The versatile behavior of a 1,2λ⁵-azaphosphete towards protic nucleophiles

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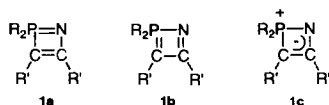[b] *Instituto de Quimica, Universidade Federal do Rio Grande do Sul, Avenido B. Gonçalves 9500, CEP 91501-970, Porto Alegre, RS, Brazil*

Abstract

1,2λ⁵-azaphosphete 1 reacts with cyclohexylamine leading to five-membered phosphazenes 7 and 8. This result has been rationalized by the protonation of the ring nitrogen atom followed by nucleophilic attack of the amide at the β-carbon of the ring. Addition of *p*-cresol and *p*-thiocresol to 1 affords the linear phosphazenes 12 and 13, resulting from protonation of the α-carbon atom of the ring followed by nucleophilic attack at phosphorus. Compounds 7 and 12 have been characterized by single crystal X-ray diffraction studies.

1. Introduction

We have recently shown that the stability of cyclobutadiene derivatives is considerably increased by replacing a carbon atom by a λ⁵-phosphorus atom [1,2]. 1,2λ⁵-Azaphosphete 1 [1] was the first representative of this new class of four-π-electron four-membered rings. In contrast to cyclobutadiene [3], compound 1 does not exist as a mixture of valence isomers, i.e. 1a, an imine of phosphorus, and 1b, an ylide of phosphorus. According to a single crystal X-ray diffraction study [1], the major canonical structure is the zwitterionic form 1c. The positive charge is located at the phosphorus atom, while the negative charge is delocalized on the three other ring atoms. In fact, 1,2λ⁵-azaphosphete 1 is a non-antiaromatic four-π-electron four-membered heterocycle (Scheme 1).
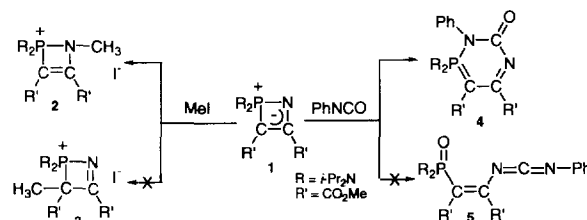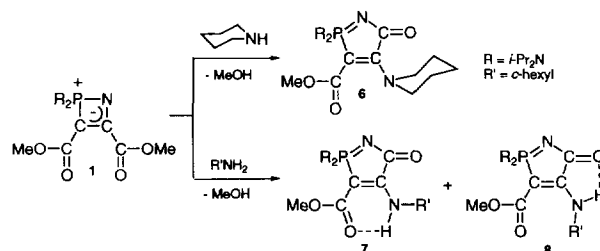
Scheme 2.

To date, 1 has always reacted via its phosphazene fragment and never via its ylide moiety. For instance, alkylation of 1 with methyl iodide does not occur at carbon to give 3, but affords compound 2 [1b]. However, owing to the cyclic structure, unusual reactivities of the PN moiety are sometimes observed: phenyliso-

Scheme 1.

Scheme 3.

Table 1
Comparison of selected spectroscopic data for compounds 6 [5], 7 and 8

Compound	$\delta\,^{31}P$	$\delta\,^{13}C(J_{PC})$ [a]			
		PC	PCC	CO [b]	CO(OMe)
6	+54.08	90.6 (118.5)	163.3 (2.0)	169.5 (14.6)	163.8 (29.7)
7	+62.12	85.8 (126.4)	166.8 (7.9)	168.5 (13.7)	164.2 (39.6)
8	+53.89	84.3 (121.0)	163.8 (6.1)	169.2 (18.0)	155.4 (43.5)

[a] Chemical shifts in ppm, coupling constants in hertz. [b] Endocyclic carbonyl group.

cyanate reacts with 1 to give the six-membered hetero-cycle 4 and not the carbodiimide 5, as expected from a classical aza-Wittig reaction [4] (Scheme 2).

During investigations of the ligand behavior of 1 towards transition metals [5], we have accidentally discovered that 1 reacts with piperidine, giving rise to the five-membered phosphazene 6 (Scheme 3). This intriguing reaction led us to investigate in detail the chemical behavior of 1 towards protic nucleophiles, and here we report the results observed with amines, phenols, and thiophenols.

2. Results and discussion

Derivative 1 is inert towards tertiary amines but reacts readily at room temperature with piperidine and cyclohexylamine. With piperidine, the five-membered phosphazene 6 [5] is the only product of the reaction, whereas with cyclohexylamine, according to ^{31}P NMR spectroscopy, a mixture of two products 7 and 8 (+62.1

Fig. 1. ORTEP drawing of 7 showing the numbering used. The only H atom shown is that involved in the hydrogen bond, illustrated by a dotted line.

and +53.9) is formed in an 80/20 ratio (95% total yield). All attempts to separate these two products by fractional crystallization or sublimation failed. A ^{13}C NMR study showed that both compounds have a very similar structure and, interestingly, the spectroscopic data compare well with those of compound 6 (Table 1).

Single crystals were grown from a pentane solution of 7 and 8 at −30°C. The ORTEP plot of 7 is shown in Fig. 1, and pertinent data are collected in Table 2. The result of this X-ray diffraction revealed a five-membered phosphazene ring structure, featuring an endocyclic carbonyl moiety, and a cyclohexylamino substituent in the β-position with respect to the phosphorus atom. The ring is almost planar [maximum deviation 0.032(3) Å], all the bond lengths and angles are quite usual. Notably, there is an intramolecular hydrogen-bonding interaction between the exocyclic carbonyl fragment and the NH moiety [N(2) ··· O(2), 2.756(4) Å; H(N2) ··· O(2), 2.054(4) Å; N(2)–H(N2), 0.970 Å; N(2)–H(N2)–O(2), 127.7(3)°]. It is important to note that the melting points of several crystals were identical (149°C), and that the ^{31}P NMR spectrum of a THF solution of these crystals was identical to that of the crude mixture, demonstrating that in solution 7 and 8 are in equilibrium. Comparing the ^{13}C NMR spectrum of 7 and 8, it appears that the most perturbated signal can be attributed to the exocyclic carbonyl moiety (Δδ = 8.8 ppm); therefore, we propose that in the second isomer 8 the intramolecular hydrogen-bonding interaction involves the endocyclic carbonyl fragment instead of the exocyclic one (Scheme 3).

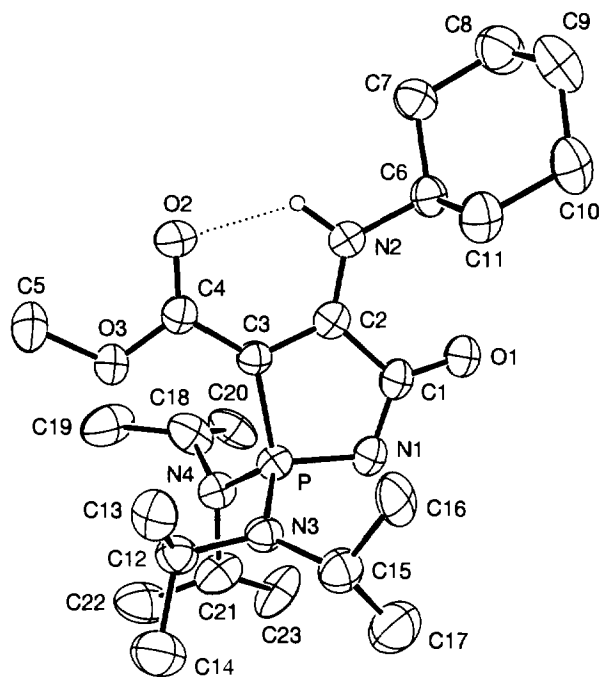Two mechanisms, which differ mainly in the first

Table 2
Selected bond lengths (Å) and angles (deg) for 7

| P–N(1)	1.618(3)	P–N(1)–C(1)	110.7(2)
N(1)–C(1)	1.347(5)	N(1)–C(1)–C(2)	113.1(3)
C(1)–C(2)	1.529(5)	C(1)–C(2)–C(3)	112.1(3)
C(2)–C(3)	1.393(5)	C(2)–C(3)–P	104.9(2)
C(3)–P	1.776(4)	N(1)–P–N(3)	109.0(2)
P–N(3)	1.650(3)	C(3)–P–N(4)	111.7(2)
P–N(4)	1.640(3)	C(2)–C(3)–C(4)	122.7(3)
C(3)–C(4)	1.440(5)	C(3)–C(4)–O(2)	125.2(3)
C(4)–O(2)	1.208(5)	C(1)–C(2)–N(2)	123.6(3)
C(2)–N(2)	1.331(4)	C(2)–N(2)–C(6)	127.6(3)
N(2) ··· O(2)	2.756(4)	N(2)–H(N2) ··· O(2)	127.7(3)
H(N2)–O(2)	2.054(4)		
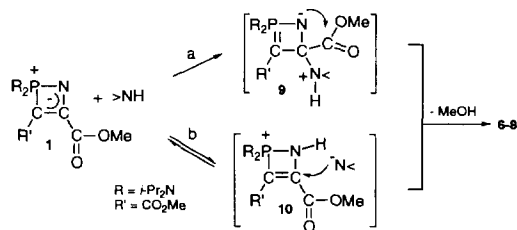
Scheme 4.

Scheme 6.

step (pathway a and b), could rationalize the formation of the five-membered heterocycles **6–8** (Scheme 4). According to ab initio calculations performed on **1'** ($R = NH_2$, $R' = CO_2H$), the LUMO ($+3.20$ eV) is located at the carbon in the β-position with respect to the λ^5-phosphorus center. Thus, the first step could be a nucleophilic attack of the amine at this carbon atom leading to intermediate **9** (pathway a). Then, the nucleophilic endocyclic nitrogen atom of **9** could attack the β-carbomethoxy group leading, after expulsion of methoxide and ring opening of the [2.0.1]bicyclic intermediate, to products **6–8**. However, $1,2\lambda^5$-azaphosphete **1** is a base [2e], and thus in the presence of a protic amine an equilibrium with the cyclic phosphonium salt **10** can exist, even though largely displaced towards **1** (pathway b). Then, **10** could act as a Michael acceptor towards the amide, giving a tautomer of **9** (Scheme 4).

An argument in favor of pathway b is provided by the reaction of the cyclic phosphonium salt **2** [1b] with the lithium salt of piperidine, which led to the cationic five-membered heterocycle **11** (85% yield). Compound **11** has also been obtained by adding iodomethane to derivative **6** (87% yield) (Scheme 5).

Using more acidic protic nucleophiles, a completely different pattern of reactivity was observed. Clean, but slow (several days), reactions occurred with *p*-cresol or *p*-thiocresol leading to derivatives **12** and **13**, which were isolated in 85 and 90% yield respectively (Scheme 6). According to NMR spectroscopy, these compounds have a similar structure, although **12** crystallized with a molecule of *p*-cresol. The ^{31}P NMR chemical shifts (**12**, $+6.6$; **13**, $+28.8$) were in the range expected for non-cyclic phosphazenes, and according to the ^{13}C NMR spectra, no carbon atom was directly bound to phosphorus. These data as a whole strongly suggest that an unprecedented cleavage of the phosphorus–carbon bond
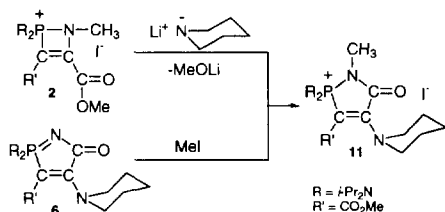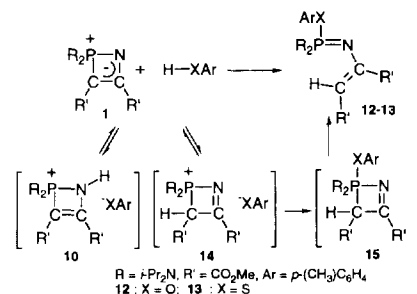
of **1** had occurred. The definitive structure of these compounds was established by a single crystal X-ray diffraction study of derivative **12** (Fig. 2, Table 3). Compound **12** is an α,β-unsaturated phosphazene formally resulting from the 1,2-addition of the phenol across the P–C ylidic bond, followed by a ring-opening reaction. The C–C double bond of **12** adopts the thermodynamically favored E-configuration, and the PNCC framework is planar, indicating some degree of electronic delocalization. Note that derivatives of type **12**, **13** are starting materials for the synthesis of electron-poor 2-azadienes [6].

It is rather tricky to rationalize the dramatic difference in the reactivity of **1** with amines, on the one hand, and *p*-cresol and *p*-thiocresol, on the other. The only reasonable hypothesis is to postulate that in protic media **1** is in equilibrium with **10**, but also to a smaller
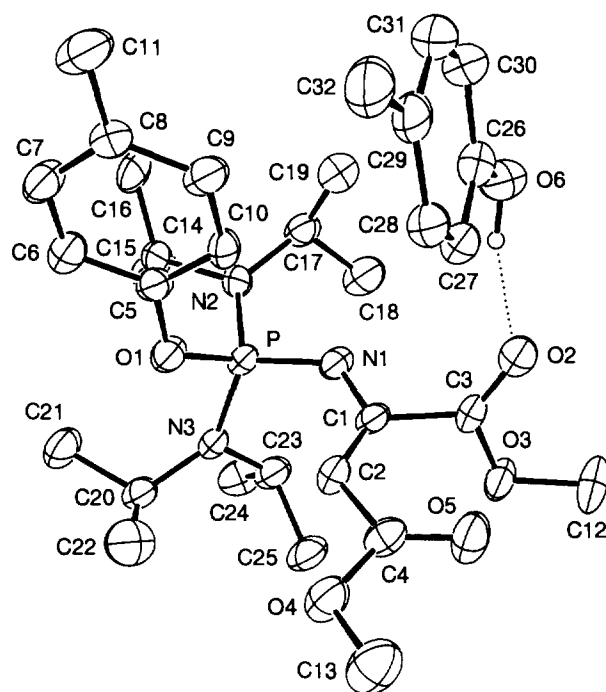

Scheme 5.

Fig. 2. ORTEP drawing of **12** showing the numbering used. The only H atom shown is that involved in the hydrogen bond, illustrated by a dotted line.

Table 3
Selected bond lengths (Å) and angles (deg) for 12

P–N(1)	1.571(5)	P–N(1)–C(1)	126.6(5)
N(1)–C(1)	1.347(8)	N(1)–C(1)–C(2)	128.8(6)
C(1)–C(2)	1.360(9)	N(1)–C(1)–C(3)	112.1(6)
C(2)–C(3)	1.520(9)	C(1)–C(2)–C(4)	122.9(6)
C(2)–C(5)	1.444(9)	N(1)–P–N(2)	105.3(3)
P–N(2)	1.623(5)	N(1)–P–N(3)	113.9(3)
P–N(3)	1.638(5)	N(2)–P–N(3)	114.4(3)
P–O(1)	1.591(4)	N(1)–P–O(1)	117.7(3)
O(1)–C(5)	1.409(8)	P–O(1)–C(5)	125.6(4)
O(2) · · · O(6)	2.747(9)	O(2)–H(O6) · · · O(6)	154(9)
H(O6)–O(2)	1.94(9)		

extent with **14**. R_2N^- can deprotonate both **10** and **14**, but cannot react at the phosphonium center because of steric hindrance. In contrast, phenoxide and thiophenoxide can deprotonate **10** but not **14**, and can also react with the phosphonium center, leading to the $\lambda^5\sigma^5$-phosphorus intermediate **15**, which undergoes a ring-opening reaction.

3. Conclusion

The comparison of the results observed in the reaction of **1** with various protic reagents clearly demonstrates the versatility of $1,2\lambda^5$-azaphosphetes (Scheme 7). Protonation can occur at the nitrogen or at the α-carbon atom of the ring. The anionic part of the reagent can either be a spectator [2e], or react at the β-carbon of the ring or at the phosphorus. The initial four-membered ring structure can be preserved [2e], undergo a ring expansion reaction, or be cleaved at the P–N [1b] or P–C bond.

4. Experimental section

4.1. General

All experiments were performed under a dry argon atmosphere. Melting points were obtained on an electrothermal capillary apparatus and were not corrected. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on Bruker AC80, AC200, WM250 or AMX400 spectrometers. ^1H and ^{13}C chemical shifts are reported in parts per million
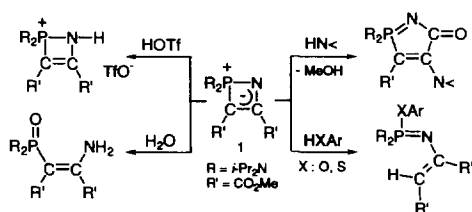
Scheme 7.

(ppm) relative to Me_4Si as external standard. ^{31}P downfield 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 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument. Conventional glassware was used.

4.2. Preparation of five-membered phosphazenes 7 and 8

Neat cyclohexylamine (3.24 μl, 2.84 mmol) was added dropwise, at room temperature, to a CH_2Cl_2 solution (10 ml) of **1** (1.0 g, 2.58 mmol). After 30 min, the solvent was removed in vacuo. The residue was crystallized at −30°C from a pentane solution. Single crystals were obtained by a second crystallization from a dilute pentane solution at −30°C. Colourless crystals. Yield 95%. M.p. 149°C. IR (CH_2Cl_2) 1647, 1572 cm^{-1} (ν CO). Anal. Found: C, 60.81; H, 9.57; N, 12.30. $C_{23}H_{43}N_4O_3P$ Calc.: C, 60.77; H, 9.53; N, 12.32%.

4.2.1. Major product (80%)
^{31}P NMR (CDCl₃) δ +62.12 ppm. ^{13}C NMR (CDCl₃) δ 22.5 and 22.8 (s, CH_3CHN), 24.2, 25.3 and 34.4 (s, CH_2), 47.0 (d, $J(PC) = 5.5$ Hz, NCHCH₃), 49.7 (s, NCH_2), 51.0 (s, CH₃O), 85.8 (d, $J(PC) = 126.4$ Hz, PC), 164.2 (d, $J(PC) = 39.6$ Hz, CO(OMe)), 166.8 (d, $J(PC) = 7.9$ Hz, PCC), 168.5 (d, $J(PC) = 13.7$ Hz, PCCC).

4.2.2. Minor product (20%)
^{31}P NMR (CDCl₃) δ +53.89 ppm. ^{13}C NMR (CDCl₃) δ 22.6 (s, CH_3CHN), 22.9 (d, $J(PC) = 1.3$ Hz, CH_3CHN), 24.3, 25.4 and 33.0 (s, CH_2), 47.2 (d, $J(PC) = 5.3$ Hz, NCHCH₃), 50.1 (s, NCH_2), 52.9 (s, CH₃O), 84.3 (d, $J(PC) = 121.0$ Hz, PC), 155.4 (d, $J(PC) = 43.5$ Hz, CO(OMe)), 163.8 (d, $J(PC) = 6.1$ Hz, PCC), 169.2 (d, $J(PC) = 18.0$ Hz, PCCC).

4.3. Five-membered phosphonium salt 11

From derivative 2: A THF solution (5 ml) of the lithium salt of piperidine (0.91 g, 1 mmol) was added dropwise at −78°C to a THF solution (5 ml) of **2** (0.53 g, 1 mmol). The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was washed three times with ether (3 × 10 ml). Compound **11** was characterized in solution by comparison of the NMR data with those of an authentic sample prepared as indicated below.

From derivative 6. Neat iodomethane (0.2 ml, 3.20 mmol) was added dropwise, at room temperature, to a dichloromethane solution (5 ml) of **6** (1.14 g, 2.58 mmol). The solution was stirred overnight at room temperature. After the solvent and excess iodomethane were removed under vacuum, the residue was washed

three times with ether (3 × 10 ml). **11** was purified by crystallization at room temperature from a CH_2Cl_2/THF solution. Colorless solid. Yield 87%. M.p. 175°C (dec.). ^{1}H NMR ($CDCl_3$) δ 1.34 (d, 12H, J(HH) = 6.9 Hz, CH_3CHN), 1.39 (d, 12H, J(HH) = 6.9 Hz, CH_3CHN), 1.77 (broad m, 6H, NCH$_2$CH_2CH_2), 3.17 (d, 3H, J(PH) = 7.2 Hz, NCH$_3$), 3.61–4.01 (sept d, 4H, J(HH) = 6.9 Hz, J(PH) = 16.4 Hz, CH$_3$CHN), 3.43 (broad s, 4H, NCH$_2$), 3.84 (s, 3H, CH$_3$O). ^{13}C NMR ($CDCl_3$) δ 22.8 (s, NCH$_2$CH$_2$CH$_2$), 23.06 (d, J(PC) = 2.7 Hz, NCHCH$_3$), 23.9 (d, J(PC) = 2.3 Hz, NCHCH$_3$), 26.8 (s, NCH$_2$CH$_2$), 30.6 (s, NCH$_3$), 43.7 (s, NCH$_2$), 49.9 (d, J(PC) = 4.8 Hz, NCHCH$_3$), 52.3 (s, CH$_3$O), 84.7 (d, J(PC) = 145.5 Hz, PC), 153.1 (d, J(PC) = 20.3 Hz, PCC), 161.7 (d, J(PC) = 11.6 Hz, CO(OMe)), 161.9 (d, J(PC) = 26.2 Hz, PCCC). ^{31}P NMR ($CDCl_3$) δ +42.70. IR (CH_2Cl_2) 1729, 1707 cm^{-1} (v CO). Anal. Found: C, 47.49; H, 7.67; N, 9.69. $C_{23}H_{44}N_4O_3$PI Calc.: C, 47.42; H, 7.61; N, 9.62%.

4.4. General procedure for the preparation of phosphazenes 12 and 13

A dichloromethane solution (10 ml) of p-cresol or p-thiocresol (30 mmol) was added dropwise, at room temperature, to a CH_2Cl_2 solution (10 ml) of **1** (1.0 g, 2.40 mmol). The solution was stirred for 5 days at room temperature and the solvent was removed in vacuo.

4.4.1. 1,1-Diisopropylamino-1-(4-methylphenoxy)-3,4-bis(methoxycarbonyl)-2-aza-1λ^5-phosphabuta-1,3-diene 12, p-cresol

Derivative **12**, p-cresol, was obtained as a pale yellow solid from a pentane solution (3 ml) at −4°C. A recrystallization at −4°C from a pentane/ether solution afforded **12**, p-cresol, as crystals. Colorless crystals. Yield 85%. M.p. 104°C. ^{1}H NMR ($CDCl_3$) δ 1.12 (d, 12H, J(HH) = 6.6 Hz, CH_3CHN), 1.27 (d, 12H, J(HH) = 6.6 Hz, CH_3CHN), 2.23 (s, 3H, C$_6$H$_4$CH_3), 2.27 (s, 3H, HOC$_6$H$_4$CH_3), 3.52 (sept d, 4H, J(HH) = 6.6 Hz, J(PH) = 20.1 Hz), 3.57 (s, 3H, CH$_3$O), 3.84 (s, 3H, CH$_3$O), 4.92 (d, 1H, J(PH) = 1.2 Hz, CHCO$_2$CH$_3$), 6.76 (d, 2H, J(HH) = 8.4 Hz, HOC$_6$$H_4CH_3$), 6.97 (d, 2H, J(HH) = 8.4 Hz, HOC$_6$$H_4CH_3$), 7.06 (s, 4H, CH$_{arom}$). The OH of HOC$_6H_4CH_3$ is not observed. ^{13}C NMR ($CDCl_3$) δ 20.4 (s, C$_6$H$_4$$CH_3$), 20.6 (s, HOC$_6H_4$$CH_3$), 22.8 and 22.9 (s, C$H_3$CHN), 45.7 (d, J(PC) = 6.1 Hz, NCHCH$_3$), 50.6 (s, CH$_3$O), 51.9 (s, CH$_3$O), 94.2 (d, J(PC) = 12.2 Hz, PNCC), 115.2 (s, HOC_6H$_4$CH$_3$), 119.6 (d, J(PC) = 5.6 Hz, C$_{arom}$), 129.9 (d, J(PC) = 19.4 Hz, C$_{arom}$), 129.8 (s, HOC_6H$_4$CH$_3$), 130.2 (s, HOC$_6$H$_4$CH$_3$), 133.9 (s, C$_{arom}$CH$_3$) 148.0 (d, J(PC) = 7.0 Hz, OC_{arom}), 154.1 (s, HOC_6H$_4$CH$_3$), 156.3 (s, PNC), 169.3 (s, CO), 169.5 (d, J(PC) = 31.9 Hz, CO). ^{31}P NMR ($CDCl_3$) δ +6.64. IR (CH_2Cl_2) 3584 cm^{-1}

(v OH), 1737, 1688 cm^{-1} (v CO). Anal Found: C, 63.56; H, 8.37; N, 6.90. $C_{32}H_{50}N_3O_6$P Calc.: C, 63.66; H, 8.34; N, 6.96%.

4.4.2. 1,1-Diisopropylamino-1-(4-methylthiophenoxy)-3,4-bis(methoxycarbonyl)-2-aza-1λ^5-phosphabuta-1,3-diene 13

The residue was washed with pentane (3 × 10 ml), and derivative **13** was obtained as a colorless solid from a CH_2Cl_2 solution (3 ml) at room temperature. Colorless solid. Yield 90%. M.p. > 300°C. ^{1}H NMR ($CDCl_3$) δ 1.09 (d, 12H, J(HH) = 6.8 Hz, CH_3CHN), 1.28 (d, 12H, J(HH) = 6.8 Hz, CH_3CHN), 2.29 (s, 3H, C$_6$H$_4$CH_3), 3.65 (s, 3H, CH$_3$O), 3.72 (sept d, 4H, J(HH) = 6.8 Hz, J(PH) = 18.8 Hz), 3.84 (s, 3H, CH$_3$O), 5.18 (d, 1H, J(PH) = 1.3 Hz, CHCO$_2$CH$_3$), 7.11 (d, 2H, J(HH) = 8.3 Hz, CH$_{arom}$), 7.46 (d, 2H, J(HH) = 8.3 Hz, CH$_{arom}$). ^{13}C NMR ($CDCl_3$) δ 20.9 (s, C$_6$H$_4$CH$_3$), 22.9 and 23.1 (s, CH_3CHN), 47.0 (d, J(PC) = 5.1 Hz, NCHCH$_3$), 50.2 (s, CH$_3$O), 51.5 (s, CH$_3$O), 93.5 (d, J(PC) = 14.8 Hz, PNCC), 122.8 (d, J(PC) = 4.4 Hz, SC_{arom}), 129.6 (d, J(PC) = 2.4 Hz, C$_{arom}$), 135.5 (d, J(PC) = 4.1 Hz, C$_{arom}$), 138.8 (d, J(PC) = 2.5 Hz, C$_{arom}$ CH$_3$), 157.6 (d, J(PC) = 2.8 Hz, PNC), 168.7 (s, CO), 168.9 (d, J(PC) = 26.1 Hz, CO).

Table 4
Crystallographic data for compounds 7 and 12

	7	12
Chemical formula	$C_{23}H_{43}N_4O_3P$	$C_{32}H_{50}N_3O_6P$
FW	454.59	603.72
T (K)	293	193
Crystal system	monoclinic	monoclinic C
Space group	$P2_1/n$	$C2/c$
a (Å)	11.2077(6)	42.686(9)
b (Å)	18.308(2)	8.312(2)
c (Å)	12.7576(6)	20.284(4)
β (deg)	92.646(4)	108.93(3)
V (Å^3)	2615.0(3)	6808(2)
F (000)	992	2608
Z	4	8
D_{calc} (g cm^{-3})	1.155	1.178
μ (Mo Kα) (mm^{-1})	0.13	0.13
$T_{min}-T_{max}$	0.959–0.999	—
2θ range (deg)	6–47	8–45
No. of data collected	4082	5377
No. of unique data	3867	4427
R (int.)	0.017	0.059
No. of observed data [a]	2302	2738
No. of parameters varied	280	395
S	1.120	1.174
$(\Delta/\sigma)_{max}$	0.004	0.000
R [b]	0.043	0.087
R_w [c]	0.042	0.259
$(\Delta/\rho)_{max, min}$ (e Å^{-3})	0.17, −0.17	0.41, −0.33

[a] $F_0 > 5\sigma(F_0)$ for **7** and $F_0 > 4\sigma(F_0)$ for **12**. [b] $R = \Sigma||F_0|-|F_0||/\Sigma|F_0|$. [c] $R_w = [\Sigma(w|F_0|-|F_0|)^2/\Sigma w|F_0|^2]^{1/2}$ for **7** and $R_w = [\Sigma w(F_0^2 - F_0^2)^2/\Sigma wF_0^4]^{1/2}$ for **12**.

Table 5

Atomic fractional coordinates and equivalent isotropic temperature factors ($\mathring{A}^2 \times 100$) for 7

Atom	x	y	z	U_{eq} *
P	0.14365(9)	0.65452(5)	0.36601(8)	4.43(5)
N(1)	0.1428(3)	0.5667(2)	0.3514(3)	5.1(2)
C(1)	0.1402(3)	0.5488(2)	0.2489(3)	4.8(3)
C(2)	0.1415(3)	0.6152(2)	0.1764(3)	4.4(2)
C(3)	0.1360(3)	0.6806(2)	0.2317(3)	4.0(2)
O(1)	0.1361(3)	0.4865(2)	0.2140(2)	6.3(2)
C(4)	0.1393(3)	0.7510(2)	0.1815(3)	4.5(2)
O(2)	0.1461(3)	0.7608(1)	0.0883(2)	5.9(2)
O(3)	0.1316(3)	0.8066(1)	0.2505(2)	6.0(2)
C(5)	0.1368(4)	0.8791(2)	0.2088(4)	7.5(3)
N(2)	0.1488(3)	0.6107(2)	0.0727(2)	4.8(2)
C(6)	0.1767(3)	0.5461(2)	0.0109(3)	5.0(2)
C(7)	0.1422(4)	0.5605(2)	−0.1035(3)	6.0(3)
C(8)	0.1744(4)	0.4965(3)	−0.1715(4)	7.8(3)
C(9)	0.3058(5)	0.4766(3)	−0.1569(4)	9.9(4)
C(10)	0.3401(4)	0.4627(3)	−0.0438(4)	8.0(4)
C(11)	0.3090(3)	0.5277(2)	0.0253(3)	6.3(3)
N(3)	0.2668(3)	0.6786(2)	0.4331(2)	4.5(2)
C(12)	0.2901(3)	0.7563(2)	0.4562(3)	5.3(3)
C(13)	0.3817(4)	0.7885(3)	0.3862(4)	7.9(3)
C(14)	0.3256(4)	0.7696(3)	0.5712(3)	8.6(4)
C(15)	0.3700(4)	0.6281(2)	0.4508(3)	6.2(3)
C(16)	0.4216(4)	0.5977(3)	0.3501(4)	8.9(4)
C(17)	0.3457(5)	0.5687(3)	0.5291(4)	9.6(4)
N(4)	0.0328(3)	0.6889(2)	0.4296(2)	5.1(2)
C(18)	−0.0798(4)	0.7040(3)	0.3724(4)	9.4(4)
C(19)	−0.1199(5)	0.7820(3)	0.3727(5)	13.6(6)
C(20)	−0.1765(5)	0.6481(4)	0.3801(5)	15.6(7)
C(21)	0.0374(5)	0.6815(2)	0.5453(4)	9.2(4)
C(22)	−0.0070(5)	0.7473(3)	0.6016(4)	12.9(5)
C(23)	−0.0167(6)	0.6126(3)	0.5847(5)	17.3(7)

* $U_{eq} = 1/3$ of the trace of the orthogonalized U_{ij} tensor.

^{31}P NMR (CDCl$_3$) δ +28.80. IR (CH$_2$Cl$_2$) 1737, 1686 cm^{-1} (ν CO). Mass spectrum (DCI-CH$_4$): m/z 512 (M$^+$ + 1). Anal Found: C, 58.66; H, 8.27; N, 8.29. C$_{25}$H$_{42}$N$_3$O$_4$PS Calc.: C, 58.68; H, 8.27; N, 8.21%.

4.5. Quantum chemical calculations

Quantum chemical calculations of the stationary point geometries (local minima and saddle points) were carried out at the RHF level [7]. A double-ζ (11s^{7}p/9s^{5}p/4s)/[6s^{4}p/4s^{2}p/2s] Dunning–Hay basis set [8] supplemented by polarization functions at all atoms was utilized in the calculations. Electron correlation correction at the RHF optimized geometries was computed with the MP2 approximation. All stationary points on the energy hypersurface were characterized by a vibrational analysis within the harmonic approximation.

4.6. Crystal structure analysis of 7

The data for 7 have been collected at 293 K on an Enraf-Nonius CAD4 diffractometer with graphite

monochromated Mo Kα radiation (λ = 0.71073 $\mathring{A}$) using ω–2θ scans. A semi-empirical absorption correction was employed [9]. The structure was solved by direct methods using SHELXS-86 [10]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier maps, and introduced in idealized geometry. The structure was refined against F with unit weights using SHELX76 [11]. Crystallographic data and fractional atomic coordinates are given in Tables 4 and 5 respectively.

Table 6

Atomic fractional coordinates and equivalent isotropic temperature factors ($\mathring{A}^2 \times 100$) for 12

Atom	x	y	z	U_{eq} *
P	0.14139(4)	0.7655(2)	0.02859(8)	0.0359(5)
N1	0.14800(12)	0.7681(6)	0.1094(3)	0.0384(13)
C1	0.16581(15)	0.6604(8)	0.1563(3)	0.036(2)
C2	0.1764(2)	0.5117(8)	0.1450(3)	0.041(2)
C3	0.1723(2)	0.7166(8)	0.2308(3)	0.042(2)
C4	0.1941(2)	0.4052(8)	0.2008(4)	0.040(2)
O1	0.12680(10)	0.6048(5)	−0.0125(2)	0.0420(11)
C5	0.0963(2)	0.5330(8)	−0.0164(3)	0.042(2)
C6	0.0773(2)	0.4771(9)	−0.0806(3)	0.052(2)
C7	0.0485(2)	0.3936(9)	−0.0853(4)	0.054(2)
C8	0.0383(2)	0.3678(9)	−0.0283(4)	0.050(2)
C9	0.0580(2)	0.4300(9)	0.0359(4)	0.047(2)
C10	0.0868(2)	0.5118(8)	0.0416(3)	0.044(2)
C11	0.0075(2)	0.2702(10)	−0.0332(4)	0.065(2)
O2	0.15267(12)	0.7219(7)	0.2607(2)	0.0598(15)
O3	0.20354(11)	0.7718(6)	0.2574(2)	0.0483(12)
C12	0.2132(2)	0.8175(11)	0.3299(3)	0.074(3)
O4	0.20401(11)	0.2705(6)	0.1760(2)	0.0509(13)
O5	0.19912(12)	0.4265(6)	0.2626(2)	0.0573(14)
C13	0.2181(2)	0.1474(9)	0.2272(4)	0.066(2)
N2	0.11503(13)	0.9093(7)	−0.0027(2)	0.0411(14)
C14	0.1000(2)	0.9209(10)	−0.0805(3)	0.054(2)
C15	0.1111(2)	1.0746(12)	−0.1070(4)	0.083(3)
C16	0.0626(2)	0.9083(11)	−0.1043(4)	0.071(2)
C17	0.1026(2)	1.0278(8)	0.0375(3)	0.045(2)
C18	0.1304(2)	1.1324(9)	0.0863(4)	0.062(2)
C19	0.0798(2)	0.9584(10)	0.0735(4)	0.059(2)
N3	0.17507(12)	0.7762(7)	0.0068(2)	0.0399(14)
C20	0.1863(2)	0.6783(10)	−0.0422(3)	0.052(2)
C21	0.1638(2)	0.6901(13)	−0.1183(3)	0.077(3)
C22	0.1940(2)	0.5023(11)	−0.0187(4)	0.074(3)
C23	0.1992(2)	0.9035(9)	0.0460(3)	0.049(2)
C24	0.2079(2)	1.0279(10)	−0.0010(4)	0.071(2)
C25	0.2307(2)	0.8247(11)	0.0944(4)	0.062(2)
O6	0.0856(2)	0.6886(10)	0.2331(3)	0.085(2)
H6O	0.1059(24)	0.6710(114)	0.2351(46)	0.092(34)
C26	0.0739(2)	0.5329(13)	0.2240(4)	0.066(2)
C27	0.0945(2)	0.4021(12)	0.2297(3)	0.059(2)
C28	0.0812(2)	0.2478(12)	0.2198(3)	0.062(2)
C29	0.0472(2)	0.2226(13)	0.2039(4)	0.068(3)
C30	0.0402(2)	0.5080(15)	0.2094(4)	0.075(3)
C31	0.0274(2)	0.3582(15)	0.1998(4)	0.075(3)
C32	0.0329(2)	0.0543(13)	0.1923(4)	0.087(3)

* $U_{eq} = 1/3$ of the trace of the orthogonalized U_{ij} tensor.

4.7. Crystal structure analysis of 12

The data for **12** have been collected at 193 K on a Stoe-Siemens diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using $\omega-2\theta$ scans. The structure was solved by direct methods using SHELXS-90 [12]. All non-hydrogen atoms were refined anisotropically. The hydrogen atom bonded to O(6) was located by a difference Fourier map, and its position was refined isotropically. For the other hydrogen atoms, the riding model was used. The structure was refined against F^2 with a weighting scheme of $\omega^{-1} = \sigma^2(F_o^2) + (0.0879P)^2 + 33.5919P$ with $P = (F_o^2 + 2F_c^2)/3$ using SHELXL93 [13]. Crystallographic data and fractional atomic coordinates are given in Tables 4 and 6 respectively.

Acknowledgements

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