Diphosphabenzenes V [1]
5,5'-(1,ω-Alkanediyl) -bis{λ⁵-[1,3]diphosphinines}. A new ethynyl-λ⁵-[1,3]diphosphinine

Ekkehard Fluck [a,*], Gernot Heckmann [b], Ekaterina Gorbunowa [b], Matthias Westerhausen [b], Frank Weller [c]

[a] *Gmelin-Institut für Anorganische Chemie der Max-Planck-Gesellschaft, Varrentrappstr. 40 / 42, D-60486 Frankfurt am Main, Germany*
[b] *Institut für Anorganische Chemie der Universität, Pfaffenwaldring 55, D-70569 Stuttgart, Germany*
[c] *Fachbereich Chemie der Universität, Hans-Meerwein-Straße, D-35043 Marburg / Lahn, Germany*

Abstract

Reaction of 1,1,3,3-tetrakis(dimethylamino)-1λ⁵,3λ⁵-diphosphete (1) with 1,4-diphenyl-1,3-butadiyne, 1,5-hexadiyne and 1,7-octadiyne yields octa-N-methyl-5-phenyl-4-(phenylethynyl)-1λ⁵,3λ⁵-[1,3]diphosphinine-1,1,3,3-tetramine (2), 5,5'-(1,2-ethanediyl)-bis-{octa-N-methyl-1λ⁵,3λ⁵-[1,3]diphosphinine-1,1,3,3-tetramine} (5), and 5,5'-(1,4-butanediyl)-bis-{octa-N-methyl-1λ⁵,3λ⁵-[1,3]diphosphinine-1,1,3,3-tetramine} (7), respectively. The new products 2, 5 and 7 are characterized by NMR, mass and IR spectra. X-ray structure analyses of 2, 5 and 7 were performed. Compounds 4 and 6 are intermediate products of the reaction of 1 and 1,5-hexadiyne and 1,7-octadiyne, respectively.

Keywords: Diphosphete; Diphosphinines; Crystal structure; NMR

1. Introduction

In 1987 we synthesized the first 1λ⁵,3λ⁵-diphosphabenzene by reacting 1,1,3,3-tetrakis(dimethylamino)-1λ⁵,3λ⁵-diphosphete (1) with dimethyl acetylenedicarboxylate [1]. Subsequently we prepared numerous other λ⁵-[1,3]diphosphinines by reacting λ⁵-1,3-diphosphetes with acetylene as well as different mono- and disubstituted acetylenes [2–5]. The formation of the λ⁵-[1,3]diphosphinines proceeds according to our proposal by a [2 + 2]-cycloaddition which leads to a bicyclic system, followed by a spontaneous valence isomerization (see Eq. (1)).
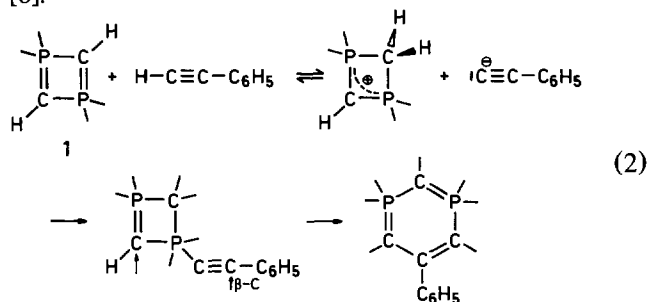

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(1)
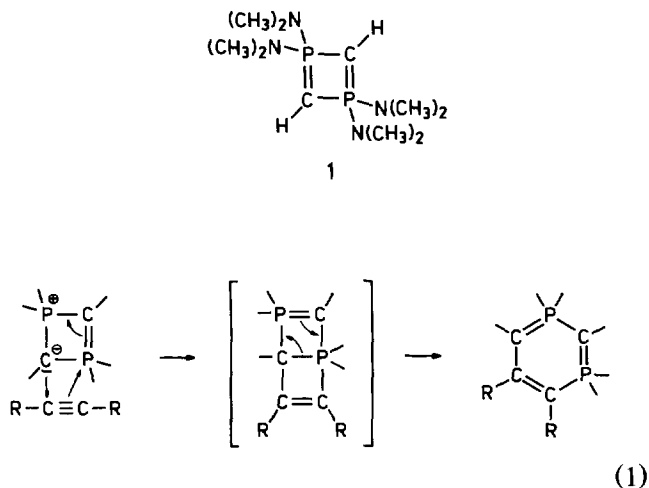
It was suggested that the reaction between λ⁵-1,3-diphosphetes and fairly acidic monosubstituted acetylenes, e.g. phenylacetylene, is preceded by an acid–base reaction (see Eq. (2)) [4]. A review of all λ⁵-[1,3]diphos-

phinines prepared by us so far was recently published [6].

(2)

The reaction of λ^5-1,3-diphosphete (1) with bis(trimethylsilyl)butadiyne-1,3 yields 1,1,3,3-tetrakis(dimethylamino)-5-trimethylsilyl-4-(trimethylsilylethynyl)-1λ^5,3λ^5-[1,3]diphosphinine (3), a compound containing a C≡C triple bond in the $(CH_3)_3Si$–C≡C substitutent. Even in the presence of excess λ^5-1,3-diphosphete (1), a second [2 + 2]-cycloaddition did not occur, and thus formation of a compound in which two λ^5-[1,3]diphosphinine rings are joined did not happen [3]. This result led to the question of whether the bulky trimethylsilyl groups and/or the distance between the two acetylene groups of the diacetylene were responsible for this behavior. In order to clarify this problem we reacted 1 with diphenylbutadiyne-1,3,hexadiyne-1,5 and octadiyne-1,7.

2. Reaction of 1 with diphenylbutadiyne-1,3

Equimolar amounts of 1,1,3,3-tetrakis(dimethylamino)-1λ^5,3λ^5-diphosphete (1) and 1,4-diphenylbutadiyne-1,3 in boiling toluene reacted during the course of several days to octa-N-methyl-5-phenyl-4-(phenylethynyl)-1λ^5,3λ^5-[1,3]diphosphinine-1,1,3,3-tetramine (2) which was isolated as yellow crystals, m.p. 146 °C (see Eq. (3)). An analogous reaction with two equivalents of 1 also yields 2, indicating that the C≡C triple bond of the side chain of 2 cannot be inserted into the four-membered ring of 1 for steric reasons.

(3)
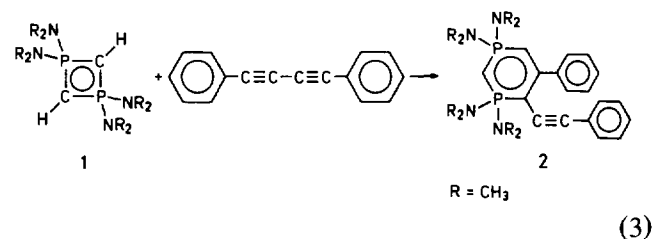
3. Reaction of 1 with hexadiyne-1,5 and octadiyne-1,7

If 1 and the hexadiyne-1,5 in a molar ratio of 2:1 are slightly warmed in toluene, an insertion reaction takes place with only one of the two C≡C triple bonds of the

hexadiyne-1,5. Even after days the ^{31}P{^{1}H} NMR spectrum shows only the resonance signal of 5-but-3-ynyl-octa-N-methyl-1λ^5,3λ^5-[1,3]diphosphinine-1,1,3,3-tetramine (4) at 61.00 ppm. Only after refluxing of the reaction mixture can formation of 5,5'-(1,2-ethanediyl)-bis-{octa-N-methyl-1λ^5,3λ^5-[1,3]diphosphinine-1,1,3,3-tetramine} (5) be observed (see Eq. (4)).

(4)
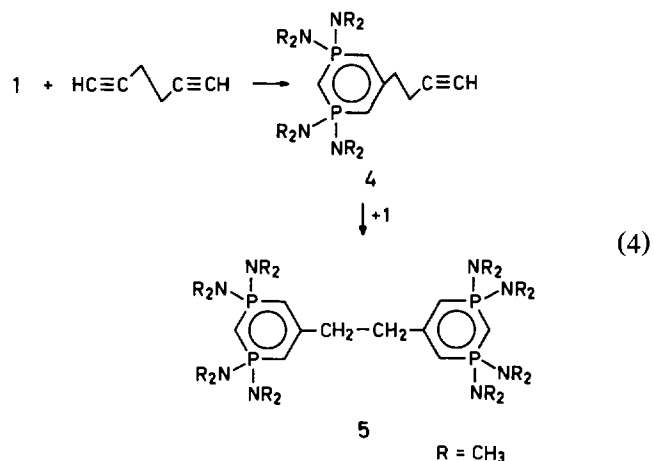
The chemical shift value of 5 amounts to δ^{31}P = 61.47 ppm. After 12 h the molecular ratio of the reaction products 4 and 5 is 1:2, after 36 h 1:5 and after 60 h 1:10. Compound 5 can be isolated in good yields as colorless air- and moisture-sensitive crystals which melt at 188–189 °C.

The diphosphete 1 reacts analogously with the octadiyne-1,7. Interaction between the octadiyne with twice the molar amount of 1 yields at first 5-hex-5-ynyl-octa-N-methyl-1λ^5,3λ^5-[1,3]diphosphinine-1,1,3,3-tetramine (6). The ^{31}P{^{1}H} NMR spectrum exhibits a signal at 61.06 ppm. The subsequent reaction of 1 with 6 leads to the formation of 5,5'-(1,4-butanediyl)-bis-{octa-N-methyl-1λ^5,3λ^5-[1,3]diphosphinine-1,1,3,3-tetramine} (7). After a reaction time of 64 h 7 is the only product found. It is obtained in a yield of about 74% as large, colorless cubes (see Eq. (5)). Its chemical shift value is δ^{31}P = 61.32 ppm.
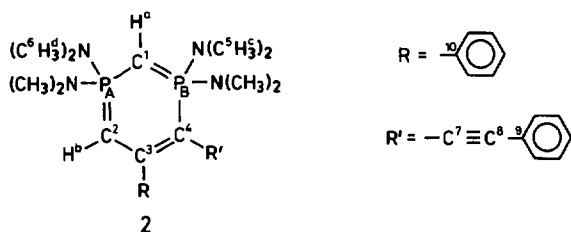

(5)
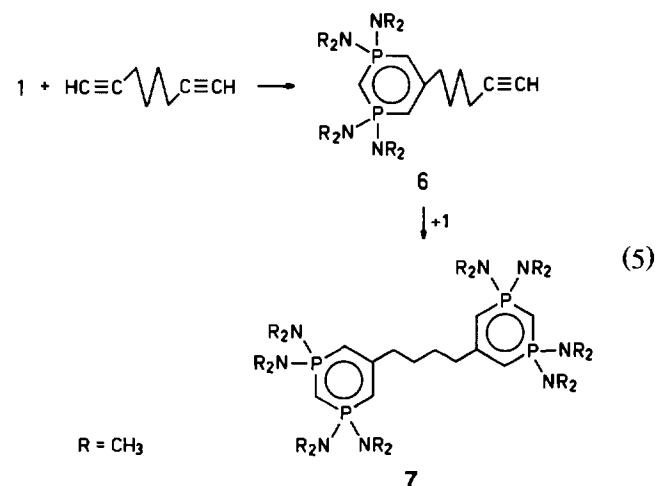
The result of this study shows that under the reaction conditions applied here it is not possible, from **1** and an alkanediyne-1,ω to synthesize derivatives of bis($2\lambda^5,4\lambda^5$-diphosphaphenyl) which are analogs of biphenyl. However, it is easily possible to prepare compounds in which the two diphosphaphenyl groups are separated by two or more methylene groups. What still needs to be investigated is whether only *one* methylene groups is sufficient, i.e. whether **1** and pentadiyne-1,4 react to yield compounds which are analogs of diphenylmethane.

4. NMR spectra

There is only a small difference in the $^{31}P\{^1H\}$ NMR spectra between $\delta^{31}P$ values of the AB spin system of the ylidic $P_AC^1P_B$ triade of **2** and those of the analogous 4-trimethylsilylethynyl substituted λ^5-[1,3]diphosphinine **3** (less than 0.4 ppm; numbering of the atoms as in Table 1). The corresponding coupling constant $^2J(P_AP_B)$

Table 1
NMR parameters of 1,1,3,3-tetrakis(dimethylamino)-5-phenyl-$1\lambda^5,3\lambda^5$-[1,3]diphosphinine (**2**) in C_6D_6 at 300 K

δ (ppm)			^nJ, n = 1–4 (Hz)		
^{31}P:	P_A [a]	55.1	n = 1:	C^1P_A	132.0
	P_B	59.1		C^1P_B	132.0
^{13}C:	C^1	2.4		C^2P_A	130.9
	C^2	66.2		C^4P_B	133.9
	C^3	164.9	n = 2:	P_AP_B	57.2
	C^4	55.5		$C^3P_{A,B}$ [a]	18.2
	C^5,C^6 [a]	36.6			12.4
		37.2		C^5P_A	2.8
	C^7	97.0		C^6P_B	2.6
	C^8	91.1		C^7P_B	5.8
	C^9	[b]		H^aP_A	11.8
	C^{10}	146.8		H^aP_B	11.8
^1H:	H^a	0.80		H^bP_A	7.3
	H^b	3.72	n = 3:	C^2P_B	1.3
	H^c,H^d	2.37		C^8P_B	4.7
		2.68		$C^{10}P_{A,B}$ [a]	19.8
	[c]				15.2
				H^cP_B,H^dP_A [a]	11.3
					11.8
			n = 4:	H^aH^b	3.5
				H^bP_B	1.3

[a] Not assigned.
[b] Hidden under C_6D_6 lines.
[c] Range δ^1H of phenyl groups 6.85–7.85 ppm.
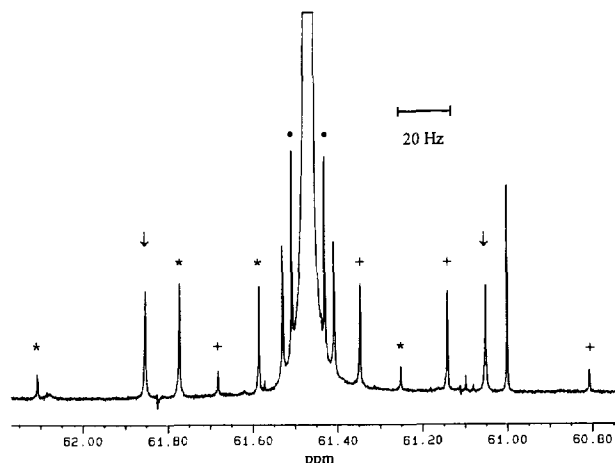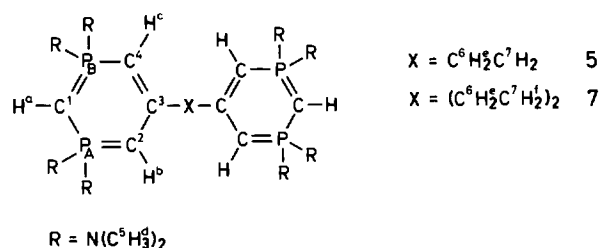

Fig. 1. ^{13}C satellites in the 161.977 MHz $^{31}P\{^1H\}$ NMR spectrum of 1,2-ethylen-bis-{λ^5-[1,3]diphosphinine} (**5**) in C_6D_6 at 305 K (3400 scans; total experimental time 21.7 h; digital resolution 0.02 Hz per point). The lines denoted ' + ' and ' * ' form, in each case, the two ab subspectra of the ABX spin system of the [mono-$^{13}C^{2,4}$] isotopomer of **5** (see Table 2, where the atoms are identified). The signals marked ' ↓ ' and ' • ' show the $^{31}P^{13}C$ doublets of an individual [mono-$^{13}C^i$] isotopomer, i = 1, 3, respectively. The third doublet represents the vicinal coupling constant $^3J(^{31}P^{13}C^6)$. The intensity ratio of the main peak of the [per-^{12}C] isotopomer and the smallest signal of the ab subspectra is about 2600:1. The singlet at 61.000 ppm belongs to the λ^5-[1,3]diphosphinine intermediate **4**, $R_2PC(H)PR_2C(H)C(R')C(H)$, $R = N(CH_3)_2$, $R' = CH_2CH_2CCH$ (see text).

of **2** lies in the narrow range of the 4,5-disubstituted diamino-λ^5[1,3]diphosphabenzenes (53.6–57.8 Hz; cf. Ref. [6]), which is significantly different from the *geminal* PP coupling of **3** (44.3 Hz) [3].

The $^{13}C\{^1H\}$ NMR spectrum of **2** shows, for C^1 and C^3, typically high or low field positions, respectively, generally characteristic of 4,5-di- and 5-monosubstituted $1\lambda^5,3\lambda^5$-diphosphabenzenes [3,7]. $^{13}C\{^1H\}$ DEPT experiments, the position and the splitting pattern of the carbon atoms C^i, i = 1–10, confirm the structure of the heterocycle **2**. The twice doubled doublet of the hydrogen atom H^b and the triply split triplet of H^a in the ^1H NMR spectrum serve to ascertain the two long-range couplings $^4J(H^aH^b)$ and $^4J(H^bP_B)$. The former has been found so far in all diamino-λ^5-[1,3]diphosphabenzenes [4].

The chemical shifts $\delta^{31}P$ of the bis(λ^5-diaminodiphosphabenzenes) **5** and **7** differ only slightly among each other and from the $\delta^{31}P$ shifts of the at the ring carbon atoms unsubstituted λ^5-diphosphabenzene 1,1,3,3-tetrakis(di-methylamino)-$1\lambda^5,3\lambda^5$-[1,3]diphosphinine (**8**) (60.210 ppm [4]; see Table 2). Both ring systems show, in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of their [mono-$^{13}C^{2,4}$] isotopomers, complete ABX systems (see Fig. 1) which are nearly identical. Their analysis and simulation (cf. Ref. [8]) result in ^{13}C isotope shifts of $^1\Delta^{31}PC^{2,4}$ = −0.012 ppm relative to the [per-^{12}C] isotopomer, which are comparably large

Table 2

NMR spectral data of bis(λ^5-1,3-diphosphabenzenes) 5 and 7 at 305 K in C_6D_6 (concentration 0.1 mol l^{-1})

X = $C^6H_2^5C^7H_2$ 5

X = $(C^6H_2^5C^7H_2')_2$ 7

R = $N(C^5H_3^d)_2$

δ (ppm)				$^nJ, n = 1$–4 (Hz)			
		5	7			5	7
^{31}P [a]:	P_A, P_B	61.467	61.323	$n = 1$:	$C^1P_{A,B}$	129.8	129.7
^{13}C:	C^1	0.44	0.51			129.8	129.7
	$C^{2,4}$	51.37	51.57		$C^{2,4}P_{A,B}$	+137.4 [β]	+137.2 [β]
	C^3	166.08	165.80	$n = 2$:	P_AP_B	54.2 [γ]	54.1
	C^5	37.03	37.16		$C^3P_{A,B}$	12.6	12.5
	C^6	47.39	44.9		$P_{A,B}H^a$	11.2	11.0
	C^7	47.39	31.49		$P_{A,B}H^{b,c}$	8.1	7.7
^1H:	H^a	0.836	0.837	$n = 3$:	$C^{2,4}P_{B,A}$	+3.7	+3.8
	$H^{b,c}$	3.272	3.158		$C^6P_{A,B}$	19.6	19.7
	H^d	2.492	2.511	$n = 4$:	$C^7P_{A,B}$	0.6	0.6
	H^e	2.990	2.51		$H^aH^{b,c}$ [δ]	3.2	2.9
	H^f	—	1.930				

[a] $\delta^{31}P$ of [per-^{12}C] isotopomer.

[β] Positive sign of $^1J(\lambda^5$-PC), cf. Ref. [2].

[γ] From ^{13}C satellites of $^{31}P\{^1H\}$ spectrum (see Fig. 1).

[δ] $^4J(P_{A,B}H^{c,b})$ and $^4J(H^bH^c) < 0.1$ Hz respectively, (see text).

like those of 8 [4], of some 1,4-dihydro-1λ^5,4λ^5-[1,4]diphosphinines [8], and of dihydro-λ^5-phosphetes [9]. $^3\Delta^{31}PC$ values could not be found. The ^{31}P shifts of the intermediates 4 and 6, which still occur in traces (less than 0.015%) in the C_6D_6 solutions of 5 and 7, have values of 61.000 and 61.063 ppm respectively (see Fig. 1).

In the $^{13}C\{^1H\}$ NMR spectrum of 5 one finds, for the exocyclic carbon atoms C^7 (for numbering of atoms see Table 2), a triplet of triplets which should be interpreted

as the X part of an $A_2A_2'X$ spin system. The coupling constant $^4J(C^7P)$ of 0.6 Hz, which was also observed at C^7 of compound 7, confirms the occurrence of two equal λ^5-diphosphabenzene heterocycles in the molecule of 5. Since in compounds 5 and 7 the three long range ^4J couplings between H^b and H^c, H^b and P_B, and also H^c and P_A are smaller than 0.1 Hz, the values of the expected (see above) interring coupling constants $^4J(H^aH^{b,c})$ and of the geminal $P_{A,B}H^{b,c}$ coupling con-
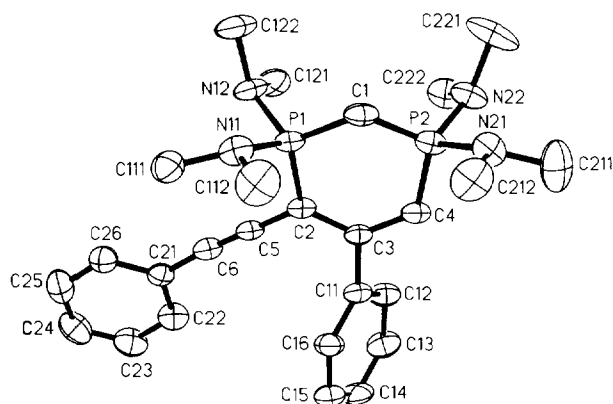

Fig. 2. Molecular structure of 2 with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Fig. 3. Molecular structure of 5 with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. The atoms generated by the crystallographically enforced symmetry are marked with a prime.

stants could be determined by first order analysis. In the ^1H NMR spectrum of **7** the multiplet belonging to H^e is hidden under the lines of the dimethylamino groups. This finding was verified by ^1H homodecoupling experiments and further corroborated by the cross-peaks in the (H,H)-COSY spectrum belonging to the $H^{b,c}$ and H^f lines.

5. Molecular and crystal structures of 2, 4 and 6

Single crystals of **2** suitable for X-ray analysis were obtained from diethyl ether/tetrahydrofuran at $-32\,°C$. In Fig. 2 the molecular structure and the numbering scheme of compound **2** are given.

Compound **5** crystallizes from toluene/diethyl ether at $-18\,°C$ in the triclinic crystal system. The molecular structure of **5** and the numbering scheme are given in Fig. 3. The atoms of the second half of the molecule generated by the crystallographic inversion center are marked with a prime.

Single crystals of compound **7** were obtained from diethyl ether at $2.5\,°C$ with a unit cell belonging to the triclinic crystal system. The molecular structure of **7** and the numbering scheme are shown in Fig. 4. The atoms of the second half of the molecule generated by the crystallographic inversion center are denoted with a prime.

The six-membered P_2C_4-ring system is common to all three compounds and is numbered in the same way for **2**, **5** and **7**. The P1–C1 and P2–C1 bond lengths are shorter by about 170 pm than the other two P–C bonds. Most notable are the differences at compound **2**; similar large differences were also observed at the 4-trimethyl-silylethynyl substituted λ^5-[1,3]diphosphinine derivate **3** [3]. Solvated bond lengths and bond angles for compound **2** are given in Table 3 and for compounds **5** and **7** these values are listed in Table 4.

The six-membered ring is almost planar, the largest deviations from the best plane are for C1 of compound
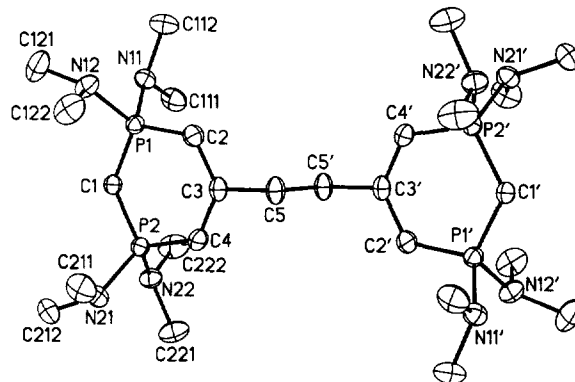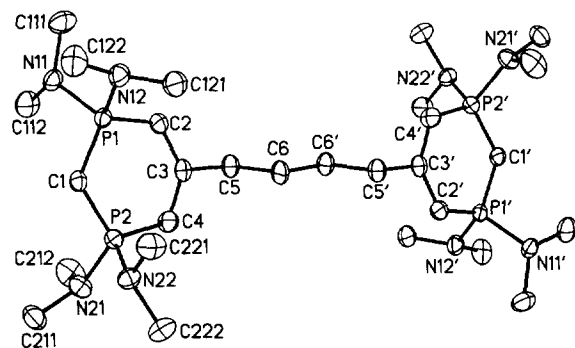

Fig. 4. Molecular structure of **7** with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted. The atoms generated by the crystallographically enforced symmetry are marked with a prime.

Table 3
Selected bond lengths (pm) and angles (°) of **2**

Bond lengths	
P1–C1	170.7(7)
P1–C2	175.4(6)
P2–C1	168.6(7)
P2–C4	175.7(6)
C2–C3	141.1(8)
C2–C5	141.9(8)
C3–C4	137.1(8)
C3–C11	151.1(6)
C5–C6	122.1(9)
C6–C21	142.8(7)
Bond angles	
C1–P1–C2	109.5(3)
C1–P2–C4	109.6(3)
P1–C1–P2	123.4(4)
P1–C2–C3	123.2(4)
P1–C2–C5	116.0(4)
C3–C2–C5	120.7(5)
C4–C3–C2	128.4(6)
C2–C3–C11	116.2(5)
C4–C3–C11	115.4(5)
P2–C4–C3	123.7(5)
C2–C5–C6	178.6(7)
C5–C6–C21	174.9(6)

5 at 3.9 pm and of compound **7** at 6.7 pm, and thus are smaller than at the alkynyl substituted derivatives **2** and **3** [3]. The PN_2-planes are nearly perpendicular to the six-membered rings.

The alkyl-(**5** and **7**) or aryl groups, respectively, which are linked to C3, exhibit single bonds in the

Table 4
Selected bond lengths (pm) and angles (°) of **5** and **7**

	5	7
Bond lengths		
P1–C1	170.21(14)	170.0(2)
P1–C2	171.94(13)	172.3(2)
P2–C1	170.20(12)	169.8(2)
P2–C4	171.73(13)	171.7(2)
C2–C3	139.0(2)	139.2(2)
C3–C4	139.2(2)	139.1(2)
C3–C5	152.2(2)	152.0(2)
C5–C5′	152.6(2)	—
C5–C6	—	152.7(2)
C6–C6′	—	152.5(3)
Bond angles		
C1–P1–C2	110.06(6)	110.11(8)
C1–P2–C4	110.18(7)	110.03(8)
P1–C1–P2	122.88(7)	122.75(9)
P1–C2–C3	124.70(10)	124.03(12)
C2–C3–C4	127.31(11)	127.54(14)
C2–C3–C5	116.42(11)	116.28(14)
C4–C3–C5	116.26(11)	116.15(14)
P2–C4–C3	124.57(10)	124.62(12)
C3–C5–C5′	112.37(12)	—
C3–C5–C6	—	112.04(13)
C5–C6–C6′	—	113.1(2)

expected range. The axis normal to the two planar six-membered rings of compound **2** enclose an angle of 59.0°. The alkynyl group of **2** which is linked to C2 shows, in spite of the expected short C2–C5 bond of 142 pm, no interaction with the six-membered ring. The alkynyl fragment occurs in a conformation similar to diphenylacetylene (tolane) [10–12]. In crystalline tolane the phenyl rings are coplanar. In compound **2** the rings are out of plane by a torsion angle of 6.2°.

6. Experimental

All operations were done under strict exclusion of moisture in an atmosphere of dried and purified argon.

The solvents were dried according to known procedures and saturated with argon.

The NMR spectra were taken with AC 250 NMR (^{1}H: 250, 133 MHz) and AM 400 (^{1}H: 400, 133 MHz) NMR spectrometers from Bruker Analytische Meßtechnik GmbH, Rheinstetten, Germany. The δ^{31}P chemical shifts were referenced to 85% aqueous ortho-phosphoric acid as external standard, while the shifts δ^{13}C and δ^1H were referred to tetramethylsilane using, in each case, the respective signals of the deuterated solvents. Positive values mean shifts to lower field strengths. The simulation of the spectra were carried out using the PANIC program (Bruker Software) with an Aspect 3000 computer.

The mass spectra were recorded with a VARIAN

Table 5
Crystal parameters and details of structure determinations of **2**, **5** and **7**

Compound	2	5	7
Formula	$C_{26}H_{36}N_4P_2$	$C_{26}H_{58}N_8P_4$	$C_{28}H_{62}N_8P_4$
Formula weight [g mol^{-1}]	466.53	606.68	634.74
Crystal dimensions [mm^3]	$0.07 \times 0.09 \times 0.23$	$0.3 \times 0.3 \times 0.4$	$0.4 \times 0.4 \times 0.5$
Temperature [°C]	−50	−80	−80
Crystal system	orthorhombic	triclinic	triclinic
Space group	$Pca2_1$ (No. 29 [15])	$P\bar{1}$ (No. 2 [15])	$P\bar{1}$ (No. 2 [15])
a [pm]	1408.5(3)	799.0(2)	910.5(1)
b [pm]	1140.0(2)	915.4(2)	975.2(1)
c [pm]	1630.9(3)	1251.3(3)	1186.4(1)
α [°]	90	104.18(3)	69.038(5)
β [°]	90	96.26(3)	81.845(5)
γ [°]	90	98.35(3)	68.490(6)
Volume V [nm^3]	2.6187(9)	0.8679(4)	0.9151(2)
Z	4	1	1
$F(000)$	1000	330	346
Density d_{calc} [g cm^{-3}]	1.183	1.161	1.152
μ (Mo Kα) [mm^{-1}]		0.246	0.236
μ (Cu Kα) [mm^{-1}]	1.652		
Diffractometer	CAD4	Syntex P2$_1$	Siemens P4
Scan modus and width	$2\Theta/\omega$; 1.4	Wyckoff; 1.4	ω-scan; 1.0
Scan speed [° min^{-1}]	variable, 4–30	variable, 2–29.3	variable, 2–60
Measuring range [°]	$3.9 < \Theta < 74.8$	$3.4 < \Theta < 56$	$3.7 < 2\Theta < 56$
Index ranges	$-17 \leq h \leq 0$	$0 \leq h \leq 10$	$0 \leq h \leq 11$
	$0 \leq k \leq 14$	$-12 \leq k \leq 11$	$-11 \leq k \leq 12$
	$0 \leq l \leq 20$	$-16 \leq l \leq 16$	$-15 \leq l \leq 15$
Measured reflections	2777	4210	4570
Independent reflections (R_{int})	2777	4195 (0.0089)	4303 (0.0506)
Data N_0	2774	4195	4278
Restraints	0	0	0
Parameters N_P	308	288	305
N_0/N_P	9.01	14.56	14.03
Goodness-of-fit s (on F^2) [a]	1.054	1.089	1.154
R values: all data			
wR_2 (on F^2) [a]	0.2111	0.0873	0.1272
R_1	0.0947	0.0325	0.0529
R values: ($I < 2\sigma(I)$) [a]; data	2340	3895	3701
wR_2	0.1951	0.0848	0.1185
R_1	0.0777	0.0300	0.0438
Max./min. residual electron density [e nm^{-3}]	927/−930	293/−352	492/−404
Atom form factors	[16,17]	[16,17]	[16,17]

[a] Definition of R values: $R_1 = (\Sigma\|F_0| - |F_C\|)/|F_0|$, $wR_2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/[w(F_0^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_0^2) + aP)^2$, $s = \{\Sigma[w(F_0^2 - F_C^2)^2]/(N_0 - N_P)\}^{1/2}$.

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} [a] (pm^2 × 10^{-1}) of 2

Atom	x	y	z	U_{eq}
P(1)	7917(1)	3496(1)	5228(1)	30(1)
P(2)	7650(1)	897(1)	5203(1)	32(1)
C(1)	8088(4)	2130(6)	5631(4)	37(1)
C(2)	7057(4)	3425(5)	4452(4)	30(1)
C(3)	6572(4)	2385(5)	4242(4)	30(1)
C(4)	6757(4)	1261(5)	4496(4)	34(1)
C(5)	6878(4)	4486(5)	4024(4)	31(1)
C(6)	6732(4)	5387(6)	3640(4)	37(1)
N(11)	7683(4)	4444(5)	5983(4)	41(1)
C(111)	7617(6)	5703(6)	5797(6)	51(2)
C(112)	7041(7)	4098(10)	6640(6)	67(3)
N(12)	8891(4)	4124(5)	4831(4)	41(1)
C(121)	9197(5)	3692(7)	4032(6)	52(2)
C(122)	9696(5)	4231(8)	5399(6)	60(2)
N(21)	7277(4)	-8(5)	5938(4)	41(1)
C(211)	6980(8)	-1192(7)	5744(6)	69(3)
C(212)	6733(6)	482(8)	6619(5)	56(2)
N(22)	8418(4)	-5(6)	4730(4)	44(1)
C(221)	9183(7)	-513(10)	5214(7)	80(3)
C(222)	8722(6)	303(8)	3917(5)	50(2)
C(11)	5751(2)	2515(4)	3653(3)	34(1)
C(12)	5760(2)	1946(4)	2899(3)	40(1)
C(13)	4996(3)	2065(4)	2367(2)	49(2)
C(14)	4222(3)	2752(5)	2588(3)	54(2)
C(15)	4212(2)	3320(4)	3342(3)	53(2)
C(16)	4977(3)	3202(4)	3874(3)	41(1)
C(21)	6477(3)	6436(3)	3215(3)	32(1)
C(22)	5855(3)	6369(3)	2555(3)	44(2)
C(23)	5557(4)	7388(4)	2164(3)	54(2)
C(24)	5880(4)	8474(3)	2433(3)	57(2)
C(25)	6502(4)	8541(3)	3094(3)	55(2)
C(26)	6800(3)	7522(4)	3484(3)	43(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

MAT 711 spectrometer. A Perkin–Elmer IR 283 spectrophotometer was utilized to obtain the IR spectra.

6.1. Crystal structures of compounds 2, 5 and 7

Information on the crystal data and determination of reflection intensities of compounds **2, 5** and **7** are given in Table 5. After 98 reflections for compounds **5** and **7** two intensity and orientation reflections were measured, however no significant decrease in intensity was found; no absorption or extinction corrections were made. The solution of the structure succeeded by using the program system SHELXTL PLUS [13]. For refinement of the F^2 values at the complete matrix according to the least-squares method the program system SHELXL-93 was available [14]. All heavy atoms were anisotropically refined. The hydrogen atoms of the compounds were isotropically refined. The C–C bond length and bond angle within the phenyl groups of **2** were set at 139 pm and 120°, respectively. The atom coordinates and equivalent isotropic displacement parameters for

compound **2** are summarized in Table 6, and for compounds **5** and **7** they are listed in Table 7.

More details relating to the X-ray studies can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, under the deposition number CSD-404979 (**2**) and CSD-404983, -404984 (**5, 7**) on quoting the names of the authors and the journal citation.

6.2. Octa-N-methyl-5-phenyl-4-(phenylethynyl)-1λ^5,3λ^5-[1,3]diphosphinine-1,1,3,3-tetramine, 2

To a solution of 0.63 g (2.4 mmol) of **1** in 10 ml toluene was added dropwise a solution of 0.48 g (2.4 mmol) 1,4-diphenylbutadiyne in 10 ml toluene. This reaction mixture was refluxed for 140 h. After cooling the solvent was distilled off. The remaining dark brown residue was dissolved in 10 ml diethyl ether and recrystallized several times at − 32 °C from diethyl ether/tetrahydrofuran (1:1) to give **2** in the form of small yellow crystals; m.p. 146 °C; yield 0.61 g (54.5%). Anal. Found: C, 66.93; H, 7.99; N, 12.06. C$_{26}$H$_{36}$N$_4$P$_2$ (466.53) Calc.: C, 66.93; H, 7.77; N, 12.01%. Mass spectrum, see Table 8. IR (rubbing in Nujol, capillary between CsBr discs, cm^{-1}): 2770w, 2140s {ν(–C≡C)}, 1590w, 1490w, 1433s, 1305m, 1295m, 1260m, 1215m, 1185sh, 1170sh, 1150s, 1115w, 1085m, 1045m, 1015w, 970s, 945vs, 900m, 870vs, 855sh, 815w, 765vw, 745w, 735m, 705s, 690m, 680m, 670m, 650m, 635w, 530w, 480vw, 465vw, 445vw (vs = very strong, s = strong, m = middle, w = weak, vw = very weak, sh = shoulder).

6.3. 5,5'-(1,2-Ethanediyl)-bis-[octa-N-methyl-1λ^5,3λ^5-[1,3]diphosphinine-1,1,3,3-tetramine], 5

To a solution of 1.06 g (4 mmol) of **1** in 10 ml toluene was added dropwise at room temperature a solution of 0.156 g (2 mmol) 1,5-hexadiyne (50 wt.% in n-pentane) in 5 ml toluene to give within minutes a dark red reaction mixture. After refluxing for 60 h the toluene was distilled off under vaccum at room temperature to leave a dark brown crystalline residue which was taken up in a mixture of 10 ml diethylether/2 ml toluene. Compound **5** crystallizes from this solution after keeping it at − 35 °C. After several recrystallizations from a mixture of diethyl ether/toluene (5:1) at − 18 °C, compound **5** is obtained as colorless, moisture-sensitive crystals; m.p. 188–189 °C; yield 0.77 g (63.5%). Anal. Found: C, 51.68; H, 9.80; N, 18.41. C$_{26}$H$_{58}$N$_8$P$_4$ (606.7) Calc.: C, 51.47; H, 9.63; N, 18.47%. Mass spectrum, see Table 9. IR (rubbing in Nujol, capillary between CsBr discs, cm^{-1}): 2760s, 1245s, 1195m, 1170s, 1145s, 1115m, 1100m, 1085w, 1040s, 990s, 940vs, 930sh, 875s, 850s, 750w, 695vs, 635m, 595m, 530m, 490vw, 440m.

Table 7

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients U_{eq} [a] ($pm^2 \times 10^{-1}$) of 5 and 7

Atom	5				7			
	x	y	z	U_{eq}	x	y	z	U_{eq}
P(1)	1926(1)	2388(1)	3032(1)	22(1)	3552(1)	2862(1)	1305(1)	22(1)
P(2)	1193(1)	−985(1)	1964(1)	22(1)	2571(1)	4630(1)	3040(1)	22(1)
C(1)	1131(2)	852(1)	1923(1)	23(1)	3620(2)	4259(2)	1815(1)	25(1)
C(2)	2904(2)	1800(2)	4107(1)	29(1)	2037(2)	2195(2)	2015(2)	28(1)
C(3)	3029(1)	290(1)	4068(1)	25(1)	1146(2)	2607(2)	2973(1)	25(1)
C(4)	2341(2)	−1007(1)	3201(1)	29(1)	1255(2)	3640(2)	3491(2)	30(1)
C(5)	4069(2)	26(2)	5075(1)	28(1)	−45(2)	1790(2)	3551(2)	28(1)
C(6)	—	—	—	—	561(2)	458(2)	4725(2)	29(1)
N(11)	3213(1)	3735(1)	2629(1)	27(1)	3467(2)	3577(2)	−214(1)	27(1)
C(111)	4477(2)	3181(2)	1951(1)	39(1)	3640(3)	2498(3)	−864(2)	41(1)
C(112)	3999(2)	5133(2)	3497(1)	41(1)	2192(3)	5053(2)	−726(2)	40(1)
N(12)	505(1)	3480(1)	3527(1)	30(1)	5213(2)	1291(2)	1448(1)	30(1)
C(121)	−332(2)	4260(2)	2791(2)	47(1)	5494(3)	55(2)	2621(2)	40(1)
C(122)	−732(2)	2789(2)	4123(2)	44(1)	6666(2)	1549(3)	908(2)	42(1)
N(21)	−728(1)	−2145(1)	1790(1)	28(1)	1560(2)	6518(2)	2883(1)	31(1)
C(211)	−1673(2)	−1827(2)	2734(1)	42(1)	2400(3)	7598(2)	2690(2)	39(1)
C(212)	−1866(2)	−2394(2)	738(1)	38(1)	132(3)	7249(3)	2164(3)	49(1)
N(22)	1903(1)	−1931(1)	811(1)	28(1)	3814(2)	4260(2)	4135(1)	27(1)
C(221)	2030(3)	−3537(2)	703(2)	44(1)	5147(2)	2793(2)	4360(2)	39(1)
C(222)	3393(2)	−1132(2)	486(2)	49(1)	3071(3)	4473(3)	5266(2)	40(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 8

Abstracts of the EI mass spectrum of 2 (70eV, 400K; me = CH_3; M* = $R_2PC(H)PR_2C(H)C(H)C$, R = Nme_2)

m/e	Rel. Intensity (%)	Fragment
466	100	$[M]^+$
422	8.2	$[M - Nme_2]^+$
379	34.3	$[M - 2Nme_2 + H]^+$
347	26.4	$[M - P(Nme_2)_2]^+$
334	16.1	$[M - 3Nme_2]^+$
291	2.9	$[M - 4Nme_2 + H]^+$
247	7.1	$[\{M^* H\} - Nme_2 + H]^+$
119	91.4	$[P(Nme_2)_2]^+$
91	2.5	$[CH_3PNme_2 + H]^+$
76	53.9	$[HPNme_2]^+$
60	4.6	$[PNme]^+$
44	9.3	$[Nme_2]^+$

Table 9

Results of the EI mass spectrum of 5 (70eV, 440K; me = CH_3; M* = $R_2PC(H)PR_2C(H)C(H)C$, R = Nme_2)

m/e	Rel. Intensity (%)	Fragment
606	73.6	$[M]^+$
562	5.7	$[M - Nme_2]^+$
519	97.5	$[M - 2Nme_2 + H]^+$
472	5.4	$[M - 3Nme_2 - 2H]^+$
444	4.3	$[M - P(Nme_2)_2 + H - Nme_2]^+$
399	5.7	$[M - P(Nme_2)_2 - 2Nme_2]^+$
355	8.2	$[M - P(Nme_2)_2 - 3Nme_2]^+$
318	20.0	$[\{M^*(CH_2)_2\} + H]^+$
304	21.8	$[\{M^* CH_2\} + H]^+$
260	6.8	$[\{M^* CH_2\} + H - Nme_2]^+$
246	12.5	$[\{M^* H\} - Nme_2]^+$
119	100	$[P(Nme_2)_2]^+$
76	45.4	$[HPNme_2]^+$
44	12.9	$[Nme_2]^+$

Table 10

Abstracts of the EI mass spectrum of 7 at 70eV and 430K (me = CH_3; M* = $R_2PC(H)PR_2C(H)C(H)C$, R = Nme_2)

m/e	Rel. Intensity (%)	Fragment
634	57.5	$[M]^+$
590	29.3	$[M - Nme_2]^+$
547	82.5	$[M - 2Nme_2 + H]^+$
502	2.9	$[M - 3Nme_2]^+$
459	4.3	$[M - 4Nme_2 + H]^+$
330	40.0	$[\{M^*(CH_2)_3\} - H]^+$
318	18.9	$[\{M^*(CH_2)_2\} + H]^+$
304	23.6	$[\{M^* CH_2\} + H]^+$
260	19.3	$[\{M^* CH_2\} + H - Nme_2]^+$
217	21.1	$[\{M^* CH_2\} - 2Nme_2 + 2H]^+$
185	7.1	$[\{M^* CH_2\} + H - P(Nme_2)_2]^+$
119	100	$[P(Nme_2)_2]^+$
76	42.1	$[HPNme_2]^+$
44	7.8	$[Nme_2]^+$

6.4. 5,5'-(1,4-Butanediyl)-bis-[octa-N-methyl-1λ⁵,3λ⁵-[1,3]diphosphinine-1,1,3,3-tetramine], 7

To a solution of 2.06 g (7.8 mmol) of 1 in 10 ml toluene was slowly added at room temperature a solution of 0.42 g (3.9 mmol) 1,7-octadiyne in 5 ml toluene to give a dark red reaction mixture which was refluxed for 64 h. After cooling to room temperature the toluene was distilled off under vacuum. The remaining dark brown residue was dissolved in 5 ml diethyl ether from which, after standing for 2–3 days at −30°C, compound 7 precipitates. Pure 7 is obtained as large, colorless cubes by repeated recrystallization from diethyl ether at −8°C. Additional product was obtained from

the mother liquor at $-30\,^\circ$C; m.p. 95–96$\,^\circ$C; yield 1.83 g (73.9%). Anal. Found: C, 53.11; H, 10.13; N, 17.63. $C_{28}H_{62}N_8P_4$ (634.74) Calc.: C, 52.98; H, 9.84; N, 17.65%. Mass spectrum, see Table 10. IR (rubbing in Nujol, capillary between CsBr discs, cm^{-1}): 2760m, 1480vs, 1390w, 1280m, 1260m, 1240sh, 1220w, 1175s, 1150s, 1135sh, 1110vw, 1100w, 1040m, 1015m, 945vs, 900m, 880s, 830m, 720m, 710m, 690s, 660vw, 640m, 615m, 590vw, 550vw, 450w.

Acknowledgements

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