), 2870 (m, C−H), 2202 (w, C≡N), 1604 (vs, C=C), 1469 (w), 1380 (m), 1368 (m), 1266 (w), 1220 (w), 1118 (w). MS (EI, 35 eV): *m/z* (%) = 376 (7) [M$^+$], 208 (8) [M$^+$ − Et$_2$NCCNEt$_2$], 193 (26) [M$^+$ − Et$_2$NCCNEt$_2$ − Me], 168 (100) [Et$_2$NCCNEt$_2^+$], 139 (33) [Et$_2$NCCNEt$^+$], 83 (16) [*t*BuCN$^+$], 69 (20) [C*t*Bu$^+$], 57 (49) [*t*Bu$^+$], 41 (42) [CH$_2$CNH$^+$]. $C_{19}H_{29}N_4PS$ (376.51): calcd. C 60.61, H 7.76, N 14.88; found C 60.66, H 7.75, N 15.50.

Dimethyl 6,7-Bis(diethylamino)-3-(1,1-dimethylpropyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarboxylate (4f): This compound was produced from 1,2-thiaphosphole **1d** (42 mg, 0.15 mmol) and ynamine **2a** (57 μL, 49 mg, 0.29 mmol). Yield: 10 mg (15%); bright yellow oil. ^{1}H NMR (C_6D_6): δ = 0.97 [pt, 3 H, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.3 Hz, C(CH$_3$)$_A$(CH$_3$)$_B$ CH$_A$H$_B$CH$_3$], 1.15 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.16, $^3J_{H,H}$ = 7.05 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.23 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 6.98, $^3J_{H,H}$ = 6.98 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.44 [s, 3 H, C(CH$_3$)$_A$(CH$_3$)$_B$CH$_A$H$_B$CH$_3$], 1.47 [s, 3 H, C(CH$_3$)$_A$(CH$_3$)$_B$CH$_A$H$_B$CH$_3$], 1.82 [pq, 2 H, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.3 Hz, C(CH$_3$)$_A$(CH$_3$)$_B$ CH$_A$H$_B$CH$_3$], 2.83 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.65, $^3J_{H,H}$ = 7.05 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 2.86 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.65, $^3J_{H,H}$ = 7.16 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.07 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.91, $^3J_{H,H}$ = 6.98 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.51 (s, 6 H, CO$_2$CH$_3$), 3.63 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.91, $^3J_{H,H}$ = 6.98 Hz, N(CH$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 9.5 (s, *t*Pen-CH$_2$CH$_3$), 13.1 [s, 6-N(CH$_2$CH$_3$)$_2$], 13.7 [d, $^4J_{C,P}$ = 1.5 Hz, 7-N(CH$_2$CH$_3$)$_2$], 28.4 (s, *t*Pen-CH$_3$), 28.4 (s, *t*Pen-CH$_3$), 36.7 (s, *t*Pen-CH$_2$CH$_3$), 42.3 (d, $^3J_{C,P}$ = 5.4 Hz, *t*Pen-C_q), 42.4 [s, 6-N(CH$_2$CH$_3$)$_2$], 49.5 [d, $^3J_{C,P}$ = 5.4 Hz, 7-N(CH$_2$CH$_3$)$_2$], 51.4 (s, CO$_2$CH$_3$), 52.0 (s, CO$_2$CH$_3$), 67.7 (s, C-5), 118.0 (d, $^1J_{C,P}$ = 28.3 Hz, C-7), 126.7 (s, C-4), 148.1 (d, $^2J_{C,P}$ = 19.9 Hz, C-6), 159.7 (s, 4-CO$_2$Me), 169.1 (d, $^2J_{C,P}$ = 3.8 Hz, 5-CO$_2$Me), 171.7 (d, $^2J_{C,P}$ = 3.1 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 55.3 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2977 (vs, C−H), 1738 (s, C=O), 1726 (s, C=O), 1462 (w), 1382 (w), 1120 (m). $C_{22}H_{37}N_2O_4PS$ (456.59): calcd. C 57.87, H 8.17, N 6.14; found C 57.36, H 7.57, N 5.71.

Dimethyl 6,7-Bis(diethylamino)-3-(1-methylcyclopentyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarboxylate (4g): This compound was produced from 1,2-thiaphosphole **1e** (56 mg, 0.19 mmol) and ynamine **2a** (72 μL, 62 mg, 0.37 mmol). Yield: 54 mg (62%); bright yellow solid, m.p. 78 °C (dec.). ^{1}H NMR (C_6D_6): δ = 1.13 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.07, $^3J_{H,H}$ = 6.72 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.21 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.25, $^3J_{H,H}$ = 7.07 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.55 (s, 3 H, Me^{c}Pen-CH$_3$), 1.55−1.61 (m, 4 H, Me^{c}Pen-CH$_2$), 1.83−1.94 (m, 2 H, Me^{c}Pen-CH$_2$), 1.94−2.05 (m, 1 H, Me^{c}Pen-CH$_2$), 2.08−2.18 (m, 1 H, Me^{c}Pen-CH$_2$), 2.82 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.31, $^3J_{H,H}$ = 7.07 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 2.84 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.31, $^3J_{H,H}$ = 7.25 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.01 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.20, $^3J_{H,H}$ = 7.07 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.52 (s, 3 H, 4-CO$_2$CH$_3$), 3.53 (d, 3 H, $^5J_{H,P}$ = 0.7 Hz, 5-CO$_2$CH$_3$), 3.63 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.20, $^3J_{H,H}$ = 6.72 Hz, N(CH$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.2 [s, 6-N(CH$_2$CH$_3$)$_2$], 13.7 [d, $^4J_{C,P}$ = 2.0 Hz, 7-N(CH$_2$CH$_3$)$_2$], 23.8 (s, Me^{c}Pen-CH$_2$), 24.2 (s, Me^{c}Pen-CH$_2$), 26.2 (s, Me^{c}Pen-CH$_3$), 39.2 (s, Me^{c}Pen-CH$_2$), 40.9 (s, Me^{c}Pen-CH$_2$), 42.4 [s, 6-N(CH$_2$CH$_3$)$_2$], 49.7 [d, $^3J_{C,P}$ = 5.5 Hz, 7-N(CH$_2$CH$_3$)$_2$], 50.3 (d, $^3J_{C,P}$ = 5.5 Hz, Me^{c}Pen-C_q), 51.3 (s, CO$_2$CH$_3$), 52.0 (s, CO$_2$CH$_3$), 67.1 (s, C-5), 118.4 (d, $^1J_{C,P}$ = 28.2 Hz, C-7), 125.6 (s, C-4), 148.2 (d, $^2J_{C,P}$ = 19.2 Hz, C-6), 163.2 (s, 4-CO$_2$Me), 168.7 (d, $^2J_{C,P}$ = 3.9 Hz, 5-CO$_2$Me), 171.8 (d, $^2J_{C,P}$ = 3.1 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 58.6 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2969 (m, C−H), 1726 (vs, C=O), 1600 (m), 1432 (w), 1378 (w), 1273 (m), 1136 (w). $C_{23}H_{37}N_2O_4PS$ (468.60): calcd. C 58.95, H 7.96, N 5.98; found C 58.69, H 7.89, N 5.79.

6,7-Bis(diethylamino)-3-(1-methylcyclopentyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile (4h): This compound was produced from 1,2-thiaphosphole **1f** (122 mg, 0.52 mmol) and ynamine **2a** (200 μL, 175 mg, 1.04 mmol). Yield: 126 mg (60%); dark red oil that slowly solidified, m.p. 44 °C. ^{1}H NMR (C_6D_6): δ = 0.97 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.07, $^3J_{H,H}$ = 6.72 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.05 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.12, $^3J_{H,H}$ = 6.98 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.30 (s, 3 H, Me^{c}Pen-CH$_3$), 1.45−1.60 (m, 4 H, Me^{c}Pen-CH$_2$), 1.84−2.10 (m, 4 H, Me^{c}Pen-CH$_2$), 2.59 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.80, $^3J_{H,H}$ = 6.98 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 2.64 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.80, $^3J_{H,H}$ = 7.12 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.41 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.20, $^3J_{H,H}$ = 7.07 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.45 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.20, $^3J_{H,H}$ = 6.72 Hz, N(CH$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.5 [d, $^4J_{C,P}$ = 2.3 Hz, 7-N(CH$_2$CH$_3$)$_2$], 13.7 [s, 6-N(CH$_2$CH$_3$)$_2$], 23.8 (s, 2 × Me^{c}Pen-CH$_2$), 26.5 (s, Me^{c}Pen-CH$_3$), 39.9 (s, Me^{c}Pen-CH$_2$), 39.9 (s, Me^{c}Pen-CH$_2$), 43.6 [s, 6-N(CH$_2$CH$_3$)$_2$], 48.7 [d, $^3J_{C,P}$ = 4.7 Hz, 7-N(CH$_2$CH$_3$)$_2$], 49.4 (s, C-5), 50.3 (d, $^3J_{C,P}$ = 5.5 Hz, Me^{c}Pen-C_q), 103.5 (d, $^3J_{C,P}$ = 1.6 Hz, 4-CN), 116.9 (d, $^2J_{C,P}$ = 2.7 Hz, 5-CN), 117.2 (d, $^2J_{C,P}$ = 5.1 Hz, C-4), 122.0 (d, $^1J_{C,P}$ = 25.4 Hz, C-7), 144.5 (d, $^2J_{C,P}$ = 21.5 Hz, C-6), 178.8 (d, $^2J_{C,P}$ = 1.6 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 60.1 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2970 (vs, C−H), 2874 (m, C−H), 2216 (w, C≡N), 2214 (w, C≡N), 1607 (s, C=C), 1468 (s), 1451 (s), 1379 (s), 1064 (w). $C_{21}H_{31}N_4PS$ (402.55): calcd. C 62.66, H 7.76, N 13.92; found C 62.81, H 8.05, N 13.53.

6,7-Bis(diethylamino)-3-(1-methylcyclopentyl)-4,5-bis(trifluoromethyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene (4i): This compound was produced from 1,2-thiaphosphole **1g** (150 mg, 0.47 mmol) and ynamine **2a** (145 μL, 126 mg, 0.75 mmol). Yield: 208 mg (91%); bright yellow crystals, m.p. 49 °C. ^{1}H NMR (C_6D_6): δ = 1.06 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.07, $^3J_{H,H}$ = 6.72 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.06 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.25, $^3J_{H,H}$ = 7.20 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 1.30 (s, 3 H, Me^{c}Pen-CH$_3$), 1.43−1.66 (m, 4 H, Me^{c}Pen-CH$_2$), 1.80−1.90 (m, 1 H, Me^{c}Pen-CH$_2$), 1.99−2.19 (m, 3 H, Me^{c}Pen-CH$_2$), 2.81 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.50, $^3J_{H,H}$ = 7.20 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 2.84 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.50, $^3J_{H,H}$ = 7.25 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 2.95 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.20, $^3J_{H,H}$ = 7.07 Hz, N(CH$_A$H$_B$CH$_3$)$_2$], 3.41 [A part of an ABX$_3$ spin system,

2 H, $^2J_{H,H}$ = 14.20, $^3J_{H,H}$ = 6.72 Hz, N(CH_AH$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.3 [d, $^4J_{C,P}$ = 1.2 Hz, 7-N(CH$_2$*C*H$_3$)$_2$], 13.7 [s, 6-N(CH$_2$*C*H$_3$)$_2$], 22.4 (s, Me^{c}Pen-*C*H$_2$), 23.9 (s, Me^{c}Pen-*C*H$_2$), 25.4 (q, $^5J_{C,F}$ = 3.1 Hz, Me^{c}Pen-*C*H$_3$), 37.3 (q, $^5J_{C,F}$ = 5.3 Hz, Me^{c}Pen-*C*H$_2$), 42.5 (s, Me^{c}Pen-*C*H$_2$), 44.7 [s, 6-N(*C*H$_2$CH$_3$)$_2$], 47.1 [d, $^3J_{C,P}$ = 6.3 Hz, 7-N(*C*H$_2$CH$_3$)$_2$], 51.6 (d, $^3J_{C,P}$ = 5.5 Hz, Me^{c}Pen-*C*$_q$), 70.6 (q, $^2J_{C,F}$ = 30.1 Hz, C-5), 119.9 (q, $^2J_{C,F}$ = 33.5 Hz, C-4), 124.2 (qd, $^1J_{C,F}$ = 273.9, $^3J_{C,P}$ = 3.3 Hz, 4-*C*F$_3$), 126.9 (qd, $^1J_{C,F}$ = 279.7, $^2J_{C,P}$ = 7.4 Hz, 5-*C*F$_3$), 132.7 (d, $^1J_{C,P}$ = 24.3 Hz, C-7), 135.5 (d, $^2J_{C,P}$ = 19.2 Hz, C-6), 168.2 (q, $^3J_{C,F}$ = 3.5 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 29.5 (q, $^3J_{P,F}$ = 34.7 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2970 (m, C−H), 2876 (w, C−H), 1277 (vs, C−F), 1186 (s), 1170 (s), 1151 (s), 1122 (m). $C_{21}H_{31}F_6N_2PS$ (488.53): calcd. C 51.63, H 6.40, N 5.74; found C 51.62, H 6.40, N 5.55.

6,7-Bis(diethylamino)-3-(1-methylcyclohexyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile (4j): This compound was produced from 1,2-thiaphosphole **1h** (126 mg, 0.51 mmol) and ynamine **2a** (172 μL, 149 mg, 0.89 mmol). Yield: 147 mg (69%); dark red oil. ^{1}H NMR (C_6D_6): δ = 0.99 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.10, $^3J_{H,H}$ = 7.09 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.05 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.21, $^3J_{H,H}$ = 6.87 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.32 (s, 3 H, Me^{c}Hex-C*H*$_3$), 1.42−1.56 (m, 8 H, Me^{c}Hex-C*H*$_2$), 2.12−2.22 (m, 1 H, Me^{c}Hex-C*H*$_2$), 2.35−2.45 (m, 1 H, Me^{c}Hex-C*H*$_2$), 2.63 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.74, $^3J_{H,H}$ = 6.87 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 2.66 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.74, $^3J_{H,H}$ = 7.21 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$], 3.38 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.82, $^3J_{H,H}$ = 7.10 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.47 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.82, $^3J_{H,H}$ = 7.09 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.6 [d, $^4J_{C,P}$ = 2.3 Hz, 7-N(CH$_2$*C*H$_3$)$_2$], 13.7 [s, 6-N(CH$_2$*C*H$_3$)$_2$], 23.2 (s, Me^{c}Hex-*C*H$_2$), 23.2 (s, Me^{c}Hex-*C*H$_2$), 25.8 (s, Me^{c}Hex-*C*H$_2$), 27.2 (s, Me^{c}Hex-*C*H$_3$), 37.9 (s, Me^{c}Hex-*C*H$_2$), 38.2 (s, Me^{c}Hex-*C*H$_2$), 43.2 (d, $^3J_{C,P}$ = 5.4 Hz, Me^{c}Pen-*C*$_q$), 43.7 [s, 6-N(*C*H$_2$CH$_3$)$_2$], 48.7 [d, $^3J_{C,P}$ = 5.4 Hz, 7-N(*C*H$_2$CH$_3$)$_2$], 50.1 (s, C-5), 103.7 (d, $^3J_{C,P}$ = 1.5 Hz, 4-*C*N), 116.9 (d, $^2J_{C,P}$ = 3.1 Hz, 5-*C*N), 117.2 (d, $^2J_{C,P}$ = 4.6 Hz, C-4), 122.7 (d, $^1J_{C,P}$ = 26.8 Hz, C-7), 144.7 (d, $^2J_{C,P}$ = 20.7 Hz, C-6), 178.0 (s, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 54.2 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2972 (m, C−H), 2935 (m, C−H), 2203 (w, C≡N), 1607 (vs), 1468 (w), 1380 (w), 1267 (w). $C_{22}H_{33}N_4PS$ (416.58): calcd. C 63.43, H 7.99, N 13.45; found C 61.76, H 8.03, N 13.47.

6-(Diethylamino)-7-ethyl-3-(1-methylcyclohexyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile (4k): This compound was produced from 1,2-thiaphosphole **1h** (116 mg, 0.47 mmol) and ynamine **2c** (118 mg, 0.94 mmol). Yield: 68 mg (39%); bright yellow oil. ^{1}H NMR (C_6D_6): δ = 0.96 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.06, $^3J_{H,H}$ = 6.86 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.00 (M part of an ABM$_3$X spin system, 3 H,$^3J_{H,H}$ = 7.58, $^3J_{H,H}$ = 7.67 Hz, 7-CH$_A$H$_B$C*H*$_3$), 1.28 (s, 3 H, Me^{c}Hex-C*H*$_3$), 1.30−1.60 (m, 8 H, Me^{c}Hex-C*H*$_2$), 1.97 (B part of an ABM$_3$X spin system, 1 H, $^2J_{H,H}$ = 15.33, $^3J_{H,H}$ = 7.58, $^3J_{H,P}$ = 9.40 Hz, 7-CH$_A$*H*$_B$CH$_3$), 2.05 (A part of an ABM$_3$X spin system, 1 H, $^2J_{H,H}$ = 15.33, $^3J_{H,H}$ = 7.67, $^3J_{H,P}$ = 11.65 Hz, 7-C*H*$_A$H$_B$CH$_3$), 2.10−2.23 (m, 1 H, Me^{c}Hex-C*H*$_2$), 2.38−2.48 (m, 1 H, Me^{c}Hex-C*H*$_2$), 3.03 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.36, $^3J_{H,H}$ = 6.86 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.34 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.36, $^3J_{H,H}$ = 7.06 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.9 [s, N(CH$_2$*C*H$_3$)$_2$], 14.7 (d, $^3J_{C,P}$ = 9.2 Hz, 7-CH$_2$*C*H$_3$), 21.8 (d, $^2J_{C,P}$ = 13.0 Hz, 7-*C*H$_2$CH$_3$), 23.2 (s, Me^{c}Hex-*C*H$_2$), 23.3 (s, Me^{c}Hex-*C*H$_2$), 25.8 (s, Me^{c}Hex-*C*H$_2$), 27.4 (s, Me^{c}Hex-*C*H$_3$), 37.8 (s, Me^{c}Hex-*C*H$_2$), 38.5 (s, Me^{c}Hex-*C*H$_2$), 43.2 (d, $^3J_{C,P}$ = 5.4 Hz, Me^{c}Hex-*C*$_q$), 43.6 [s, N(*C*H$_2$CH$_3$)$_2$], 50.6 (s, C-5), 103.2 (s, *C*N), 111.2 (d, $^1J_{C,P}$ = 19.9 Hz, C-7), 116.8 (s, *C*N), 116.9 (s, C-4), 148.3 (d, $^2J_{C,P}$ = 13.8 Hz, C-6), 178.4 (d, $^2J_{C,P}$ = 1.5 Hz, C-3) ppm. ^{31}P NMR (C_6D_6): δ = 51.6 (X part of an ABM$_3$X spin system, $^3J_{P,H}$ = 9.40, $^3J_{P,H}$ = 11.65 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2971 (m, C−H), 2934 (s, C−H), 2866 (m, C−H), 2203 (m, C≡N), 1594 (vs), 1452 (m), 1407 (m), 1380 (m), 1267 (m), 1169 (w). $C_{20}H_{28}N_3PS$ (373.50).

6-(Diethylamino)-3-(1-methylcyclohexyl)-7-(trimethylsilyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile (4l): This compound was produced from 1,2-thiaphosphole **1h** (127 mg, 0.51 mmol) and ynamine **2d** (173 mg, 1.02 mmol). Yield: 178 mg (84%); yellow oil. ^{1}H NMR (C_6D_6): δ = 0.20 [s, 9 H, Si(C*H*$_3$)$_3$], 0.95 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.10, $^3J_{H,H}$ = 7.11 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.16−1.24 (m, 3 H, Me^{c}Hex-C*H*$_2$), 1.25 (s, 3 H, Me^{c}Hex-C*H*$_3$), 1.32−1.52 (m, 5 H, Me^{c}Hex-C*H*$_2$), 2.12−2.23 (m, 1 H, Me^{c}Hex-C*H*$_2$), 2.46−2.56 (m, 1 H, Me^{c}Hex-C*H*$_2$), 3.10 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.24, $^3J_{H,H}$ = 7.10 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.46 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 14.24, $^3J_{H,H}$ = 7.11 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 1.0 [d, $^3J_{C,P}$ = 6.1 Hz, Si(*C*H$_3$)$_3$], 13.1 [s, N(CH$_2$*C*H$_3$)$_2$], 23.3 (s, Me^{c}Hex-*C*H$_2$), 23.3 (s, Me^{c}Hex-*C*H$_2$), 25.8 (s, Me^{c}Hex-*C*H$_2$), 27.8 (s, Me^{c}Hex-*C*H$_3$), 38.0 (s, Me^{c}Hex-*C*H$_2$), 38.8 (s, Me^{c}Hex-*C*H$_2$), 42.0 [s, N(*C*H$_2$CH$_3$)$_2$], 43.0 (d, $^3J_{C,P}$ = 5.4 Hz, Me^{c}Hex-*C*$_q$), 52.6 (s, C-5), 102.8 (s, 4-*C*N), 103.0 (d, $^1J_{C,P}$ = 16.8 Hz, C-7), 116.2 (d, $^2J_{C,P}$ = 3.1 Hz, 5-*C*N), 116.8 (s, C-4), 157.5 (d, $^2J_{C,P}$ = 9.9 Hz, C-6), 178.3 (s, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 53.7 (s, P-1). $C_{21}H_{32}N_3PSSi$ (417.64): calcd. C 60.39, H 7.72, N 10.06; found C 60.62, H 7.73, N 9.96.

Dimethyl 6,7-Bis(diethylamino)-3-(1-methylcyclohexyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarboxylate (4m): This compound was produced from 1,2-thiaphosphole **1i** (166 mg, 0.53 mmol) and ynamine **2a** (205 μL, 178 mg, 1.06 mmol). Yield: 194 mg (76%); yellow oil. ^{1}H NMR (C_6D_6): δ = 1.13 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 6.99, $^3J_{H,H}$ = 6.98 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.23 [X part of an ABX$_3$ spin system, 6 H, $^3J_{H,H}$ = 7.18, $^3J_{H,H}$ = 7.02 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.28−1.50 (m, 2 H, Me^{c}Hex-C*H*$_2$), 1.54 (s, 3 H, Me^{c}Hex-C*H*$_3$), 1.55−1.63 (m, 2 H, Me^{c}Hex-C*H*$_2$), 1.64−1.93 (m, 2 H, Me^{c}Hex-C*H*$_2$), 1.95−2.05 (m, 1 H, Me^{c}Hex-C*H*$_2$), 2.20−2.30 (m, 2 H, Me^{c}Hex-C*H*$_2$), 2.33−2.42 (m, 1 H, Me^{c}Hex-C*H*$_2$), 2.82 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.36, $^3J_{H,H}$ = 7.02 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 2.85 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 12.36, $^3J_{H,H}$ = 7.18 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$], 3.06 [B part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.98, $^3J_{H,H}$ = 6.99 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.50 (s, 3 H, 4-CO$_2$C*H*$_3$), 3.53 (d, 3 H, $^5J_{H,P}$ = 0.6 Hz, 5-CO$_2$C*H*$_3$), 3.64 [A part of an ABX$_3$ spin system, 2 H, $^2J_{H,H}$ = 13.98, $^3J_{H,H}$ = 6.98 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.1 [s, 6-N(CH$_2$*C*H$_3$)$_2$], 13.8 [d, $^4J_{C,P}$ = 1.5 Hz, 7-N(CH$_2$*C*H$_3$)$_2$], 23.5 (s, Me^{c}Hex-*C*H$_2$), 23.8 (s, Me^{c}Hex-*C*H$_2$), 26.4 (s, Me^{c}Hex-*C*H$_2$), 28.0 (s, Me^{c}Hex-*C*H$_3$), 39.1 (s, Me^{c}Hex-*C*H$_2$), 39.8 (s, Me^{c}Hex-*C*H$_2$), 42.4 [s, 6-N(*C*H$_2$CH$_3$)$_2$], 42.7 (d, $^3J_{C,P}$ = 5.4 Hz, Me^{c}Hex-*C*$_q$), 49.8 [d, $^3J_{C,P}$ = 5.4 Hz, 7-N(*C*H$_2$CH$_3$)$_2$], 51.4 (s, CO$_2$*C*H$_3$), 52.0 (s, CO$_2$*C*H$_3$), 67.7 (s, C-5), 118.1 (d, $^1J_{C,P}$ = 28.3 Hz, C-7), 126.2 (s, C-4), 148.6 (d, $^2J_{C,P}$ = 19.1 Hz, C-6), 159.5 (s, 4-*C*O$_2$Me), 169.4 (s, 5-*C*O$_2$Me), 171.7 (d, $^2J_{C,P}$ = 2.3 Hz, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 55.2 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2932 (m, C−H), 1725 (vs, C=O), 1600 (m), 1446 (w), 1378 (w), 1271 (w). MS (EI, 35 eV): *m*/*z* (%) = 482 (3) [M$^+$], 314 (100) [M$^+$ − Et$_2$NCCNEt$_2$], 168 (36) [Et$_2$NCCNEt$_2^+$]. $C_{24}H_{39}N_2O_4PS$ (482.63): calcd. C 59.73, H 8.15, N 5.81; found C 60.10, H 8.17, N 5.81.

6,7-Bis(diethylamino)-3-(1-methylcyclohexyl)-4,5-bis(trifluoromethyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene (4n): This compound was produced from 1,2-thiaphosphole **1j** (139 mg, 0.42 mmol) and ynamine **2a** (162 µL, 140 mg, 0.83 mmol). Yield: 176 mg (84%); bright yellow crystals, m.p. 41 °C. ^{1}H NMR (C_6D_6): δ = 1.06 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.02, $^3J_{H,H}$ = 6.94 Hz, N(CH$_A$H$_B$CH_3)$_2$], 1.06 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.09, $^3J_{H,H}$ = 6.52 Hz, N(CH$_A$H$_B$CH_3)$_2$], 1.22−1.33 (m, 2 H, Me^{c}Hex-CH_2), 1.36 (s, 3 H, Me^{c}Hex-CH_3), 1.38−1.70 (m, 5 H, Me^{c}Hex-CH_2), 1.72−1.88 (m, 1 H, Me^{c}Hex-CH_2), 2.25−2.36 (m, 1 H, Me^{c}Hex-CH_2), 2.52−2.62 (m, 1 H, Me^{c}Hex-CH_2), 2.81 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.42, $^3J_{H,H}$ = 6.52 Hz, N(CH$_A$$H_BCH_3$)$_2$], 2.83 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.42, $^3J_{H,H}$ = 7.09 Hz, N(CH_AH$_B$CH$_3$)$_2$], 2.93 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.73, $^3J_{H,H}$ = 6.94 Hz, N(CH$_A$$H_BCH_3$)$_2$], 3.42 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.73, $^3J_{H,H}$ = 7.02 Hz, N(CH_AH$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.3 [d, $^4J_{C,P}$ = 1.5 Hz, 7-N(CH$_2$$CH_3$)$_2$], 13.7 [s, 6-N(CH$_2$$CH_3$)$_2$], 24.0 (s, Me^{c}Hex-$CH_2$), 24.4 (s, Me^{c}Hex-$CH_2$), 26.3 (s, Me^{c}Hex-$CH_2$), 27.9 (s, Me^{c}Hex-$CH_3$), 38.0 (q, $^5J_{C,F}$ = 5.4 Hz, Me^{c}Hex-CH$_2$), 42.4 (s, Me^{c}Hex-CH$_2$), 44.7 [s, 6-N(CH$_2$CH$_3$)$_2$], 44.9 (d, $^3J_{C,P}$ = 5.4 Hz, Me^{c}Pen-C_q), 47.2 [d, $^3J_{C,P}$ = 6.1 Hz, 7-N(CH$_2$CH$_3$)$_2$], 71.7 (qd, $^2J_{C,F}$ = 32.1, $^1J_{C,P}$ = 2.1 Hz, C-5), 120.7 (q, $^2J_{C,F}$ = 33.9 Hz, C-4), 124.3 (qd, $^1J_{C,F}$ = 273.3, $^2J_{C,P}$ = 3.6 Hz, 5-CF$_3$), 127.0 (q, $^1J_{C,F}$ = 280.4 Hz, 4-CF$_3$), 132.9 (d, $^1J_{C,P}$ = 24.5 Hz, C-7), 135.5 (d, $^2J_{C,P}$ = 19.1 Hz, C-6), 167.9 (s, C-3) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 24.9 (q, $^3J_{P,F}$ = 36.5 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2933 (w, C−H), 1270 (vs, C−F), 1186 (s), 1170 (s), 1121 (m). MS (EI, 35 eV): *m*/*z* (%) = 502 (17) [M$^+$], 168 (100) [Et$_2$NCCNEt$_2^+$], 139 (13) [Et$_2$NCCNEt$_2^+$ − Et]. $C_{22}H_{33}F_6N_2PS$ (502.56): calcd. C 52.58, H 6.62, N 5.58; found C 52.92, H 6.68, N 5.53.

General Procedure for the Synthesis of the Tungsten Complexes 5: A solution of the bicyclic compound **4** in 10 mL of THF was added at 0 °C to a solution of pentacarbonyl(tetrahydrofuran)tungsten(0) (generated by irradiation of hexacarbonyltungsten in THF for 20 min). After removal of the ice bath, volatile materials were evaporated under vacuum, and the residue was taken up in *n*-pentane/diethyl ether (1:1) and filtered through silica gel (D3 glass sinter, Ø 3.5 cm, filled to a height of 2 cm). After removal of the solvent under vacuum, the tungsten complexes **5** were obtained in analytical purity.

η^1-{3-*tert*-Butyl-6,7-bis(diethylamino)-4,5-bis(methoxycarbonyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}pentacarbonyltungsten(0) (5a): This compound was produced from **4a** (341 mg, 0.77 mmol) and hexacarbonyltungsten(0) (275 mg, 0.78 mmol) in THF (35 mL). Yield: 514 mg (87%); bright yellow solid, m.p. 89 °C. ^{1}H NMR (C_6D_6): δ = 1.03 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.06, $^3J_{H,H}$ = 7.03 Hz, 7-N(CH$_A$H$_B$CH_3)$_2$], 1.19 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 6.99, $^3J_{H,H}$ = 6.96 Hz, 6-N(CH$_A$H$_B$CH_3)$_2$], 1.29 [s, 9 H, C(CH_3)$_3$], 2.71 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.90, $^3J_{H,H}$ = 6.99 Hz, 6-N(CH$_A$$H_BCH_3$)$_2$], 3.03 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 12.80, $^3J_{H,H}$ = 7.03, $^4J_{H,P}$ = 1.89 Hz, 7-N(CH$_A$$H_BCH_3$)$_2$], 3.18 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 12.80, $^3J_{H,H}$ = 7.06, $^4J_{H,P}$ = 1.34 Hz, 7-N(CH_AH$_B$CH$_3$)$_2$], 3.45 (s, 3 H, CO$_2$CH_3), 3.66 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.90, $^3J_{H,H}$ = 6.96 Hz, 6-N(CH_AH$_B$CH$_3$)$_2$], 3.70 (d, 3 H, $^5J_{H,P}$ = 0.8 Hz, 5-CO$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.3 [s, N(CH$_2$$CH_3$)$_2$], 14.4 [s, N(CH$_2$$CH_3$)$_2$], 30.5 [s, C($CH_3$)$_3$], 38.9 [s, C(CH$_3$)$_3$], 43.1 [s, 6-N(CH$_2CH_3$)$_2$], 49.3 [d, $^3J_{C,P}$ = 4.6 Hz, 7-N(CH$_2$CH$_3$)$_2$], 51.5 (s, CO$_2$$CH_3$), 52.5 (s, CO$_2$$CH_3$), 72.1 (d, $^1J_{C,P}$ = 21.5 Hz, C-5), 121.8 (d, $^1J_{C,P}$ = 22.2 Hz, C-7), 125.1 (s, C-4), 150.1 (d, $^2J_{C,P}$ = 21.5 Hz, C-6), 163.2 (s, 4-CO$_2$Me), 167.6 (d, $^2J_{C,P}$ = 10.0 Hz, 5-CO$_2$Me), 169.9 (s, C-3), 196.2 (d, $^2J_{C,P}$ = 6.9, $^1J_{C,W}$ = 125.8 Hz, CO$_{eq}$), 199.1 (d, $^2J_{C,P}$ = 29.1 Hz, CO$_{ax}$) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 68.7 (s, $^1J_{P,W}$ = 255.1 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2968 (w, C−H), 2074 (vs, C≡O), 1980 (s, C≡O), 1947 (vs, C≡O), 1725 (m, C=O), 1592 (m, C=C), 1433 (w), 1378 (w), 1262 (w). MS (EI, 35 eV): *m*/*z* (%) = 766 (6) [M$^+$], 168 (100) [Et$_2$NCCNEt$_2^+$], 139 (11) [Et$_2$NCCNEt$^+$]. $C_{26}H_{35}N_2O_9PSW$ (766.47): calcd. C 40.74, H 4.60, N 3.66; found C 40.72, H 4.62, N 3.65.

η^1-{3-*tert*-Butyl-6-(diethylamino)-4,5-bis(methoxycarbonyl)-7-methyl-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}pentacarbonyltungsten(0) (5b): This compound was produced from **4b** (47 mg, 0.12 mmol) and hexacarbonyltungsten(0) (47 mg, 0.13 mmol) in THF (20 mL). Yield: 49 mg (58%); bright yellow solid, m.p. 93 °C (dec.). ^{1}H NMR (C_6D_6): δ = 0.98 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.14, $^3J_{H,H}$ = 7.06 Hz, 6-N(CH$_A$H$_B$CH_3)$_2$], 1.28 [s, 9 H, C(CH_3)$_3$], 1.85 (d, 3 H, $^3J_{H,P}$ = 17.1 Hz, 7-CH_3), 2.70 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.21, $^3J_{H,H}$ = 7.14 Hz, 6-N(CH$_A$$H_BCH_3$)$_2$], 3.13 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.21, $^3J_{H,H}$ = 7.06 Hz, 6-N(CH_AH$_B$CH$_3$)$_2$], 3.41 (s, 3 H, 4-CO$_2$CH_3), 3.73 (d, 3 H, $^5J_{H,P}$ = 0.9 Hz, 5-CO$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 12.6 (d, $^2J_{C,P}$ = 9.8 Hz, 7-CH$_3$), 13.4 [s, 6-N(CH$_2$$CH_3$)$_2$], 30.4 [s, C($CH_3$)$_3$], 38.8 [d, $^3J_{C,P}$ = 1.6 Hz, C(CH$_3$)$_3$], 43.6 [s, 6-N(CH$_2$CH$_3$)$_2$], 51.7 (s, CO$_2$$CH_3$), 52.5 (s, CO$_2$$CH_3$), 74.6 (d, $^1J_{C,P}$ = 23.1 Hz, C-5), 106.8 (d, $^1J_{C,P}$ = 34.4 Hz, C-7), 125.3 (s, C-4), 151.8 (d, $^2J_{C,P}$ = 5.1 Hz, C-6), 163.3 (s, 4-CO$_2$Me), 167.9 (d, $^2J_{C,P}$ = 11.0 Hz, 5-CO$_2$Me), 169.4 (d, $^2J_{C,P}$ = 4.7 Hz, C-3), 195.7 (d, $^2J_{C,P}$ = 7.8, $^1J_{C,W}$ = 126.2 Hz, CO$_{eq}$), 199.1 (d, $^2J_{C,P}$ = 29.7 Hz, CO$_{ax}$) ppm. ^{31}P NMR (C_6D_6): δ = 64.4 (q, $^3J_{P,H}$ = 17.1, $^1J_{P,W}$ = 269.9 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2970 (w, C−H), 2076 (s, C≡O), 1979 (s, C≡O), 1951 (vs, C≡O), 1726 (m, C=O), 1591 (m, C=C), 1434 (w), 1276 (w). MS (EI, 35 eV): *m*/*z* (%) = 709 (18) [M$^+$], 570 (19) [M$^+$ − Et$_2$NCCMe − CO], 542 (95) [M$^+$ − Et$_2$NCCMe − 2 CO], 458 (10) [M$^+$ − Et$_2$NCCMe − 5 CO], 111 (100) [Et$_2$NCCNMe$^+$]. $C_{23}H_{28}NO_9PSW$ (709.37): calcd. C 38.94, H 3.98, N 1.98; found C 40.00, H 3.92, N 1.84.

η^1-{3-*tert*-Butyl-6,7-bis(diethylamino)-4,5-bis(trifluoromethyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}pentacarbonyltungsten(0) (5c): This compound was produced from **4d** (71 mg, 0.15 mmol) and hexacarbonyltungsten(0) (59 mg, 0.17 mmol) in THF (20 mL). Yield: 120 mg (100%); bright yellow solid, m.p. 89 °C. ^{1}H NMR (C_6D_6): δ = 0.95 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.13, $^3J_{H,H}$ = 7.05 Hz, 7-N(CH$_A$H$_B$CH_3)$_2$], 1.06 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.12, $^3J_{H,H}$ = 6.69 Hz, 6-N(CH$_A$H$_B$CH_3)$_2$], 1.30 [s, 9 H, C(CH_3)$_3$], 2.62 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.83, $^3J_{H,H}$ = 7.05 Hz, 7-N(CH$_A$$H_BCH_3$)$_2$], 2.86 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.83, $^3J_{H,H}$ = 7.13, $^4J_{H,P}$ = 2.76 Hz, 7-N(CH_AH$_B$CH$_3$)$_2$], 3.32 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.52, $^3J_{H,H}$ = 6.69 Hz, 6-N(CH$_A$$H_BCH_3$)$_2$], 3.37 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.52, $^3J_{H,H}$ = 7.12 Hz, 6-N(CH_AH$_B$CH$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.6 [s, N(CH$_2$$CH_3$)$_2$], 14.3 [s, N(CH$_2$$CH_3$)$_2$], 31.0 [q, $^5J_{C,F}$ = 3.6 Hz, C(CH$_3$)$_3$], 40.5 [s, C(CH$_3$)$_3$], 44.4 [s, 6-N(CH$_2$CH$_3$)$_2$], 47.1 [d, $^3J_{C,P}$ = 5.4 Hz, 7-N(CH$_2$CH$_3$)$_2$], 73.6 (qd, $^2J_{C,F}$ = 31.1, $^1J_{C,P}$ = 26.2 Hz, C-5), 120.2 (q, $^2J_{C,P}$ = 34.9 Hz, C-4), 123.4 (qd, $^1J_{C,F}$ = 274.8, $^2J_{C,P}$ = 8.6 Hz, 5-CF$_3$), 126.0 (q, $^1J_{C,F}$ = 280.4 Hz, 4-CF$_3$), 132.6 (d, $^1J_{C,P}$ = 31.4 Hz, C-7), 138.1 (d, $^2J_{C,P}$ = 17.6 Hz, C-6), 169.9 (m, not resolved, C-3), 196.1 (d, $^2J_{C,P}$ = 6.5, $^1J_{C,W}$ = 127.0 Hz, CO$_{eq}$), 198.4 (d, $^2J_{C,P}$ =

32.1 Hz, *C*O$_{ax}$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 58.4 (q, $^3J_{P,F}$ = 16.1, $^1J_{P,W}$ = 266.6 Hz, P-1) ppm. IR (CCl_4): ṽ = 2973 (w, C−H), 2871 (w, C−H), 2078 (m, C≡O), 1951 (vs, C≡O), 1586 (w), 1273 (w), 1170 (w). MS (EI, 35 eV): *m*/*z* (%) = 786 (14) [M^+], 168 (100) [$Et_2NCCNEt_2^+$]. $C_{24}H_{29}F_6N_2O_5PSW$ (786.40): calcd. C 36.66, H 3.72, N 3.56; found C 37.08, H 3.72, N 3.52.

η^1-{6,7-Bis(diethylamino)-4,5-bis(methoxycarbonyl)-3-(1-methylcyclopentyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}pentacarbonyltungsten(0) (5d): This compound was produced from **4g** (20 mg, 0.04 mmol) and hexacarbonyltungsten(o) (18 mg, 0.05 mmol) in THF (15 mL). Yield: 34 mg (100%); bright yellow solid, m.p. 89 °C. ^1H NMR (C_6D_6): δ = 1.05 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.00, $^3J_{H,H}$ = 6.65 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.21 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.11, $^3J_{H,H}$ = 6.89 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.42 (s, 3 H, Me^{c}Pen-C*H*$_3$), 1.44−1.55 (m, 5 H, Me^{c}Pen-C*H*$_2$), 1.65−1.76 (m, 1 H, Me^{c}Pen-C*H*$_2$), 1.76−1.86 (m, 1 H, Me^{c}Pen-C*H*$_2$), 1.88−1.98 (m, 1 H, Me^{c}Pen-C*H*$_2$), 2.72 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.20, $^3J_{H,H}$ = 6.89 Hz, 7-N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.04 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.20, $^3J_{H,H}$ = 7.11, $^4J_{H,P}$ = 1.66 Hz, 7-N(C*H*$_A$H$_B$CH$_3$)$_2$], 3.22 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.57, $^3J_{H,H}$ = 6.65 Hz, 6-N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.44 (d, 3 H, $^5J_{H,P}$ = 0.8 Hz, 5-CO$_2$C*H*$_3$), 3.74 (s, 3 H, 4-CO$_2$C*H*$_3$), 3.74 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.57, $^3J_{H,H}$ = 7.00 Hz, 6-N(C*H*$_A$H$_B$CH$_3$)$_2$] ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 72.9 (s, $^1J_{P,W}$ = 253.1 Hz, P-1) ppm. IR (CCl_4): ṽ = 2970 (w, C−H), 2075 (m, C≡O), 1980 (m, C≡O), 1949 (vs, C≡O), 1722 (w, C=O), 1595 (w), 1434 (w), 1274 (m).

η^1-{6,7-Bis(diethylamino)-3-(1-methylcyclopentyl)-4,5-bis(trifluoromethyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}pentacarbonyltungsten(0) (5e): This compound was produced from **4i** (89 mg, 0.18 mmol) and hexacarbonyltungsten(o) (71 mg, 0.20 mmol) in THF (15 mL). Yield: 144 mg (97%); bright yellow solid, m.p. 103 °C. ^1H NMR (C_6D_6): δ = 0.96 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.05, $^3J_{H,H}$ = 6.99 Hz, 7-N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.08 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.08, $^3J_{H,H}$ = 6.88 Hz, 6-N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.21 (s, 3 H, Me^{c}Pen-C*H*$_3$), 1.30−1.60 (m, 4 H, Me^{c}Pen-C*H*$_2$), 1.65−1.72 (m, 1 H, Me^{c}Pen-C*H*$_2$), 1.85−2.10 (m, 3 H, Me^{c}Pen-C*H*$_2$), 2.63 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.91, $^3J_{H,H}$ = 7.05 Hz, 7-N(CH$_A$*H*$_B$CH$_3$)$_2$], 2.87 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.91, $^3J_{H,H}$ = 6.99, $^4J_{H,P}$ = 2.96 Hz, 7-N(C*H*$_A$H$_B$CH$_3$)$_2$], 3.34 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.97, $^3J_{H,H}$ = 6.88 Hz, 6-N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.48 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.97, $^3J_{H,H}$ = 7.08 Hz, 6-N(C*H*$_A$H$_B$CH$_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.6 [s, N(CH$_2$*C*H$_3$)$_2$], 14.4 [s, N(CH$_2$*C*H$_3$)$_2$], 22.4 (s, Me^{c}Pen-*C*H$_2$), 23.8 (s, Me^{c}Pen-*C*H$_2$), 25.4 (q, $^5J_{C,F}$ = 2.9 Hz, Me^{c}Pen-*C*H$_3$), 36.9 (q, $^5J_{C,F}$ = 5.6 Hz, Me^{c}Pen-*C*H$_2$), 42.5 (s, Me^{c}Pen-*C*H$_2$), 44.4 [s, 6-N(*C*H$_2$CH$_3$)$_2$], 47.1 [d, $^3J_{C,P}$ = 5.1 Hz, 7-N(*C*H$_2$CH$_3$)$_2$], 51.7 (d, $^3J_{C,P}$ = 5.5 Hz, Me^{c}Pen-*C*$_q$), 73.0 (qd, $^2J_{C,F}$ = 30.1, $^1J_{C,P}$ = 26.1 Hz, C-5), 119.3 (q, $^2J_{C,F}$ = 34.4 Hz, C-4), 123.4 (qd, $^1J_{C,F}$ = 283.9, $^2J_{C,P}$ = 10.2 Hz, 5-*C*F$_3$), 126.1 (q, $^1J_{C,F}$ = 280.4 Hz, 4-*C*F$_3$), 132.8 (d, $^1J_{C,P}$ = 30.5 Hz, C-7), 137.9 (d, $^2J_{C,P}$ = 17.2 Hz, C-6), 170.5 (q, $^3J_{C,F}$ = 3.1 Hz, C-3), 196.2 (d, $^2J_{C,P}$ = 5.3, $^1J_{C,W}$ = 127.0 Hz, *C*O$_{eq}$), 198.4 (d, $^2J_{C,P}$ = 31.3 Hz, *C*O$_{ax}$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 61.2 (q, $^3J_{P,F}$ = 15.3, $^1J_{P,W}$ = 265.5 Hz, P-1) ppm. IR (CCl_4): ṽ = 2970 (w, C−H), 2078 (m, C≡O), 1996 (m, C≡O), 1951 (vs, C≡O), 1275 (w), 1171 (w), 1128 (w). MS (EI, 35 eV): *m*/*z* (%) = 812 (12) [M^+], 488 (12) [M^+ − W(CO)$_5$], 374 (56) [M^+ − W(CO)$_5$ − Me^{c}Pen − P], 168 (100) [$Et_2NCCNEt_2^+$], 139 (13) [$Et_2NCCNEt^+$]. $C_{26}H_{31}F_6N_2O_5PSW$ (812.43): calcd. C 38.44, H 3.85, N 3.45; found C 38.90, H 3.86, N 3.38.

General Procedure for the Synthesis of the Iron Complexes 6: A 1.1-fold excess of nonacarbonyldiiron(o) was added at 0 °C to a magnetically stirred solution of the respective bicyclic compound **4** in 5 mL of THF. The cooling bath was removed, the mixture was allowed to warm to room temperature, and stirring was continued for a further 12 h at 25 °C. All volatile materials were then removed under vacuum and the residue was filtered through silica gel (D3 glass sinter, Ø 3.5 cm, filled to a height of 3 cm) with *n*-pentane/diethyl ether (1:1). After removal of the solvents under vacuum, the corresponding iron complexes **6** were obtained in analytical purity.

η^1-{3-*tert*-Butyl-6,7-bis(diethylamino)-4,5-bis(methoxycarbonyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}tetracarbonyliron(0) (6a): This compound was produced from **4a** (51 mg, 0.12 mmol) and nonacarbonyldiiron(o) (46 mg, 0.13 mmol). Yield: 34 mg (47%); yellowish-brown oil. ^1H NMR (C_6D_6): δ = 1.05 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.07, $^3J_{H,H}$ = 6.72 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.22 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.31, $^3J_{H,H}$ = 6.55 Hz, N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.29 [s, 9 H, C(C*H*$_3$)$_3$], 2.80 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.03, $^3J_{H,H}$ = 7.31 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.14 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.03, $^3J_{H,H}$ = 6.55 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$], 3.16 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.94, $^3J_{H,H}$ = 7.07 Hz, N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.42 (s, 3 H, CO$_2$C*H*$_3$), 3.72 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.94, $^3J_{H,H}$ = 6.72 Hz, N(C*H*$_A$H$_B$CH$_3$)$_2$], 3.77 (s, 3 H, CO$_2$C*H*$_3$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.1 [s, N(CH$_2$*C*H$_3$)$_2$], 14.4 [s, N(CH$_2$*C*H$_3$)$_2$], 30.3 [s, C(*C*H$_3$)$_3$], 38.8 [s, *C*(CH$_3$)$_3$], 42.8 [s, 6-N(*C*H$_2$CH$_3$)$_2$], 49.7 [d, $^3J_{C,P}$ = 3.8 Hz, 7-N(*C*H$_2$CH$_3$)$_2$], 51.6 (s, CO$_2$*C*H$_3$), 52.5 (s, CO$_2$*C*H$_3$), 72.8 (d, $^1J_{C,P}$ = 19.9 Hz, C-5), 122.2 (d, $^1J_{C,P}$ = 23.8 Hz, C-7), 125.2 (s, C-4), 149.3 (d, $^2J_{C,P}$ = 29.9 Hz, C-6), 162.7 (s, 4-*C*O$_2$Me), 167.8 (d, $^2J_{C,P}$ = 11.5 Hz, 5-*C*O$_2$Me), 168.8 (d, $^2J_{C,P}$ = 3.1 Hz, C-3), 212.8 (d, $^2J_{C,P}$ = 18.4 Hz, *C*O) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 133.6 (s, P-1) ppm. IR (CCl_4): ṽ = 2968 (w, C−H), 2054 (vs, C≡O), 1984 (m, C≡O), 1960 (vs, C≡O), 1944 (s, C≡O), 1720 (m, C=O), 1588 (m), 1434 (w), 1360 (w), 1254 (w). MS (EI, 70 eV): *m*/*z* (%) = 610 (7) [M^+], 526 (47) [M^+ − 3CO], 498 (97) [M^+ − 4 CO], 380 (42) [M^+ − PSFe(CO)$_4$], 168 (100) [$Et_2NCCNEt_2^+$ and/or Fe(CO)$_4^+$], 139 (11) [$Et_2NCCNEt^+$], 57 (41) [*t*Bu$^+$]. $C_{25}H_{35}FeN_2O_8PS$ (610.44): calcd. C 49.19, H 5.78, N 4.59; found C 49.15, H 6.03, N 4.68.

η^1-{3-*tert*-Butyl-6-(diethylamino)-4,5-bis(methoxycarbonyl)-7-methyl-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}tetracarbonyliron(0) (6b): This compound was produced from **4b** (39 mg, 0.10 mmol) and nonacarbonyldiiron(o) (41 mg, 0.11 mmol). Yield: 18 mg (33%); light brown solid, m.p. 118 °C (dec.). ^1H NMR (C_6D_6): δ = 0.97 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.06, $^3J_{H,H}$ = 7.01 Hz, 6-N(CH$_A$H$_B$C*H*$_3$)$_2$], 1.27 [s, 9 H, C(C*H*$_3$)$_3$], 1.89 (d, 3 H, $^3J_{H,P}$ = 18.0 Hz, 7-CH$_3$), 2.71 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.99, $^3J_{H,H}$ = 7.06 Hz, 6-N(CH$_A$*H*$_B$CH$_3$)$_2$], 3.11 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.99, $^3J_{H,H}$ = 7.01 Hz, 6-N(C*H*$_A$H$_B$CH$_3$)$_2$], 3.40 (s, 3 H, 4-CO$_2$C*H*$_3$), 3.76 (d, 3 H, $^5J_{H,P}$ = 0.8 Hz, 5-CO$_2$C*H*$_3$) ppm. ^{31}P NMR (C_6D_6): δ = 133.0 (q, $^3J_{P,H}$ = 18.0 Hz, P-1) ppm. IR (CCl_4): ṽ = 2970 (w, C−H), 2056 (s, C≡O), 1986 (m, C≡O), 1960 (vs, C≡O), 1738 (w, C=O), 1725 (w, C=O), 1590 (w, C=C), 1277 (w). MS (EI, 35 eV): *m*/*z* (%) = 553 (1) [M^+], 525 (14) [M^+ − CO], 469 (100) [M^+ − 3 CO], 441 (63) [M^+ − 4 CO]. $C_{22}H_{28}FeNO_8PS$ (553.36): calcd. C 47.75, H 5.10, N 2.53; found C 48.84, H 5.19, N 2.24.

η^1-{3-*tert*-Butyl-4,5-dicyano-6,7-bis(diethylamino)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}tetracarbonyliron(0) (6c): This compound was produced from **4e** (32 mg, 0.09 mmol) and nonacarbon-

yldiiron(o) (35 mg, 0.10 mmol). Yield: 29 mg (62%); dark brown oil. ^{1}H NMR (C_6D_6): δ = 0.95 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.02, $^3J_{H,H}$ = 6.92 Hz, 7-N($CH_AH_BCH_3$)$_2$], 1.02 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.14, $^3J_{H,H}$ = 7.10 Hz, 6-N($CH_AH_BCH_3$)$_2$], 1.19 [s, 9 H, C(CH_3)$_3$], 2.92 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 12.34, $^3J_{H,H}$ = 6.92, $^4J_{H,P}$ = 2.54 Hz, 7-N($CH_AH_BCH_3$)$_2$], 2.94 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 12.34, $^3J_{H,H}$ = 7.02, $^4J_{H,P}$ = 1.74 Hz, 7-N($CH_AH_BCH_3$)$_2$], 3.00 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.21, $^3J_{H,H}$ = 7.14 Hz, 6-N($CH_AH_BCH_3$)$_2$], 3.77 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 14.21, $^3J_{H,H}$ = 7.10 Hz, 6-N($CH_AH_BCH_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.5 [s, 6-N(CH_2CH_3)$_2$], 14.0 [d, $^4J_{C,P}$ = 1.5 Hz, 7-N(CH_2CH_3)$_2$], 29.6 [s, C(CH_3)$_3$], 39.4 [s, C(CH_3)$_3$], 43.8 [s, 6-N(CH_2CH_3)$_2$], 49.3 [d, $^3J_{C,P}$ = 3.8 Hz, 7-N(CH_2CH_3)$_2$], 55.8 (d, $^1J_{C,P}$ = 26.8 Hz, C-5), 101.7 (d, $^2J_{C,P}$ = 3.1 Hz, C-4), 114.8 (d, $J_{C,P}$ = 3.1 Hz, CN), 115.7 (br. s, CN), 125.1 (d, $^1J_{C,P}$ = 24.5 Hz, C-7), 147.1 (d, $^2J_{C,P}$ = 29.9 Hz, C-6), 178.9 (d, $^2J_{C,P}$ = 4.6 Hz, C-3), 211.7 (d, $^2J_{C,P}$ = 18.4 Hz, CO) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 144.9 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2974 (w, C−H), 2206 (w, C≡N), 2061 (vs, C≡O), 1996 (m, C≡O), 1966 (vs, C≡O), 1951 (s, C≡O), 1598 (w, C=C), 1468 (w), 1382 (w), 1119 (w). MS (EI, 35 eV): *m/z* (%) = 544 (6) [M^+], 460 (17) [M^+ − 3 CO], 432 (98) [M^+ − 4 CO], 168 (17) [$Et_2NCCNEt_2^+$ and/or $Fe(CO)_4^+$], 69 (44) [CtBu$^+$], 57 (100) [tBu$^+$]. $C_{23}H_{29}FeN_4O_4PS$ (544.39): calcd. C 50.74, H 5.37, N 10.29; found C 49.23, H 5.53, N 9.88.

η^1-{3-*tert*-Butyl-6,7-bis(diethylamino)-4,5-bis(trifluoromethyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}tetracarbonyliron(0) (6d): This compound was produced from **4d** (72 mg, 0.16 mmol) and nonacarbonyldiiron(o) (63 mg, 0.17 mmol). Yield: 93 mg (95%); bright yellow oil. ^{1}H NMR (C_6D_6): δ = 0.94 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.17, $^3J_{H,H}$ = 7.04 Hz, 7-N($CH_AH_BCH_3$)$_2$], 1.06 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.09, $^3J_{H,H}$ = 7.07 Hz, 6-N($CH_AH_BCH_3$)$_2$], 1.27 [s, 9 H, C(CH_3)$_3$], 2.60 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.65, $^3J_{H,H}$ = 7.04 Hz, 7-N($CH_AH_BCH_3$)$_2$], 2.95 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.65, $^3J_{H,H}$ = 7.17, $^4J_{H,P}$ = 2.69 Hz, 7-N($CH_AH_BCH_3$)$_2$], 3.26 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.71, $^3J_{H,H}$ = 7.09, $^5J_{H,P}$ = 1.40 Hz, 6-N($CH_AH_BCH_3$)$_2$], 3.37 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.71, $^3J_{H,H}$ = 7.07 Hz, 6-N($CH_AH_BCH_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.5 [s, 6-N(CH_2CH_3)$_2$], 14.4 [d, $^4J_{C,P}$ = 2.3 Hz, 7-N(CH_2CH_3)$_2$], 31.1 [q, $^5J_{C,F}$ = 3.6 Hz, C(CH_3)$_3$], 40.6 [s, C(CH_3)$_3$], 44.2 [s, 6-N(CH_2CH_3)$_2$], 47.7 [d, $^3J_{C,P}$ = 3.8 Hz, 7-N(CH_2CH_3)$_2$], 73.9 (qd, $^2J_{C,F}$ = 31.5, $^1J_{C,P}$ = 24.9 Hz, C-5), 120.8 (q, $^2J_{C,F}$ = 34.4 Hz, C-4), 123.4 (qd, $^1J_{C,F}$ = 275.2, $^2J_{C,P}$ = 9.8 Hz, 5-CF_3), 125.8 (q, $^1J_{C,F}$ = 280.7 Hz, 4-CF_3), 131.0 (d, $^1J_{C,P}$ = 31.4 Hz, C-7), 140.6 (d, $^2J_{C,P}$ = 23.7 Hz, C-6), 169.7 (qd, $^3J_{C,F}$ = 3.7, $^2J_{C,P}$ = 3.6 Hz, C-3), 212.8 (d, $^2J_{C,P}$ = 16.1 Hz, CO) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 119.8 (q, $^3J_{P,F}$ = 11.1 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2974 (w, C−H), 2871 (w, C−H), 2059 (m, C≡O), 1991 (m, C≡O), 1965 (vs, C≡O), 1947 (s, C≡O), 1580 (w), 1273 (w, C−F), 1176 (w), 1154 (w). MS (EI, 35 eV): *m/z* (%) = 630 (6) [M^+], 546 (20) [M^+ − 3 CO], 518 (70) [M^+ − 4 CO], 462 (5) [M − $Et_2NCCNEt_2^+$ and/or M − $Fe(CO)_4^+$], 243 (100), 168 (100) [$Et_2NCCNEt_2^+$ and/or $Fe(CO)_4^+$], 57 (10) [tBu$^+$]. $C_{23}H_{29}F_6FeN_2O_4PS$ (630.39): calcd. C 43.82, H 4.64, N 4.44; found C 44.18, H 4.80, N 4.54.

η^1-{6,7-Bis(diethylamino)-4,5-bis(methoxycarbonyl)-3-(1-methylcyclopentyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}tetracarbonyliron(0) (6e): This compound was produced from **4g** (15 mg, 0.03 mmol) and nonacarbonyldiiron(o) (15 mg, 0.04 mmol). Yield: 3 mg (15%); brown oil. ^{1}H NMR (C_6D_6): δ = 1.05 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 6.98, $^3J_{H,H}$ = 6.85 Hz, 6-N($CH_AH_BCH_3$)$_2$], 1.24 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.23, $^3J_{H,H}$ = 7.02 Hz, 7-N($CH_AH_BCH_3$)$_2$], 1.40 (s, 3 H, Me^{c}Pen-CH_3), 1.40−1.55 (m, 3 H, Me^{c}Pen-CH_2), 1.60−1.85 (m, 4 H, Me^{c}Pen-CH_2), 1.90−2.00 (m, 1 H, Me^{c}Pen-CH_2), 2.79 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 14.00, $^3J_{H,H}$ = 7.02 Hz, 7-N($CH_AH_BCH_3$)$_2$], 3.15 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.80, $^3J_{H,H}$ = 6.85 Hz, 6-N($CH_AH_BCH_3$)$_2$], 3.18 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 14.00, $^3J_{H,H}$ = 7.23, $^4J_{H,P}$ = 2.00 Hz, 7-N($CH_AH_BCH_3$)$_2$], 3.40 (s, 3 H, CO_2CH_3), 3.80 (s, 3 H, CO_2CH_3), 3.81 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.80, $^3J_{H,H}$ = 6.98 Hz, 6-N($CH_AH_BCH_3$)$_2$] ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 136.8 (s, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2969 (w, C−H), 2055 (s, C≡O), 1985 (m, C≡O), 1960 (vs, C≡O), 1946 (s, C≡O), 1723 (w, C=O).

η^1-{6,7-Bis(diethylamino)-3-(1-methylcyclopentyl)-4,5-bis(trifluoromethyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}tetracarbonyliron(0) (6f): This compound was produced from **4i** (80 mg, 0.16 mmol) and nonacarbonyldiiron(o) (66 mg, 0.18 mmol). Yield: 95 mg (88%); brown oil. ^{1}H NMR (C_6D_6): δ = 0.95 [M part of an ABM_3X spin system, 6 H, $^3J_{H,H}$ = 7.06, $^3J_{H,H}$ = 6.95 Hz, 7-N($CH_AH_BCH_3$)$_2$], 1.10 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.5, $^3J_{H,H}$ = 6.87 Hz, 6-N($CH_AH_BCH_3$)$_2$], 1.19 (s, 3 H, Me^{c}Pen-CH_3), 1.30−1.56 (m, 4 H, Me^{c}Pen-CH_2), 1.60−1.70 (m, 1 H, Me^{c}Pen-CH_2), 1.80−2.08 (m, 3 H, Me^{c}Pen-CH_2), 2.60 [B part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.91, $^3J_{H,H}$ = 7.06 Hz, 7-N($CH_AH_BCH_3$)$_2$], 2.96 [A part of an ABM_3X spin system, 2 H, $^2J_{H,H}$ = 13.91, $^3J_{H,H}$ = 6.95, $^4J_{H,P}$ = 2.56 Hz, 7-N($CH_AH_BCH_3$)$_2$], 3.27 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.73, $^3J_{H,H}$ = 6.87 Hz, 6-N($CH_AH_BCH_3$)$_2$], 3.59 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.73, $^3J_{H,H}$ = 7.05 Hz, 6-N($CH_AH_BCH_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 13.5 [s, 6-N(CH_2CH_3)$_2$], 14.4 [d, $^4J_{C,P}$ = 1.2 Hz, 7-N(CH_2CH_3)$_2$], 22.1 (s, Me^{c}Pen-CH_2), 23.6 (s, Me^{c}Pen-CH_2), 25.3 (d, $^4J_{C,P}$ = 2.3 Hz, Me^{c}Pen-CH_3), 36.8 (m, not resolved, Me^{c}Pen-CH_2), 42.4 (s, Me^{c}Pen-CH_2), 44.2 [s, 6-N(CH_2CH_3)$_2$], 47.7 [d, $^3J_{C,P}$ = 3.9 Hz, 7-N(CH_2CH_3)$_2$], 51.7 (s, Me^{c}Pen-C_q), 73.4 (m, not resolved, C-5), 120.0 (q, $^2J_{C,F}$ = 34.8 Hz, C-4), 123.4 (qd, $^1J_{C,F}$ = 275.0, $^2J_{C,P}$ = 9.5 Hz, 5-CF_3), 125.8 (q, $^1J_{C,F}$ = 280.3 Hz, 4-CF_3), 131.3 (d, $^1J_{C,P}$ = 31.7 Hz, C-7), 140.4 (m, not resolved, C-6), 169.9 (m, not resolved, C-3), 212.8 (d, $^2J_{C,P}$ = 18.0 Hz, CO) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 122.9 (q, $^3J_{P,F}$ = 10.6 Hz, P-1) ppm. IR (CCl_4): $\tilde{\nu}$ = 2970 (w, C−H), 2059 (s, C≡O), 1991 (m, C≡O), 1965 (vs, C≡O), 1947 (s, C≡O), 1275 (w), 1177 (w). MS (EI, 35 eV): *m/z* (%) = 656 (9) [M^+], 572 (13) [M^+ − 3 CO], 544 (50) [M^+ − 4 CO], 488 (5) [M^+ − $Fe(CO)_4$ and/or M^+ − $Et_2NCCNEt_2$], 438 (100) [M^+ − $Fe(CO)_4$ − PF], 409 (35) [M^+ − $Fe(CO)_4$ − PF − Et], 354 (65) [M^+ − $Fe(CO)_4$ − PF − HMe^{c}Pen], 168 (81) [$Fe(CO)_4^+$ and/or $Et_2NCCNEt_2^+$]. $C_{25}H_{31}F_6FeN_2O_4PS$ (656.42): calcd. C 45.74, H 4.76, N 4.27; found C 46.59, H 4.94, N 4.34.

η^1-{4,5-Dicyano-6,7-bis(diethylamino)-3-(1-methylcyclohexyl)-2-thia-1-phosphabicyclo[3.2.0]hepta-3,6-diene}tetracarbonyliron(0) (6g): This compound was produced from **4j** (83 mg, 0.20 mmol) and nonacarbonyldiiron(o) (80 mg, 0.22 mmol). Yield: 68 mg (59%); orange-brown oil. ^{1}H NMR (C_6D_6): δ = 0.96 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.00, $^3J_{H,H}$ = 6.96 Hz, N($CH_AH_BCH_3$)$_2$], 1.05 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.12, $^3J_{H,H}$ = 7.12 Hz, N($CH_AH_BCH_3$)$_2$], 1.22 (s, 3 H, Me^{c}Hex-CH_3), 1.23−1.46 (m, 8 H, Me^{c}Hex-CH_2), 1.92−2.04 (m, 1 H, Me^{c}Hex-CH_2), 2.16−2.32 (m, 1 H, Me^{c}Hex-CH_2), 2.95 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.43, $^3J_{H,H}$ = 6.96 Hz,

N($CH_AH_BCH_3$)$_2$], 2.96 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 12.85, $^3J_{H,H}$ = 7.12 Hz, N($CH_AH_BCH_3$)$_2$], 3.00 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.43, $^3J_{H,H}$ = 7.00 Hz, N($CH_AH_BCH_3$)$_2$], 3.80 [A part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 12.85, $^3J_{H,H}$ = 7.12 Hz, N($CH_AH_BCH_3$)$_2$] ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 13.6 [s, 6-N(CH_2CH_3)$_2$], 14.1 [d, $^4J_{C,P}$ = 1.5 Hz, 7-N(CH_2CH_3)$_2$], 23.1 (s, Me^{c}Hex-CH_2), 23.1 (s, Me^{c}Hex-CH_2), 25.5 (s, Me^{c}Hex-CH_2), 27.3 (s, Me^{c}Hex-CH_3), 37.6 (s, Me^{c}Hex-CH_2), 37.9 (s, Me^{c}Hex-CH_2), 43.8 [s, 6-N(CH_2CH_3)$_2$], 43.9 (d, Me^{c}Hex-C_q), 49.4 [d, $^3J_{C,P}$ = 3.1 Hz, 7-N(CH_2CH_3)$_2$], 56.1 (d, $^1J_{C,P}$ = 26.8 Hz, C-5), 101.5 (d, $^2J_{C,P}$ = 3.8 Hz, C-4), 114.9 (d, $^3J_{C,P}$ = 3.1 Hz, 4-CN), 115.8 (d, $^2J_{C,P}$ = 9.2 Hz, 5-CN), 125.7 (d, $^1J_{C,P}$ = 23.7 Hz, C-7), 147.3 (d, $^2J_{C,P}$ = 29.8 Hz, C-6), 179.1 (d, $^2J_{C,P}$ = 3.8 Hz, C-3), 211.7 (d, $^1J_{C,P}$ = 19.1 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 145.1 (s, P-1) ppm. $C_{26}H_{33}FeN_4O_4PS$ (584.47): calcd. C 53.43, H 5.69, N 9.59; found C 52.05, H 6.17, N 9.39.

Treatment of 4a with Mesitylenecarbonitrile Oxide: Mesitylenecarbonitrile oxide (**7**, 39 mg, 0.24 mmol) was added at −78 °C to a solution of the bicyclic compound **4a** (99 mg, 0.22 mmol) in toluene (5 mL). After removal of the cooling bath and allowing the mixture to warm to room temperature, stirring at 25 °C was continued for a further 12 h. Volatile materials were then removed under vacuum and the residue was separated by column chromatography on silica gel, eluting with *n*-pentane/diethyl ether (1:1). The [3+2] cycloadduct **8** was obtained in analytical purity as a colorless fraction with R_f = 0.76.

Dimethyl *trans*-6-*tert*-Butyl-3a,7b-bis(diethylamino)-3-mesityl-7a,7b-dihydro-3a*H*-[1,2]thiaphospholo[2′,3′:1,4]phospheto[2,3-*d*]-isoxazole-7,7a-dicarboxylate (8): Yield: 107 mg (81%); colorless solid, m.p. 89 °C (dec.). ^1H NMR (C_6D_6): δ = 1.06 [X part of an ABX_3 spin system, 6 H, $^3J_{H,H}$ = 7.00, $^3J_{H,H}$ = 7.20 Hz, 7b-N($CH_AH_BCH_3$)$_2$], 1.36 [pt, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.1 Hz, 6 H, 3a-N($CH_AH_BCH_3$)$_2$], 1.41 [d, $^5J_{H,P}$ = 0.6 Hz, 9 H, C(CH_3)$_3$], 2.12 (d, $^4J_{H,H}$ = 1.7 Hz, 3 H, Mes-CH_3), 2.65 (d, $^4J_{H,H}$ = 1.7 Hz, 3 H, Mes-CH_3), 2.68 (d, $^4J_{H,H}$ = 1.7 Hz, 3 H, Mes-CH_3), 2.78 (d, $^5J_{H,P}$ = 0.7 Hz, 3 H, 7a-CO_2CH_3), 2.93 [B part of an ABX_3 spin system, 2 H, $^2J_{H,H}$ = 13.50, $^3J_{H,H}$ = 7.00 Hz, 7b-N($CH_AH_BCH_3$)$_2$], 3.19−3.29 [m, 2 H, N(CH_2CH_3)$_2$], 3.30−3.38 [m, 2 H, N(CH_2CH_3)$_2$], 3.37 (s, 3 H, 7-CO_2CH_3), 3.85−4.05 [m, 2 H, N(CH_2CH_3)$_2$], 6.72−6.74 (m, 1 H, Mes-CH), 6.80−6.82 (m, 1 H, Mes-CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 12.8 [s, 7b-N(CH_2CH_3)$_2$], 14.3 [d, $^4J_{C,P}$ = 2.3 Hz, 3a-N(CH_2CH_3)$_2$], 21.2 (s, Mes-CH_3), 21.4 (s, Mes-CH_3), 21.4 (s, Mes-CH_3), 30.4 [s, C(CH_3)$_3$], 38.5 [d, $^3J_{C,P}$ = 4.3 Hz, C(CH_3)$_3$], 43.1 [br. s, 3a-N(CH_2CH_3)$_2$], 49.6 [d, $^3J_{C,P}$ = 2.3 Hz, 7b-N(CH_2CH_3)$_2$], 51.2 (s, CO_2CH_3), 51.4 (s, CO_2CH_3), 66.1 (s, C-7a), 74.3 (d, $^2J_{C,P}$ = 2.7 Hz, C-7b), 107.3 (d, $^1J_{C,P}$ = 88.4 Hz, C-3a), 121.1 (d, $^2J_{C,P}$ = 4.2 Hz, C-7), 128.5 (s, Mes-CH), 128.5 (s, Mes-CH), 138.7 (d, $J_{C,P}$ = 2.3 Hz, Mes-CCH_3), 139.0 (d, $J_{C,P}$ = 4.6 Hz, Mes-CCH_3), 139.2 (d, $J_{C,P}$ = 3.1 Hz, Mes-CCH_3), 142.0 (s, Mes-*i*-C), 157.1 (s, 7-CO_2Me), 157.9 (d, $^2J_{C,P}$ = 54.6 Hz, C-3), 169.9 (d, $^2J_{C,P}$ = 8.4 Hz, 7a-CO_2Me), 171.5 (d, $^2J_{C,P}$ = 3.1 Hz, C-6) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = −46.5 (s, P-1) ppm. IR (CCl_4): ṽ = 2970 (m, C−H), 1722 (vs, C=O), 1583 (m), 1256 (m). $C_{31}H_{46}N_3O_5PS$ (603.77): calcd. C 61.67, H 7.68, N 6.96; found C 61.60, H 7.60, N 6.86.

General Procedure for the Synthesis of the Phosphabarrelenes 10 and the Tricyclic Compounds 11: A solution of the respective 1,2-thiaphosphole **1** and 2 equiv. of cyclooctyne (**9**) in toluene was heated at 100 °C for 20 h in a pressure tube. After cooling to room temperature and removal of volatile materials under vacuum, the residue was worked up by column chromatography on silica gel. Elution with *n*-pentane/diethyl ether (1:1) gave as the first, pale yellow fraction a mixture containing the barrelenes **10**, from which only the tetracyclic product **10a** could be isolated in pure form (in the case of the reaction with **1a**), and a second, colorless fraction containing the respective tricyclic product **11**. Both fractions were further purified by recrystallization from *n*-pentane/diethyl ether (3:1) at −20 °C. The following compounds were obtained starting from 1,2-thiaphosphole **1a** (214 mg, 0.78 mmol), cyclooctyne (195 μL, 169 mg, 1.56 mmol), and toluene (10 mL).

Dimethyl 10-*tert*-Butyl-1-phosphatetracyclo[8.8.2.0^{2,9}.0^{11,18}]eicosa-2(9),11(18),19-triene-19,20-dicarboxylate 1-Sulfide (10a): Yield: 131 mg (34%); bright yellow crystals, m.p. 170 °C. ^1H NMR (C_6D_6): δ = 1.22−1.54 (m, 10 H, CH_2), 1.59 [s, 3 H, C(CH_3)$_2$CH_3], 1.59−1.66 (m, 2 H, CH_2), 1.74 [s, 6 H, C(CH_3)$_2$CH_3], 1.86−1.95 (m, 2 H, CH_2), 2.01−2.12 (m, 2 H, CH_2), 2.58−2.68 (m, 4 H, CH_2), 2.68−2.90 (m, 4 H, CH_2), 3.43 (s, 3 H, CO_2CH_3), 3.54 (s, 3 H, CO_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 27.3 (d, $J_{C,P}$ = 10.0 Hz, CH_2), 27.6 (d, $J_{C,P}$ = 11.5 Hz, CH_2), 29.9 (s, CH_2), 32.1 (s, CH_2), 32.2 (s, CH_2), 32.5 (d, $^2J_{C,P}$ = 2.3 Hz, CH_2), 35.5 [s, C(CH_3)$_2$CH$_3$], 35.8 [s, C(CH_3)$_2$CH$_3$], 36.0 [s, C(CH_3)$_2$CH$_3$], 52.3 (s, CO_2CH_3), 52.5 (s, CO_2CH_3), 75.1 (d, $^3J_{C,P}$ = 29.1 Hz, C-10), 142.3 (d, $^1J_{C,P}$ = 64.4 Hz, C-2 and C-18), 145.0 (d, $^1J_{C,P}$ = 53.7 Hz, C-19), 160.6 (d, $^3J_{C,P}$ = 2.3 Hz, 20-CO_2Me), 160.9 (d, $^2J_{C,P}$ = 1.5 Hz, C-9 and C-11), 164.3 (d, $^2J_{C,P}$ = 8.4 Hz, C-20), 168.5 (d, $^2J_{C,P}$ = 14.6 Hz, 19-CO_2Me) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 13.5 (s, P-1) ppm. IR (CCl_4): ṽ = 2927 (m, C−H), 1741 (vs, C=O), 1727 (vs, C=O), 1610 (m, C=C), 1431 (m), 1261 (m), 1097 (w). MS (EI, 70 eV): *m*/*z* (%) = 490 (10) [M$^+$], 475 (7) [M$^+$ − Me], 458 (12) [M$^+$ − S], 433 (70) [M$^+$ − *t*Bu], 402 (35) [M$^+$ − P*t*Bu], 373 (28) [M$^+$ − 2 CO_2CH_3], 69 (34) [C*t*Bu$^+$], 57 (100) [*t*Bu$^+$]. $C_{27}H_{39}O_4PS$ (490.64): calcd. C 66.10, H 8.01; found C 65.62, H 7.86.

Methyl 2-*tert*-Butyl-4-methoxy-6,7,8,9,10,11-hexahydrocycloocta[*b*]-[1,2]thiaphospholo[2,3-*d*][1,4]oxaphosphinine-3-carboxylate 12-Sulfide (11a): Yield: 103 mg (64%); colorless crystals, m.p. 137 °C (dec.). ^1H NMR (C_6D_6): δ = 1.25−1.38 (m, 3 H, CH_2), 1.40−1.50 (m, 2 H, CH_2), 1.46 [d, 9 H, $^5J_{H,P}$ = 0.4 Hz, C(CH_3)$_3$], 1.50−1.63 (m, 1 H, CH_2), 1.75−1.85 (m, 1 H, CH_2), 1.90−1.98 (m, 1 H, CH_2), 2.04−2.24 (m, 2 H, CH_2), 2.41−2.55 (m, 1 H, CH_2), 2.62−2.75 (m, 1 H, CH_2), 3.11 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 26.0 (s, CH_2), 26.5 (s, CH_2), 28.1 (d, $J_{C,P}$ = 7.7 Hz, CH_2), 28.8 (d, $J_{C,P}$ = 1.5 Hz, CH_2), 29.7 (d, $J_{C,P}$ = 8.4 Hz, CH_2), 31.2 [s, C(CH_3)$_3$], 31.8 (s, CH_2), 38.0 [d, $^3J_{C,P}$ = 2.3 Hz, C(CH_3)$_3$], 52.0 (s, OCH_3), 55.8 (s, OCH_3), 94.2 (d, $^1J_{C,P}$ = 83.6 Hz, C-3a), 110.5 (d, $^1J_{C,P}$ = 82.0 Hz, C-11a), 118.9 (d, $^2J_{C,P}$ = 13.0 Hz, C-3), 146.0 (s, CO_2Me), 156.3 (d, $^2J_{C,P}$ = 1.5 Hz, C-5a or C-4), 158.3 (d, $^2J_{C,P}$ = 14.6 Hz, C-4 or C-5a), 167.7 (d, $^2J_{C,P}$ = 12.3 Hz, C-2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 47.0 (s, P-12) ppm. IR (CCl_4): ṽ = 2928 (m, C−H), 1728 (m, C=O), 1644 (vs, C=C), 1462 (w), 1270 (m). MS (EI, 70 eV): *m*/*z* (%) = 414 (26) [M$^+$], 399 (6) [M$^+$ − Me], 371 (6) [M$^+$ − COMe], 351 (9) [M$^+$ − PS], 274 (38) [M$^+$ − S − C_8H_{12}], 259 (19) [M$^+$ − S − C_8H_{12} − Me], 243 (28) [M$^+$ − S − C_8H_{12} − P], 227 (100) [M$^+$ − 2 S − C_8H_{12} − Me]. $C_{19}H_{27}O_4PS_2$ (414.52): calcd. C 55.05, H 6.57; found C 54.34, H 6.52.

Methyl 2-(1,1-Dimethylpropyl)-4-methoxy-6,7,8,9,10,11-hexahydrocycloocta[*b*][1,2]thiaphospholo[2,3-*d*][1,4]oxaphosphinine-3-carboxylate 12-Sulfide (11b): This compound was produced from 1,2-thiaphosphole **1d** (47 mg, 0.16 mmol) and cyclooctyne (41 μL, 35 mg, 0.33 mmol) in toluene (5 mL). Yield: 8 mg (26%); colorless solid. ^1H NMR (C_6D_6): δ = 1.15 [pt, 3 H, $^3J_{H,H}$ = $^3J_{H,H}$ = 7.4 Hz, C(CH_3)$_A$(CH_3)$_B$ $CH_AH_BCH_3$], 1.25−1.35 (m, 2 H, CH_2), 1.37 [s, 3 H, C(CH_3)$_A$(CH_3)$_B$$CH_AH_BCH_3$], 1.38−1.60 (m, 3 H, CH_2), 1.51 [s, 3 H, C(CH_3)$_A$(CH_3)$_B$$CH_AH_BCH_3$], 1.64−1.69 (m, 1 H, CH_2),

1.75−1.82 (m, 1 H, CH_2), 1.87−1.94 (m, 2 H, CH_2), 2.04−2.18 (m, 3 H, CH_2), 2.42−2.53 (m, 1 H, CH_2), 2.61−2.69 (m, 1 H, CH_2), 3.09 (s, 3 H, OCH_3), 3.65 (s, 3 H, OCH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 47.0 (s, P-12) ppm. IR (CCl_4): $\tilde{\nu}$ = 2933 (m, C−H), 1729 (s, C=O), 1642 (vs, C=C), 1462 (w), 1271 (m), 1193 (m), 932 (w).

Methyl 4-Methoxy-2-(1-methylcyclopentyl)-6,7,8,9,10,11-hexahydrocycloocta[*b*][1,2]thiaphospholo[2,3-*d*][1,4]oxaphosphinine-3-carboxylate 12-Sulfide (11c): This compound was produced from 1,2-thiaphosphole **1e** (36 mg, 0.12 mmol) and cyclooctyne (30 μL, 26 mg, 0.24 mmol) in toluene (5 mL). Yield: 20 mg (76%); colorless solid. ^1H NMR (C_6D_6): δ = 1.25−1.45 (m, 7 H, CH_2), 1.46 (s, 3 H, Me^{c}Pen-CH_3), 1.48−1.70 (m, 3 H, CH_2), 1.75−2.35 (m, 8 H, CH_2), 2.41−2.55 (m, 1 H, CH_2), 2.65−2.75 (m, 1 H, CH_2), 3.08 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 48.0 (s, P-12) ppm. IR (CCl_4): $\tilde{\nu}$ = 2949 (w, C−H), 1728 (s, C=O), 1643 (vs, C=C), 1273 (m). MS (EI, 35 eV): *m/z* (%) = 440 (100) [M^+], 425 (21) [M^+ − Me], 408 (10) [M^+ − S], 381 (10) [M^+ − CO_2Me], 377 (24) [M^+ − PS], 300 (25) [M^+ − S − C_8H_{12}], 285 (20) [M^+ − S − C_8H_{12} − Me], 269 (35) [M^+ − S − C_8H_{12} − P], 268 (31) [M^+ − 2 S − C_8H_{12}]. $C_{21}H_{29}O_4PS_2$ (440.55): calcd. C 57.25, H 6.64; found C 57.28, H 6.88.

Methyl 4-Methoxy-2-(1-methylcyclohexyl)-6,7,8,9,10,11-hexahydrocycloocta[*b*][1,2]thiaphospholo[2,3-*d*][1,4]oxaphosphinine-3-carboxylate 12-Sulfide (11d): This compound was produced from 1,2-thiaphosphole **1i** (133 mg, 0.42 mmol) and cyclooctyne (105 μL, 92 mg, 0.85 mmol) in toluene (5 mL). Yield: 31 mg (32%); colorless solid, m.p. 167 °C (dec.). ^1H NMR (C_6D_6): δ = 1.25−1.40 (m, 4 H, CH_2), 1.40−1.49 (m, 2 H, CH_2), 1.50 (s, 3 H, Me^{c}Hex-CH_3), 1.50−1.66 (m, 6 H, CH_2), 1.75−1.85 (m, 2 H, CH_2), 1.88−2.05 (m, 1 H, CH_2), 2.05−2.25 (m, 4 H, CH_2), 2.30−2.40 (m, 1 H, CH_2), 2.45−2.55 (m, 1 H, CH_2), 2.60−2.75 (m, 1 H, CH_2), 3.09 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.5 (s, *C*H$_2$), 26.0 (s, *C*H$_2$), 26.2 (s, *C*H$_2$), 26.5 (s, *C*H$_2$), 28.1 (d, $J_{C,P}$ = 7.3 Hz, *C*H$_2$), 28.5 (s, Me^{c}Hex-*C*H$_3$), 29.7 (d, $J_{C,P}$ = 8.1 Hz, *C*H$_2$), 31.8 (s, *C*H$_2$), 38.0 (s, *C*H$_2$), 41.9 (s, *C*H$_2$), 42.0 (s, Me^{c}Hex-C_q), 52.0 (s, O*C*H$_3$), 55.8 (s, O*C*H$_3$), 94.3 (d, $^1J_{C,P}$ = 83.4 Hz, C-3a), 110.4 (d, $^1J_{C,P}$ = 81.8 Hz, C-11a), 119.7 (d, $^2J_{C,P}$ = 13.0 Hz, C-3), 145.1 (s, *C*O$_2$Me), 156.4 (s, C-5a or C-4), 158.1 (d, $^2J_{C,P}$ = 13.8 Hz, C-4 or C-5a), 167.9 (d, $^2J_{C,P}$ = 11.5 Hz, C-2) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 46.9 (s, P-12) ppm. IR (CCl_4): $\tilde{\nu}$ = 2933 (m, C−H), 1727 (s, C=O), 1643 (vs, C=C), 1272 (s). MS (EI, 70 eV): *m/z* (%) = 454 (27) [M^+], 314 (32) [M^+ − S − C_8H_{12}], 283 (39) [M^+ − PS − C_8H_{12}], 127 (100) [$MeO_2CCCCO_2^+$]. $C_{22}H_{31}O_4PS_2$ (454.58): calcd. C 58.13, H 6.87; found C 57.85, H 6.70.

Diffraction Measurements: STOE Imaging Plate Diffraction System, graphite monochromator, Mo-K_α radiation (λ = 0.71073 Å), cell determination and refinement by STOE programs Ver. 2.75, structure solution by direct methods (SHELXS-86[26]) and structure refinement by SHELXL-93,[27] hydrogen atoms were included in the refinement using riding models. CCDC-199607 (**4a**), -199608 (**10a**) and -199609 (**11a**) 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 4a: $C_{21}H_{35}N_2O_4PS$; *M* = 442.54 g·mol^{-1}; triclinic; space group $P\bar{1}$ (no. 2); lattice constants *a* = 8.992(2), *b* = 10.563(2), *c* = 13.393(3) Å, α = 91.42(3), β = 95.51(3), γ = 101.43(3)°, *V* = 1239.8(4) Å^3; *Z* = 2; $D_{calcd.}$ = 1.185 Mg/m^3; μ = 0.222 mm^{-1}; *T* = 293(2) K; crystal size 0.40 × 0.40 × 0.10 mm; 1.97° ≤ Θ ≤ 26.07°; 10814 reflections collected, 4532 independent reflections ($R_{int.}$ = 0.0587); 262 parameters; w^{-1} = [$\sigma^2(F_o^2)$ + (0.0558*P*)^2 + 0.25*P*], *P* = [(F_o^2) + 2F_c^2]/3; R^1 = 0.0554, wR^2 = 0.1435 [$I > 2\sigma(I)$]; R^1 = 0.0769, wR^2 = 0.1507 (all data); residual electron density 1.082 and −0.456 e/Å^3, *S* = *GOF* (on F^2) = 1.250.

Crystal Structure Analysis of 10a: $C_{27}H_{39}O_4PS$; *M* = 490.61 g·mol^{-1}; monoclinic; space group $P2_1/c$ (no. 14); lattice constants *a* = 10.044(2), *b* = 26.927(5), *c* = 10.026(2) Å, β = 108.23(3)°, *V* = 2575.5(9) Å^3; *Z* = 4; $D_{calcd.}$ = 1.265 Mg/m^3; μ = 0.218 mm^{-1}; *T* = 293(2) K; crystal size 0.50 × 0.30 × 0.30 mm; 2.13° ≤ Θ ≤ 24.99°; 18463 reflections collected, 4378 independent reflections ($R_{int.}$ = 0.0806); 298 parameters; w^{-1} = [$\sigma^2(F_o^2)$ + (0.1200*P*)^2 + 1.20*P*], *P* = [(F_o^2) + 2F_c^2]/3; R^1 = 0.0682, wR^2 = 0.1826 [$I > 2\sigma(I)$]; R^1 = 0.0861, wR^2 = 0.1957 (all data); residual electron density 0.708 and −0.372 e/Å^3, *S* = *GOF* (on F^2) = 1.035.

Crystal Structure Analysis of 11a: $C_{19}H_{27}O_4PS_2$; *M* = 414.50 g·mol^{-1}; monoclinic; space group $P2_1/c$ (no. 14); lattice constants *a* = 14.529(3), *b* = 18.731(4), *c* = 8.163(2) Å, β = 105.88(3)°, *V* = 2136.5(7) Å^3; *Z* = 4; $D_{calcd.}$ = 1.289 Mg/m^3; μ = 0.344 mm^{-1}; *T* = 293(2) K; crystal size 0.40 × 0.20 × 0.20 mm; 2.62° ≤ Θ ≤ 25.96 °; 7506 reflections collected, 3915 independent reflections ($R_{int.}$ = 0.0585); 235 parameters; w^{-1} = [$\sigma^2(F_o^2)$ + (0.0100*P*)^2], *P* = [(F_o^2) + 2F_c^2]/3; R^1 = 0.0427, wR^2 = 0.0734 [$I > 2\sigma(I)$]; R^1 = 0.0820, wR^2 = 0.0775 (all data); residual electron density 0.224 and −0.231 e/Å^3, *S* = *GOF* (on F^2) = 1.040.

Acknowledgments

We are grateful to the Fonds der Chemischen Industrie (post-graduate grant for J. D.) and the Deutsche Forschungsgemeinschaft [Graduate College "Phosphorus as Connecting Link Between Various Chemical Disciplines" (post-graduate grant for J. R.)] for generous financial support.

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Received June 13, 2002
[O02316]