Organophosphorus Compounds, Part 150;[1] Imidovanadium(V)-Complexes as Reaction Partners for Kinetically Stabilized Phosphaalkynes. 1-Aza-2-phospha-4-vanada(V)-cyclobutenes: Precursors in the Synthesis of 1*H*-1,2-Azaphospholes

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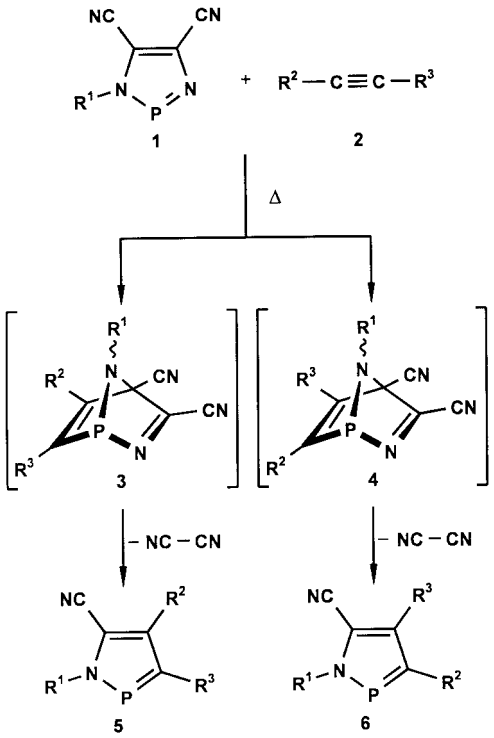
Abstract: A new synthetic pathway to the 1*H*-1,2-azaphospholes **12a**–**m** has been developed involving reactions of the 1-aza-2-phospha-4-vanada(V)-cyclobutenes **9a**–**g**, generated in situ from the imidovanadium(V) complexes **7a**–**c** and the phosphaalkynes **8a**–**e**, with the acetylenes **10a**–**g**. This synthesis affords the heterocyclic compounds **12a**–**m** in good yields and allows variation of all substituents for the first time. The structure of the 1*H*-1,2-azaphosphole **12a** has been confirmed by X-ray crystallographic analysis. A selective η^1-complexation of the azaphospholes **12a,b** to afford the transition metal complexes **13a,b** can be realized by reaction with diiron nonacarbonyl. While reactions of the alkyl trifluoromethanesulfonates **14a,b** with the heterophosphole **12a** result in the formation of the azaphospholium compounds **15a,b**, the azaphosphole **12a** reacts with the azo compound **16** to form the spirotricyclic betaine **17**. Diels–Alder reactions occur when the heterophospholes **12a,b** are treated with the electron-poor acetylenes **18a**–**e** and furnish the 1,2-azaphosphanorbornadienes **19a**–**f**, the structures of which have been confirmed by an X-ray crystallographic analysis of the bicyclic product **19e**. The phosphorus atom of the azaphosphanorbornadiene **19a** can be oxidized and sulfurized to form the bicyclic species **20** and **21** containing $\lambda^5\sigma^4$-phosphorus atoms.

Key words: 1*H*-1,2-azaphospholes, 1,2-azaphosphanorbornadienes, heterophospholes, Diels–Alder reaction, phosphorus, organometallic reagents, azo compounds, heterocycles

Introduction

Two major aspects of current research in the field of low-coordinated phosphorus compounds are, on one hand, the syntheses of phosphorus-containing cage compounds[2] and of heterophospholes[3–5] on the other hand. Although the class of the 1,3-azaphospholes has been well investigated from both synthetic and reactivity aspects,[3a] there are as yet only two approaches to the class of constitutionally isomeric heterocyclic compounds, the 1*H*-1,2-azaphospholes.[6,7] Of these two, however, only the synthetic route to the 1*H*-1,2-azaphosphole-5-carbonitriles **5** and **6** from the easily accessible 1,3,2-diazaphosphole-4,5-dinitriles **1** and acetylenes **2**, (Scheme 1) is of preparative importance.[6]

The subsequent chemistry of the 1*H*-1,2-azaphospholes is also practically unexplored. All that is known is that the 1*H*-1,2-azaphosphole-5-carbonitriles **5** and **6** are colorless, air-stable liquids possessing only very low reactivity.



Scheme 1

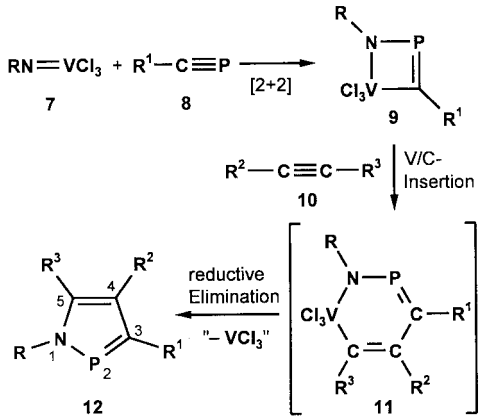
For example, they are not attacked by water, methanol, sulfur, or mixtures thereof.

Having found and initiated investigations on the enormous synthetic potential of imidovanadium(V) compounds in reactions with phosphaalkynes[8] and, in particular, of 1-aza-2-phospha-4-vanada(V)-cyclobutenes in reactions with phosphaalkynes to furnish 1,3,5-triphosphabenzenes,[9] we have now turned our attention to their reactions with alkynes. In this paper we report on the selective synthesis of 1*H*-1,2-azaphospholes and their surprising reactivity.

New Approach to 1*H*-1,2-Azaphospholes 12a–m

When the 1:1 cycloadducts **9a**–**g**, generated in situ by addition of an equimolar amount of a phosphaalkyne **8a**–**e** to the imidovanadium(V) complex **7a**–**c**, are treated with

an excess of an acetylene **10a**–**g** quantitative reactions with formation of the 1*H*-1,2-azaphospholes **12a**–**m** are observed (Scheme 2). The pure products **12a**–**m** are then isolated in 31–71% yields after workup.



7	a	b	c
R	*t*Bu	1-Ad	*i*Pr

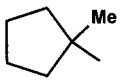
8	a	b	c	d	e
R^1	*t*Bu	*t*Pen	MecPen	MecHex	1-Ad

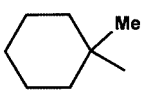
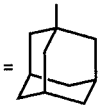
9	a	b	c	d	e	f	g
R	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	1-Ad	*i*Pr
R^1	*t*Bu	*t*Pen	MecPen	MecHex	1-Ad	*t*Bu	*t*Bu

10	a	b	c	d	e	f	g
R^2	H	H	Me	H	H	Me	Ph
R^3	Ph	Tol	Ph	Bz	Pr	Me	Ph

11, 12	a	b	c	d	e	f
R	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu
R^1	*t*Bu	*t*Pen	MecPen	MecHex	1-Ad	*t*Bu
R^2	H	H	H	H	H	H
R^3	Ph	Ph	Ph	Ph	Ph	Tol
% yield	71	71	43	47	37	38

11, 12	g	h	i	j	k	l	m
R	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	1-Ad	*i*Pr
R^1	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu	*t*Bu
R^2	Me	H	H	Me	Ph	H	H
R^3	Ph	Bz	Pr	Me	Ph	Ph	Ph
% yield	41	47	51	31	67	40	65

*t*Pen = $C(CH_3)_2C_2H_5$; MecPen = 

MecHex =  ; 1-Ad = 

Scheme 2

The compositions of the azaphospholes **12a**–**m** are elucidated unambiguously from their elemental analyses and mass spectral data. The $^{31}P\{^1H\}$ NMR spectra of **12a**–**m** each show a singlet signal between δ = 168.8 and 182.2, i.e., in the typical region for heterophospholes possessing a $\lambda^3\sigma^2$-phosphorus atom directly adjacent to a nitrogen and a carbon atom.[10] The signals in the $^{13}C\{^1H\}$ NMR spectra for the ring carbon atoms C(3), C(4), and C(5) are of high diagnostic value. Thus, the sp^2-carbon atom C(4) produces a signal between δ = 116.3 and 127.0 with a typical ^2J(C,P) coupling constant of 4.8–6.3 Hz. As a result of the direct adjacency to electronegative heteroatoms the ^{13}C NMR signals of the atoms C(3) and C(5) appear at low field: that of C(5) is seen as a singlet or doublet at δ = 142.4–149.7 with a ^2J(C,P) coupling over the nitrogen atom of 4.0–0.0 Hz. The signal for C(3) is the most significant; it appears, as expected, at lowest field (δ = 173.6–180.6) as a doublet with a characteristic ^1J(C,P) coupling constant of 40.7–44.1 Hz. The ^1H NMR chemical shifts of the hydrogen atoms on the rings of compounds **12a**–**f,h,i,l,m** are in the range δ = 6.33 – 6.72, i.e., in the generally usual aromatic region for azaphospholes.[6] Since only one signal is seen for each proton in these cases, the reaction must be regiospecific.

An X-ray crystallographic analysis of compound **12a** (see Fig. 1) was carried out in order to obtain unequivocal confirmation of the regiochemistry and structure.

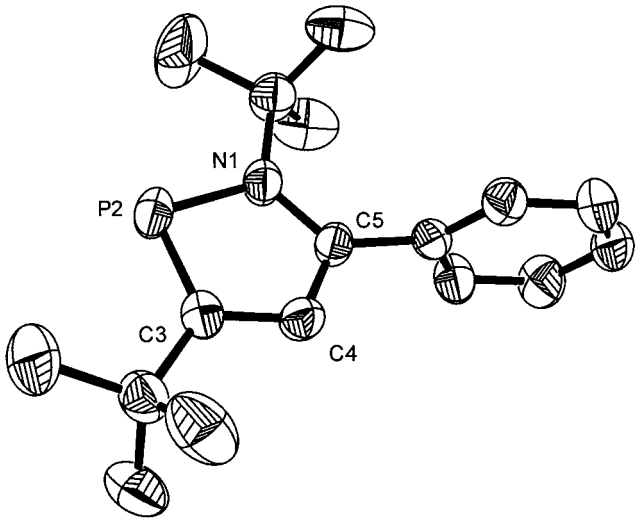


Figure 1 Crystal structure of **12a**. Selected bond lengths [Å] and angles [°]: P(2)–N(1) 1.728(4), P(2)–C(3) 1.713(5), N(1)–C(5) 1.377(5), C(3)–C(4) 1.395(6), C(4)–C(5) 1.372(6), C(5)–N(1)–P(2) 112.3(3), N(1)–P(2)–C(3) 91.5(2), P(2)–C(3)–C(4) 109.7(4), C(3)–C(4)–C(5) 115.3(4), C(4)–C(5)–N(1) 111.2(4)

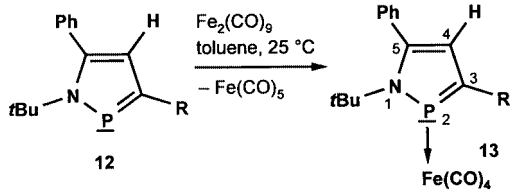
This demonstrated conclusively in the case of **12a** that the product was the 5-phenyl-substituted regioisomer. The central structural feature of **12a** is the planar five-membered ring unit. When a least squares plane is defined through N(1), P(2), C(3), C(4), and C(5), the mean deviation is merely 0.34 pm. With an angle of 85.5°, the plane of the phenyl system is almost orthogonal to that of the five-membered ring. As expected, the bond lengths of the ring atoms lie between the values for the corresponding single and double bonds and, furthermore, are in good

agreement with the bond lengths in comparable heterophospholes.[3a] Not only the planarity of the five-membered ring but also the bond lengths confirm the aromaticity of this heterocyclic skeleton.

Studies on the Reactivity of 1*H*-1,2-Azaphospholes

a) Complexation of the Azaphospholes 12a,b with Diiron Nonacarbonyl

Reactions of the heterophospholes **12a,b** with an equimolar amount of diiron nonacarbonyl furnish the η^1-complexes **13a,b** selectively in 63 and 59% yield, respectively (Scheme 3).



12, 13	a	b
R	*t*Bu	*t*Pen
% yield	63	59

Scheme 3

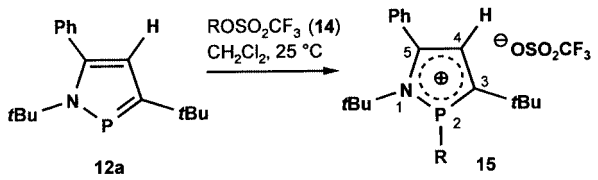
The η^1-complexation in **13a,b** is apparent from the $^{31}P\{^1H\}$ NMR spectra with a pronounced high field shift of the signals by $\Delta\delta \cong 55 - 60$ ppm to $\delta = 121.3$ (**13a**) and 126.2 (**13b**). On the other hand, the complexation is reflected in the $^{13}C\{^1H\}$ NMR spectra in some cases by a marked shift of the ring carbon signals to lower field. This phenomenon is particularly pronounced for the carbon atom C(3), the signals of which are shifted by about 30 ppm to lower field and appear at $\delta = 204.0$ and 204.5, respectively. Concomitantly, the ^1J(C,P) coupling constants decrease by about 20 Hz.

b) Alkylation of the Azaphosphole 12a with the Alkyl Trifluoromethanesulfonates 14a,b

The azaphosphole **12a** reacts under mild conditions and in remarkable selectivity with alkyl trifluoromethanesulfonates **14a,b** to afford the 1,2-azaphospholium compounds **15a,b** in quantitative yields (Scheme 4).

The EI mass spectra of compounds **15a,b** confirm the formation of the cation unit from one equivalent of the heterophosphole **12a** and a methyl or ethyl group, respectively.

The functionalization at phosphorus is clearly demonstrated in the $^{31}P\{^1H\}$ NMR spectra by the high-field shift of the signals in comparison to that of the starting material **12a**. Thus, the phosphorus signals appear at $\delta = 103.4$



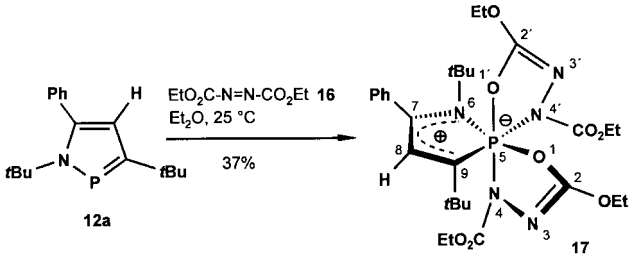
14, 15	a	b
R	Me	Et
% yield	100	100

Scheme 4

(15a) and 114.5 **(15b)**. Finally, the ^1H and $^{13}C\{^1H\}$ NMR spectra provide conclusive evidence for the constitutions and prove the preservation of the azaphosphole skeleton. In particular, the signals of the newly introduced methyl or ethyl group are of major diagnostic relevance. Thus, the P-methyl group of **15a** gives rise to a signal at $\delta = 15.7$ in the $^{13}C\{^1H\}$ NMR spectrum and unambiguously demonstrates the alkylation at phosphorus with its characteristic ^1J(C,P) coupling constant of 27.3 Hz. This alkylation position is also supported by the signals of the ethyl group in **15b**: thus, the methylene group gives a doublet signal at $\delta = 23.8$ with a significant ^1J(C,P) coupling constant of 29.8 Hz, while the signal of the methyl group appears at $\delta = 7.4$ with a ^2J(C,P) coupling constant of 2.2 Hz.

c) Reaction of the 1*H*-1,2-Azaphosphole 12a with the Azo Compound 16

The reaction of the azaphosphole **12a** with two equivalents of the azo compound **16** occurs at 25°C and furnishes the zwitterionic 2:1-adduct **17**, isolated in 37% yield after workup (Scheme 5).



Scheme 5

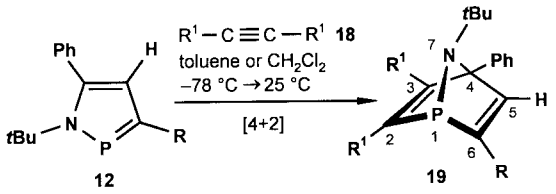
In addition to its EI mass spectrum which confirms its composition, the structural elucidation of compound **17** is based mainly on NMR spectral data.

The extreme high-field shift of the ^{31}P NMR signal by more than 220 ppm in comparison to that of the azaphosphole **12a** confirms the formation of a betaine possessing a hexacoordinated, negatively charged phosphorus atom. The observed chemical shift of $\delta = -41.0$ is in good agree-

ment with literature data for related compounds.[11,12] The ^{1}H NMR spectrum is also in accord with the constitution of **17** and, in addition, demonstrates the existence of a bis-adduct as a consequence of the correct integration ratio of the *t*-butyl to the ethyl protons. The ^{13}C{^{1}H} NMR spectrum again plays major role in the determination of the constitution. Of particular diagnostic relevance is the signal of the carbon atom C(9) adjacent to the spiro center. As a result of the increase of the coordination and the presence of a formal negative charge at phosphorus, this signal experiences not only a shift to higher field of more than 75 ppm but also an appreciable increase in the magnitude of the $^1J_{C,P}$ coupling constant to 113.7 Hz. Similar values have been reported for a structurally related spirocyclic betaine[12] and are also found for zwitterionic 2:1-adducts of tetrahalo-*ortho*-benzoquinones with 1,3-aza- and 1,2,4-diazaphospholes.[13]

d) Diels–Alder Reaction of the 1*H*-1,2-Azaphospholes 12a,b with Electron-Poor Acetylenes 18a–e

When the azaphospholes **12a,b** are allowed to react with the electron-poor acetylenes **18a–e** the azaphosphanorbornadienes **19a–f** are obtained selectively and in high yields (63 – 73%) (Scheme 6).



12	a	b
R	*t*Bu	*t*Pen

18	a	b	c	d	e
R^1	CO_2Me	CO_2Et	CO_2tBu	CF_3	CN

19	a	b	c	d	e	f
R	*t*Bu	*t*Pen	*t*Bu	*t*Bu	*t*Bu	*t*Bu
R^1	CO_2Me	CO_2Me	CO_2Et	CO_2tBu	CF_3	CN
% yield	71	73	67	63	73	63

Scheme 6

The 1:1 composition of the azaphosphanorbornadienes **19a–f** from one equivalent of the azaphosphole **12a** or **12b** and one equivalent of the acetylene **18** is supported by elemental analyses and mass spectral data.

The ^{31}P{^{1}H} NMR spectra of the bicyclic compounds **19a–f** contain singlet signals at much higher field in comparison to those of the starting compounds. The positions of the signals, between $\delta = 53.0 - 60.6$, are typical for aminophosphanes and thus unambiguously confirm the transition from $\lambda^3\sigma^2$- to $\lambda^3\sigma^3$-phosphorus atoms.[14] The ^{1}H and ^{13}C NMR data support the conclusions drawn from the ^{31}P NMR spectrum and a X-ray crystallographic analysis of product **19e** provided definitive confirmation of the structure of the cage compounds **19a–f** (see Figure 2).

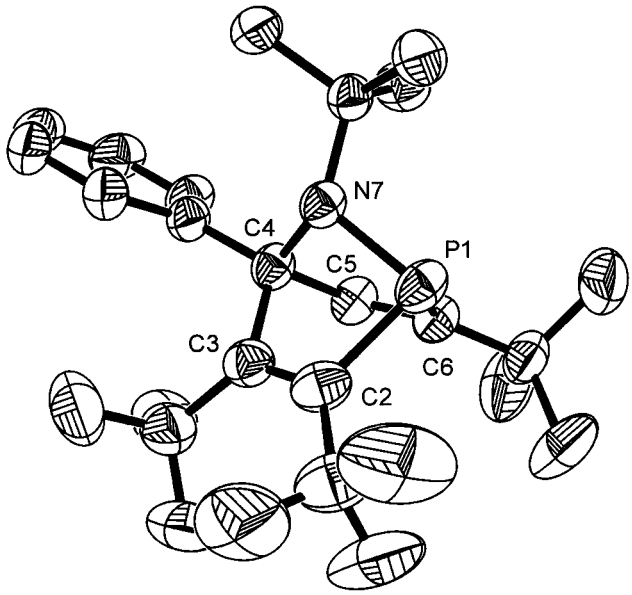
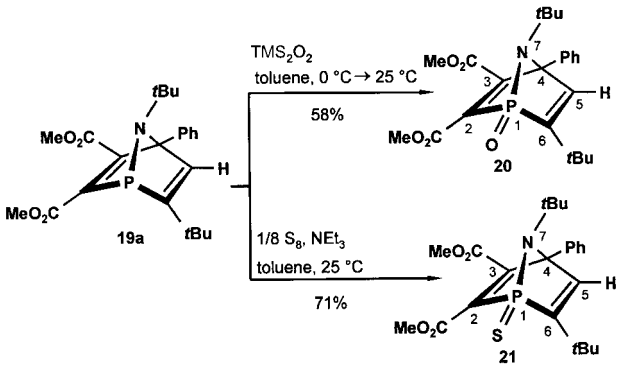


Figure 2 Crystal structure of **19e**. Selected bond lengths [Å] and angles [°]: P(1)–N(7) 1.737(2), P(1)–C(2) 1.855(2), P(1)–C(6) 1.895(2), N(7)–C(4) 1.508(2), C(2)–C(3) 1.331(2), C(3)–C(4) 1.555(2), C(4)–C(5) 1.555(2), C(5)–C(6) 1.317(3), N(7)–P(1)–C(2) 86.34(8), N(7)–P(1)–C(6) 91.91(7), C(2)–P(1)–C(6) 92.21(9), C(4)–N(7)–P(1) 99.51(10), C(3)–C(2)–P(1) 108.04(14), C(2)–C(3)–C(4) 110.90(2), N(7)–C(4)–C(3) 100.25(13), N(7)–C(4)–C(5) 105.78(13), C(3)–C(4)–C(5) 102.42(14), C(4)–C(5)–C(6) 112.90(2), C(5)–C(6)–P(1) 106.17(13)

The central structural increment of compound **19e** is a distorted norbornadiene skeleton in which the phosphorus atom is present at one bridgehead (position 1) and the nitrogen atom is in the bridge (position 7). The *tert*-butyl group on the nitrogen atom is inclined towards the lesser substituted double bond. The bond lengths P(1)–C(2) [1.855(2) Å] and P(1)–C(6) [1.895(2) Å] are within the range of the experimentally determined average value (1.86 Å)[15] and are markedly longer than the corresponding bond lengths for C(3)–C(4) [1.555(2) Å] and C(4)–C(5) [1.555(2) Å]. Together with the appreciably smaller bond angle for C(2)–P(1)–C(6) [92.21(9)°] as compared with C(3)–C(4)–C(5) [102.42(14)°], these bond length differences characterize the distortion of the norbornadiene skeleton. In addition, the nitrogen bridge is not positioned symmetrically between P(1) and C(4), as revealed by the bond lengths P(1)–N(7) [1.737(2) Å] and N(7)–C(4) [1.508(2) Å] in combination with the angle P(1)–N(7)–C(4) of 99.51(10)°. The C/C double bond lengths of 1.317(3) Å [C(5)–C(6)] and 1.331(2) Å [C(2)–C(3)] are of the usual size.[15] A comparison of the geometric parameters of the bicyclic product **19e** with those of a 1-phosphanorbornadiene[16] or, of a tungsten-complexed azaphosphanorbornadiene[17] shows characteristic agreements for comparable structural increments.

e) Oxidation and Sulfurization of the 1,2-Azaphosphanorbornadiene 19a

When the azaphosphanorbornadiene **19a** is allowed to react with an equimolar amount of an oxidizing agent such as bis(trimethylsilyl) peroxide or sulfur in the presence of an equimolar amount of triethylamine, the respective chalcogen-containing bicyclic compounds **20** (58%) and **21** (71%) are obtained after workup (Scheme 7).



Scheme 7

The chalcogenation of **19a** is immediately confirmed by the mass spectra of products **20** and **21**. Thus, the respective molecular ion peaks are seen in the EI mass spectra at m/z = 431 (**20**) and 447 (**21**). The IR spectra of compounds **20** and **21** also support the chalcogenation of phosphorus by the appearance of characteristic and intense P/chalcogen bands at 1267 cm^{-1} (**20**) and 1260 cm^{-1} (**21**), respectively.

The $^{31}P\{^1H\}$ NMR spectra do not reveal a uniform trend with regard to the chemical shifts of the phosphorus atoms of **20** and **21** in comparison to that of the starting compound **19a**. While oxidation resulted in a slight shift to higher field of the phosphorus atom of **20** (δ = 42.6), the sulfuration in compound **21** effected a slight deshielding of the ^{31}P NMR signal to δ = 67.8. However, these observations are in good harmony with phenomena reported in the literature, namely that the ^{31}P NMR signal of a pentavalent phosphorus atom bearing a doubly bonded chalcogen atom experiences a shift to lower field on going from oxygen to sulfur.[14,18] The ^1H and $^{13}C\{^1H\}$ NMR spectral data are also in accord with the constitutions of **20** and **21**, thus unequivocally confirming the retention of the bicyclic structure.

All reactions were performed under argon (purity >99.998%) using Schlenk techniques. The solvents were dried by standard procedures, distilled, and stored under argon until used. Compounds **7a**,[19] **7b**,[20] **7c**,[20] **8a**,[21] **8b**,[22] **8c**,[23,24] **8d**,[23,24] **8e**,[21] **18e**,[25] and bis(trimethylsilyl) peroxide[26] were prepared by published methods. The bulb-to-bulb distillations were carried out in a Büchi GKR 50 apparatus, the temperatures stated are oven temperatures. Mps were determined on a Mettler FP61 apparatus (heating rate 2°C/min) and are uncorrected. Microanalyses were performed with a Perkin-Elmer Analyzer 2400. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AC 200 and Bruker AMX 400 spectrometers and referenced to the solvent as internal standard. ^{31}P NMR spectra were measured on a Bruker AC 200 (81.1 MHz) spectrometer with 85% H_3PO_4 as external standard. MS were recorded on a Finnigan MAT 90 spectrometer at 70 eV ionization voltage. IR spectra were measured on a Perkin-Elmer 16 PC FT-IR spectrophotometer.

1*H*-1,2-Azaphospholes 12a–m, General Procedure

Method A: To a stirred solution of the imidovanadium(V) complex **7** in toluene was added an equimolar amount of the respective phosphaalkyne **8** at −78°C. The reaction mixture was allowed to warm to 25°C and then a threefold excess of the respective alkyne **10** was added. After 18 h all volatile components were removed at 25°C/0.001 mbar and the residue dissolved in toluene (25 mL). Impurities were filtered over Celite and the solvent was evaporated. Depending on the constitution of the residue, the products were either purified by crystallization from CH_2Cl_2 at −30°C or by bulb-to-bulb distillation (if the residue was dark-brown and oily).

Method B: To a stirred solution of the imidovanadium(V) complex **7** and a threefold excess of the respective alkyne **10** in toluene was added an equimolar amount of the respective phosphaalkyne **8** (related to **7**) at −78°C. The reaction mixture was allowed to warm to r.t. and stirred for additional 18 h. The workup was analogous to that of Method A.

1,3-Di-*tert*-butyl-5-phenyl-1*H*-1,2-azaphosphole (12a)

Method B: From imidovanadium(V) complex **7a** (0.28g, 1.20 mmol) in toluene (5 mL), phenylacetylene (**10a**; 0.37 g, 3.60 mmol) and *t*-butylphosphaalkyne (**8a**; 0.12 g, 1.20 mmol); yield (bulb-to-bulb distillation): 0.23 g (71%); bp 120°C/0.001 mbar.

^1H NMR (C_6D_6, 25°C, 200.1 MHz): δ = 1.40 [d, 9 H, ^4J(H,P) = 1.4 Hz] and 1.50 [d, 9 H, ^4J(H,P) = 1.5 Hz] (*t*-C_4H_9 at N-1 and C-3), 6.70 [d, 1 H, ^3J(H,P) = 5.9 Hz, H-4], 7.10–7.30 (m, 5 H, C_6H_5).

$^{13}C\{^1H\}$ NMR (C_6D_6, 25°C, 50.3 MHz): δ = 33.0 [d, ^3J(C,P) = 10.2 Hz] and 33.6 [d, ^3J(C,P) = 11.4 Hz] [C(*C*H_3)$_3$ at N-1 and C-3], 34.4 [d, ^2J(C,P) = 16.8 Hz, *C*(CH$_3$)$_3$ at C-3], 59.4 [d, ^2J(C,P) = 11.4 Hz, *C*(CH$_3$)$_3$ at N-1], 120.4 [d, ^2J(C,P) = 6.0 Hz, C-4], 127.4 (s, Ph-C), 127.8 (s, Ph-C), 131.2 [d, ^4J(C,P) = 1.8 Hz, Ph-C], 139.4 [d, ^3J(C,P) = 4.2 Hz, Ph-C], 148.7 [d, ^2J(C,P) = 1.8 Hz, C-5], 177.7 [d, ^1J(C,P) = 43.7 Hz, C-3].

$^{31}P\{^1H\}$ NMR (C_6D_6, 25°C, 81.0 MHz): δ = 182.2 (s).

Anal. Calcd for $C_{17}H_{24}NP$ (273.4): C, 74.6; H, 8.9; N, 5.1. Found C, 74.1; H, 8.9; N, 5.2.

MS (EI, 70 eV): *m*/*z* (%) = 273 (M^+, 100), 217 ([M − C_4H_8]$^+$, 14), 202 ([M − C_4H_9N]$^+$, 58).

1-*tert*-Butyl-3-(1,1-dimethylpropyl)-5-phenyl-1*H*-1,2-azaphosphole (12b)

Method A: From imidovanadium(V) complex **7a** (0.664 g, 2.91 mmol) in toluene (18 mL), (1,1-dimethylpropyl)phosphaalkyne (**8b**; 0.332 g, 2.91 mmol, as a 26% solution in hexamethyldisiloxane)), and phenylacetylene (**10a**, 0.892 g, 8.73 mmol); yield: 0.594 g (71%); mp 76°C (crystallization from CH_2Cl_2 at −30°C); bp 120°C/0.001 mbar.

^1H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 0.86 [t, 3 H, ^3J(H,H) = 7.5 Hz, CH_2CH_3], 1.32 [d, 6 H, ^4J(H,P) = 1.6 Hz, C(CH_3)$_2$Et], 1.53 [d, 9 H, ^4J(H,P) = 1.1 Hz, *t*-C_4H_9 at N-1], 1.63 [q, 2 H, ^3J(H,H) = 7.5 Hz, CH_2CH_3], 6.45 [d, 1 H, ^3J(H,P) = 6.0 Hz, H-4), 7.31–7.39 (m, 5 H, C_6H_5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 9.3 [d, ^4J(C,P) = 1.8 Hz, CH_2CH_3], 29.6 [d, ^3J(C,P) = 10.8 Hz, C(*C*H$_3$)$_2$Et], 33.4 [d, ^3J(C,P) = 10.8 Hz, C(*C*H$_3$)$_3$ at N-1], 37.2 [d, ^3J(C,P) = 9.9 Hz, *C*H_2CH$_3$], 37.5 [d, ^2J(C,P) = 6.2 Hz, *C*(CH$_3$)$_2$Et], 59.0 [d, ^2J(C,P) = 10.8 Hz, *C*(CH$_3$)$_3$ at N-1], 120.0 [d, ^2J(C,P) = 6.3 Hz, C-

4], 127.1 (s, Ph-C), 127.6 (s, Ph-C), 130.7 [d, ^4J(C,P) = 2.7 Hz, Ph-C], 138.8 [d, ^3J(C,P) = 3.6 Hz, Ph-C], 148.3 [d, ^2J(C,P) = 1.8 Hz, C-5], 175.9 [d, ^1J(C,P) = 44.0 Hz, C-3].

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C, 81.0 MHz): δ = 181.2 (s).

IR (CCl_4): ν = 2972 (C−H), 1622, 1532, 1298, 1216, 1186, 1113, 929, 790 cm^{-1}.

Anal. Calcd for $C_{18}H_{26}NP$ (287.4): C, 75.23; H, 9.12; N, 4.87. Found C, 74.81; H, 10.11; N, 4.96.

MS (EI, 70 eV): *m*/*z* (%) = 287 (M^+, 20), 231 ([M − C_4H_8]$^+$, 23), 216 ([M − C_4H_9N]$^+$, 7), 202 ([M − $C_5H_{11}N$]$^+$, 100).

1-*tert*-Butyl-3-(1-methylcyclopentyl)-5-phenyl-1*H*-1,2-azaphosphole (12c)

Method A: From imidovanadium(V) complex **7a** (0.237 g, 1.04 mmol) in toluene (10 mL), (1-methylcyclopentyl)methylidynephosphane (**8c**; 0.131 g, 1.04 mmol, as a 16% solution in hexamethyldisiloxane), and phenylacetylene (**10a**; 0.319 g, 3.12 mmol); yield (bulb-to-bulb distillation): 0.134 g (43%); mp 79°C; bp 140°C/0.001 mbar.

^1H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 1.42 [s, 3 H, $C(CH_2)_2CH_3$], 1.57 [d, 9 H, ^4J(H,P) = 1.2 Hz, *t*-C_4H_9 at N-1], 1.73−2.05 (m, 8 H, cyclopentyl-CH_2), 6.53 [d, 1 H, ^3J(H,P) = 5.7 Hz, H-4], 7.35−7.45 (m, 5 H, C_6H_5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 24.5 [s, $C(CH_2)_2CH_3$], 29.9 (s, cyclopentyl-CH_2), 30.0 (s, cyclopentyl-CH_2), 33.5 [d, ^3J(C,P) = 11.2 Hz, cyclopentyl-CH_2], 42.4 [d, ^3J(C,P) = 10.8 Hz, $C(CH_3)_3$ at N-1], 45.2 [d, ^2J(C,P) = 15.3 Hz, $C(CH_2)_2CH_3$], 59.0 [d, ^2J(C,P) = 11.3 Hz, $C(CH_3)_3$ at N-1], 120.3 [d, ^2J(C,P) = 5.6 Hz, C-4], 127.2 (s, Ph-C), 127.7 (s, Ph-C), 130.8 [d, ^4J(C,P) = 1.4 Hz, Ph-C], 138.9 [d, ^3J(C,P) = 3.2 Hz, Ph-C], 148.7 (s, C-5), 177.1 [d, ^1J(C,P) = 43.4 Hz, C-3].

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 81.0 MHz): δ = 179.7 (s).

IR ($CDCl_3$): ν = 2964 (C−H), 1621, 1530, 1295, 1262, 1229, 1204, 1189, 1113, 1074, 1022, 810 cm^{-1}.

MS (EI, 70 eV): *m*/z (%) = 299 (M^+, 35), 243 ([M − C_4H_8]$^+$, 100), 228 ([M − C_4H_9N]$^+$, 30), 57 ([*t*-C_4H_9]$^+$, 21).

1-*tert*-Butyl-3-(1-methylcyclohexyl)-5-phenyl-1*H*-1,2-azaphosphole (12d)

Method A: From imidovanadium(V) complex **7a** (0.396 g, 1.73 mmol) in toluene (12 mL), (1-methylcyclohexyl)methylidynephosphane (**8d**; 0.243 g, 1.73 mmol, as a 16% solution in hexamethyldisiloxane), and phenylacetylene (**10a**; 0.530 g, 5.19 mmol); yield: (bulb-to-bulb distillation): 0.255 g (47%); mp 81°C; bp 140°C/0.001 mbar.

^1H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 1.35 [d, 3 H, ^4J(H,P) = 1.0 Hz, $C(CH_2)_2CH_3$], 1.50−1.92 (m, 10 H, cyclohexyl-CH_2), 1.57 [d, 9 H, ^4J(H,P) = 1.7 Hz, *t*-C_4H_9 at N-1], 6.52 [d, 1 H, ^3J(H,P) = 5.9 Hz, H-4], 7.35−7.43 (m, 5 H, C_6H_5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 23.7 [s, $C(CH_2)_2CH_3$], 27.4 (s, cyclohexyl-CH_2), 30.4 (m_c, cyclohexyl-CH_2), 34.4 [d, ^3J(C,P) = 11.7 Hz, cyclohexyl-CH_2], 38.4 [d, ^2J(C,P) = 14.5 Hz, $C(CH_2)_2CH_3$], 40.9 [d, ^3J(C,P) = 9.9 Hz, $C(CH_3)_3$ at N-1], 60.0 [d, ^2J(C,P) = 10.8 Hz, $C(CH_3)_3$ at N-1], 120.5 [d, ^2J(C,P) = 6.3 Hz, C-4], 128.1 (s, Ph-C), 128.6 (s, Ph-C), 131.7 [d, ^4J(C,P) = 1.8 Hz, Ph-C], 139.9 [d, ^3J(C,P) = 3.6 Hz, Ph-C], 149.2 [d, ^2J(C,P) = 1.8 Hz, C-5], 178.8 [d, ^1J(C,P) = 43.1 Hz, C-3].

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 25°C, 81.0 MHz): δ = 182.1 (s).

IR (CCl_4): ν = 2932 (C−H), 1711, 1622, 1448, 1368, 1312, 1287, 1262, 1188, 1112, 944, 909 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 313 (M^+, 35), 257 ([M − C_4H_8]$^+$, 100), 242 ([M − C_4H_9N]$^+$, 5), 57 ([*t*-C_4H_9]$^+$, 87).

3-(1-Adamantyl)-1-*tert*-butyl-5-phenyl-1*H*-1,2-azaphosphole (12e)

Method A: From imidovanadium(V) complex **7a** (0.457 g, 2.00 mmol) in toluene (15 mL), (1-adamantyl)methylidynephosphane (**8e**; 0.340 g, 2.00 mmol), and phenylacetylene (**10a**; 0.613 g, 6.00 mmol); yield (bulb-to-bulb distillation): 0.260 g (37%); mp 93°C; bp 170°C/0.001 mbar.

^1H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 1.42 (s, 9 H, *t*-C_4H_9 at N-1), 1.69 (br s, 6 H, Ad-H), 1.97 (br s, 3 H, Ad-H), 2.12 (br s, 6 H, Ad-H), 6.68 [d, 1 H, ^3J(H,P) = 6.0 Hz, H-4], 7.00−7.13 (m, 3 H, C_6H_5), 7.23−7.27 (m, 2 H, C_6H_5).

$^{13}C\{^1H\}$ NMR (C_6D_6, 25°C, 100.6 MHz): δ = 29.5 [d, ^4J(C,P) = 1.7 Hz, Ad-C], 33.6 [d, ^3J(C,P) = 11.0 Hz, $C(CH_3)_3$ at N-1], 36.6 [d, ^2J(C,P) = 16.1 Hz, Ad-C], 37.1 (s, Ad-C), 45.6 [d, ^3J(C,P) = 10.2 Hz, Ad-C], 59.0 [d, ^2J(C,P) = 11.0 Hz, $C(CH_3)_3$ at N-1], 119.2 [d, ^2J(C,P) = 5.1 Hz, C-4], 127.4 (s, Ph-C), 128.5 (s, Ph-C), 131.2 [d, ^4J(C,P) = 1.7 Hz, Ph-C], 139.6 [d, ^3J(C,P) = 4.2 Hz, Ph-C], 148.4 (s, C-5), 178.4 [d, ^1J(C,P) = 43.2 Hz, C-3].

$^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C, 81.0 MHz): δ = 181.7 (s).

IR (CCl_4): ν = 2963 (C−H), 2908 (*C*−H), 2850 (*C*−H), 1261, 1100, 1032 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 351 (M^+, 31), 295 ([M − C_4H_8]$^+$, 100), 135 ([1-Ad]$^+$, 27), 57 ([*t*-C_4H_9]$^+$, 24).

1,3-Di-*tert*-butyl-5-*p*-tolyl-1*H*-1,2-azaphosphole (12f)

Method A: From imidovanadium(V) complex **7a** (0.536 g, 2.35 mmol) in toluene (13 mL), *t*-butylphosphaalkyne (**8a**, 0.235 g, 2.35 mmol), and *p*-tolylacetylene (**10b**, 0.819 g, 7.05 mmol); yield (bulb-to-bulb distillation): 0.257 g (38%), mp 79°C; bp 120°C/0.001 mbar.

^1H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 1.35 [d, 9 H, ^4J(H,P) = 1.4 Hz, *t*-C_4H_9 at C-3], 1.52 [d, 9 H, ^4J(H,P) = 1.1 Hz, *t*-C_4H_9 at N-1], 2.39 (s, 3 H, Tol-CH_3), 6.48 [d, 1 H, ^{3}(H,P) = 6.0 Hz, H-4], 7.15 [AA´BB´ spin system, 2 H, ^3J(H,H) = 8.3 Hz, Tol-H], 7.25 [AA´BB´ spin system, 2 H, ^3J(H,H) = 8.3 Hz, Tol-H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 21.2 (s, Tol-CH_3), 32.6 [d, ^3J(C,P) = 9.9 Hz, $C(CH_3)_3$ at C-3], 33.4 [d, ^3J(C,P) = 11.7 Hz, $C(CH_3)_3$ at N-1], 34.1 [d, ^2J(C,P) = 7.3 Hz, $C(CH_3)_3$ at C-3], 58.9 [d, ^2J(C,P) = 11.7 Hz, $C(CH_3)_3$ at N-1], 120.0 [d, ^2J(C,P) = 5.4 Hz, C-4], 127.8 (s, Tol-C), 130.5 [d, ^4J(C,P) = 1.8 Hz, Tol-C], 135.7 [d, ^3J(C,P) = 3.6 Hz, Tol-C], 137.4 (s, Tol-C), 148.5 (s, C-5), 177.6 [d, ^1J(C,P) = 43.1 Hz, C-3].

$^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C, 81.0 MHz): δ = 178.5 (s).

IR ($CDCl_3$): ν = 2971 (C−H), 1621, 1536, 1504, 1321, 1296, 1216, 1185, 1112, 821 cm^{-1}.

Anal. Calcd for $C_{18}H_{26}NP$ (287.4): C, 75.23; H, 9.12; N, 4.87. Found C, 74.13; H, 8.90; N, 3.80.

MS (EI, 70 eV): *m*/*z* (%) = 287 (M^+, 32), 231 ([M − C_4H_8]$^+$, 72), 216 ([M − C_4H_9N]$^+$, 100).

1,3-Di-*tert*-butyl-4-methyl-5-phenyl-1*H*-1,2-azaphosphole (12g)

Method A: From imidovanadium(V) complex **7a** (0.572 g, 2.50 mmol) in toluene (14 mL), *t*-butylphosphaalkyne (**8a**, 0.250 g, 2.50 mmol), and 1-phenylprop-1-yne (**10c**, 0.871 g, 7.50 mmol); yield (bulb-to-bulb distillation): 0.295 g (41%); mp 75°C; bp 140°C/0.001 mbar.

^1H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 1.44 [d, 9 H, ^4J(H,P) = 2.4 Hz] and 1.45 [d, 9 H, ^4J(H,P) = 1.4 Hz] (*t*-C_4H_9 at N-1 and C-3), 2.78 (s, 3 H, CH_3 at C-4), 7.22−7.25 (m, 2 H, C_6H_5), 7.34−7.38 (m, 3 H, C_6H_5).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 14.8 (s, C-4-CH_3), 31.5 [d, ^3J(C,P) = 13.7 Hz, $(CH_3)_3$ at C-3], 33.3 [d, ^3J(C,P) = 11.2 Hz, $C(CH_3)_3$ at N-1], 34.9 [d, ^2J(C,P) = 8.4 Hz, $C(CH_3)_3$ at C-3], 58.9 [d, ^2J(C,P) = 11.3 Hz, $C(CH_3)_3$ at N-1], 125.1 [d, ^2J(C,P) = 5.6

Hz, C-4], 127.7 (s, Ph-C), 127.8 (s, Ph-C), 131.7 [d, ^4J(C,P) = 1.6 Hz, Ph-C], 138.9 [d, ^3J(C,P) = 3.2 Hz, Ph-C], 147.8 (s, C-5), 173.9 [d, ^1J(C,P) = 41.8 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 170.7 (s).

IR ($CDCl_3$): ν = 2966 (C−H), 1693, 1622, 1539, 1477, 1396, 1367, 1282, 1111, 1008, 923, 757, 722, 644, 619 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 287 (M^+, 43), 231 ([M − C_4H_8]$^+$, 66), 216 ([M − C_4H_9N]$^+$, 100).

5-Benzyl-1,3-di-*tert*-butyl-1*H*-1,2-azaphosphole (12h):
Method A: From imidovanadium(V) complex **7a** (0.463 g, 2.03 mmol) in toluene (13 mL), *t*-butylphosphaalkyne (**8a**; 0.203 g, 2.03 mmol) and 3-phenylprop-1-yne (**10d**; 0.707 g; 6.09 mmol); yield (bulb-to-bulb distillation): 0.274 g (47%); mp 78°C; bp 120°C/ 0.001 mbar.

^{1}H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 1.28 [d, 9 H, ^4J(H,P) = 1.6 Hz, *t*-C_4H_9 at C-3], 1.67 [d, 9 H, ^4J(H,P) = 1.6 Hz, *t*-C_4H_9 at N-1], 4.26 (s, 2 H, CH_2 at C-5), 7.06−7.29 (m, 5 H, C_6H_5).

^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 32.6 [d, ^3J(C,P) = 9.6 Hz], 32.7 [d, ^3J(C,P) = 12.6 Hz] (C(CH_3)$_3$ at N-1 and C-3), 34.0 [d, ^2J(C,P) = 16.9 Hz, C(CH_3)$_3$ at C-3], 38.0 [d, ^3J(C,P) = 4.0 Hz, CH_2 at C-5], 57.9 [d, ^2J(C,P) = 11.3 Hz, C(CH_3)$_3$ at N-1], 119.7 [d, ^2J(C,P) = 4.8 Hz, C-4], 126.1 (s, Ph-C), 128.3 (s, Ph-C), 128.5 (s, Ph-C), 140.3 (s, Ph-C), 146.9 [d, ^2J(C,P) = 4.0 Hz, C-5], 177.8 [d, ^1J(C,P) = 43.4 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 81.0 MHz): δ = 179.4 (s).

IR ($CDCl_3$): ν = 2965 (C−H), 2867 (*C*−H), 1700, 1600, 1585, 1504, 1263, 1206, 1184, 1116, 1028, 1013, 919, 817, 733, 651 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 287 (M^+, 47), 231 ([M − C_4H_8]$^+$, 48), 216 ([M − C_4H_9N]$^+$, 100), 91 ([Ph − CH_2]$^+$, 35).

1,3-Di-*tert*-butyl-5-propyl-1*H*-1,2-azaphosphole (12i)
Method A: From imidovanadium(V) complex **7a** (0.776 g, 3.40 mmol) in toluene (15 mL), *t*-butylphosphaalkyne (**8a**; 0.340 g, 3.40 mmol), and pent-1-yne (**10e**; 0.695 g (10.20 mmol); yield (bulb-to-bulb distillation): 0.439 g (51%); bp 70°C/0.001 mbar.

^{1}H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 1.00 [t, 3 H, ^3J(H,H) = 7.4 Hz, $CH_2CH_2CH_3$], 1.33 [d, 9 H, ^4J(H,P) = 1.7 Hz, *t*-C_4H_9 at C-3], 1.68 [d, 9 H, ^4J(H,P) = 1.7 Hz, *t*-C_4H_9 at N-1], 1.69 [tq, 2 H, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 7.4 Hz, $CH_2CH_2CH_3$], 2.82 [dt, 2 H, ^3J(H,H) = 8.0 Hz, ^4J(H,P) = 1.7 Hz, CH_2 at C-5], 6.57 [d, 1 H, ^3J(H,P) = 5.7 Hz, H-4].

^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C, 100.6 MHz): δ = 14.1 (s, $CH_2CH_2CH_3$), 23.6 (s, $CH_2CH_2CH_3$), 32.4 [d, ^3J(C,P) = 11.4 Hz] and 32.5 [d, ^3J(C,P) = 9.5 Hz] (C(CH_3)$_3$ at N-1 and C-3), 33.8 [d, ^2J(C,P) = 16.2 Hz, C(CH_3)$_3$ at C-3], 34.1 [d, ^3J(C,P) = 3.8 Hz, CH_2 at C-5], 57.4 [d, ^2J(C,P) = 11.4 Hz, C(CH_3)$_3$ at N-1], 116.3 [d, ^2J(C,P) = 4.8 Hz, C-4], 149.7 (s, C-5), 177.6 [d, ^1J(C,P) = 42.0 Hz, C-3].

^{31}P{^{1}H} NMR ($CDCl_3$, 25 °C, 81.0 MHz): δ = 177.8 (s).

IR (CCl_4): ν = 2968 (C−H), 2906 (C−H), 2874 (C−H), 1711, 1476, 1463, 1396, 1368, 1291, 1269, 1206, 1131, 1068, 1059, 1027, 946, 910, 885, 843 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 239 (M^+, 7), 183 ([M − C_4H_8]$^+$, 6), 168 ([M − C_4H_9N]$^+$, 15), 57 ([*t*-C_4H_9]$^+$, 100).

1,3-Di-*tert*-butyl-4,5-dimethyl-1*H*-1,2-azaphosphole (12j)
Method A: From imidovanadium(V) complex **7a** (0.250 g, 1.10 mmol) in toluene (5 mL), *t*-butylphosphaalkyne (**8a**; 0.110 g, 1.10 mmol), and but-2-yne (**10f**; 0.192 g, 3.30 mmol); yield (bulb-to-bulb distillation): 0.080 g (31%); bp 140°C/0.001 mbar.

^{1}H NMR (C_6D_6, 25°C, 200.1 MHz): δ = 1.41 [d, 9 H, ^4J(H,P) = 1.7 Hz] and 1.41 [d, 9 H, ^4J(H,P) = 2.4 Hz, *t*-C_4H_9 at N-1 and C-3], 2.11 [d, 3 H, ^4J(H,P) = 2.2 Hz, CH_3 at C-4], 2.14 (s, 3 H, CH_3 at C-5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 50.3 MHz): δ = 14.6 (s, CH_3 at C-5), 16.9 [d, ^3J(C,P) = 4.2 Hz CH_3 at C-4], 31.9 [d, ^3J(C,P) = 13.6 Hz] and 32.0 [d, ^3J(C,P) = 11.0 Hz] (C(CH_3)$_3$ at N-1 and C-3), 34.5 [d, ^2J(C,P) = 11.0 Hz, C(CH_3)$_3$ at C-3], 57.2 [d, ^2J(C,P) = 11.9 Hz, C(CH_3)$_3$ at N-1], 123.8 [d, ^2J(C,P) = 5.1 Hz, C-4], 142.4 [d, ^2J(C,P) = 2.5 Hz, C-5], 173.6 [d, ^1J(C,P) = 40.7 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 168.8 (s).

MS (EI, 70 eV): *m*/*z* (%) = 225 (M^+, 89), 168 ([M − C_4H_8]$^+$, 100), 57 ([*t*-C_4H_9]$^+$, 66).

1,3-Di-*tert*-butyl-4,5-diphenyl-1*H*-1,2-azaphosphole (12k)
Method A: From imidovanadium(V) complex **7a** (0.290 g, 1.29 mmol) in toluene (5 mL), *t*-butylphosphaalkyne (**8a**; 0.130 g, 1.30 mmol), and 1,2-diphenylacetylene (**10g**; 0.460 g, 2.56 mmol); yield (bulb-to-bulb distillation): 0.240 g (67%); bp 220°C/0.001 mbar.

^{1}H NMR (C_6D_6, 25°C, 200.1 MHz): δ = 1.43 [d, 9H, ^4J(H,P) = 1.5 Hz] and 1.48 [d, 9H, ^4J(H,P) = 2.4 Hz, *t*-Bu at *N*-1 and C-3], 6.77−7.23 (m, 10H, Ph-H).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 50.3 MHz): δ = 33.1 [d, ^3J(C,P) = 13.6 Hz] and 33.5 [d, ^3J(C,P) = 11.9 Hz, C(CH_3)$_3$ at *N*-1 and C-3], 35.7 [d, ^2J(C,P) = 18.7 Hz, C(CH_3)$_3$ at C-3], 59.3 [d, ^2J(C,P) = 11.0 Hz, C(CH_3)$_3$ at *N*-1], 126.2 (s, Ph-C), 127.0 [d, ^2J(C,P) = 5.9 Hz, C-4], 128.3 (s, Ph-C), 132.5 [d, J(C,P) = 2.6 Hz, Ph-C], 133.8 (s, Ph-C), 133.9 [d, J(C,P) = 5.9 Hz, Ph-C], 138.2 [d, J(C,P) = 3.4 Hz, Ph-C], 140.2 (s, Ph-C), 140.2 (s, Ph-C), 148.1 [d, ^2J(C,P) = 1.7 Hz, C-5], 174.4 [d, ^1J(C,P) = 44.1 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 173.4 (s).

1-(1-Adamantyl)-3-*tert*-butyl-5-phenyl-1*H*-1,2-azaphosphole (12l)
Method A: From imidovanadium(V) complex **7b** (0.100 g, 0.31 mmol) in toluene (15 mL), *t*-butylphosphaalkyne (**8a**; 0.031 g, 0.31 mmol), and phenylacetylene (**10a**; 0.095 g, 0.93 mmol); yield (bulb-to-bulb distillation): 0.040 g (40%); bp 170°C/0.001 mbar.

^{1}H NMR (C_6D_6, 25°C, 200.1 MHz): δ = 1.34 [t, 6 H, ^3J(H,H) = 3.1 Hz, ad-H], 1.50 [d, 9 H, ^4J(H,P) = 1.7 Hz, *t*-C_4H_9 at C-3], 1.80 (m, 3 H, ad-H), 2.26 [d, 6 H, ^3J(H,H) = 3.1 Hz, Ad-H], 6.72 [d, 1 H, ^3J(H,P) = 7.1 Hz, H-4], 7.02−7.36 (m, 5 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 50.3 MHz): δ = 30.5 [d, ^4J(C,P) = 2.2 Hz, Ad-C], 33.0 [d, ^3J(C,P) = 10.2 Hz, C(CH_3)$_3$ at C-3], 34.4 [d, ^2J(C,P) = 17.4 Hz, C(CH_3)$_3$ at C-3], 36.1 (s, Ad-C), 46.0 [d, ^3J(C,P) = 12.4 Hz, Ad-C], 60.6 [d, ^2J(C,P) = 9.5 Hz, C(CH_2)$_3$ at N-1], 120.4 [d, ^2J(C,P) = 5.8 Hz, C-4], 127.4 (s, Ph-C), 128.1 (s, Ph-C), 131.1 [d, ^4J(C,P) = 2.2 Hz, Ph-C], 140.1 [d, ^3J(C,P) = 3.6 Hz, Ph-C], 148.2 (s, C-5), 177.7 [d, ^1J(C,P) = 43.6 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 179.2 (s).

MS (EI, 70 eV): *m*/*z* (%) = 351 (M^+, 12), 135 ([$C_{10}H_{15}$]$^+$, 26), 135 ([C_8H_6]$^+$, 100).

3-*tert*-Butyl-5-phenyl-1-isopropyl-1*H*-1,2-azaphosphole (12m)
Method B: From imidovanadium(V) complex **7c** (0.210 g, 0.98 mmol) in toluene (5 mL), *t*-butylphosphaalkyne (**8a**; 0.098 g, 0.98 mmol), and phenylacetylene (**10a**; 0.100 g, 0.98 mmol); yield (bulb-to-bulb distillation): 0.160 g (65%), bp 140°C/0.001 mbar.

^{1}H NMR (C_6D_6, 25°C, 200.1 MHz): δ = 1.27 [d, 6 H, ^3J(H,H) = 6.6 Hz, CH(CH_3)$_2$], 1.49 [d, 9 H, ^4J(H,P) = 1.7 Hz, *t*-C_4H_9 at C-3], 4.39 [pseudo-oct, 1 H, ^3J(H,H) = ^3J(H,P) = 6.6 Hz, C*H*(CH_3)$_2$], 6.77 [d, 1 H, ^3J(H,P) = 6.1 Hz, H-4], 7.10−7.26 (m, 5 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 50.3 MHz): δ = 26.7 [d, ^3J(C,P) = 10.5 Hz, CH(CH_3)$_2$], 33.1 [d, ^3J(C,P) = 9.5 Hz, C(CH_3)$_3$ at C-3], 34.6 [d, ^2J(C,P) = 17.2 Hz, C(CH_3)$_3$ at C-3], 50.0 [d, ^2J(C,P) = 12.4 Hz, *C*H(CH_3)$_2$], 116.7 [d, ^2J(C,P) = 5.7 Hz, C-4], 127.8 (s, Ph-C), 128.5 (s, Ph-C), 129.5 [d, ^4J(C,P) = 1.9 Hz, Ph-C], 135.7 [d, ^3J(C,P) = 3.8 Hz, Ph-C], 149.2 (s, C-5), 180.6 [d, ^1J(C,P) = 43.8 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 172.5 (s).

MS (EI, 70 eV): *m/z* (%) = 259 (M^+, 94), 244 ([M − CH_3]$^+$, 100), 202 ([M − C_4H_9]$^+$, 64), 77 ([C_6H_5]$^+$, 5).

1*H*-1,2-Azaphospholetetracarbonyliron(0) Complexes 13a,b; General Procedure

To a stirred suspension of nonacarbonyldiiron(0) in toluene was added an equimolar amount of the respective 1*H*-1,2-azaphosphole **12a,b** at 25°C. After 18 h the reaction mixture was filtered over Celite and the solvent evaporated. The dark red residue was dissolved in pentane and crystallized at −30°C providing a black-red, crystalline powder of the respective complex **13a,b**.

(2-η^1-1,3-Di-*tert*-butyl-5-phenyl-1*H*-1,2-azaphosphole)tetracarbonyliron(0) (13a)

From nonacarbonyldiiron(0) (0.265 g, 0.73 mmol) in toluene (12 mL) and azaphosphole **12a** (0.199 g, 0.73 mmol); yield: 0.203 g (63%); mp 105°C (dec.).

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 1.39 [d, 9 H, ^4J(H,P) = 1.4 Hz] and 1.40 [d, 9 H, ^4J(H,P) = 0.5 Hz, *t*-C_6H_4 at N-1 and C-3], 6.69 [d, 1 H, ^3J(H,P) = 10.3 Hz, H-4], 6.99−7.17 (m, 5 H, C_6H_5).

^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 31.5 [d, ^3J(C,P) = 8.7 Hz] and 32.7 [d, ^3J(C,P) = 9.4 Hz, C(*C*H_3)$_3$ at N-1 and C-3], 35.6 [d, ^2J(C,P) = 13.1 Hz, *C*(CH_3)$_3$ at C-3], 62.2 [d, ^2J(C,P) = 7.3 Hz, *C*(CH_3)$_3$ at N-1], 124.7 [d, ^2J(C,P) = 5.1 Hz, C-4], 127.5 (s, Ph-C), 128.7 (s, Ph-C), 129.0 [d, ^4J(C,P) = 5.1 Hz, Ph-C], 137.5 [d, ^3J(C,P) = 5.8 Hz, Ph-C], 162.7 [d, ^2J(C,P) = 8.7 Hz, C-5], 204.6 [d, ^1J(C,P) = 25.5 Hz, C-3], 218.2 [d, ^2J(C,P) = 5.8 Hz, CO].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 121.3 (s).

IR (CCl_4): ν = 2968 (*C*−H), 2047 (*CO*), 1969 (*CO*), 1940 (*CO*), 1186, 1028, 676, 634 cm^{-1}.

Anal. Calcd for $C_{21}H_{24}FeNO_4P$ (441.3): C, 57.16; H, 5.48; N, 3.17. Found C, 56.13; H, 5.64; N, 3.08.

MS (EI, 70 eV): *m/z* (%) = 441 (M^+, 1), 273 ([M − Fe(CO)$_4$]$^+$, 27), 217 ([M − Fe(CO)$_4$ − C_4H_8]$^+$, 51), 202 ([M − Fe(CO)$_4$ − C_4H_9N]$^+$, 100), 57 ([*t*-C_4H_9]$^+$, 5).

(2-η^1-1-*tert*-Butyl-3-(1,1-dimethylpropyl)-5-phenyl-1*H*-1,2-azaphosphole)tetracarbonyliron(0) (13b)

From nonacarbonyldiiron(0) (0.224 g, 0.78 mmol) in toluene (12 mL) and azaphosphole **12b (**0.284 g, 0.78 mmol); yield : 0.210 g (59%); mp 107°C (dec.).

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 0.84 [t, 3 H, ^3J(H,H) = 7.4 Hz, CH_2CH_3], 1.36 [d, 6 H, ^4J(H,P) = 1.7 Hz, C(CH_3)$_2$Et], 1.41 [d, 9 H, ^4J(H,P) = 1.0 Hz, *t*-C_4H_9 at N-1], 1.68 [dq, 2 H, ^3J(H,H) = 7.5 Hz, ^4J(H,P) = 1.7 Hz, CH_2CH_3], 6.65 [d, 1 H, ^3J(H,P) = 10.5 Hz, H-4], 6.97−7.20 (m, 5 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 9.2 (s, CH_2CH_3), 28.9 [d, ^3J(C,P) = 10.2 Hz, C(*C*H_3)$_2$Et], 32.9 [d, ^3J(C,P) = 9.3 Hz, C(*C*H_3)$_3$ at N-1], 36.9 [d, ^2J(C,P) = 5.9 Hz, *C*(CH$_3$)$_2$Et], 39.6 [d, ^3J(C,P) = 11.9 Hz, *C*H_2CH$_3$], 62.7 [d, ^2J(C,P) = 7.6 Hz, *C*(CH_3)$_3$ at N-1], 125.7 [d, ^2J(C,P) = 5.5 Hz, C-4], 127.4 (s, Ph-C), 129.0 (s, Ph-C), 129.6 [d, ^4J(C,P) = 5.1 Hz, Ph-C], 138.2 [d, ^3J(C,P) = 5.1 Hz, Ph-C], 163.1 [d, ^2J(C,P) = 9.3 Hz, C-5], 204.0 [d, ^1J(C,P) = 24.6 Hz, C-3], 219.2 [d, ^2J(C,P) = 5.9 Hz, CO].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 126.2 (s).

IR (CCl_4): ν = 2965 (C−H), 2047 (CO), 1970 (CO), 1960 (CO), 1940 (CO), 1479, 1190, 1029, 705, 634 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 455 (M^+, 16), 437 ([M − CO]$^+$, 59), 287 ([M − Fe(CO)$_4$]$^+$, 100), 231 ([M − Fe(CO)$_4$ − C_4H_8]$^+$, 32), 216 ([M − Fe(CO)$_4$ − C_4H_9N]$^+$, 32), 57 ([*t*-C_4H_9]$^+$, 50).

1,2-Azaphospholium Triflates 15a,b; General Procedure

To a stirred solution of the 1*H*-1,2-azaphosphole **12a** in CH_2Cl_2 was added an equimolar amount of the respective alkyl trifluoromethanesulfonate **14a,b** at −78°C. The reaction mixture was allowed to warm to 25°C and after 18 h all volatile components were removed at 25°C/0.001 mbar, whereby the respective products **15a,b** were obtained as colorless, viscous oils.

1,3-Di-*tert*-butyl-2-methyl-5-phenyl-1,2-azaphospholium Triflate (15a)

From azaphosphole **12a** (0.183 g, 0.67 mmol) in CH_2Cl_2 (8 mL) and methyl triflate (**14a**; 0.110 g, 0.67 mmol); yield: 0.293 g (~100%); bp >250°C/0.001 mbar.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 1.18 (s, 9 H) and 1.35 (s, 9 H, *t*-C_4H_9 at N-1 and C-3), 2.06 [d, 3 H, ^2J(H,P) = 5.7 Hz, CH_3 at P-2], 6.59 [d, 1 H, ^3J(H,P) = 10.8 Hz, H-4], 7.30−7.36 (m, 3 H,C_6H_5), 7.63−7.70 (m, 2H,C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 15.7 [d, ^1J(C,P) = 27.3 Hz, CH_3 at P-2], 30.6 [d, ^3J(C,P) = 6.4 Hz] and 31.6 [d, ^3J(C,P) = 6.4 Hz, C(*C*H_3)$_3$ at N-1 and C-3], 36.5 [d, ^2J(C,P) = 10.4 Hz, *C*(CH_3)$_3$ at C-3], 66.5 [d, ^2J(C,P) = 7.2 Hz, *C*(CH_3)$_3$ at N-1], 121.7 [q, ^1J(C,F) = 322.2 Hz, $CF_3SO_3^-$], 127.5 [d, ^2J(C,P) = 4.4 Hz, C-4], 128.4 (s, Ph-C), 130.8 (s, Ph-C), 132.7 (s, Ph-C), 133.3 [d, ^3J(C,P) = 4.0 Hz, Ph-C], 180.3 [d, ^2J(C,P) = 8.8 Hz, C-5], 192.5 [d, ^1J(C,P) = 24.9 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 103.4 (s).

IR (CCl_4): ν = 2960 (C−H), 2926 (C−H), 2873 (C−H), 1495, 1262, 1098, 1030, 727, 694 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 288 (M^+, 3), 217 ([M − CH_3 − C_4H_8]$^+$, 9), 202 ([M − CH_3 − C_4H_9N]$^+$, 13), 56 ([C_4H_8]$^+$, 100).

1,3-Di-*tert*-butyl-2-ethyl-5-phenyl-1,2-azaphospholium Triflate (15b)

From azaphosphole **12a** (0.231 g, 0.84 mmol) in CH_2Cl_2 (10 mL) and ethyl triflate (**14b**; 0.150 g, 0.84 mmol); yield: 0.381 g (~100%); bp >250°C/0.001 mbar.

^{1}H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 1.00 [dt, 3 H, ^3J(H,P) = 10.4 Hz, ^3J(H,H) = 7.3 Hz, CH_2CH_3 at P-2], 1.43 [d, 9 H, ^4J(H,P) = 1.2 Hz, *t*-C_4H_9 at C-3], 1.61 (s, 9H, *t*-C_4H_9 at N-1), 2.93 [dq, 2 H, ^2J(H,P) = 34.1 Hz, ^3J(H,H) = 7.3 Hz, CH_2CH$_3$ at P-2], 7.03 [d, 1 H, ^3J(H,P) = 10.3 Hz, H-4], 7.50−7.67 (m, 5 H, C_6H_5).

^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 7.4 [d, ^2J(C,P) = 2.2 Hz, CH_2CH_3 at P-2], 23.8 [d, ^1J(C,P) = 29.8 Hz, *C*H_2CH$_3$ at P-2], 30.5 [d, ^3J(C,P) = 6.5 Hz] and 31.4 [d, ^3J(C,P) = 6.5 Hz, C(*C*H_3)$_3$ at N-1 and C-3], 36.9 [d, ^2J(C,P) = 11.6 Hz, *C*(CH_3)$_3$ at C-3], 67.0 [d, ^2J(C,P) = 7.3 Hz, *C*(CH_3)$_3$ at N-1], 120.5 [q, ^1J(C,F) = 321.4 Hz, $CF_3SO_3^-$], 126.7 [d, ^2J(C,P) = 4.4 Hz, C-4], 128.6 (s, Ph-C), 131.1 (s, Ph-C), 132.1 [d, ^3J(C,P) = 4.4 Hz, Ph-C], 134.4 (s, Ph-C), 181.7 [d, ^2J(C,P) = 8.0 Hz, C-5], 190.8 [d, ^1J(C,P) = 28.3 Hz, C-3].

^{31}P{^{1}H} NMR ($CDCl_3$, 25°C, 81.0 MHz): δ = 114.5 (s).

IR (CCl_4): ν = 2960 (C−H), 2928 (C−H), 2872 (C−H), 1458, 1265, 1152, 1030, 909 cm^{-1}.

MS (EI, 70 eV): *m/z* (%) = 302 (M^+, 2), 217 ([M − C_2H_5 − C_4H_8]$^+$, 66), 202 ([M − C_2H_5 − C_4H_9N]$^+$, 8), 56 ([C_4H_8]$^+$, 54), 41 ([C_3H_5]$^+$, 100).

6,9-Di-*tert*-butyl-2,2′-diethoxy-4,4′-bis(ethoxycarbonyl)-7-phenyl-1,1′-dioxa-3,3′,4,4′,6-pentaaza-5-phosphaspiro[4.4.4]trideca-2,2′,7-triene (17)

Diethyl azodicarboxylate (**16**, 0.293 g, 1.68 mmol)) was added to a stirred solution of azaphosphole **12a** (0.230 g, 0.84 mmol) in Et_2O (5 mL) at 25°C. After 3 d all volatile components were removed at 25°C/0.001 mbar and the residue was suspended in cold (3°C) hexane (3 mL), whereby a colorless precipitate was separated. The precipitate was washed with cold hexane (3 × 3 mL) and then dried at 25°C/0.001 mbar providing the spirotricyclic betaine **17**; yield: 0.193 g (37%); mp 103°C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 0.92 [t, 6 H, ^3J(H,H) = 7.1 Hz, OCH_2CH_3], 1.01 [t, 6 H, ^3J(H,H) = 7.1 Hz, OCH_2CH_3], 1.30 (s, 9 H, *t*-C_4H_9 at C-9), 1.56 (s, 9 H, *t*-C_4H_9 at N-6), 3.64−4.12 (m, 8 H, OCH_2CH_3), 6.45 [d, 1 H, ^3J(H,P) = 73.0 Hz, H-8], 7.09−7.23 (m, 3 H, C_6H_5), 7.89−7.93 (m, 2 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 14.0 (s, OCH_2CH_3), 14.1 (s, OCH_2CH_3), 14.2 (s, OCH_2CH_3), 14.3 (s, OCH_2CH_3), 29.7 [d, ^3J(C,P) = 4.6 Hz, $C(CH_3)_3$ at C-9], 31.4 [s, $C(CH_3)_3$ at N-6], 38.1 [d, ^2J(C,P) = 15.3 Hz, $C(CH_3)_3$ at C-9], 58.3 [s, $C(CH_3)_3$ at N-6], 63.1 (s, OCH_2CH_3), 64.9 (s, OCH_2CH_3), 100.4 [d, ^1J(C,P) = 113.7 Hz, C-9], 124.7 [d, ^2J(C,P) = 4.0 Hz, C-8], 127.7 (s, Ph-C), 128.1 (s, Ph-C), 128.8 (s, Ph-C), 141.7 (s, Ph-C), 148.5 (s, C-7), 150.4 (s) and 153.4 [d, ^2J(C,P) = 14.5 Hz] (C2 and C2´), 156.2 [d, ^2J(C,P) = 10.7 Hz] and 156.9 [d, ^2J(C,P) = 25.2 Hz] (CO_2Et at N-4 and N-4´).

^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 81.0 MHz): δ = −41.0 (s).

IR (CCl_4): ν = 2978 (C−H), 2936 (C−H), 2910 (C−H), 1747 (CO), 1669, 1478, 1428, 1382, 1369, 1346, 1320, 1306, 1271, 1247, 1176, 1145, 1072, 1017, 696, 644 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 621 (M^+, 1), 564 ($[M - C_4H_9]^+$, 5), 390 ($[M - C_6H_{10}N_2O_4 - C_4H_9]^+$, 11), 273 ($[M - 2(C_6H_{10}N_2O_4)]^+$, 37), 202 ($[M - 2(C_6H_{10}N_2O_4) - C_4H_9N]^+$, 37), 185 ($[M - 2(C_6H_{10}N_2O_4) - C_7H_4]^+$, 100), 57 ($[C_4H_9]^+$, 33).

7-Aza-1-phosphanorbornadienes 19a-d; General Procedure

To a stirred solution of the respective 1*H*-1,2-azaphosphole **12a,b** in toluene was added an equimolar amount of the respective dialkyl acetylenedicarboxylate **18a**−**d** at −78°C. The reaction mixture was allowed to warm to 25°C and after 18 h all volatile components were removed at 25°C/0.001 mbar. The residue was dissolved in pentane and impurities were filtered over Celite. The filtrate was concentrated and the azaphosphanorbornadienes **19a**−**d** were obtained by crystallization at −30°C as colorless to yellow, microcrystalline solids.

Dimethyl 6,7-Di-*tert*-butyl-4-phenyl-7-aza-1-phosphabicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (19a)

From azaphosphole **12a** (0.772 g, 2.83 mmol) in toluene (10 mL) and dimethyl acetylenedicarboxylate (**18a**; 0.402 g (2.83 mmol); yield: 0.835 g (71%); mp 85°C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 0.91 [d, 9 H, ^4J(H,P) = 0.5 Hz, *t*-C_4H_9 at N-7], 1.12 [d, 9 H, ^4J(H,P) = 0.5 Hz, *t*-C_4H_9 at C-6], 3.39 (s, 3 H, OCH_3), 3.46 (s, 3 H, OCH_3), 7.13−7.20 (m, 3 H, C_6H_5), 7.32 [d, 1 H, ^3J(H,P) = 8.1 Hz, H-5], 7.61−7.65 (m, 2 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 28.9 [d, ^3J(C,P) = 5.1 Hz, $C(CH_3)_3$ at C-6], 32.0 [d, ^3J(C,P) = 11.0 Hz, $C(CH_3)_3$ at N-7], 34.4 [d, ^2J(C,P) = 16.1 Hz, $C(CH_3)_3$ at C-6], 51.3 (s, OCH_3), 51.4 (s, OCH_3), 56.1 [d, ^2J(C,P) = 8.5 Hz, $C(CH_3)_3$ at N-7], 93.1 [d, ^2J(C,P) = 11.0 Hz, C-4], 128.1 (s, Ph-C), 128.5 (s, Ph-C), 130.1 (s, Ph-C), 137.8 (s, Ph-C), 142.2 (s, C-5), 156.0 [d, ^1J(C,P) = 33.9 Hz, C-2], 164.3 [d, ^2J(C,P) = 20.3 Hz, C-3], 166.9 (s, CO_2Me), 168.1 (s, CO_2Me), 177.4 [d, ^1J(C,P) = 33.9 Hz, C-6].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 54.0 (s).

IR (CCl_4): ν = 2964 (C−H), 1731 (CO), 1652, 1474, 1458, 1434, 1363, 1261, 1234, 1197, 1029 cm^{-1}.

Anal. Calcd for $C_{23}H_{30}NO_4P$ (415.5): C, 66.49; H, 7.28; N, 3.37. Found C, 66.51; H, 7.41; N, 3.28.

MS (EI, 70 eV): *m*/*z* (%) = 415 (M^+, 5), 273 ($[M - C_6H_6O_4]^+$, 34), 217 ($[M - C_6H_6O_4 - C_4H_8]^+$, 67), 202 ($[M - C_6H_6O_4 - C_4H_9N]^+$, 100), 57 ($[C_4H_9]^+$, 83).

Dimethyl 7-*tert*-Butyl-6-(1,1-dimethylpropyl)-4-phenyl-7-aza-1-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (19b)

From azaphosphole **12b** (0.188 g, 0.65 mmol) in toluene (5 mL) and dimethyl acetylenedicarboxylate (**18a**; 0.093 g, 0.65 mmol); yield: 0.204 g (73%); mp 83°C.

^{1}H NMR ($CDCl_3$, 25°C, 400.1 MHz): δ = 0.63 [t, 3 H, ^3J(H,H) = 7.4 Hz, CH_2CH_3], 0.80 (s, 9 H, *t*-C_4H_9 at N-7), 1.03 [s, 3 H, $C(CH_3)(CH_3)Et$], 1.13 [s, 3 H, $C(CH_3)(CH_3)Et$], 1.37−1.49 (m, 2 H, CH_2CH_3), 3.56 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 7.20 [d, 1 H, ^3J(H,P) = 8.1 Hz, H-5], 7.23−7.29 (m, 3 H, C_6H_5),), 7.51−7.55 (m, 2 H, C_6H_5).

^{13}C{^{1}H} NMR ($CDCl_3$, 25°C, 100.6 MHz): δ = 8.6 (s, CH_2CH_3), 25.6 [d, ^3J(C,P) = 4.8 Hz, $C(CH_3)(CH_3)_3Et$], 27.2 [d, ^3J(C,P) = 6.4 Hz, $C(CH_3)(CH_3)_3Et$], 32.1 [d, ^3J(C,P) = 11.2 Hz, $C(CH_3)_3$ at N-7], 34.1 [d, ^3J(C,P) = 4.8 Hz, CH_2CH_3], 37.9 [d, ^2J(C,P) = 15.3 Hz, CMe_2Et], 51.9 [d, ^2J(C,P) = 9.6 Hz, $C(CH_3)_3$ at N-7], 56.2 (s, OCH_3), 56.3 (s, OCH_3), 92.9 [d, ^2J(C,P) = 10.4 Hz, C-4], 128.0 (s, Ph-C), 128.5 (s, Ph-C), 129.9 (s, Ph-C), 137.4 (s, Ph-C), 143.5 (s, C-5), 155.2 [d, ^1J(C,P) = 34.5 Hz, C-2], 164.5 [d, ^2J(C,P) = 19.3 Hz, C-3], 167.4 (s, CO_2Me), 168.7 (s, CO_2Me), 176.2 [d, ^1J(C,P) = 37.7 Hz, C-6].

^{31}P{^{1}H} NMR ($CDCl_3$, 25°C, 81.0 MHz): δ = 53.7 (s).

IR (CCl_4): ν = 2967 (C−H), 1731 (CO), 1653, 1435, 1363, 1263, 1239, 1197, 1028, 909, 701, 668 cm^{-1}.

Anal. Calcd for $C_{24}H_{32}NO_4P$ (429.5): C, 67.12; H, 7.51; N, 3.26. Found C, 66.51; H, 7.41; N, 3.28.

MS (EI, 70 eV): *m*/*z* (%) = 429 (M^+, 1), 287 ($[M - C_6H_6O_4]^+$, 28), 231 ($[M - C_6H_6O_4 - C_4H_8]^+$, 24), 216 ($[M - C_6H_6O_4 - C_4H_9N]^+$, 9), 202 ($[M - C_6H_6O_4 - C_4H_9N - CH_3]^+$, 100), 57 ($[C_4H_9]^+$, 83).

Diethyl 6,7-Di-*tert*-butyl-4-phenyl-7-aza-1-phosphabicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (19c)

From azaphosphole **12a** (0.347 g, 1.27 mmol) in toluene (8 mL) and diethyl acetylenedicarboxylate (**18b**; 0.216 g, 1.27 mmol); yield: 0.377 g (67%); mp 87°C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 0.88 [t, 3 H, ^3J(H,H) = 7.2 Hz, OCH_2CH_3], 0.93 [d, 9 H, ^4J(H,P) = 1.2 Hz, *t*-Bu at N-7], 0.97 [t, 3 H, ^3J(H,H) = 7.2 Hz, OCH_2CH_3], 1.15 (s, 9 H, *t*-C_4H_9 at C-6), 3.84−4.16 (m, 4 H, OCH_2CH_3), 7.10−7.14 (m, 3 H, C_6H_5), 7.36 [d, 1 H, ^3J(H,P) = 8.1 Hz, H-5], 7.66−7.71 (m, 2 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 13.1 (s, OCH_2CH_3), 14.3 (s, OCH_2CH_3), 29.4 [d, ^3J(C,P) = 4.6 Hz, $C(CH_3)_3$ at C-6], 32.6 [d, ^3J(C,P) = 11.4 Hz, $C(CH_3)_3$ at N-7], 35.0 [d, ^2J(C,P) = 16.0 Hz, $C(CH_3)_3$ at C-6], 56.6 [d, ^2J(C,P) = 8.4 Hz, $C(CH_3)_3$ at N-7], 60.9 (s, OCH_2CH_3), 61.0 (s, OCH_2CH_3), 93.6 [d, ^2J(C,P) = 10.7 Hz, C-4], 128.4 (s, Ph-C), 128.8 (s, Ph-C), 130.8 (s, Ph-C), 138.4 (s, Ph-C), 141.8 (s, C-5), 156.2 [d, ^1J(C,P) = 32.0 Hz, C-2], 164.4 [d, ^2J(C,P) = 19.8 Hz, C-3], 166.7 (s, CO_2Et), 168.9 (s, CO_2Et), 178.0 [d, ^1J(C,P) = 35.1 Hz, C-6].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 54.0 (s).

IR (CCl_4): ν = 2965 (C−H), 2903 (C−H), 1717 (CO), 1620, 1473, 1462, 1447, 1391, 1364, 1292, 1276, 1228, 1198, 1035 cm^{-1}.

Anal. Calcd for $C_{25}H_{34}NO_4P$ (443.5): C, 67.70; H, 7.73; N, 3.16. Found C, 66.47; H, 7.40; N, 3.00.

MS (EI, 70 eV): *m*/*z* (%) = 443 (M^+, 1), 273 ($[M - C_8H_{10}O_4]^+$, 46), 217 ($[M - C_8H_{10}O_4 - C_4H_8]^+$, 53), 202 ($[M - C_8H_{10}O_4 - C_4H_9N]^+$, 100), 57 ($[C_4H_9]^+$, 83).

Di-*tert*-butyl 6,7-Di-*tert*-Butyl-4-phenyl-7-aza-1-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (19d)

From) azaphosphole **12a** (0.161 g, 0.59 mmol) in toluene (4 mL) and di-*tert*-butyl acetylenedicarboxylate (**18c**; 0.133 g, 0.59 mmol); yield: 0.186 g (63%); mp 93 °C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 0.97 [d, 9 H, ^4J(H,P) = 1.1 Hz, *t*-Bu at N-7], 1.23 (s, 9 H, *t*-C_4H_9 at C-6), 1.32 [s, 9 H, $OC(CH_3)_3$], 1.46 [s, 9 H, $OC(CH_3)_3$], 7.11−7.20 (m, 3 H, C_6H_5), 7.37 [d, 1 H, ^3J(H,P) = 8.2 Hz, H-5], 7.69−7.74 (m, 2 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 27.8 [s, $OC(CH_3)_3$], 28.1 [s, $OC(CH_3)_3$], 29.4 [d, ^3J(C,P) = 4.8 Hz, $C(CH_3)_3$ at C-6], 32.6 [d, ^3J(C,P) = 10.5 Hz, $C(CH_3)_3$ at N-7], 34.9 [d, ^2J(C,P) = 16.2 Hz, $C(CH_3)_3$ at C-6], 56.3 [d, ^2J(C,P) = 8.6 Hz, $C(CH_3)_3$ at N-7], 80.7 [s, $OC(CH_3)_3$], 81.4 [s, $OC(CH_3)_3$], 93.2 [d, ^2J(C,P) = 10.5 Hz, C-4], 128.2 (s, Ph-C), 128.6 (s, Ph-C), 138.5 (s, Ph-C), 140.2 (s, C-5), 155.9 [d, ^1J(C,P) = 29.6 Hz, C-2], 163.6 [d, ^2J(C,P) = 20.0 Hz, C-3], 165.1 (s, CO_2*t*Bu), 169.3 (s, CO_2*t*Bu), 177.7 [d, ^1J(C,P) = 38.1 Hz, C-6].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 54.2 (s).

IR (CCl_4): ν = 2970 (C−H), 2933 (C−H), 1712 (CO), 1624, 1476, 1459, 1392, 1367, 1299, 1259, 1167, 1113, 1028, 702 cm^{-1}.

Anal. Calcd for $C_{29}H_{42}NO_4P$ (499.6): C, 69.72; H, 8.48; N, 2.80. Found C, 68.23; H, 8.27; N, 3.57.

MS (EI, 70 eV): *m*/*z* (%) = 499 (M^+, 3), 273 ($[M - C_{12}H_{18}O_4]^+$, 31), 217 ($[M - C_{12}H_{18}O_4 - C_4H_8]^+$, 59), 202 ($[M - C_{12}H_{18}O_4 - C_4H_9N]^+$, 100), 57 ($[C_4H_9]^+$, 78).

6,7-Di-*tert*-butyl-2,3-bis(trifluoromethyl)-4-phenyl-7-aza-1-phosphabicyclo[2.2.1]hepta-2,5-diene (19e)

Hexafluorobut-2-yne (**18d**; 0.240 g, 1.48 mmol) was condensed at −196°C in a glass-pressure tube and then warmed up to −78°C. Then the azaphosphole **12a** (0.403 g, 1.48 mmol dissolved in CH_2Cl_2 (5 mL) was added at −78°C and the reaction mixture was allowed to warm to 25°C. After 18 h all volatile components were removed at 25°C/0.001 mbar, the residue was dissolved in pentane and filtered over Celite. Crystallization at −28°C from CH_2Cl_2 provided the azaphosphanorbornadiene **19e** as colorless crystals; yield: 0.470 g (73%); mp 93°C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 0.86 [d, 9 H, ^4J(H,P) = 1.6 Hz, *t*-C_4H_9 at N-7], 1.15 (s, *t*-C_4H_9 at C-6), 7.15−7.18 (m, 3 H, C_6H_5), 7.27 [d, 1 H, ^3J(H,P) = 8.4 Hz, H-5], 7.56−7.62 (m, 2 H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 29.2 [d, ^3J(C,P) = 5.1 Hz, $C(CH_3)_3$ at C-6], 32.6 [d, ^3J(C,P) = 11.3 Hz, $C(CH_3)_3$ at N-7], 34.9 [d, ^2J(C,P) = 15.3 Hz, $C(CH_3)_3$ at C-6], 57.1 [d, ^2J(C,P) = 8.9 Hz, $C(CH_3)_3$ at N-7], 94.3 [dq, ^2J(C,P) = 12.7, ^3J(C,F) = 1.3 Hz, C-4], 121.8 [qq, ^1J(C,F) = 274.3 Hz, ^4J(C,F) = 1.5 Hz, CF_3 at C-3], 124.2 [qdq, ^1J(C,F) = 270.2 Hz, ^2J(C,P) = 21.6 Hz, ^4J(C,F) = 1.5 Hz, CF_3 at C-2], 127.5 (s, Ph-C), 129.3 (s, Ph-C), 136.4 (s, Ph-C), 139.3 (d, ^2J(C,P) = 1.9 Hz, C-5), 160.0 (m_c) and 163.3 (m_c, C-2 and C-3), 179.8 [d, ^1J(C,P) = 38.2 Hz, C-6].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 53.0 [q, ^3J(P,F) = 15.8 Hz].

IR (CCl_4): ν = 2966 (C−H), 2905 (C−H), 1651, 1463, 1450, 1364, 1299, 1253, 1168, 1150, 1017, 703 cm^{-1}.

Anal. Calcd for $C_{21}H_{24}F_6NP$ (435.4): C, 57.93; H, 5.56; N, 3.22. Found C, 57.63; H, 5.52; N, 3.70.

MS (EI, 70 eV): *m*/*z* (%) = 435 (M^+, 5), 273 ($[M - C_4F_6]^+$, 26), 217 ($[M - C_4F_6 - C_4H_8]^+$, 62), 202 ($[M - C_4F_6 - C_4H_9N]^+$, 100), 162 ($[C_4F_6]^+$, 15), 57 ($[C_4H_9]^+$, 39).

6,7-Di-*tert*-butyl-4-phenyl-7-aza-1-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dinitrile (19f)

To a stirred solution of the azaphosphole **12a** (0.332 g, 1.40 mmol) in CH_2Cl_2 (5 mL) was added dicyanoacetylene (**18e**; 0.106 g, 1.40 mmol) at −78°C. The reaction mixture was allowed to warm to 25°C and after 18 h all volatile components were removed at 25°C/0.001 mbar. The residue was dissolved in pentane/Et_2O (3:1) and filtered over Celite. The filtrate was concentrated and the azaphosphanorbornadiene **19f** was obtained by crystallization at −78°C as pale yellow crystals; yield: 0.308 g (63%); mp 105°C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 0.64 [d, 9 H, ^4J(H,P) = 1.4 Hz, *t*-C_4H_9 at N-7], 0.87 (s, 9H, *t*-C_4H_9 at C-6), 6.65 [d, 1H, ^3J(H,P) = 7.8 Hz, H-5], 7.02−7.18 (m, 5H, C_6H_5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 27.7 [d, ^3J(C,P) = 6.4 Hz, $C(CH_3)_3$ at C-6], 30.8 [d, ^3J(C,P) = 10.4 Hz, $C(CH_3)_3$ at N-7], 33.9 [d, ^2J(C,P) = 17.7 Hz, $C(CH_3)_3$ at C-6], 56.6 [d, ^2J(C,P) = 8.8 Hz, $C(CH_3)_3$ at N-7], 92.8 [d, ^2J(C,P) = 12.9 Hz, C-4], 113.6 (s, CN), 113.7 (s, CN), 128.0 (s, Ph-C), 129.0 (s, Ph-C), 129.8 (s, Ph-C), 134.4 (s, Ph-C), 144.7 (s, C-5), 151.9 [d, ^2J(C,P) = 4.8 Hz, C-3], 152.7 [d, ^1J(C,P) = 47.4 Hz, C-2], 177.0 [d, ^1J(C,P) = 29.7 Hz, C-6].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 60.6 (s).

IR (CCl_4): ν = 2930 (C−H), 2857 (C−H), 2179, 1684, 1636, 1447, 1360, 1264, 1216, 1089, 1030, 726, cm^{-1}.

Anal. Calcd for $C_{21}H_{24}N_3P$ (349.4): C, 72.19; H, 6.92; N, 12.03. Found C, 70.43; H, 7.28; N, 10.89.

MS (EI, 70 eV): *m*/*z* (%) = 349 (M^+, 8), 292 ($[M - C_4H_9]^+$, 12), 273 ($[M - C_4N_2]^+$, 24), 217 ($[M - C_4N_2 - C_4H_8]^+$, 56), 202 ($[M - C_4N_2 - C_4H_9N]^+$, 100), 57 ($[C_4H_9]^+$, 15).

Dimethyl 6,7-Di-*tert*-butyl-1-oxo-4-phenyl-7-aza-1λ^5-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (20)

Bis(trimethylsilyl) peroxide (0.049 g, 0.28 mmol) was added to a stirred solution of the azaphosphanorbornadiene **19a** (0.115 g, 0.28 mmol) in hexane (4 mL) at 0°C. The reaction mixture was allowed to warm to 25°C and after 18 h all volatile components were removed at 25°C/0.001 mbar. The residue was dissolved in pentane and the solution cooled to −28°C, whereby a colorless precipitate formed. The oxidized bicyclic product **20** was obtained as a yellow solid after evaporation of the solvent; yield: 0.070 g (58%); mp 103°C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 1.14 (s, *t*-C_4H_9 at N-7), 1.32 (s, *t*-C_4H_9 at C-6), 3.28 (s, 3H, OCH_3), 3.44 (s, 3 H, OCH_3), 7.02−7.45 (m, 5H, C_6H_5), 7.56 [d, 1H, ^3J(H,P) = 38.4 Hz, H-5).

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 27.8 [d, ^3J(C,P) = 5.1 Hz, $C(CH_3)_3$ at C-6], 31.5 [d, ^3J(C,P) = 4.5 Hz, $C(CH_3)_3$ at N-7], 34.3 [d, ^2J(C,P) = 8.9 Hz, $C(CH_3)_3$ at C-6], 51.5 (s, OCH_3), 51.6 (s, OCH_3), 58.7 [d, ^2J(C,P) = 1.3 Hz, $C(CH_3)_3$ at N-7], 68.9 [d, ^2J(C,P) = 35.0 Hz, C-4], 127.3 (s, Ph-C), 127.8 (s, Ph-C), 128.6 (s, Ph-C), 136.0 [d, ^3J(C,P) = 12.7 Hz, Ph-C], 142.3 [d, ^1J(C,P) = 83.9 Hz, C-2], 147.9 [d, ^2J(C,P) = 8.9 Hz, C-5], 157.4 [d, ^1J(C,P) = 85.8 Hz, C-6], 162.8 (s, CO_2Me), 165.0 (s, CO_2Me), 168.0 [d, ^2J(C,P) = 6.5 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 42.6 (s).

IR (CCl_4): ν = 2960 (C−H), 1730 (CO), 1685, 1670, 1635, 1603, 1594, 1552, 1538, 1433, 1395, 1368, 1267 (P = O), 1257, 1193, 1094, 1030, 1019, 975, 867 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 431 (M^+, 1), 375 ($[M - C_4H_8]^+$, 100), 343 ($[M - C_4H_9 - OCH_3]^+$, 57), 57 ($[C_4H_9]^+$, 17).

Dimethyl 6,7-Di-*tert*-butyl-4-phenyl-1-thio-7-aza-1λ^5-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (21)

Sulfur (S_8) (0.120 g, 0.47 mmol) and Et_3N (0.048 g, 0.47 mmol) were added to a stirred solution of the azaphosphanorbornadiene **19a** (0.196 g, 0.47 mmol) in toluene (4 mL) at 25°C. After 7 d all volatile components were removed at 25°C/0.001 mbar. The residue was dissolved in pentane and filtered over Celite. After concentrating the filtrate, crystallization at −28°C afforded the sulfurized azaphosphanorbornadiene **21** as an orange-red solid; yield: 0.149 g (71%); mp 96°C.

^{1}H NMR (C_6D_6, 25°C, 400.1 MHz): δ = 1.18 (s, 9 H, *t*-C_4H_9 at N-7), 1.40 (s,) H, *t*-C_4H_9 at C-6), 3.22 (s, 3 H, OCH_3), 3.52 (s, 3 H, OCH_3), 6.98−7.26 (m, 5 H, C_6H_5), 7.63 [d, 1 H, ^3J(H,P) = 38.4 Hz, H-5].

^{13}C{^{1}H} NMR (C_6D_6, 25°C, 100.6 MHz): δ = 28.0 [d, ^3J(C,P) = 4.4 Hz, C(CH_3)$_3$ at C-6], 32.2 [d, ^3J(C,P) = 5.2 Hz, C(CH_3)$_3$ at N-7], 35.5 [d, ^2J(C,P) = 9.6 Hz, C(CH_3)$_3$ at C-6], 51.6 (s, OCH_3), 51.9 (s, OCH_3), 60.8 [d, ^2J(C,P) = 1.2 Hz, C(CH_3)$_3$ at N-7], 76.2 [d, ^2J(C,P) = 26.1 Hz, C-4], 128.2 (s, Ph-C), 128.3 (s, Ph-C), 128.8 (s, Ph-C), 136.9 [d, ^3J(C,P) = 11.7 Hz, Ph-C], 146.5 [d, ^2J(C,P) = 8.4 Hz, C-5], 147.5 [d, ^1J(C,P) = 66.3 Hz, C-2], 160.1 [d, ^1J(C,P) = 60.6 Hz, C-6], 163.0 [d, ^2J(C,P) = 13.1 Hz, CO_2Me], 163.6 [d, ^3J(C,P) = 4.0 Hz, CO_2Me], 164.2 [d, ^2J(C,P) = 14.9 Hz, C-3].

^{31}P{^{1}H} NMR (C_6D_6, 25°C, 81.0 MHz): δ = 67.8 (s).

IR (CCl_4): ν = 2954 (C−H), 1733 (CO), 1435, 1295, 1260 (P = S), 1192, 1105, 1019, 949 cm^{-1}.

MS (EI, 70 eV): *m*/*z* (%) = 447 (M^+, 12), 391 ([M − C_4H_8]$^+$, 14), 359 ([M − C_4H_8 − S]$^+$, 37), 215 ([M − $C_6H_6O_4$ − S − C_4H_9 − H]$^+$, 100), 57 ([C_4H_9]$^+$, 72).

Crystal Structure Analysis of 12a

Crystal Data: $C_{17}H_{24}NP$, M_r = 273.37, monoclinic, space group $P2_{1/C}$, *a* = 5.925(2), *b* = 10.3776(14), *c* = 26.598(4) Å, α = 90°, β = 90.140(13)°, γ = 90°, *V* = 1635.4(5) Å^3, *Z* = 4, d_c = 1.100 Mg/m^3.

Data Collection: The data collection was performed using an automatic four circle diffractometer (Siemens P4) at r.t. Crystal dimensions:0.30 × 0.20 × 0.15 mm. The measurements were made in the range 1.53<θ<25.00°, λ = 0.71073 Å MoK_α (graphite monochromator), $-1 \le h \le 7$, $-1 \le k \le 12$, $-31 \le l \le 31$, a total of 4278 reflections, of which 2847 were independent reflections.

Structure Solution and Refinement: The structure was solved using direct methods (SHELX-86)[27] and refined with the full matrix least squares procedure against F^2 (SHELXL-93).[28] The anisotropic refinement converged at R1 = 0.0840 and wR2 = 0.1150 [I>2σ(I)] and R1 = 0.1797, wR2 = 0.1557 [all data]. The difference Fourier synthesis on the basis of the final structural model showed a maximum of 0.183 e/Å^3 and a minimum of −0.231 e/Å^3.[29]

Crystal Structure Analysis of 19e

Crystal Data: $C_{21}H_{24}F_6NP$, M_r = 435.38, monoclinic, space group $C_{2/C}$, *a* = 14.719(3), *b* = 11.771(2), *c* = 24.879(5) Å, α = 90.0°, β = 94.78(3)°, γ = 90.0°, *V* = 4296(2) Å^3, *Z* = 8, d_c = 1.346 Mg/m^3.

Data Collection: The data collection was performed using a STOE-IPDS diffractometer at r.t. Crystal dimensions: 0.30 × 0.20 × 0.20 mm. The measurements were made in the range 2.33<θ<26.05°, λ = 0.71073 Å MoK_α (graphite monochromator), $-18 \le h \le 18$, $-14 \le k \le 13$, $-30 \le l \le 30$, a total of 16994 reflections, of which 4138 were independent reflections.

Structure Solution and Refinement: The structure was solved using direct methods (SHELX*S*-86)[27] and refined with the full matrix least squares procedure against F^2 (SHELXL-93).[28] The anisotropic refinement converged at R1 = 0.0444 and wR2 = 0.1327 [I>2σ(I)] and R1 = 0.0602, wR2 = 0.1430 [all data]. The difference Fourier synthesis on the basis of the final structural model showed a maximum of 0.295 e/Å^3 and a minimum of −0.190 e/Å^3.[29]

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(29) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-136910 (**12a**) and CCDC-136909 (**19e**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail:deposit@chemcrys.cam.ac.uk].

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