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Reactions of 1,1,3,3-Tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphete with Diphenylchlorophosphane and Methyl Iodide

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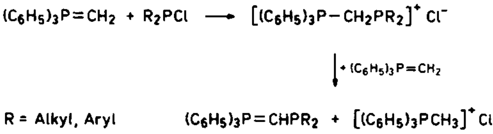
ABSTRACT

1,1,3,3-Tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphete, 1, reacts with diphenylchlorophosphane to yield 1,1,3,3-tetrakis(dimethylamino)-4-diphenylphosphanyl-1,2-dihydro-$3\lambda^5$-[1,3]diphosphetium chloride, 2, or, depending on the reaction conditions, the isomer compound 3. The cation of 2 is deprotonated by $LiN[Si(CH_3)_3]_2$ to give the diphenylphosphanyl-substituted derivative of 1, i.e., compound 4. Methyl iodide adds to 1 to form 1,1,3,3-tetrakis(dimethylamino)-4-methyl-1,2-dihydro-$3\lambda^5$-[1,3]diphosphetium iodide, 6. Deprotonation of 6 with n-butyllithium leads to the monomethyl derivative of 1, i.e., compound 7. Physical properties, NMR spectra, and mass spectra of compounds 2–4, 6, and 7 are described. The results of the X-ray structural analysis of 6 are reported and discussed.

INTRODUCTION

As part of phosphorus chemistry, the synthesis of $1\lambda^3,3\lambda^3$- and $1\lambda^5,3\lambda^5$-diphosphetes as well as that of $1\lambda^3,2\lambda^3$-diphosphetes and λ^3-phosphetes and the chemistry of these classes of compound are still in the center of interest. For references to the recent literature, see Refs. [1–3].

Phosphorus ylids such as triphenylmethylenephosphorane react with dialkyl- or diaryl-halogen phosphoranes, according to Equation 1, to yield phosphonium salts.



$$(C_6H_5)_3P{=}CH_2 + R_2PCl \longrightarrow [(C_6H_5)_3P{-}CH_2PR_2]^+ Cl^- \xrightarrow{+ (C_6H_5)_3P=CH_2} (C_6H_5)_3P{=}CHPR_2 + [(C_6H_5)_3PCH_3]^+ Cl^- \qquad (1)$$

R = Alkyl, Aryl

With an excess of methylenephosphorane, *trans*-ylidation to (1-phosphanoalkylidene)-phosphoranes occurs (see Equation 1) [4,5]. Triaminoalkylidenephosphoranes behave similarly [6]. Therefore, the question of the behavior of the double ylid 1,1,3,3-tetrakis(dimethylamino)-$1\lambda^5,3\lambda^5$-diphosphete, 1 [7],

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Dedicated to Professor Louis D. Quin on the occasion of his retirement from the Department of Chemistry of the University of Massachusetts at Amherst.

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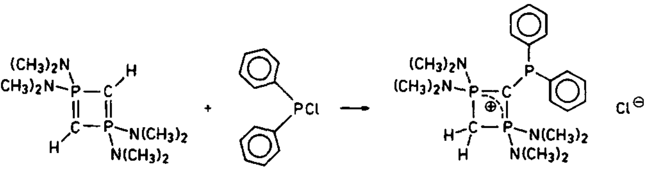
toward diphenylchlorophosphane came up. In addition to this reaction, this article describes the reaction of 1 with methyl iodide.

The Reaction of 1 *with Diphenylchlorophosphane*

Compound 1 reacts in diethyl ether with equimolar amounts of diphenylchlorophosphane already at room temperature, according to Equation 2, to yield 1,1,3,3-tetrakis(dimethylamino)-4-diphenylphosphanyl-1,2-dihydro-3λ^5-[1,3]diphosphetium chloride, 2, in high yield.

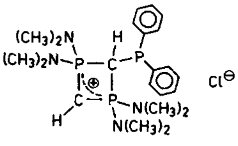


1 2

(2)

The needlelike crystals melt between 207 and 211°C. The structure assignment of 2 is confirmed by its elemental analysis, the mass spectrum (see Experimental), and the NMR-spectroscopical investigations (see NMR section).

A change of reaction conditions leads to formation of compound 3, which is isomeric with 2. Thus, by slowly dropping an ether solution of diphenylchlorophosphane into an ether solution of twice the eqimolar amount of 1, cooling to −40°C, and stirring after warming to room temperature for an additional 12 hours, a voluminous precipitate is obtained that consists of nearly pure 3, while the reaction solution still contains much of compound 1.



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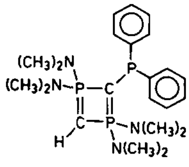
Compound 3, dissolved in $CDCl_3$, rearranges at room temperature within 5 days almost totally to compound 2. After an additional 5 days, the rearrangement is complete. At this point, the reaction mixture still contains a large amount of compound 1. On substituting the diethyl ether by toluene and refluxing this mixture for 1 hour, formation of a clear solution is observed from which, upon cooling, a colorless solid precipitates. The $^{31}P\{^1H\}$ NMR spectrum of this solution exhibits the AB_2 spin system of the diphenylphosphanyl-substituted λ^5-diphosphete 4 (see NMR section) and the singlet of the diphosphetium chloride 5. In addition, small amounts of 2 and traces of impurities are present. The solid is mainly composed of 2 and 5. Clarification of the question whether the deprotonation of 3 occurs directly or proceeds via the intermediate formation of 2 needs further investigation.



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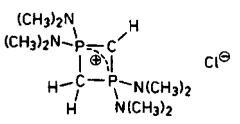

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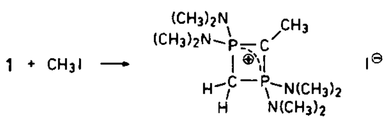
Deprotonation of 2

Strong bases such as *n*-butyllithium or lithium-[bis(trimethylsilyl)amide] deprotonate at low temperatures the cation of 2 to form the already-mentioned diphenylphosphanyl-substituted λ^5-diphosphete 4. Using *n*-butyllithium for this reaction, the diphenylphosphanyl group is partially cleaved off. This side reaction has not been observed by using lithium-[bis(trimethylsilyl)amide] for the deprotonation. However, in both cases, compound 4 could not be isolated in a very pure state. Nevertheless, the structure of 4 could be ascertained on the basis of its $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra as well as its mass spectra, which were taken under different conditions (see Experimental). The molecular peaks appear in both spectra with a high intensity. The calculated and the, at an ionization energy of 20 eV, experimentally obtained values for the isotope distribution of the molecular peak are also given.

The Reaction of 1 *with Methyl Iodide*

The diphosphete 1 adds in an ether solution an equimolar amount of methyl iodide in a straightforward reaction to give 1,1,3,3-tetrakis(dimethylamino)-4-methyl-1,2-dihydro-3λ^5-[1,3]diphosphetium iodide 6 (see Equation 3). This salt occurs in cubiclike crystals and melts without decomposition at 212°C. It is very soluble in methylene chloride or chloroform, slightly soluble in tetrahydrofuran and insoluble in *n*-pentane, diethyl ether, or toluene. Using an excess of compound 1 or of methyl iodide in this reaction leads also to formation of 6 as the only product. This reaction proceeds analogously to the one between 1 and cinnamyl chloride and *cis*-1,4-dichloro-2-butene, as was reported earlier by us [8]. In all cases, a proton migration occurs with formation of a methylene group. Excess diphosphete does not cause a deprotonation. The peak in the mass spectrum with the *m*/*e* value corresponding to the cation of 6 shows the highest relative intensity. The fragmentation pattern is in agreement with those generally observed of 1λ⁵,3λ⁵-diphosphetes [8–10]. Compound **6** exhibits in its $^{31}P\{^1H\}$ NMR spectra a singlet at $\delta^{31}P = 34.9$ (CD_2Cl_2). The $^{13}C\{^1H\}$ and ^1H NMR spectra are in agreement with the results of the X-ray crystal structure analysis of compound **6**.

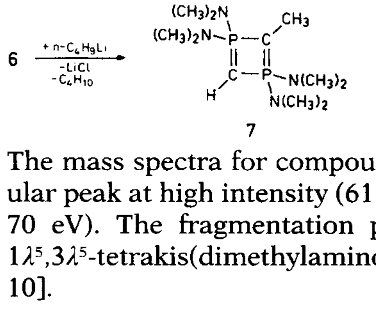


(3)

6

Deprotonation of 6*: 1,1,3,3-Tetrakis(dimethylamino)-2-methyl-1λ⁵,3λ⁵-diphosphete,* 7

While the λ⁵-diphosphete **1** does not deprotonate **6**, this reaction, however, proceeds well with *n*-butyllithium. This reaction, which proceeds without formation of side products, gives **7** as cubical crystals, mp 38–41°C, in a high yield. Compound **7** is rather moisture sensitive. It can be distilled under a high vacuum and is soluble in most common organic solvents. However, polar or acidic solvents such as chlorinated hydrocarbons, alcohols, acetonitrile, or acetone react with **7**.

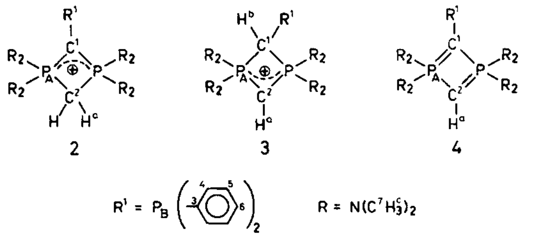


(4)

7

The mass spectra for compound **7** show the molecular peak at high intensity (61.5% at 20 eV; 27.2% at 70 eV). The fragmentation pattern is typical for 1λ⁵,3λ⁵-tetrakis(dimethylamino)diphosphetes [8–10].

TABLE 1 NMR Parameters of the Isomers **2** and **3** of Diphenylphosphanyl-Substituted 1λ⁵,3λ⁵-Diphosphetium Chloride in $CDCl_3$ at 300 K and of the Corresponding 1λ⁵,3λ⁵-Diphosphete **4** in C_6D_6 at 300 K



		δ			^nJ/Hz; n = 1–4			
		2	**3**	**4**		**2**	**3**	**4**
					n = 1:			
^{31}P:	P_A	37.9	37.3	48.3	P_AC^1	94.7	62.1	92.0
	P_B	−23.2	−22.8	−21.0	P_AC^2	63.7	122.4	106.6
					P_BC^1	33.2	32.8	22.0
					P_BC^3	7.6	13.4	10.5
^{13}C:	C^1	43.7	48.4	23.4	n = 2:			
	C^2	30.6	29.0	9.4	P_AP_B	50.0	20.8	54.4
	C^3	138.2	135.5	146.0	P_BC^4	19.8	23.6	19.5
	C^4	132.3	133.2	133.2	P_AH^a	15.6	<0.5	*a*
	C^5	128.3	129.1	127.9	P_AH^b	—	13.6	—
	C^6	128.6	130.4	126.8	P_BH^b	—	2.4	—
	C^7	37.5	37.7	38.2				
			37.9					
^1H:	H^a	4.02	1.95	*a*	n = 3:			
	H^b	—	5.27	—	P_AC^3	7.6	6.7	7.4
	H^c	2.63	2.51	2.53	P_BC^2	5.7	4.3	9.5
			2.75		P_BC^5	7.0	8.6	6.3
					n = 4:$^\beta$			
					P_BH^a	2.0	1.8	*a*
					H^aH^b	—	1.8	—

a: not assigned.
β: for **2–4**: $^4J(P_bC^b) < 0.5$ Hz.

The NMR Spectra of 2–4, 6, *and* 7

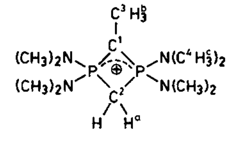
The $^{31}P\{^1H\}$ NMR spectra of **2**, **3**, and **4**, consist of an A_2X spin system, those of compounds **6** and **7** of a singlet with ^{13}C satellite pairs, of which the $^1J(PC^{1,2})$ values of **6** (121.2 and 66.5 Hz; see Tables 1 and 2 with the denomination of the atoms) point to two differently hybridized carbon atoms. There is only an insignificant difference (<3 ppm) between the chemical shifts $\delta^{31}P_A$ of **2**, **3**, and **6** that lie in the range of the λ⁵-diaminodiphosphetium cations [11]. The $^{31}P_A$ line of **4** and **7** that is shifted downfield by about 10 ppm almost coincides with the one of the educt **1** (48.9 ppm [7]). The chemical shift $\delta^{31}P_B$ of **2**, **3**, and **4** points to the existence of a diphenylphosphane group (cf. [12]). In comparison with **2** and **4**, the observed $^2J(P_AP_B)$ value (20.8 Hz) for **3** is only half as large; however, it is characteristic for a geminal PP-coupling via an sp^3-hybridized carbon atom [13].

The lines of the two triplets appearing in the $^{13}C\{^1H\}$ NMR spectrum of **2–4**, **6**, and **7** are split into doublets in the case of **2–4** by the exocyclic phosphorus atom P_B. This pattern is typical for mono C-substituted four-membered cyclic 1,3-diphospha compounds. The methine-$C^{1,2}$, methylene-C^2, and the quaternary C^1-carbon atom, relevant for the four-ring structure, were determined for the five heterocycles by ^{13}C-DEPT spectroscopy. For the isomeric compounds **2** and **3**, the almost equally large $^1J(P_AC^2)$

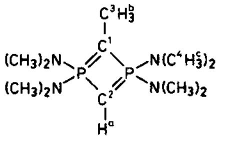
and ${}^1J(P_AC^1)$ values (63.7 and 62.1 Hz, respectively) determine the ring position of the sp^3-hybridized carbon atom. When compared with the nearly twice as large ${}^1J(PC)$ couplings, the position of the $P^V{=}C{-}P^{V\oplus}$ triad of the ring becomes evident. The $\delta^{13}C^{1,2}$ values of 2 and 6 appear in the expected range of the λ^5-diaminodiphosphetium ions [11]. Compound 3 can be considered as a, at the methylene carbon, diphenylphosphanyl-substituted derivative of 5. As anticipated, it exhibits for symmetry reasons the two $\delta^{13}C^7$ and the two δ^1H^c values. Of note is the high field position of ${}^{13}C^2$ of 7, which surpasses the one of 1 [7] by 4.3 ppm and the one of the 2,4-dimethyl-substituted derivative of 1 [9] by 8.3 ppm. The peaks of the endocyclic carbon atoms of the dimethyl-substituted derivative of 1 are themselves shifted upfield by 4.8 ppm relative to C^1 of compound 7. This finding is indicative for an enhanced concentration of negative charge at the unsubstituted ring carbon atom C^2 of 7.

The chemical shifts δ^1H^a of 2 and 6 as well as δ^1H^b of 3 appear in the δ^1H region of the methylene hydrogen atoms of the λ^5-diphosphetium ions; the methine H^a atoms of 3 and 7 are recognizable in the ${}^1H$ NMR spectrum by their high field position and their small nonresolved geminal ${}^{31}P_AH^a$-couplings [9,11]. The observed triplet of the ${}^1H$ NMR spectrum of 3 of the H^a and the twice-split triplet of the H^b methine hydrogen atom also confirms the structure of 3. Through homodecoupling and selective ${}^1H[{}^{31}P_{A,B}(CW)]$ decoupling experiments, it was possible to assign to these multiplets, besides the expected geminal coupling P_AH^b of 13.5 Hz, the two coupling constants ${}^4J(P_BH^a)$ and ${}^4J(H^aH^b)$ of the same value (1.8 Hz) (compare compound 5: ${}^4J(HH) = 1.7$ Hz [14]). A long-range coupling constant ${}^5J(H^aH^b)$ of 1.2 Hz was detected for 6.

TABLE 2 NMR Data of the Methyl-Substituted $1\lambda^5,3\lambda^5$-Diphosphetium Iodide 6 in CD_2Cl_2 at 300 K and the Corresponding $1\lambda^5,3\lambda^5$-Diphosphate 7 in C_6D_6 at 300 K



6



7

		δ 6	δ 7		ⁿJ/Hz; n = 1–5 6	7
				n = 1:		
${}^{31}P$:		34.9	48.5	PC^1	121.2	109.3
				PC^2	66.5	91.1
${}^{13}C$:	C^1	38.9	17.0	*n* = 2:		
	C^2	28.3	3.9	PC^3	2.1	2.6
	C^3	7.1	9.8	PH^a	16.2	<0.3
	C^4	37.0	38.1[a]	*n* = 3:		
${}^1H$:	H^a	3.09	0.55	PH^b	18.8	17.3
	H^b	1.42	1.69	*n* = 5		
	H^c	2.68	2.62	H^aH^b	1.2	—

a: singlet.

X-ray Structure Determination of 6

Compound 6 possesses a planar P_2C_2 four-membered ring with an alternating PCPC sequence (Figure 1). The cation of 6 is disordered; two planar four-membered rings are intercrossing each other along the C1 . . . C2 axis with an angle of 17° (Figure 2). Each P_2C_2 ring is separated into two subunits. The first unit is a P–C–P fragment with a highly ylidic

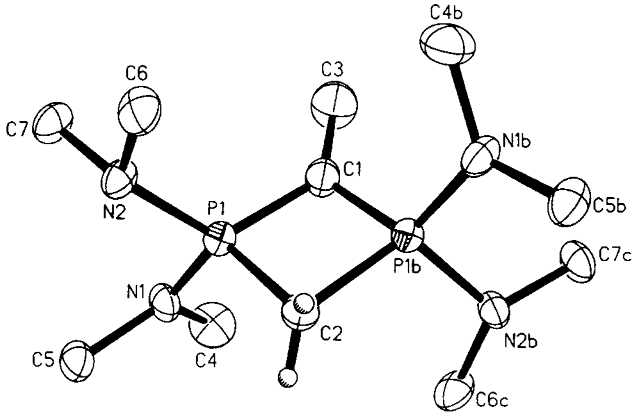


FIGURE 1 Graphic representation of a cation of 6 (without H atoms, except H2 and H2a; probability level 50%).

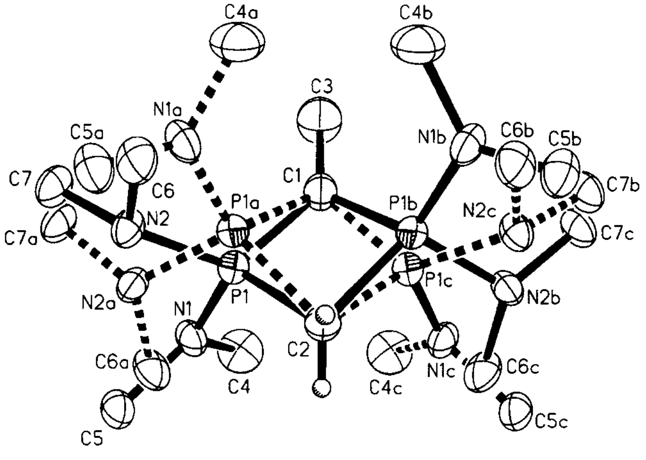


FIGURE 2 Structure of the cation of 6 with disorder behavior of the four-membered ring.

character, recognizable by the short bond length P1–C1 of 170.2(5) pm. However, this value is characteristic for undisturbed λ^5-diphosphetes [7,10,15]. The ylidic P–C–P sequences of the coordination complexes of 1 with MCl_2 (M = Ge, Sn) [16] and $M(CO)_n$ fragments (M = Cr, n = 5; M = Fe, n = 4) [17] show very similar P–C atomic distances (Table 6). The second unit represents a P–C–P sequence containing the methylene group of **6**. This sequence and the unit with the metal fragment of the complexes exhibit significantly longer P–C distances, which can be looked upon as P–C single bonds. A distance of 182.7(5) pm for this bond has been established for **6**.

As a consequence of the subdivision of the four-membered ring in two separate parts, there results a distorted quadrangular geometry with an interior angle of 94.7(4)° at the planar-coordinated carbon atom C1 (angular sum 360°) and a strongly distorted tetrahedral environment at C2 with an interior angle of 86.4(3)°.

Although the P–N distances are almost identical [P1–N1 164.3(7); P1–N2 164.7(5)°], the dimethylamino groups are quite different concerning the angular sums at N1 and N2. While a value of 357° is found for N1, N2 exhibits, with a value of 345°, a significant pyramidalization. This effect is also observed for other compounds containing λ^5-diphosphete units. The iodide ion is not coordinated to the cation. Only weak I . . . H contacts could be observed (shortest I . . . H distance: 314 pm).

EXPERIMENTAL

All operations are performed under an argon blanket. A high vacuum system was provided to evacuate the equipment to 10^{-3} torr and then to flush with dry high-purity argon. The solvents were dried by the usual procedures and saturated with dry argon [18].

The NMR spectra were taken with a temperature-controlled AM 200 (^{1}H: 200.133 MHz) and an AC 250 (^{1}H: 250.133 MHz) NMR spectrometer of Bruker Analytische Meßtechnik GmbH, Rheinstetten, Germany. The δ^1H and δ^{13}C chemical shifts were referenced to tetramethylsilane (TMS). The δ^{31}P chemical shifts were measured using 85% aqueous orthophosphoric acid as an external standard. The digital resolution was <0.3 Hz in each case. As usual, downfield shifts are taken to be positive. The mass spectra were registered with a Varian Type MAT 711 spectrometer.

X-ray Analysis of 6

A crystal of **6** was covered with a high-boiling paraffin oil and mounted on the top of a glass capillary under the flow of cool gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections on a four-circle diffractometer with graphite-monochromated MoK_α radiation (λ = 71.073 pm; Siemens P4). The final cell parameters were determined from 25 high-angle reflections.

The intensities have been corrected for Lorentz and polarization effects (for cell parameters and collecting of the intensities, see Table 3). The structure has been solved by direct methods with SHELXTL-Plus [19] and refined against F^2 by full-matrix least squares using SHELXL-93 [20]. The positions of the hydrogen atoms were calculated for ideal positions and refined with a common displacement parameter. The H atoms H21, H22, H31, and H32 have been refined without constraints. The H atoms on C6 and C7 were not considered for the refinement. The calculation of the bond lengths, bond angles, and U_{eq} was performed using the program PLATON [21].

No corrections of the absorption effects were made. The structure was refined for the space group Cmcm. The four-membered ring is disordered; two positions have been observed. We chose the planar PCPC arrangement because all structurally characterized λ^5-diphosphetes or their derivatives possess a planar or almost planar P_2C_2 backbone. Refinement in the lower symmetric space groups $Cmc2_1$ and

TABLE 3 Crystallographic Data for **6**

Formula	$C_{11}H_{29}IN_4P_2$
Formula weight	406.24
Crystal size (mm)	0.3 × 0.2 × 0.25
a (pm)	1146.0(3)
b (pm)	991.5(1)
c (pm)	1569.4(1)
V ($pm^3 \cdot 10^6$)	1783.2(5)
Z	4
ρ_{calc} (g/cm^3)	1.513
Temp [K]	213
Space group	Cmcm, No. 63 [22]
2θ range (°)	4–50
h, k, l values	$-11 \leq h \leq 11$ $-1 \leq k \leq 13$ $-1 \leq l \leq 13$
μ (cm^{-1})	19.7
No. of reflections	2013
Unique reflections	853
Reflections with $F_0 > 4\sigma(F_0)$	644
No. of parameters	91
R_1 $[F_o > 4\sigma(F_o)]^a$	0.0276
wR_2^b	0.0786
Max/min residual electron density ($e/pm^3 \cdot 10^6$)	0.42/−0.41

$^a R_1 = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$.
$^b wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0492 \cdot P)^2]$, and $P = [Max(F_o^2, 0) + 2F_c^2]/3$.

Ama2$_1$ were not successful. Atomic coordinates and equivalent isotropic displacement coefficients of **6** are given in Table 4. Selected bond lengths and bond angles are listed in Table 5.

1,1,3,3-Tetrakis(dimethylamino)-4-diphenylphosphanyl-1,2-dihydro-3λ^5-[1,3]diphosphetium Chloride, 2

An amount of 1.5 g (5.7 mmol) of **1** [7] was dissolved in 30 mL diethyl ether, cooled to −60°C, when 1.26 g (5.7 mmol) diphenylchlorophosphane in 20 mL diethyl ether was added dropwise slowly to furnish immediately a colorless precipitate. After the solution had been warmed to room temperature with constant stirring for a total of 3 hours, a colorless product was collected, washed with 10 mL diethyl ether and dried under vacuum. Recrystallization from hot tetrahydrofuran gave compound **2** as needlelike crystals, mp 207–211°C; yield 2.5 g (81.1%), soluble in methylene chloride and chloroform, insoluble in diethyl ether and *n*-pentane. Anal. Calcd for $C_{22}H_{36}ClN_4P_3$ (484.9): C, 54.49; H, 7.48; N, 11.55. Found: C, 54.04; H, 7.88; N, 11.00. Abstracts of the EI mass spectrum, 480 K (*m*/*e*; rel. int. (%) at 20 eV; fragment; R = N(CH$_3$)$_2$): 449; 27.7; [M–Cl]$^+$ – 448; 100; [M–HCl]$^+$ = [M*]$^+$ – 405; 17.5; [M*–R + H]$^+$ –361; 56.1; [M*–2R + H]$^+$ – 282; 14.4; [M*–2R–C$_6$H$_5$]$^+$ – 239; 11.5; [M*–3R–C$_6$H$_5$]$^+$ – 220; 50.6; [M*–R + P(C$_6$H$_5$)$_2$]$^+$ – 196; 22.9; [M*–4R–C$_6$H$_5$ + H]$^+$ – 44; 11.6; [R]$^+$.

TABLE 4 Atomic Coordinates and Isotropical Equivalent Displacement Parameters (10^{-22} m^2) of the Nonhydrogen Atoms in **6**^{a} [23]

Atom	*x*	*y*	*z*	U_{eq}
I1	0	0.5	0	4.20(2)
P1	0.3953(1)	0.3320(2)	0.22739(8)	2.07(5)
N1	0.3415(6)	0.3375(7)	0.1304(5)	2.6(2)
N2	0.2757(4)	0.3157(5)	0.2153(3)	2.4(1)
C1	0.5	0.4483(7)	0.25	2.7(2)
C2	0.5	0.1977(6)	0.25	2.3(2)
C3	0.5	0.6018(8)	0.25	4.5(3)
C4	0.4007(7)	0.4060(7)	0.0628(4)	4.0(3)
C5	0.2536(9)	0.2401(9)	0.1041(5)	3.0(3)
C6	0.2941(9)	0.288(1)	0.1233(6)	3.3(4)
C7	0.1805(5)	0.4158(6)	0.2277(4)	2.9(2)

$^a U_{eq}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5 Selected Bond Lengths (pm) and Angles (°) in **6**

P1–N1	164.3(7)	N1–P1–N2	101.4(3)
P1–N2	164.7(5)	N1–P1–C1	115.8(3)
P1–C1	170.2(5)	N1–P1–C2	89.4(2)
P1–C2	182.7(5)	C1–P1–C2	89.4(2)
N1–C4	143.0(9)	P1–N1–C4	121.6(5)
N1–C5	145.5(9)	P1–N1–C5	120.0(6)
N2–C6	148(1)	C4–N1–C5	115.7(7)
N2–C7	148.8(8)	C6–N2–C7	110.8(5)
C1–C3	152(1)	P1–N2–C6	115.5(5)
		P1–N2–C7	118.3(5)
		P1–C1–C3	132.7(2)
		P1–C1–P1b	94.7(4)
		P1–C2–P1b	86.4(3)

1,1,3,3-Tetrakis(dimethylamino)-2-diphenylphosphanyl-1λ^5-3λ^5-diphosphete, 4

To a suspension of 2.0 g (4.1 mmol) of **2** in 20 mL diethyl ether, when cooled to −50°C, was added with stirring dropwise 4.1 mL of a 1 molar solution of lithium-bis(trimethylsilyl)amide in tetrahydrofurane. This mixture, while being stirred, was warmed to room temperature and let stand for 2 hours, during which a clear yellow solution formed. The solvents were removed completely and the residue was extracted with 20 mL diethyl ether. The insoluble LiCl was extracted twice with 10 mL diethyl ether and the combined ether solution was reduced to 5–7 mL. After this solution had been maintained at −16°C for about 15 hours, impure compound **4** precipitated. Additional attempts to purify **4** were not successful; melting range 140–175°C; yield 0.55 g (29.3%). **4** is soluble in all commonly used organic solvents. Because of a lack of purity, no elemental analysis was obtained ($C_{22}H_{35}N_4P_3$: 448.4). Abstracts of the EI mass spectra (*m*/*e*; rel. int. (%) at 20 eV (360 K); rel. int. (%) at 70 eV (350 K); fragment; R = N(CH$_3$)$_2$): 448; 100; 50.3; [M]$^+$ – 361; 69.5; 100; [M–2R + H]$^+$ – 195; 2.2; 12.0; [M–4R–C$_6$H$_5$]$^+$ – 183; –; 12.3; [P(C$_6$H$_5$)$_2$–2H]$^+$ – 119; 5.6; 36.5; [PR$_2$]$^+$ – 76; –; 41.1; [HPR]$^+$ – 44; 1.0; 23.1; [R]$^+$. Isotope distribution of [M]$^+$, 360 K (*m*/*e*; rel. int. (%) at 20 eV; exp; calc.): 448; 100; 100 – 449; 25.2; 25.9 – 450; 3.3; 3.2.

TABLE 6 P–C Bond Lengths in Selected Compounds Containing a λ^5-Diphosphete Unit

	C–P		
Compound	*Ylidic*	*Nonylidic*	*Ref.*
6	170.2(5)	182.7(5)	*a*
1 · GeCl$_2$	169.6(4); 170.2(4)	180.8(3); 181.1(4)	[16]
1 · SnCl$_2$	170.6(3)	180.2(3); 181.3(3)	[16]
1 · Cr(CO)$_5$	166.9(9); 168.2(8)	179.1(7); 179.4(7)	[17]
1 · Fe(CO)$_4$	168.9(4); 170.0(4)	180.6(3); 181.0(3)	[17]

^{a}This work.

1,1,3,3-Tetrakis(dimethylamino)-4-methyl-1,2-dihydro-3λ^5-[1,3]diphosphetium Iodide, 6

A solution of 2 g (7.6 mmol) of **1** in 20 mL diethyl ether was cooled to $-60°C$ when, under stirring, a solution of 1.1 g (7.6 mmol) methyl iodide in 10 mL diethyl ether was added to yield an immediate colorless precipitate. After the reaction mixture was slowly brought to room temperature and stirred for an additional 1/2 hour, the precipitate was filtered off and dried under vacuum; yield 2.7 g (81.8%), mp 212°C (recrystallized from acetonitrile). Anal. calcd for $C_{11}H_{29}IN_4P_2$ (406.2): C, 32.52; H, 7.20; N, 13.79. Found: C, 32.61; H, 7.22; N, 13.81. Abstracts of the EI mass spectrum, 430 K (*m/e*; rel. int. (%) at 70 eV; fragment; $R = N(CH_3)_2$): 279; 100; $[M{-}I]^+ = [M^*]^+$ – 191; 54.7; $[M^*{-}2R]^+$ – 148; 17.4; $[M^*{-}3R + H]^+$ – 128; 11.0; $[HI]^+$ – 119; 45.1; $[PR_2]^+$ – 76; 42.6; $[HPR]^+$ – 44; 37.2; $[R]^+$.

1,1,3,3-Tetrakis(dimethylamino)-2-methyl-1λ^5,3λ^5-diphosphete, 7

An amount of 3.0 g (7.4 mmol) of finely powdered **6** was suspended in 40 mL tetrahydrofuran and cooled to $-45°C$. With stirring, 3 mL of a 2.5 molar solution of *n*-butyllithium in hexane were added dropwise. A clear solution was obtained during warming of the suspension to room temperature. After 1 hour, the solvents were distilled off under vacuum; the residue was extracted in 20 mL *n*-pentane to leave insoluble LiI. After distillation of the *n*-pentane, impure compound **7** remained as a light yellow oil. After dissolution of it in a small amount of *n*-pentane, compound **7** precipitated within 2 days in the form of cubiclike colorless crystals. An additional amount of **7** could be obtained by a vacuum distillation of the mother liquor. Compound **7** distills as a light yellow oil at 0.003 torr in a temperature range of 85–93°C. The product slowly solidifies and melts in a range between 38 and 41°C; yield 1.7 g (82.5%). Due to the extreme moisture sensitivity, an elemental analysis of compound **7** could not be obtained. Abstracts of the EI mass spectra (*m/e*; rel. int. (%) at 20 eV (295 K); rel. int. (%) at 70 eV (295 K); fragment; $R = N(CH_3)_2$): 278; 61.5; 27.2 $[M]^+$ – 235; 17.8; 8.4; $[M{-}R + H]^+$ – 191; 100; 100; $[M{-}2R + H]^+$ – 148; 5.8; 14.4; $[M{-}3R + 2H]^+$ – 119; 52.0; 53.4; $[PR_2]^+$ – 76; 1.5; 39.3; $[HPR]^+$ – 44; 4.6; 24.7; $[R]^+$.

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[23] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-59253, the authors, and the journal citation.