λ^5-Phosphetes, Benzo-λ^5-Phosphetes, Naphtho-λ^5-Phosphetes: Four-π-, Eight-π-, and Twelve-π-Electron Systems

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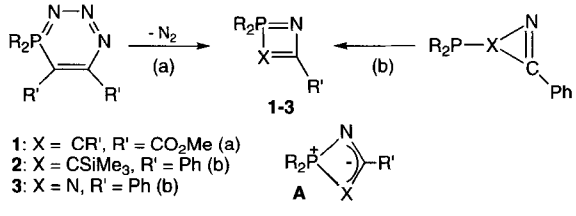
Dedicated to Professor Manfred Regitz on the occasion of his 60th birthday

Abstract: A number of possible strategies for the preparation of λ^5-phosphetes were tested as follows: cyclopropenium **6** was treated with the lithium salt of diphenylphosphine to give phosphinocyclopropene **7**, but **7** did not undergo ring expansion upon photolysis or thermolysis. *P*-chloro-*C*-trimethylsilyl-substituted ylide **8b** reacted with two equivalents of dimethyl acetylenedicarboxylate to afford phosphinine **13** via a transient λ^5-phosphete **12**. Addition of aluminum trichloride to *P*-halogenated ylides **17a–b** led to dihydrophosphetium salts **19a–b**, which, upon treatment with pyridine, isomerized into the 1,2-dihydrophosphet-2-ium salts **20a–b**. Hydrolysis of derivatives **20a–b** cleanly afforded phosphoniums **21a–b**, which reacted with $NaN(SiMe_3)_2$ to give rise to the corresponding λ^5-phosphetes **22a–b**. The benzo-λ^5-phosphete **22a** underwent ring expansion reactions with dimethyl acetylenedicarboxylate and acetonitrile, leading to benzo-λ^5-phosphinine and benzo-1,4λ^5-azaphosphinine in good yields. Derivative **22b** was characterized by X-ray crystal structure analysis. Ab initio SCF calculations, IGLO-^{13}C chemical shifts and $\Delta\chi$ for various benzannulated derivatives and phosphorus heterocycles are presented.

Keywords
ab initio calculations · cyclic ylides · heterocycles · phosphorus ylides

Introduction

We have recently shown that the stability of four-π-electron four-membered rings[1] is considerably increased by replacing a carbon atom with a heteroatom possessing no p orbital available for the π system. 1,2λ^5-Azaphosphetes **1**[2a,b] and **2**[2c] and 1,3,2λ^5-diazaphosphete **3**[2d,e] have been prepared either by ring-contraction (route a) or ring-expansion reactions (route b) (Scheme 1). According to X-ray crystal-structure analyses[2a,e] and ab initio calculations,[2f] heterocycles **1–3** are rhombic four-π-electron ylides (**A**). Their stability has been explained by the strongly polarized and relatively long P–N and P–C bonds, which prevent these heterocycles from possessing any anti-aromatic character and also partially release the ring strain.



Scheme 1.

Here we report on the synthesis and chemical behavior of λ^5-phosphetes and of their benzo- and naphtho-derivatives.[3] In order to gain more insight into the electronic structures of these compounds, we have calculated and evaluated their magnetic susceptibilities.

Results and Discussion

In a previous paper[2b] we showed that λ^5-phosphete **5** was not accessible through route (a); all attempts to eliminate dinitrogen from 1,2,3λ^5-diazaphosphinine **4** failed. Route (b) requires the preparation of phosphanyl-substituted cyclopropenes, which are potentially accessible through the reaction of cyclopropenium cations with phosphorus nucleophiles.[4] Cyclopropenium **6** is inert towards bis(diisopropylamino)(trimethylstannyl)-phosphine, probably because of the considerable steric bulk of both reactants, but readily reacts with the lithium salt of diphenylphosphine, affording phosphinocyclopropene **7** in 85% isolated yield (Scheme 2). The position of the phosphanyl

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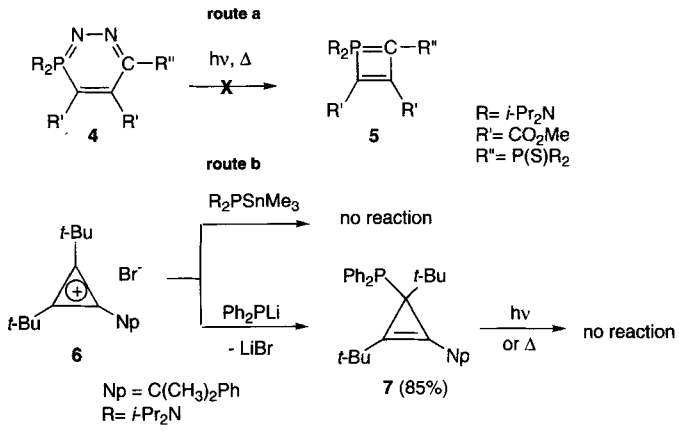
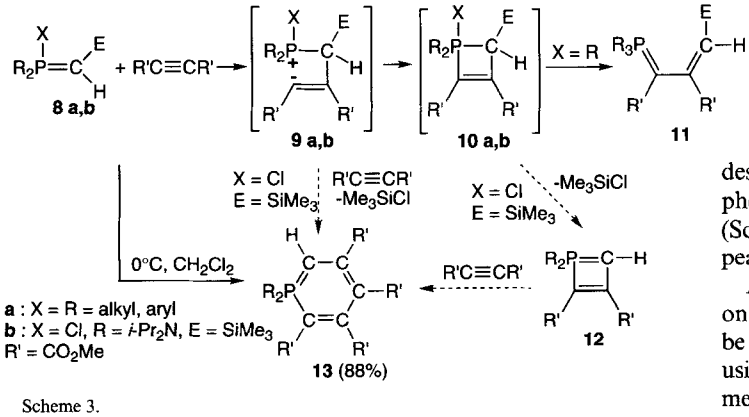


Scheme 2.

substituent was unambiguously assigned by NMR, the two *t*BuC fragments being inequivalent. However, all attempts to induce a ring-expansion reaction failed (heating for days at 180 °C, irradiation at $\lambda = 254$ or 320 nm, or addition of Lewis acids).

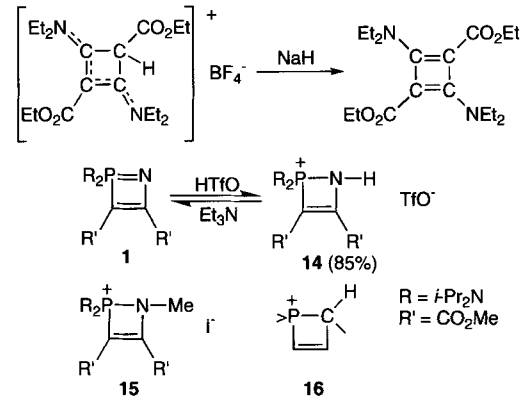
Since known strategies proved fruitless, a new approach was sought. It is known that electron-poor alkynes insert into the P=C bond of phosphorus ylides **8a** leading to vinyl ylides **11** via transient betaines **9a** and λ^5-phosphacyclobutenes **10a**.[5] Starting from the *P*-chloro-*C*-trimethylsilyl phosphorus ylide **8b**,[6] one can anticipate elimination of trimethylchlorosilane from the intermediate **10b** leading to λ^5-phosphete **12**. However, according to ^{31}P NMR spectroscopy, ylide **8b** reacted at room temperature with two equivalents of dimethyl acetylenedicarboxylate, affording derivative **13** (M.p. = 129 °C) in 88% isolated yield (Scheme 3). Mass spectrometry and elemental analysis confirmed that **13** arose from the addition of two molecules of the alkyne. In the ^{13}C{H} NMR spectrum, all the carbon atoms appeared as doublets, two being directly bound to the phosphorus atom, strongly supporting the cyclic structure. Lastly, the location of the hydrogen atom was clearly established from the ^{13}C NMR spectrum ($\delta = 100.47$ (dd, ^1J(C,H) = 160.7 Hz, ^1J(P,C) = 117.5 Hz)).



Scheme 3.

Two reasonable mechanisms can be postulated: either the desired λ^5-phosphete **12** is formed but a second molecule of alkyne inserts rapidly, or the betaine intermediate **9b** reacts with the alkyne and undergoes a [1,6] electrocyclization followed by elimination of trimethylchlorosilane. We favor the first hypothesis since, despite the numerous reported reactions involving phosphorus ylides and dimethyl acetylenedicarboxylate, or *P*-chloro-substituted phosphorus ylides and electrophiles,[5, 6] to the best of our knowledge the formation of a six-membered ring has not yet been described.

From these results, it appeared necessary to prepare a λ^5-phosphete in the absence of potential trapping agents, and thus a new approach reminiscent of the preparation of the first stable cyclobutadiene was developed. In 1968, Gompper and Seybold prepared a stabilized "[1,3]-push–[2,4]-pull" substituted cyclobutadiene by deprotonation of the corresponding cyclobutadienyl salt (Scheme 4).[7] To check this possibility, we used the azaphosphete **1** as a model. Addition of a stoichiometric amount of trifluoromethanesulfonic acid to **1** afforded the cyclic phosphonium **14** (M.p. = 170 °C), in 85% isolated yield. The presence of the $(i\mathrm{Pr}_2\mathrm{N})_2$PNH sequence was confirmed by the observation of a doublet of quintets (J(P,H) = 5.6 and 19.9 Hz) in the ^{31}P NMR spectrum, while the other NMR data compared well with that for the cyclic phosphonium **15** obtained by reacting **1** with iodomethane.[2b] Addition of an excess of triethylamine to a dichloromethane solution of **14** indeed regenerates the λ^5-azaphosphete **1** in 95% yield, according to ^{31}P NMR spectroscopy. Therefore, the desired precursor of λ^5-phosphetes would be 1,2-dihydrophosphet-2-ium salts **16**, but they seem not to be easily available (Scheme 4). In contrast, the benzo- and naphtho-analogues appeared to be accessible according to the procedure below.[3]



Scheme 4.

P-chloro-substituted phosphorus ylides bearing alkyl groups on the phosphorus center possess a reactive P–Cl bond that can be heterolytically cleaved using Lewis acids to yield methylene phosphonium salts.[8] For the present studies, we used the ylides **17a,b**; **17a** was characterized by X-ray analysis. The molecular structure is shown in Figure 1. The P1–C1 bond (1.674(3) Å) is comparable to distances found in other *P*-halogenated ylides.[8b] The p-type orbital used to describe the electron density located at the ylidic carbon center C1 is orientated in plane with the P–Cl bond

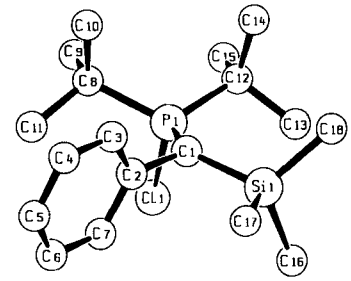
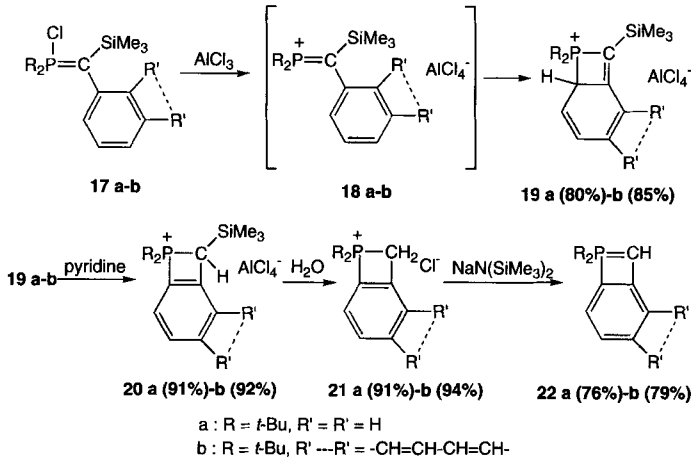


Fig. 1. Molecular structure of **17a**. Selected bond lengths (Å) and angles (°): P1–C1 1.674(3), P1–C8 1.889(3), P1–C12 1.875(3), P1–Cl1 2.166(2), C1–C2 1.506(4), C1–Si1 1.880(3), C1-P1-C8 114.5(2), C1-P1-C12 114.1(2), C1-P1-Cl1 115.14(11), C2-C1-P1 117.6(2), P1-C1-Si1 131.0(2), C2-C1-Si1 107.8(2). Hydrogen atoms are omitted for clarity.

(2.166(2) Å). This eclipsed orientation in the crystal is the cause of the rather long P–Cl bond (bond order 0.69 according to Allmann)[9] as explained by the model of negative hyperconjugation whereby electron density is transferred from the ylidic carbon atom C1 into the σ* orbital of the P–Cl bond.[10] Weakening of the P–Cl bond is essential for the successful preparation of methylene phosphonium salts, that is, ylide **8b** is not a suitable precursor.[11] Addition of freshly sublimed (colorless!) aluminum trichloride to CH_2Cl_2 solutions of *P*-halogenated ylides **17a–b** afforded transient methylene phosphonium salts **18a–b**, which possess a highly electrophilic phosphorus center owing to the polarizing effect of the *C*-silyl substituent (Scheme 5).[8a] An intramolecular electrocyclic ring closure occurred, leading to dihydrophosphetium salts **19a–b**, which were isolated in good yield. Upon treatment with a strong base, a complicated mixture of products was obtained. However, in the presence of pyridine, an irreversible and quantitative isomerization to the 1,2-dihydrophosphet-2-ium salts **20a–b** occurred. Addition of a strong base such as sodium bis(trimethylsilyl)amide to **20a** afforded among other products *C*-silylated benzo-λ^5-phosphete, which was only characterized by ^1H and ^{31}P NMR spectroscopy.[3] All attempts to obtain this four-π-electron ylide in a pure form failed.



Scheme 5.

Addition of water to a THF solution of **20a–b** cleanly afforded dihydrophosphet-2-ium salts **21a–b**. Under these slightly acidic reaction conditions, the carbon–silicon bond was cleaved, and no by-products were observed after recrystallization. The phosphonium salts **21a–b** reacted cleanly with $NaN(SiMe_3)_2$ in toluene solution to yield the desired benzo-λ^5-phosphetes **22a–b**, which were obtained as highly moisture- and oxygen-sensitive deep red crystals from cold *n*-hexane solution. Crystals of **22a** proved to be unsuitable for X-ray analysis; however, the structure of **22b** could be solved by diffraction studies. Two independent molecules were found in the unit cell, of which one is severely disordered. The SCHAKAL plot of the nondisordered one is shown in Figure 2, and selected geometrical data are collected in Table 1 together with those previously obtained for dihydrophosphet-2-ium salt **20b**.[3]

As expected for a naphthocyclobutadiene derivative, all the ring atoms of **22b** lie in the same plane (maximum deviation: 0.042 Å). As already observed for the related four-π-electron four-membered heterocycles **1** and **3**, the value of the inner ring angle at P1 is small (C1-P1-C3, 78.9(3)°), and that of the opposite angle is large (C1-C2-C3, 106.7(6)°), inducing a short diagonal P···C2 distance (2.206(7) Å). The four-membered ring is almost a symmetrical rhombus: the two P–C bond lengths (P1–C1, 1.772(8) Å; P1–C3, 1.773(6) Å) are in the range of those reported for semi-stabilized phosphorus ylides.[5] Furthermore the two C–C bond lengths (C1–C2, 1.401(8) Å; C2–C3, 1.406(7) Å) lie halfway between those of single and double bonds. In other words, a positive charge is located at phosphorus while the negative charge is delocalized on the carbon framework, even though this destroys the potential aromatic $4n + 2$ electron configuration of the naphthalene moiety. The electronic perturbation of the naphthalene rings is obvious on comparing the measurements for derivatives **20b** and **22b** (Table 1), keeping in mind that the bond lengths in naphthalene itself alternate just as in **20b**.[1a, 12]

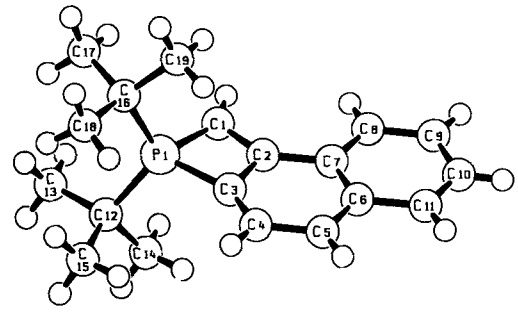


Fig. 2. Molecular structure of **22b** showing the numbering scheme used.

Table 1. Selected bond lengths (Å) and angles (°) for derivatives **20b** and **22b**.

	20b	**22b**		**20b**	**22b**
P1–C1	1.859(3)	1.772(8)	C1-P1-C3	78.7(1)	78.9(3)
C1–C2	1.549(5)	1.401(8)	P1-C1-C2	83.8(2)	87.2(5)
C2–C3	1.360(5)	1.406(7)	C1-C2-C3	105.0(3)	106.7(6)
C3–P1	1.781(3)	1.773(6)	C2-C3-P1	92.5(2)	87.1(5)
C3–C4	1.420(5)	1.356(8)	C2-C3-C4	123.7(3)	125.8(6)
C4–C5	1.350(6)	1.428(8)	C3-C4-C5	116.7(3)	117.8(7)
C5–C6	1.409(6)	1.382(8)	C4-C5-C6	122.6(3)	118.5(7)
C6–C7	1.438(5)	1.459(9)	C5-C6-C7	121.1(3)	117.8(9)
C7–C2	1.424(4)	1.465(8)	C6-C7-C2	115.2(3)	116.1(7)
C7–C8	1.402(6)	1.309(11)	C11-C6-C7	116.2(3)	117.3(8)
C8–C9	1.360(6)	1.406(11)	C7-C2-C3	121.2(3)	116.9(6)
C9–C10	1.401(8)	1.408(10)	C6-C7-C8	120.2(3)	118.2(10)
C10–C11	1.328(8)	1.370(8)	C7-C8-C9	121.1(3)	125.1(11)
C11–C6	1.421(6)	1.407(8)	C8-C9-C10	118.2(3)	117.9(9)
			C9-C10-C11	122.1(4)	118.8(8)
			C10-C11-C6	122.1(4)	122.8(7)

In order to gain more of an insight into the bonding situation of such systems, we have performed ab initio SCF calculations on the benzannulated derivatives **23–25** and phosphorus heterocycles **26–29**. Selected calculated bond lengths and angles are listed in Table 2. Compounds **25** and **29** are included for comparison to show the effect of annulation of a saturated four-membered cycle to the benzene moiety.[13] Compounds **26** and **27** are formally derived from benzocyclobutadiene **23** by replacement of one CH unit of the four-membered ring with a P or HP^+ group, both of these groups being able to participate in the π-electron system by (p,p) π interactions. As expected for antiaromatic compounds, electron localization occurs in **23**, **26** and **27**, leading to a significant alternation of all the bond lengths; in other words, the molecules feature a bis(methylene)cyclobutene-like fragment. Comparison of the measurements calculated for anion **24** and benzocyclobutane **25** clearly indicates that the negative charge is delocalized on the benzene ring. Finally, the bond situation of λ^5-phosphete **28**

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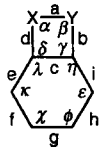
Table 2. Selected calculated SCF bond lengths (Å) and angles (°) for compounds **23**–**29**.



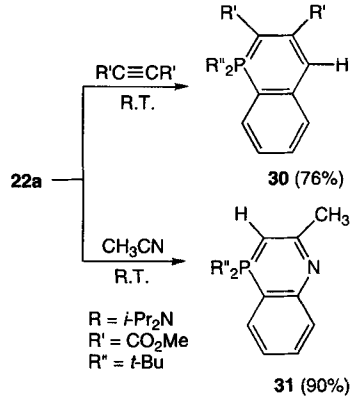
	X	Y	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*	α	β	γ	δ	η	ε	φ	χ	κ	λ
23	CH	CH	1.334	1.516	1.421	1.516	1.343	1.440	1.359	1.440	1.343	91.7	91.7	88.3	88.3	122.8	115.5	121.8	121.8	115.5	122.8
24	CH_2	CH^-	1.534	1.386	1.441	1.531	1.346	1.435	1.383	1.401	1.416	84.3	92.2	93.3	90.2	118.3	116.6	124.5	118.8	117.6	124.1
25	CH_2	CH_2	1.570	1.518	1.380	1.518	1.378	1.394	1.392	1.394	1.378	86.4	86.4	93.6	93.6	122.3	116.0	121.6	121.6	116.0	122.3
26	P	CH	1.675	1.491	1.415	1.898	1.350	1.428	1.364	1.425	1.355	75.1	97.0	97.5	90.4	122.2	116.6	121.4	121.3	116.9	121.8
27	PH^+	CH	1.650	1.494	1.423	1.833	1.340	1.435	1.361	1.429	1.353	80.8	91.1	101.7	86.3	120.6	116.7	121.7	121.7	115.1	124.2
28	PH_2	CH	1.710	1.452	1.425	1.793	1.364	1.401	1.388	1.395	1.391	80.0	89.7	103.1	87.3	117.9	117.5	123.7	119.3	117.2	124.3
29	PH_2^+	CH_2	1.847	1.526	1.391	1.774	1.387	1.381	1.400	1.387	1.382	79.0	84.9	104.3	91.8	120.7	116.5	122.4	121.2	115.8	123.4

appeared to be intermediate between those of derivatives **24** and **25**, the benzene moiety being less perturbed than in **24** because delocalization of the negative charge may also occur through the π^* orbitals of the PH_2 group (i.e., negative hyperconjugation).[8c]

In benzene and phosphabenzene $\Delta\chi$ (given in $10^{-6}\,cm^3\,mol^{-1}$) is strongly negative (C_6H_6: −63.4 (exp. −59.7)[15]; C_5H_5P: −66.1[16a]), while much larger anisotropies are observed for π systems possessing an antiaromatic character. For cyclobutadiene, the standard prototype of an antiaromatic system, $\Delta\chi$ is even positive at the MC-SCF level.[16] The calculated IGLO-^{13}C chemical shifts[17] and $\Delta\chi$ for derivatives **23**–**29** are given in Table 3. None of the parent phosphorus heterocycles **26**–**29** are known; however, the experimental NMR data for the *P-t*-butyl derivatives **22a** and **20a**–**21a** compare well with **28** and **29**, respectively.

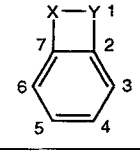
Annulation of a saturated four-membered cycle on a benzene ring (compounds **25** and **29**) reduces the value of $\Delta\chi$ by about 15%, indicating relatively little disturbance of the electronic properties of the aromatic moiety. The small negative values of $\Delta\chi$ found for **23**, **26**, and **27** are indicative of antiaromatic π systems; this confirms the electronic similarities between benzocyclobutadiene (**23**) and the heterocycles **26** and **27** incorporating (p,p) π-bonded phosphorus centers. On the other hand, the $\Delta\chi$ values of the cyclic hydrocarbon anion **24** (− 26.7) and ylide **28** (− 29.2) are similar and halfway between those of **23** (−11.0) and benzocyclobutane (**25**) (− 55.3). This is confirmed by the significant shielding observed for the protons of the benzo and naphtho groups in λ^5-phosphetes **22a** (δ = 5.84–7.20) and **22b** (δ = 6.28–7.83) compared with the "aromatic" phosphonium salts **21a** (δ = 7.16–7.78) and **21b** (δ = 7.30–8.22). Nevertheless, some care must be taken, since the effects of the delocalization of the different charges in **22a,b** and **21a,b** have to be taken in account. A careful study of the *out-of-plane* components for the proton shieldings could be helpful,[14b] but is unfortunately out of reach experimentally.

As expected, benzophosphete **22a** is very reactive. A conventional insertion of dimethyl acetylenedicarboxylate into the ylide P=CH bond of **22a** occurred at room temperature, giving rise to the bicyclic [4.4.0]heterocycle **30** (M.p. = 147 °C) in 76% isolated yield (Scheme 6). The position of the CH



Scheme 6.

Table 3. Calculated IGLO ^{13}C NMR chemical shifts and anisotropy of magnetic susceptibilities $\Delta\chi$ ($10^{-6}\,cm^3\,mol^{-1}$) for compounds **23**–**29**. Experimental values in parentheses.



	X	Y	X	1	2	3	4	5	6	7	$\Delta\chi$ [a]
23	CH	CH	150.1	150.1	153.0	110.7	126.3	126.3	110.7	153.0	−11.0
24	CH_2	CH^-	29.7	52.4	167.3	83.7	137.2	85.8	116.2	133.9	− 26.7
25	CH_2	CH_2	23.8	23.8	146.3	122.2	126.5	126.5	122.2	146.3	− 55.3
			(23.4) [b]	(23.4) [b]	(146.7)	(124.5)	(128.2)	(128.2)	(124.5)	(146.7)	
26	P	CH	–	230.6	153.7	108.5	129.7	131.9	124.6	140.8	−7.8
27	PH^+	CH	–	214.0	134.9	130.4	136.8	138.2	133.4	132.6	− 2.3
28	PH_2	CH	– [c]	8.2	184.2	105.6	144.8	105.3	135.4	107.8	− 29.2
(22a) [d]	$PtBu_2$	CH	–	(36.1)	(170.1)	(106.6)	(135.9)	(108.5)	(125.1)	(121.8)	
29	PH_2^+	CH_2	– [c]	20.4	152.7	127.3	147.9	134.4	136.1	129.1	− 54.0
(20a)	$PtBu_2$	$CHSiMe_3^-$	(34.1)	(150.5)	(125.8)	(130.6)	(130.8)	(137.8)	(127.5)		
(21a)	$PtBu_2$	CH_2	–	(28.4)	(145.7)	(126.5)	(128.6)	(130.8)	(136.3)	(124.0)	

[a] $\Delta\chi = \chi_{op} - \chi_{ip}$, where χ_{ip} is the average of the different *in-plane* components of the susceptibility (op = *out-of-plane*; ip = *in-plane*). [b] Obviously erroneous in ref. [21] where a value of 133 is given. [c] IGLO ^{31}P shift: −58.4 (**28**), −49.4 (**29**). The small downfield shift of the ^{31}P shift resonance (9 ppm) comparing ylide **28** and phosphonium salt **29** is in accord with the observed differences between **22a**/**21a** (8.7 ppm) and **22b**/**21b** (6.1 ppm) resonances. [d] An IGLO calculation of λ^5-benzophosphete using experimental distances and angles of **22a**, and including a P*t*Bu group gives the following ^{13}C shifts: C1 32.2, C2 186.3, C3 108.5, C4 144.5, C6 135.7, C7 97.0.

Table 4. Crystallographic data [a] for derivatives **17a** and **22b**.

	17a [b]	**22b** [c]
empirical formula	$C_{18}H_{32}ClPSi$	$C_{19}H_{25}P$
formula weight	342.95	284.38
temperature (K)	293(2)	293(2)
wavelength (Å)	0.71070	0.71070
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/a$
a (Å)	9.282(5)	12.209(8)
b (Å)	17.881(9)	22.157(12)
c (Å)	12.849(7)	13.841(9)
α (°)	90	90
β (°)	105.62(4)	111.23(5)
γ (°)	90	90
volume (Å^3)	2054(2)	3490.5(4)
Z	4	8
ρ_{calc} (Mgm^{-3})	1.109	1.080
Absorption coeff. (mm^{-1})	0.316	0.148
F(000)	744	1228
crystal size (mm)	0.3 × 0.4 × 0.6	0.4 × 0.5 × 0.6
θ range (°)	2.00–25.00	1.58–20.00
index ranges	$-11 \le h \le 10$	$-11 \le h \le 10$
	$0 \le k \le 21$	$0 \le k \le 21$
	$0 \le l \le 15$	$0 \le l \le 15$
reflections collected	3607	3264
independent reflections	3607	3264
refinement method	*full-matrix least-squares on F^2*	*full-matrix least-squares on F^2*
data/restraints/parameters	3606/0/222	3264/105/381
goodness-of-fit on F^2	1.015	1.047
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0470$, $wR2 = 0.1023$	$R1 = 0.0619$, $wR2 = 0.1290$
R indices (all data)	$R1 = 0.1030$, $wR2 = 0.1242$	$R1 = 0.1381$, $wR2 = 0.1626$
largest diff. peak and hole (eÅ^{-3})	0.193, −0.201	0.160, −0.164

[a] All data were collected on a Siemens-Stoe four-circle diffractometer with $Mo_{K\alpha}$ radiation (λ = 0.71070 Å) by ω-scan. Anisotropic temperature factors for all non-hydrogen atoms were used. Hydrogen atoms were included in calculated positions or as part of a rigid group (CH_3) (**22b**) with common isotropic temperature factors. All calculations were performed by using the programs SHELXS-86 [22] and SHELXL-93 [23]. [b] An empirical absorption correction was applied ($0.923 < T < 0.998$). [c] An empirical absorption correction was applied ($0.937 < T < 1.000$) [24].

phosphinine was unambiguously assigned by 2D NMR heterocorrelated spectra (^{1}H NMR: δ = 5.59 (d, ^4J(P,H) = 1.7 Hz), ^{13}C NMR: δ = 105.76 (d, ^3J(P,C) = 7.2 Hz)). The high reactivity of benzophosphete **22a** was further demonstrated through its reaction with acetonitrile. Surprisingly, according to ^{13}C NMR and 2D-heterocorrelated spectra two carbon atoms in the resulting product are directly bound to phosphorus (^{13}C NMR: δ = −2.03 (d, ^1J(P,C) = 120.3 Hz), 124.40 (d, ^1J(P,C) = 67.0 Hz)), the former bearing a hydrogen atom. All the other spectroscopic data also agree with the structure of 1,4λ^5-azaphosphinine **31**. This derivative formally results from insertion of acetonitrile into a carbon–carbon bond, and not as expected into a phosphorus–carbon bond (Scheme 6).

Conclusion

The synthesis of stable benzo- and naphtho-λ^5-phosphetes highlights the particular stability of the four-membered four-*n*-π-electron ylide structure. λ^5-Phosphetes are versatile building blocks in heterocyclic synthesis, and preparation of further rings of this type featuring other heteroatoms is under active investigation.

Experimental Section

All experiments were performed in an atmosphere of dry argon. Melting points are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC80, AC200, or WM250 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign in ppm relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin–Elmer FT-IR Spectrometer 1725X. Mass spectra were obtained on a Ribermag R10 10E instrument. Liquid chromatography was performed with silica gel or neutral alumina. Conventional glassware was used.

Computation details: The geometries of **23**–**29** were optimized at the SCF level using the TURBOMOLE package of programs [18] (basis set DZ + d for **23**–**25**, DZP for **26**–**29**). Most of the IGLO calculations were performed using the direct version of the IGLO program [19]. Basis set II was used [17]. For calculation using a geometry in accordance with the experimental structure of **22b**, a DZ basis set [17] was used for the hydrogen atoms of the methyl groups and the phenyl ring, basis II for all other atoms.

1-(1,1′-Dimethylbenzyl)-2-*t*-butylcyclopropenone: This was obtained by distillation as a yellow liquid (86%) by the procedure described for the di-*t*-butylcycloprenone [20]: B.p. 132–134 °C (5×10^{-2} mmHg); ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.76 (s, 9H; $C(CH_3)_3$), 1.24 (s, 6H; $PhCCH_3$), 6.79–7.01 (m, 5H; H_{arom}); ^{13}C NMR (50.323 MHz, $CDCl_3$, 25 °C): δ = 27.81 (s; $C(CH_3)_3$), 28.01 (s; $PhCCH_3$), 33.22 (s; $C(CH_3)_3$), 41.02 (s; $CPhCH_3$), 125.42, 127.05, 128.42 (s; C_{arom}), 144.22 (s; C*i*), 163.51 (s; $CCPhCH_3$), 164.52 (s; $CC(CH_3)_3$); IR (THF): $\tilde{\nu}$ = 1857 (C=C), 1639 cm^{-1} (CO); $C_{16}H_{20}O$ (228.32): calcd C 84.16, H 8.83; found: C 84.13, H 8.85.

1-(1,1′-Dimethylbenzyl)-2,3-*t*-butylcyclopropenium bromide (6): A pentane solution (100 mL) of *t*-butyllithium (1.7 M; 76.00 mmol) was added dropwise over 30 min at 0 °C to a pentane solution (100 mL) of 1-(1,1′-dimethylbenzyl)-2-*t*-butylcyclopropenone (14.50 g, 63.00 mmol). The solution was allowed to warm to room temperature and stirred for an additional 60 minutes, and water (100 mL) was added at 0 °C. The pentane layer was separated, washed with two portions of water (2 × 30 mL), dried over magnesium sulfate, filtered, and concentrated using a rotary evaporator. The resulting pale yellow oil was dissolved in ether (400 mL), and this solution was saturated with anhydrous HBr. The solvent was removed under vacuum, and the residue washed three times with ether (3 × 30 mL). **6** was obtained as a pale yellow solid (17.61 g, 80% yield): M.p. 120–121 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.72 (s, 9H; $C(CH_3)_3$), 1.26 (s, 6H; $PhCCH_3$), 6.66–6.81 (m, 5H; H_{arom}); ^{13}C NMR (50.323 MHz, $CDCl_3$, 25 °C): δ = 26.74 (s; $CPhCH_3$), 27.40 (s; $C(CH_3)_3$), 34.53 (s; $C(CH_3)_3$), 41.25 (s; $CPhCH_3$), 125.65, 127.84, 128.69 (s; C_{arom}), 140.70 (s; C*i*), 180.56 (s; $CCPhCH_3$), 181.69 ($CC(CH_3)_3$). $C_{20}H_{29}Br$ (349.34): calcd C 68.76, H 8.37; found: C 68.73, H 8.41.

1-[Bis(diisopropylamino)phosphino]-1,2-di-*t*-butyl-3-(1,1′-dimethylbenzyl)cyclopropene (7): To a THF solution (35 mL) of diphenylphosphine (1.63 g, 8.70 mmol) at −78 °C was added dropwise a stoichiometric amount of butyllithium in hexane. The solution was allowed to warm to room temperature, stirred for an additional 10 min, and added at −78 °C to a THF solution (5 mL) of derivative **6** (3.03 g, 8.70 mmol). The solution was allowed to warm to room temperature, stirred for an additional 60 min, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. Compound **7** was obtained as an extremely air-sensitive viscous oil (3.36 g, 85%); ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.80 (s, 9H; $C(CH_3)_3$), 1.23 (s, 9H; $C(CH_3)_3$), 1.52 (s, 3H; $PhCCH_3$), 1.64 (s, 3H; $PhCCH_3$), 7.24–7.80 (m, 15H; H_{arom}); ^{13}C NMR (50.323 MHz, $CDCl_3$, 25 °C): δ = 29.16 (s; $PhCCH_3$), 29.80 (s; $PhCCH_3$), 30.29 (s; $C(CH_3)_3$), 31.22 (s; $C(CH_3)_3$), 31.39 (d, ^3J(P,C) = 8.6 Hz; $C(CH_3)_3$), 38.56 (s; $PhCCH_3$), 39.08 (d, ^2J(P,C) = 36.2 Hz; $C(CH_3)_3$), 47.99 (d, ^1J(P,C) = 39.1 Hz; PC), 125.83, 126.61 (s; C_{arom}), 127.09 (d, ^4J(P,C) = 7.0 Hz; C_{arom}), 127.29 (d, ^3J(P,C) = 6.0 Hz; C_{arom}), 127.50 (d, ^3J(P,C) = 8.5 Hz; C_{arom}), 127.55 (s; C_{arom}), 126.37 (s; C=C), 128.01 (s; C=C), 134.19 (d, ^2J(P,C) = 18.7 Hz; C_{arom}), 136.52 (d, ^2J(P,C) = 22.5 Hz; C_{arom}), 139.02 (d, ^1J(P,C) = 14.5 Hz; C$_i$), 141.07 (d, ^1J(P,C) = 18.2 Hz; C$_i$), 148.07 (s; C$_i$), C_{arom} observed; ^{31}P NMR ($CDCl_3$, 32.438 MHz): δ = +13.77. MS (CH_4, CI) *m*/*z* (%): 455 (4) [M^+ + 1], 269 (100) [$M - PPh_2^+$]. Satisfactory elemental analysis could not be carried out because of the presence of a small amount of the corresponding phosphine oxide.

1,1-[Bis(diisopropylamino)]-2,3,4,5-carbomethoxy-λ^5-phosphinine (13): To a CH_2Cl_2 solution (15 mL) of ylide **8b** [6c] (2.65 g, 7.50 mmol) at −78 °C was added dropwise dimethyl acetylenedicarboxylate (2 equiv, 1.8 mL, 1.50 mmol). The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum and **13** was isolated by column chromatography (CH_2Cl_2/CH_3CN 90/10, $R_f \approx 0.5$) as a pale yellow solid (3.49 g, 88%): M.p. 129 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.03 (d, ^3J(H,H) = 6.7 Hz, 12H,

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CH_3CHN), 1.14 (d, ^3J(H,H) = 6.8 Hz, 12H; CH_3CHN), 3.53 (s, 3H; CH_3O), 3.56 (s, 3H; CH_3O), 3.67 (s, 3H; CH_3O), 3.73 (s, 3H; CH_3O), 5.37 (d, ^2J(P,H) = 5.8 Hz, 1H; PCH), no NCH group was observed, probably hidden by CH_3O; ^{13}C NMR (62.896 MHz, $CDCl_3$, 25 °C): δ = 23.32 (d, ^3J(P,C) = 2.7 Hz; CH_3CHN), 24.45 (d, ^3J(P,C) = 2.5 Hz; CH_3CHN), 47.41 (d, ^2J(P,C) = 5.9 Hz; CH_3CHN), 50.96 (s; CH_3O), 51.57 (s; CH_3O), 52.06 (s; CH_3O), 52.35 (s; CH_3O), 82.96 (d, ^1J(P,C) = 129.0 Hz; PCCO), 100.04 (d, ^3J(P,C) = 14.0 Hz; PCCC), 100.47 (d, ^3J(P,C) = 17.5 Hz; PCH), 144.59 (d, ^2J(P,C) = 4.3 Hz; PCHC), 148.11 (d, ^2J(P,C) = 9.0 Hz; PCHCCC), 166.49 (d, ^4J(P,C) = 0.5 Hz; CO), 166.51 (d, ^1J(P,C) = 8.2 Hz; CO), 169.33 (d, ^3J(P,C) = 16.8 Hz; CO), 169.91 (d, ^3J(P,C) = 19.9 Hz; CO); ^{31}P NMR (32.438 MHz, $CDCl_3$, 25 °C): δ = + 33.88; IR (THF): $\tilde{\nu}$ = 1737, 1673 cm^{-1} (CO); MS (NH_3, CI) *m/z* (%): 529 (100) $[M^+ + 1]$; $C_{25}H_{41}N_2O_8P$ (528.57): calcd C 56.80, H 7.82, N 5.30; found: C 56.79, H 7.84, N 5.29.

Four-membered heterocycle 14: Neat trifluoromethanesulfonic acid (0.23 mL, 2.60 mmol) was added dropwise, at −30 °C, to a dichloromethane solution (5 mL) of **1** [2a,b] (1.00 g, 2.58 mmol). The solution was allowed to warm to room temperature and stirred for an additional 4 h. The solvent was removed under vacuum and the residue washed three times with ether (3x10 mL). Compound **14** was purified by recrystallization at room temperature from a CH_2Cl_2/Et_2O solution as a colorless solid (1.18 g, 85%): M.p. 170 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.23 (d, ^3J(H,H) = 7.4 Hz, 12H; CH_3CHN), 1.27 (d, ^3J(H,H) = 7.5 Hz, 12H; CH_3CHN), 3.67 (s, 3H; CH_3O), 3.78 (sept d, ^3J(H,H) = 7.5 Hz, ^3J(P,H) = 19.9 Hz, 4H; CH_3CHN), 3.83 (s, 3H; CH_3O), 9.45 (d, ^3J(P,H) = 5.6 Hz, 1H; NH); ^{13}C NMR (50.323 MHz, $CDCl_3$, 25 °C): δ = 21.62 (d, ^3J(P,C) = 1.7 Hz; CH_3CHN), 21.84 (d, ^3J(P,C) = 2.0 Hz; CH_3CHN), 49.54 (d, ^2J(P,C) = 4.6 Hz; CH_3CHN), 52.14 (d, ^2J(P,C) = 1.5 Hz; CH_3O), 53.90 (s; CH_3O), 106.07 (d, ^1J(P,C) = 107.0 Hz; PC), 120.21 (sept, ^1J(F,C) = 319.7 Hz; CF_3), 157.26 (d, ^3J(P,C) = 40.7 Hz; CO), 158.78 (d, ^2J(P,C) = 8.2 Hz; CO), 161.97 (d, ^2J(P,C) = 12.8 Hz; CN); ^{31}P NMR (32.438 MHz, CH_2Cl_2, 25 °C): δ = + 43.11; $C_{19}H_{35}F_3N_3O_7PS$ (537.53): calcd C 42.45, H 6.56, N 7.81; found: C 42.44, H 6.60, N 7.87.

Di-*t*-butyl-[(trimethylsilylphenyl)methyl]phosphane: To a THF solution (40 mL) of benzyltrimethylsilane (6.57 g, 40.00 mmol) at 0 °C was added dropwise butyllithium in hexanes (26 mL, 1.6 M, 41.60 mmol). The solution was allowed to warm to room temperature and stirred for an additional 4 h while the solution turned bright red. Pure di-*t*-butylchlorophosphane (6.50 g, 36.00 mmol) was added to this solution at 0 °C through a syringe. The solution was allowed to warm to room temperature and stirred for an additional 15 h while the red color slowly faded. The solvent was removed under vacuum and the residue treated with hexane (60 mL). After filtration and evaporation of the solvent under vacuum, di-*t*-butyl[(trimethylsilyl)phenyl)methyl]phosphane was obtained as an oil which crystallized as colorless crystals upon standing at room temperature for several days (10.40 g, 94%): M.p. 76–78 °C; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.20 (s, 9H; $SiCH_3$), 1.12 (d, ^3J(P,H) = 10.7 Hz, 9H; CCH_3), 1.24 (d, ^3J(P,H) = 10.7 Hz, 9H; CCH_3), 2.67 (d, ^2J(P,H) = 3.9 Hz, 1H; CH), 6.88–7.35 (m, 5H; H_{arom}); ^{13}C NMR (50.323 MHz, C_6D_6, 25 °C): δ = 0.72 (d, ^3J(P,C) = 6.5 Hz; $SiMe_3$), 31.70 (d, ^1J(P,C) = 60.7 Hz; PCH), 31.82 (d, ^2J(P,C) = 14.9 Hz; CCH_3), 31.91 (d, ^2J(P,C) = 14.8 Hz; CCH_3), 33.85 (d, ^1J(P,C) = 32.4 Hz; CCH_3), 34.15 (d, ^1J(P,C) = 33.6 Hz; CCH_3), 125.12, 128.22, 131.51 (s; C_{arom}), 142.54 (s; C_i); ^{31}P NMR (32.438 MHz, C_6D_6, 25 °C): δ = + 43.31; MS (70 eV, EI) *m/z* (%): 308 (7) $[M^+]$.

Di-*t*-butyl[(1-naphthyltrimethylsilyl)methyl]phosphane: The above procedure was used starting from 1-naphthylmethyl-trimethylsilane (6.43 g, 30.00 mmol). The product was obtained as colorless crystals from a hexane solution at −30 °C (8.50 g, 85%): M.p. 87–89 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.04 (s, 9H; $SiCH_3$), 0.97 (d, ^3J(P,H) = 10.4 Hz, 9H; CCH_3), 1.34 (d, ^3J(P,H) = 10.8 Hz, 9H; CCH_3), 3.64 (d, ^2J(P,H) = 3.7 Hz, 1H; CH), 7.33–8.23 (m, 7H; H_{arom}); ^{13}C NMR (50.323 MHz, $CDCl_3$, 25 °C): δ = 1.22 (d, ^3J(P,C) = 2.8 Hz; $SiMe_3$), 24.90 (d, ^1J(P,C) = 54.3 Hz; PCH), 31.44 (d, ^2J(P,C) = 12.7 Hz; CCH_3), 31.62 (d, ^2J(P,C) = 13.8 Hz; CCH_3), 33.22 (d, ^1J(P,C) = 27.6 Hz; CCH_3), 34.44 (d, ^1J(P,C) = 30.8 Hz; CCH_3), 124.22, 124.90, 125.00, 125.22, 128.01, 128.35, 129.17, 132.54, 134.11, 140.02 (s; C_{arom}); ^{31}P NMR (32.438 MHz, $CDCl_3$, 25 °C): δ = + 57.82. MS (70 eV, EI) *m/z* (%): 358 (4) $[M^+]$.

Di-*t*-butylchloro[(phenyltrimethylsilyl)methylene]phosphorane (17a): Neat CCl_4 (4.61 g, 30.00 mmol) was added to a hexane solution (40 mL) of di-*t*-butyl-[(trimethylsilylphenyl)methyl]phosphane (4.63 g, 15.00 mmol) at −40 °C through a syringe. The solution was allowed to warm to room temperature and stirred for an additional 1 h. The solvent was removed under vacuum and **17a** was obtained as yellow-brownish needles at −30 °C from a hexane solution. After sublimation at 85 °C/0.01 Torr, **17a** was isolated as yellow crystals (4.05 g, 79%): M.p. 82–83 °C; NMR data are listed in ref [5]; MS (70 eV, EI) *m/z* (%): 342 (4) $[M^+]$; $C_{18}H_{32}ClSiP$ (342.95): calcd C 63.04, H 9.40, Cl 10.34, P 9.03; found: C 63.14, H 9.24, Cl 10.38, P 8.88.

Di-*t*-butyl-chloro[(1-naphthyltrimethylsilyl)methylene]phosphorane (17b): Neat CCl_4 (4.61 g, 30.00 mmol) was added to a hexane solution (50 mL) of di-*t*-butyl-[(1-naphthyltrimethylsilyl)methyl]phosphane (5.38 g, 15.00 mmol) at −40 °C through a syringe. The solution was allowed to warm to room temperature and stirred for an additional 2.5 hours. The solvent was removed under vacuum and **17b** was obtained as yellow crystals at −30 °C from an acetonitrile solution (5.20 g, 88%): M.p. 106–107 °C; NMR data are listed in ref [5]; MS (70 eV, EI) *m/z* (%): 392 (2) $[M^+]$.

Compounds 19a–b and 20a–b: Synthetic and analytical data are listed in ref [3].

1,1-Di-t-butyl-1,2-dihydrobenzophosphet-1-ium chloride (21a): To a *THF* solution (20 mL) of **20a** (0.95 g, 2.00 mmol) was added water (4 mL). After the solution had been stirred for 3 h at room temperature, the solvent was removed under vacuum. The residue was treated with CH_2Cl_2 and filtered. Colloidal suspended aluminum salts were removed by briefly refluxing the mixture followed by repeated filtration. The solvent was removed under vacuum, and after crystallization from a hot toluene suspension, **21a** was obtained as a white solid (0.49 g, 91%): M.p. 197 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.51 (d, ^3J(P,H) = 19.9 Hz, 18H; CCH_3), 4.28 (d, ^2J(P,H) = 10.3 Hz, 2H; CH_2), 7.16–7.78 (m, 4H; H_{arom}); ^{13}C NMR (50.323 MHz, $CDCl_3$, 25 °C): δ = 26.60 (s; CCH_3), 28.42 (d, ^1J(P,C) = 46.9 Hz; CH_2), 35.44 (d, ^1J(P,C) = 20.5 Hz; CCH_3), 123–147(s; C_{arom}); ^{31}P NMR (32.438 MHz, $CDCl_3$, 25 °C): δ = + 82.33; $C_{15}H_{24}ClP$ (270.78): calcd C 66.54, H 8.93, Cl 13.09, P 11.44; found: C 66.41, H 8.89, Cl 13.12, P 11.60.

2,2-Di-*t*-butyl-1,2-dihydronaphtho[2,1,*b*]phosphet-1-ium chloride (21b): To a THF solution (20 mL) of **20b** (1.05 g, 2.00 mmol) was added water (4 mL). After the solution had been stirred for 4 h at room temperature, the solvent was removed under vacuum. The residue was treated with CH_2Cl_2 and filtered. Colloidal suspended aluminum salts were removed by briefly refluxing the mixture followed by repeated filtration. The solvent was removed under vacuum, and after crystallization from a hot toluene suspension, **21b** was obtained as a white solid (0.60 g, 94%): M.p. 137 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.61 (d, ^3J(P,H) = 17.1 Hz, 18H; CCH_3), 4.57 (d, ^2J(P,H) = 11.2 Hz, 2H; CH_2), 7.30–8.22 (m, 6H; H_{arom}); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C): δ = 26.62 (d, ^1J(P,C) = 46.9 Hz; CH_2), 26.92 (s; CCH_3), 35.72 (d, ^1J(P,C) = 20.5 Hz; CCH_3), 120–147 (s; C_{arom}); ^{31}P NMR (32.438 MHz, $CDCl_3$, 25 °C): δ = +79.08; $C_{19}H_{26}ClP$ (320.84): calcd C 71.13, H 8.17, Cl 11.05, P 9.65; found: C 71.08, H 8.12, Cl 11.02, P 9.71.

1,1-Di-*t*-butyl-1-benzophosphete (22a): To a toluene suspension (10 mL) of **21a** (0.41 g, 1.50 mmol) at −78 °C was added $NaN(SiMe_3)_2$ (0.28 g, 1.50 mmol). The solution was allowed to warm to room temperature, the mixture becoming deep red. Precipitated NaCl was filtered off and the solvent was removed under vacuum. **22a** was obtained as deep red plates from a hexane solution at −30 °C (0.27 g, 76%): M.p. 94–95 °C; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 1.14 (d, ^3J(P,H) = 14.3 Hz, 18H; CCH_3), 2.77 (d, ^2J(P,H) = 27.8 Hz, 1H; CH), 5.84–7.20 (m, 4H; H_{arom}); ^{13}C NMR (50.323 MHz, C_6D_6, 25 °C): δ = 27.76 (s; CCH_3), 34.64 (d, ^1J(P,C) = 26.4 Hz; CCH_3), 36.44 (d, ^1J(P,C) = 82.1 Hz; PCH), 106.65 (d, ^3J(P,C) = 26.9 Hz; CH_{arom}), 108.47 (d, ^3J(P,C) = 11.6 Hz; CH_{arom}), 121.77 (d, ^1J(P,C) = 72.5 Hz; PC_{arom}), 125.14 (s; CH_{arom}), 135.88 (d, ^4J(P,C) = 2.2 Hz; CH_{arom}), 170.13 (d, ^2J(P,C) = 3.8 Hz; PCHC); ^{31}P NMR (32.438 MHz, C_6D_6, 25 °C): δ = +73.60; MS (70 eV, EI) *m/z* (%): 234 (32) $[M^+]$; $C_{15}H_{23}P$ (234.32): calcd C 76.89, H 9.89, P 13.22; found: C 76.85, H 9.83, P 13.34.

2,2-Di-*t*-butyl-1-naphtho[2,1,*b*]phosphete (22b): To a toluene suspension (10 mL) of **21b** (0.48 g, 1.50 mmol) at −78 °C was added $NaN(SiMe_3)_2$ (0.28 g, 1.50 mmol). The solution was allowed to warm to room temperature, the mixture becoming deep red. Precipitated NaCl was filtered off, and the solvent was removed under vacuum. **22b** was obtained from a hexane solution at −30 °C as deep red plates suitable for X-ray analysis (0.34 g, 79%): M.p. 126–127 °C; ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 1.18 (d, ^3J(P,H) = 14.3 Hz, 18H; CCH_3), 3.38 (d, ^2J(P,H) = 26.0 Hz, 1H; CH), 6.28–7.83 (m, 6H; H_{arom}); ^{13}C NMR (50.323 MHz, C_6D_6, 25 °C): δ = 27.41 (s; CCH_3), 33.72 (d, ^1J(P,C) = 27.9 Hz; CCH_3), 41.34 (d, ^1J(P,C) = 77.6 Hz; PCH), 106.01 (d, ^1J(P,C) = 76.9 Hz; PC_{arom}), 106.05 (d, ^3J(P,C) = 11.7 Hz; CH_{arom}), 122.05 (d, ^3J(P,C) = 25.0 Hz; C_{arom}), 121.42 (s; CH_{arom}), 123.21 (s; CH_{arom}), 123.35 (s; CH_{arom}), 125.74 (s; CH_{arom}), 128.62 (s; CH_{arom}), 140.61 (s; C_{arom}), 170.11 (d, ^2J(P,C) = 3.8 Hz; PCHC); ^{31}P NMR (32.438 MHz, C_6D_6, 25 °C): δ = +73.00; MS (70 eV, EI) *m/z* (%): 284 (46) $[M^+]$; $C_{19}H_{25}P$ (284.38): calcd C 80.25, H 8.86, P 10.89; found: C 80.19, H 8.91, P 10.93.

Benzo-λ^5-phosphinine 30: To a *n*-hexane solution (10 mL) of **22a** (0.50 g, 2.1 mmol) was added dimethyl acetylenedicarboxylate (0.30 g, 2.10 mmol) at room temperature. The red color of the reaction mixture faded immediately and became yellow. After a short while, **30** started to precipitate, and crystallization was completed overnight at −30 °C. After recrystallization from hot *n*-hexane, **30** was obtained as yellow crystals (0.6 g, 76%): M.p. 147 °C; ^{1}H NMR (200 MHz, CD_3CN, 25 °C): δ = 0.94 (d, ^3J(P,H) = 15.4 Hz, 18H; CCH_3), 3.08 (s, 3H; CH_3O), 3.25 (s, 3H; CH_3O), 5.59 (d, ^4J(P,H) = 1.7 Hz, 1H; PCCH), 6.68 (m, 1H; H_{arom}), 6.76 (m, 1H; H_{arom}), 6.97 (m, 1H; H_{arom}), 7.46 (m, 1H; H_{arom}); ^{13}C NMR (50.323 MHz, CD_3CN, 25 °C): δ = 29.54 (d, ^2J(P,C) = 1.6 Hz; CCH_3), 43.28 (d, ^1J(P,C) = 41.2 Hz; CCH_3), 50.76 (s; CH_3O), 52.31 (s; CH_3O), 54.23 (d, ^1J(P,C) = 98.3 Hz; PC), 105.76 (d, ^3J(P,C) = 7.2 Hz; PCCCH), 110.44 (d, ^1J(P,C) = 71.4 Hz; PC_{arom}), 123.69 (d, ^3J(P,C) = 11.0 Hz; C_{arom}), 129.10 (d, ^3J(P,C) = 7.2 Hz; CH_{arom}), 132.45 (d, ^2J(P,C) = 2.2 Hz; CH_{arom}), 135.42 (d, ^4J(P,C) = 7.7 Hz; CH_{arom}), 140.62 (d, ^2J(P,C) = 4.9 Hz; PCCCO), 143.04 (d, ^2J(P,C) = 2.2 Hz; C_{arom}), 169.69 (d,

^3J(P,C) = 17.0 Hz; CO), 172.76 (d, ^2J(P,C) = 13.2 Hz; CO); ^{31}P NMR (32.438 MHz, CD_3CN, 25 °C): δ = + 32.20; MS (70 eV, EI) *m/z* (%): 376 (15) [M^+]; $C_{21}H_{29}O_4P$ (376.43): calcd C 67.01, H 7.76, P 8.23; found: C 67.10, H 7.83, P 8.20.

Benzo-1,4λ^5-azaphosphinine 31: A *n*-hexane solution (2 mL) of **22a** (0.5 g, 2.10 mmol) was treated with acetonitrile (2 mL). The red color faded and the solution turned slightly yellow. After evaporation of all volatiles in vacuum (0.01 Torr), the residue was dissolved in a minimum amount of *n*-hexane and stored at −30 °C. After two days, **31** was collected in the form of slightly yellow crystals by filtration (0.40 g; 69%). The mother liquor still contained **31** which was spectroscopically (^{31}P NMR) pure. M.p. 90–93 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.04 (d, ^2J(P,H) = 5.8 Hz, 1H; PCH), 1.35 (d, ^3J(P,H) = 14.5 Hz, 18H; CCH_3), 2.92 (s, 3H; CH_3CN), 7.20 (m, 2H; H_{arom}), 7.31 (m, 1H; H_{arom}), 7.61 (m, 1H; H_{arom}); ^{13}C NMR (50.323 MHz, $CDCl_3$, 25 °C): δ = − 2.03 (d, ^1J(P,C) = 120.3 Hz; PCH), 22.81 (d, ^3J(P,C) = 2.7 Hz; CH_3CN), 28.50 (s; CCH_3), 37.49 (d, ^1J(P,C) = 48.3 Hz; CCH_3), 124.40 (d, ^1J(P,C) = 67.0 Hz; PC_{arom}), 124.41 (d, ^3J(P,C) = 11.0 Hz; CH_{arom}), 131.36 (s; $PCC_{arom}N$), 131.48 (d, ^2J(P,C) = 2.7 Hz; CH_{arom}), 133.50 (d, ^3J(P,C) = 9.9 Hz; CH_{arom}), 146.19 (d, ^2J(P,C) = 6.1 Hz; PC-CCH_3); ^{31}P NMR (32.438 MHz, $CDCl_3$, 25 °C): δ = + 43.20; MS (70 eV, EI) *m/z* (%): 275 (275) [M^+]; $C_{17}H_{26}NP$ (275.36): calcd C 74.15, H 9.52, N 5.09; found: C 74.21, H 9.60, N 5.09.

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