PAPERS

Unusually Coordinated Phosphorus Compounds; 7[1].
Adamant-1-ylmethylidynephosphine, A New, Stable Phosphaalkyne

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The reaction of tris[trimethylsilyl]phosphine (4a) as well as of the lithium bis[trimethylsilyl]phosphide·2 tetrahydrofuran complex (4b) with 1-adamantoyl chloride (5) results in the formation of the phosphaalkene 7 in 67% or 96% yield, respectively. Subsequent sodium hydroxide or tetra-n-butylammonium fluoride-catalysed elimination of hexamethyldisiloxane from 7 at 20/90°C gives rise to the phosphaalkyne 8 in 83 or 71% yield. The phosphaalkyne 8 undergoes smooth [3 + 2]cycloaddition reactions with 1,3-dipoles such as the nitrile oxide 9, the diazo compounds 12a–c, and the azide 15 to produce the phospholes 11, 14a–c, and 16, respectively. The phosphaalkene 7 reacts with the dipoles 9 and 12a to give the same cycloadducts 11 and 14a, respectively. In these two reactions, the primary adducts undergo spontaneous (10 → 11) or sodium hydroxide-catalysed (13 → 14a) elimination of hexamethyldisiloxane.

Our knowledge of compounds containing phosphorus-carbon triple bonds (phosphaalkynes, alkylidynephosphines) is, in contrast to that of alkynes and nitriles which have been intensively studied and the synthetic potential of which has been systematically utilised, very limited[2,3]. The simplest member of the series, phosphaacetylene (1a), is very unstable. It was generated from phosphine by an electrical discharge between graphite electrodes, frozen out at − 196°C, and characterised by I.R. spectroscopy[4] first and by other methods later[5].
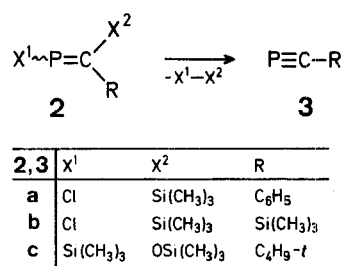
P≡C—R

1a-h

1	R	1	R
a	—H	e	—CH=CH₂
b	—F	f	—C≡CH
c	—CH₃	g	—C≡C—C≡N
d	—CF₃	h	—C≡N

Most of the phosphaalkynes so far reported have also very short life-times. They were generated by intra- or intermolecular elimination of hydrogen halides either with potassium hydroxide (1b[6]) or under gas phase pyrolysis conditions (1c[7], d[8], e[8], f[8], and g[9]) and characterised by micro-wave spectrometry in the gas phase. From fluoromethylidynephosphine (1b) even a ³¹P-N.M.R. spectrum could be recorded. Phosphaalkyne 1h[10] was obtained, albeit in traces, by a formal substitution reaction of 1a with cyanoazide. In all cases mentioned above, the preparation of pure compounds is difficult and this fact has prevented studies on the synthetic applications of these highly interesting compounds.

The phenyl- and trimethylsilyl-substituted phosphaalkynes 3a and 3b, accessible from the corresponding phosphaalkenes 2a and 2b by thermal elimination of chlorotrimethylsilane (Scheme A), are considerably more stable, but they also have only limited half-life-times under normal conditions (3a: $\tau_{1/2} = 7$ min at 0°C[11]; 3b: $\tau_{1/2} = 50$ min at 20°C[12]).

$$X^1\text{\textasciitilde}P=C\begin{array}{c}X^2\\ \diagup\\ \diagdown\\ R\end{array} \xrightarrow[-X^1-X^2]{} P\equiv C-R$$

2   **3**

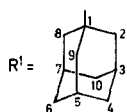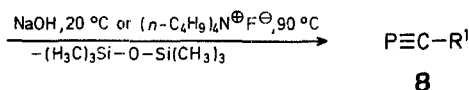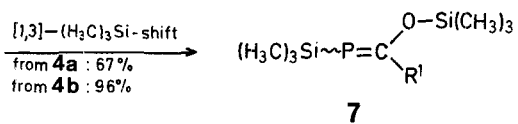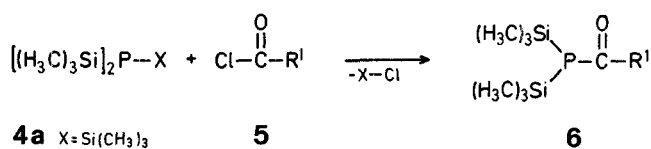| 2,3	X¹	X²	R
a	Cl	Si(CH₃)₃	C₆H₅
b	Cl	Si(CH₃)₃	Si(CH₃)₃
c	Si(CH₃)₃	OSi(CH₃)₃	C₄H₉-t

Scheme A

Phosphaalkyne 3c, the first compound of this type which is stable at room temperature, was prepared from the corresponding phosphaalkene 2c by a sodium hydroxide-catalysed elimination of hexamethyldisiloxane[13] (Scheme A). In the present work we describe the synthesis of adamant-1-ylmethylidynephosphine (8), a further thermally stable, crystalline phosphaalkyne and its behaviour in cycloaddition reactions with some 1,3-dipoles.

1. Syntheses of Adamant-1-ylmethylidynephosphine (8)

As is also the case with 3c[14,15], starting materials for the preparation of 8 are either tris[trimethylsilyl]phosphine (4a) or the lithium bis[trimethylsilyl]phosphide·2 tetrahydrofuran complex (4b). Tris[trimethylsilyl]phosphine (4a) is treated with 1-adamantoyl chloride (5) in a molar ratio of 1:1 in pentane at 20°C. After reaction for 7 days (¹H-N.M.R.-monitoring) the acyl chloride has been completely consumed, but some phosphine is still present in the mixture as this compound is, at least partially, doubly or triply acylated[14]. Product 7, however, can be separated as a viscous oil from the reaction mixture by distillation. Under the conditions mentioned above, the primary product 6 cannot be detected[16] (Scheme B).

$$[(H_3C)_3Si]_2P-X + Cl-\overset{O}{\underset{\|}{C}}-R^1 \xrightarrow{-X-Cl} (H_3C)_3Si\overset{(H_3C)_3Si}{\diagdown}P-\overset{O}{\underset{\|}{C}}-R^1$$

4a X = Si(CH₃)₃   **5**   **6**
4b X = Li · 2THF

$$\xrightarrow[\text{from 4b : 96\%}]{\substack{[1,3]-(H_3C)_3Si-\text{shift} \\ \text{from 4a : 67\%}}} (H_3C)_3Si\sim P=C\overset{O-Si(CH_3)_3}{\underset{R^1}{\diagup}}$$

7

$$\xrightarrow[-(H_3C)_3Si-O-Si(CH_3)_3]{\text{NaOH, 20 °C or } (n-C_4H_9)_4N^{\oplus}F^{\ominus}, 90 °C} P\equiv C-R^1$$

8

R¹ =

Scheme B

Lithium bis[trimethylsilyl]phosphide · 2 tetrahydrofuran (**4b**) and 1-adamantoyl chloride (**5**) in a molar ratio of 1 : 1 react in cyclopentane at $-40\,^\circ$C to give initially 1-adamantoylbis[trimethylsilyl]phosphine (**6**). This compound can be detected even at room temperature by ^{31}P- and ^{1}H-N.M.R. spectrometry. A ^{31}P chemical shift value of -110.6 ppm, which is very similar to that found for the corresponding 2,2-dimethylpropanoyl derivative (-107 ppm)[14], and the appearance of only one doublet in the trimethylsilyl region ($\delta = 0.31$ ppm; $^3J_{\mathrm{H,P}} = 4.3$ Hz) prove the formation of an acylbis[trimethylsilyl]phosphine. As to be expected, the compound rearranges rapidly within 15 min by the well-known 1,3-migration of one trimethylsilyl group to form the phosphaalkene **7**. After the removal of lithium chloride and solvent in vacuum, again a viscous oil is

initially isolated, but in this case it solidifies in the refrigerator. The almost pure solid compound could be recrystallised from pentane; on distillation it decomposes partially by elimination of hexamethyldisiloxane.
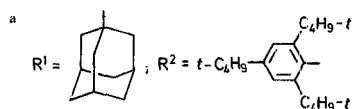
The constitution of phosphaalkene **7** was unequivocally confirmed by microanalytical and spectral data as well as by the cryoscopic determination of its molecular weight. Apart from an unresolved multiplet of the adamantyl substituent, the ^{1}H-N.M.R. spectrum obtained from a solution in benzene, shows a singlet ($\delta = 0.44$ ppm) and a doublet ($\delta = 0.54$ ppm; $^3J_{\mathrm{H,P}} = 3.8$ Hz) assigned to the trimethylsilyl groups at the phosphorus and the oxygen atom. A similar pattern with two $J_{\mathrm{Si,P}}$ coupling constants of very different magnitude (O—Si: $\delta = 13.9$ ppm; $^3J_{\mathrm{Si,P}} = 3.2$ Hz; P—Si: $\delta = -4.7$ ppm; $^1J_{\mathrm{Si,P}} = 52.1$ Hz) is found in the ^{29}Si-N.M.R. spectrum. Finally the observation of a ^{31}P- ($\delta = 120.2$ ppm) and a ^{13}C-N.M.R. signal ($\delta = 226.8$ ppm; $^1J_{\mathrm{C,P}} = 78.6$ Hz) at very low field is characteristic for the trivalent, bicoordinate (λ^3, σ^2) phosphorus atom and the olefinic carbon atom of the P=C moiety[17].

As several authors[18,19] have demonstrated in N.M.R. spectroscopic studies on different $(Z)/(E)$-isomeric phosphaalkenes, the occurrence of a higher absolute value of the $J_{\mathrm{P,X}}$ coupling constant is indicative that the atom X is part of a substituent which is arranged cis with respect to the nonbonding electron pair at phosphorus. From a comparison of appropriate values for compound **7** (c.f. Experimental Section) with those of $(Z)/(E)$-[2,2-dimethyl-1-(trimethylsiloxy)-propylidene]phosphine[20] and $(Z)/(E)$-[1-(t-butyldimethylsiloxy-benzylidene]-(2,4,6-tri-t-butylphenyl)-phosphine[19] (c.f. Table) it is quite clear that **7** consists mainly of the (Z)-isomer. A very weak ^{31}P-resonance at $\delta = +102.3$ ppm with an intensity of only 3 % relative to that of the (Z)-isomer might be attributable to the (E)-isomer.

The constitution of compound **7** is also confirmed by a more detailed analysis of its I. R. and Raman spectra. A very weak

Table. Coupling Constants (J in Hz) and Configuration Assignment in $(Z)/(E)$-Isomeric Phosphaalkenes

Phosphaalkene[a]	Ref.	$^3J_{\mathrm{P=C-O-Si}}$	$^4J_{\mathrm{P=C-O-Si-C}}$	$^5J_{\mathrm{P=C-O-Si-C-H}}$	$^2J_{\mathrm{P=C-C}}$	$^3J_{\mathrm{P=C-C-C}}$	$^4J_{\mathrm{P=C-C-C-H}}$
(Z)-Isomers							
	20	–[b]	0.9	<0.3	25.0	12.0	0.6
	19	–[b]	<0.3	<0.3	32.3	10.4	–[c]
	14, 20	5.5	<0.3	<0.3	24.5	12.5	1.5
	this work	3.2	<0.3	<0.3	22.3	12.9	–[c]
(E)-Isomers							
	20	–[b]	6.3	0.9	12.5	2.0	<0.3
	19	–[b]	8.6[d]	1.8	14.0	5.5	–[c]

[a]

[b] Not reported.
[c] Not resolved.
[d] Carbon atoms of the methyl group.

I. R. and a strong to medium Raman band at 445 cm^{-1} indicate the presence of an Si-P bond, whereas the P=C stretching vibration could not be unambiguously assigned [1161 or 1098 cm^{-1}, s-m (Raman); w-vw (I. R.)] due to the presence of strong lines of the adamantyl substituent in this region. We further observe a strong I. R.-absorption, but an only weak Raman line at 878 cm^{-1}; this comes from the Si—O stretching vibration which, however, is strongly coupled with the corresponding C—O movement in this type of compound. The strongest band of the Raman spectrum at 625 cm^{-1} must be ascribed to the symmetrical stretching vibration of the SiC$_3$-moiety; its I. R.-pendant is only very weak. Furthermore, the existence of two differently bonded trimethylsilyl groups can be recognized by a splitting of many of the bands characteristic for this substituent. For example, this is seen for the symmetrical bending (I. R.: 1275, 1253 vs, 1241 s-m, 1215 vs; Raman: 1258 s-m, 1237 m, 1208 s-m) and the rocking motion (I. R. only: 845, 835 vs, 758, 751 s-m) of the CH$_3$ groups.
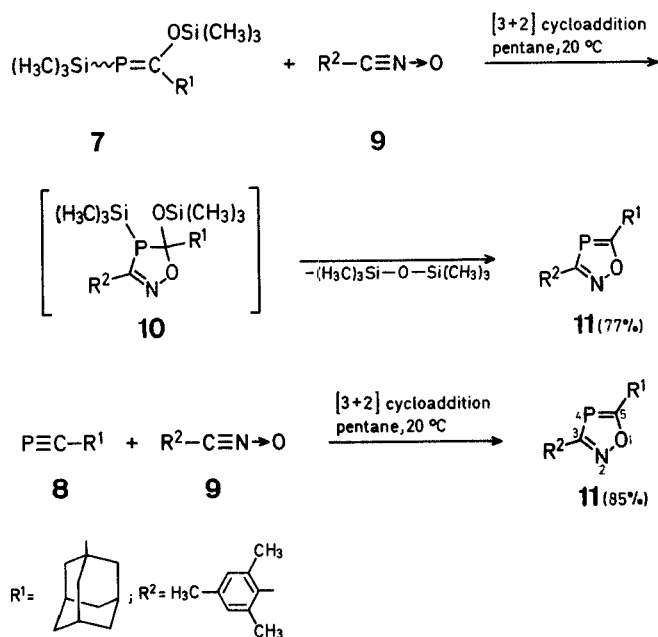
Hexamethyldisiloxane elimination from 7 to form the phosphaalkyne 8 in an optimized yield of 83%, can be achieved with very small amounts of sodium hydroxide in a solvent such as 1,2-dimethoxyethane, in analogy to the preparation of 3c[13]. The reaction can also be performed at 90°C in the absence of a solvent using tetra-n-butylammonium fluoride on kiesel gel as a catalyst (71% yield). The phosphaalkyne 8, hexamethyldisiloxane formed by elimination, and the solvent, if present, are removed from the reaction mixture under vacuum and separated by fractional condensation. Compound 8 is the first crystalline phosphaalkyne which is stable at room temperature to be reported.

The behaviour of 8 in cycloaddition reactions (see Section 2) as well as the analytical and spectral data obtained leave no doubt as to the correctness of the structural assignment for the phosphaalkyne. Considering only the structurally relevant P≡C unit, this is characterised by the intense stretching vibration at v = 1520 cm^{-1} in the I. R. spectrum, the ^{13}C-N.M.R. signal at δ = 184.7 ppm which is split into a doublet by coupling with phosphorus ($^1J_{C,P}$ = 39.0 Hz), and, finally, the ^{31}P-N.M.R. signal at δ = – 66.9 ppm. Comparable values were also reported for the phosphaalkyne 3c[13]. It should also be mentioned that the ^{13}C-N.M.R. signals of the adamantyl carbon atoms C-1 ($^2J_{C,P}$ = 18.0 Hz) as well as those of C-2, C-8, and C-9 ($^3J_{C,P}$ = 6.0 Hz) are split by coupling with phosphorus. The same observation is made for the cycloadducts of 8 described in Section 2.

2. [3 + 2]Cycloaddition Reactions of Phosphaalkene 7 and Phosphaalkyne 8

Recently, several authors have reported on the first [3 + 2]cycloaddition reactions at the phosphorus-carbon triple bond of the phosphaalkyne 3c[21, 22] and have shown that these reactions open up completely new possibilites for the syntheses of phospholes. This is also valid for the cycloaddition reactions of the new phosphaalkyne 8. Reaction of 8 with mesityl nitrile oxide (9) results in the formation of the 1,2,4-oxazaphosphole 11. This product is also obtained from the reaction of the phosphaalkene 7 with the dipole 9. As there is no plausible reason for assuming that the nitrile oxide can catalyse the reaction 7 → 8 and that 8 subsequently undergoes cycloaddition with 9, it must be assumed that the dihydrooxazaphosphole 10 is formed initially from 7 and 9.

Energetic reasons (aromatisation) would then be responsible for the subsequent, spontaneous elimination of hexamethyldisiloxane from 10 to give the final product 11 (Scheme C).

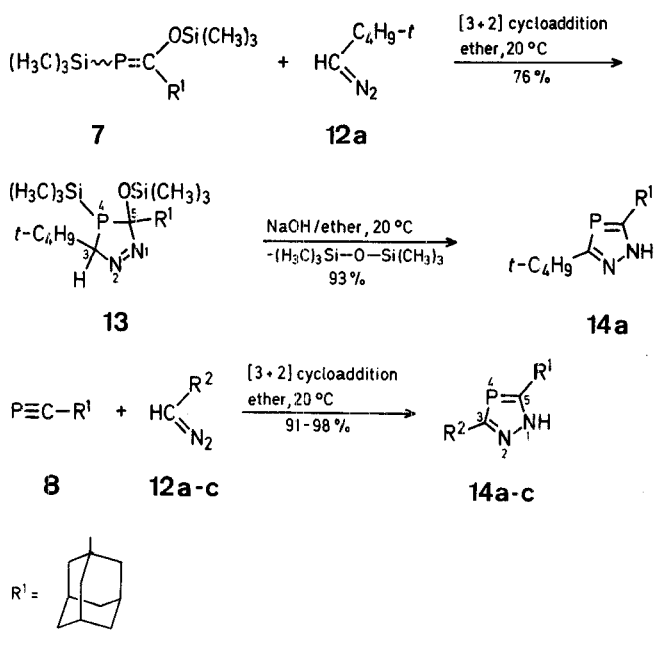Scheme C

The dipole orientations in the reactions 7 + 9 → 11 and 8 + 9 → 11 are such that an optimal separation between the adamantyl and mesityl groups results in each case. Thus, the phosphorus atom is bonded directly to two ring carbon atoms (1,2,4-oxazaphosphole ring) and this is confirmed by the ^{13}C-N.M.R. spectral data. Although the resonance for C-5 occurs, as is to be expected, at a lower field than that for C-3 (δ = 228.0 ppm as compared to δ = 181.0 ppm), the $^2J_{C,P}$ coupling constants for C-5 and C-3 are of comparable magnitudes (65.0 and 61.0 Hz, respectively). Furthermore, the phosphorus resonance of 11 at δ = 74.4 ppm excludes the possibility of the opposite dipole orientation (formation of a 1,2,5-oxazaphosphole ring) as this would result in a large shift to lower field[21, 23].

The diazo compounds 12a-c undergo smooth addition to the phosphorus-carbon triple bond of phosphaalkyne 8 to give the 1,2,4-diazaphospholes 14a-c. The position of the hydrogen atom (shown in Scheme D at N-1) is not certain, it could equally well be bonded to N-2. In the case of 3,5-di-t-butyl-1,2,4-diazaphosphole (14; R^1 = R^2 = t-C$_4$H$_9$), a rapid positional exchange between the two nitrogen atoms is observed in the ^{1}H-N.M.R. spectrum of a deuterochloroform solution[21].
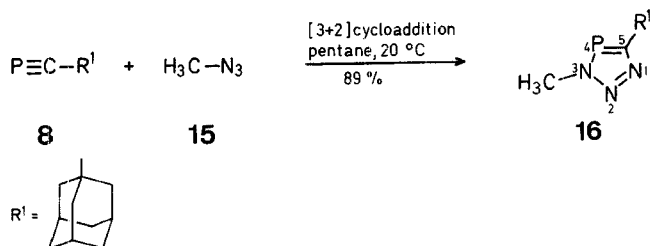
The heterocyclic product 14a can also be obtained from the reaction of the phosphaalkene 7 with the diazoalkane 12a (Scheme D). In contrast to the previously described reaction of 7 with the nitrile oxide 9, the primary adduct 13 can be isolated in this case. Although this adduct 13 could not be obtained in an analytically pure form, the N.M.R. spectral data (see Experimental Section) provide conclusive evidence for the given constitution. In addition, the sodium hydroxide-catalysed elimination of hexamethyldisiloxane from 13, resulting in the formation of the diazaphosphole 14a, unambiguously supports the dihydrodiazaphosphole structure 13. Similar reactions under the elimination of chlorotrimethylsilane are known[23, 24].

(H₃C)₃Si⌇⌇P=C⟨OSi(CH₃)₃ / R¹

7

+   HC⟨C₄H₉-t / N₂

12a

[3+2] cycloaddition
ether, 20 °C
—————————→
76%

(H₃C)₃Si \ OSi(CH₃)₃
t-C₄H₉—P—R¹
₃ ⁄N—N¹
H ²

13

NaOH/ether, 20 °C
——————————————→
−(H₃C)₃Si—O—Si(CH₃)₃
93%

t-C₄H₉⟨P=⟨R¹ / N—NH

14a

P≡C—R¹   +   HC⟨R² / N₂

8   **12a-c**

[3+2] cycloaddition
ether, 20 °C
——————————→
91–98%

R²⟨P=⟨R¹ / N—NH
²

14a-c

R¹ = [adamantyl structure]

12,14	a	b	c
R²	t-C₄H₉	H₃COOC	⟨phenyl⟩—C—‖O

Scheme D

The NH absorption in the I.R. (v = 3160–3200 cm^{-1}) and the signals in the ^{1}H-N.M.R. spectra (δ = 10.3–11.8 ppm) of **14a–c** indicate that the original diazomethyl hydrogen atom is bonded to nitrogen in the product. The expected resonances are observed in the ^{1}H-N.M.R. spectra; note-worthy is only the splitting of the resonance for the t-butyl hydrogen atoms in **14a** with $^4J_{H,P}$ = 1.1 Hz, which would be hardly imaginable for the reverse direction of addition. The ^{13}C-N.M.R. spectra of **14b** and **c** unequivocally confirm this assumption. The resonances for the carbon atoms C-3 (δ = 165.0 and 167.8 ppm, respectively) and C-5 (δ = 192.8 and 193.9 ppm, respectively) each appear as doublets with carbon-phosphorus coupling constants in the order of 60 Hz. As already mentioned for **11**, this would not be the case for the opposite dipole orientation. The splitting of the resonances of the carbonyl carbon atoms by phosphorus with comparable values of the coupling constants (22.9 and 19.0 Hz, respectively) is also indicative of the assumed dipole orientation. The ^{31}P-N.M.R. resonances are observed in the expected region; acceptor substituents in the 3-position, however, cause a shift to lower field (**14b**: δ = 95.1 ppm; **14c**: δ = 103.7 ppm)^{21}.

Finally, the [3 + 2]cycloaddition of methyl azide (**15**) with phosphaalkyne **8** results in the formation of the 1,2,3,4-triazaphosphole **16** in a specific orientation (Scheme E).

P≡C—R¹   +   H₃C—N₃

8   **15**

[3+2]cycloaddition
pentane, 20 °C
————————————→
89%

H₃C—³N⟨P=⁵⟨R¹ / N¹
N
²

16

R¹ = [adamantyl structure]

Scheme E

The same regiochemistry as for the diazo dipoles can be deduced from the coupling between the phosphorus atom and the methyl group ($^3J_{H,P}$ = 7.2 Hz). This regiochemistry also fulfils the steric requirements of both reaction partners. The phosphorus resonance (δ = 174.4 ppm) experiences a large down-field shift as a result of the direct bonding to a ring nitrogen atom.

Melting points were determined on a copper block (heating rate: 3 °C/min) and are not corrected. Microanalyses were performed with a Perkin-Elmer 240 Analyzer. I.R. spectra were recorded on a Perkin-Elmer 397 or 684 spectrophotometer, Raman spectra on a Coderg spectrophotometer PH0 [red line of a crypton gas laser (647 nm)]. ^{1}H-N.M.R. spectra were obtained with Varian EM 360, EM 390, and Bruker WP 60 spectrometers, ^{13}C-N.M.R. spectra with Bruker WP 80, WP 200, and WP 300 spectrometers [tetramethylsilane as internal (**6, 7, 8**) or external standard (**11, 13, 14, 16**)], ^{29}Si-N.M.R. spectra with a Bruker WP 300 spectrometer [tetramethylsilane as external standard (**7**)], and ^{31}P-N.M.R. spectra with Bruker WP 80 (**6, 7, 8**) and WP 200 spectrometers (**11, 13, 14, 16**) [85% orthophosphoric acid as external reference]. All solvents were anhydrous and were distilled under argon before use. All reactions were performed in flame-dried glass apparatus in an argon atmosphere.

(Adamant-1-yl-trimethylsiloxy)-methylidene-trimethylsilylphosphine (7):

Method A, from 4a and 5: To a solution of 1-adamantoyl chloride^{25} (**5**; 55.0 g, 0.28 mol) in pentane (200 ml) is added dropwise with stirring tris[trimethylsilyl]phosphine^{26} (**4a**; 70.0 g, 0.28 mol) in pentane (100 ml). The mixture is allowed to stand at room temperature for 7 days (^{1}H-N.M.R. monitoring). Evaporation at 30 °C/15 torr and subsequent fractional distillation gives product **7** as a viscous oil; yield: 63.3 g (67%); b.p. 130–135 °C/10^{-2} torr.

Method B, from 4b and 5: To a solution of 1-adamantoyl chloride^{25} (**5**; 11.4 g, 57.4 mmol) in cyclopentane (50 ml) is added slowly at −40 °C with stirring lithium bis[trimethylsilyl]phosphide·2 tetrahydrofuran^{27} (**4b**; 18.9 g, 57.4 mmol) in cyclopentane (50 ml). ^{1}H-N.M.R. monitoring shows that primarily formed 1-adamantoyl-bis[trimethylsilyl]phosphine (**6**) {^{1}H-N.M.R. (cyclopentane): δ = 0.31 ppm (d, $^3J_{H,P}$ = 4.3 Hz, P[Si(CH₃)₃]₂); ^{31}P-N.M.R. (cyclopentane): δ = −110.6 ppm} rearranges to **7**, when the reaction mixture is stirred for 15 min at room temperature. After filtration of lithium chloride and distillation of the solvent under vacuum, **7** is isolated as a viscous oil which solidifies in the refrigerator. Further purification of the yellowish compound is accomplished by recrystallisation from pentane, adding some seed crystals to the cooled solution; yield: 18.6 g (96%); m.p. 57 °C.

C₁₇H₃₃OPSi₂   calc.   C 59.95   H 9.77
(340.6)   found   59.9   9.58

Molecular weight: 348 (cryoscopically in benzene).

I.R. (film of molten **7**) and Raman (solid): see theoretical section.

(Z)-**7**, ^{1}H-N.M.R. (C₆D₆): δ = 0.44 [s, 9 H, O—Si(CH₃)₃]; 0.54 [d, $^3J_{H,P}$ = 3.8 Hz, 9 H, P—Si(CH₃)₃]; 1.7–2.2 ppm (m, 15 H$_{adamantyl}$).

(Z)-**7**, ^{13}C-N.M.R.(C₆D₆): δ = 1.4   (d, $^2J_{C,P}$ = 9.4 Hz, P—Si—CH₃); 2.6 (s, O—Si—CH₃); 29.1 (d, $^4J_{C,P}$ = 2.0 Hz, C-3, C-5, C-7); 36.9 (s, C-4, C-6, C-10); 41.9 (d, $^3J_{C,P}$ = 12.9 Hz, C-2, C-8, C-9); 47.5 (d, $^2J_{C,P}$ = 22.3 Hz, C-1); 226.8 ppm (d, $^1J_{C,P}$ = 78.6 Hz, C=P).

(Z)-**7**, ^{29}Si-N.M.R. (C₆D₆): δ = −4.7 (d, $^1J_{Si,P}$ = 52.1 Hz, P-Si); 13.9 ppm (d, $^3J_{Si,P}$ = 3.2 Hz, O-Si).

(Z)-**7**, ^{31}P-N.M.R.(C₆D₆): δ = 120.2 ppm;   (E)-**7**, ^{31}P-N.M.R.(C₆D₆): δ = 102.3 ppm.

M.S. (70 eV, source temperature 425 K, probe temperature 300 K): m/e (rel. intens. %) = 340.2 (M⁺, 1); 268.1 (M⁺ − SiC₃H₈, 15); 237.1 (M⁺ − PS:C₃H₈, 33); 147.0 (C₆H₁₈OSi₂⁺ − CH₃, 95); 135.0 (C₁₀H₁₅⁺, 100); 75.0 (C₂H₇OSi⁺, 9); 73.0 (C₃H₉Si⁺, 40).

Adamant-1-ylmethylidynephosphine (8):

Method A, from 7 by sodium hydroxide catalysis: In the presence of small amounts of solid sodium hydroxide (about 5 mg), the phosphaalkene 7 (3.64 g, 10.7 mmol), prepared from phosphide 4b and dissolved in 1,2-dimethoxyethane (10 ml), eliminates hexamethyldisiloxane quantitatively within 24 h (^{1}H-N.M.R. monitoring). Volatile compounds are removed under vacuum at room temperature and separated by trap-to-trap distillation (0°C/−78°C). The colourless crystalline compound 8 which condenses at 0°C, is purified by further sublimation; yield: 1.7 g (83%); m.p. 69–70°C.

Method B, from 7 by tetra-n-butylammonium fluoride catalysis: The phosphaalkene 7 (2.3 g, 6.7 mmol), prepared from phosphine 4a, is heated at 90°C, tetra-n-butylammonium fluoride on kiesel gel[28] (0.14 g, 0.16 mmol) is added, and a pressure of 10^{-3} torr is immediately applied to the reaction flask. The addition of the ammonium fluoride is repeated sometimes until no more 7 is detectable in the reaction mixture. The product 8 and hexamethyldisiloxane (together with other trimethylsilyl group-containing products) are collected in cold traps at 0°C (product 8) and at −78°C (hexamethyldisiloxane). The phosphaalkyne 8 separates as colourless crystals; yield: 0.85 g (71%).

$C_{11}H_{15}P$ calc. C 74.14 H 8.48
(178.2) found 74.1 8.43

Molecular weight: 179 (cryoscopically in benzene)

I.R. (film of solid 8) and Raman (solid): $v = 1528/1520\,cm^{-1}$ (C≡P).

^{1}H-N.M.R. (C_6D_6): $\delta = 1.4–2.0$ ppm (m, 15 H$_{adamantyl}$).

^{13}C-N.M.R. (C_6D_6): $\delta = 27.8$ (s, C-3, C-5, C-7); 35.7 (s, C-4, C-6, C-10); 38.5 (d, $^2J_{C,P} = 18.0$ Hz, C-1); 42.9 (d, $^3J_{C,P} = 6.0$ Hz; C-2, C-8, C-9); 184.7 ppm (d, $^1J_{C,P} = 39.0$ Hz, C≡P).

^{31}P-N.M.R. (C_6D_6): $\delta = -66.9$ ppm.

M.S. (70 eV; source temperature 425 K; probe temperature 300 K): m/e (rel. intens. %) = 178.0 (M$^+$, 100); 177.0 (M$^+$ − H, 12); 135.0 ($C_{10}H_{15}^+$, 18); 93.0 ($C_7H_9^+$, 14); 91.0 ($C_7H_7^+$, 26); 79.0 ($C_6H_7^+$, 27).

5-(Adamant-1-yl)-3-mesityl-1,2,4-oxazaphosphole (11):

Method A, from 7 and 9: To a stirred solution of mesityl nitrile oxide[29] (9; 1.13 g, 7.0 mmol) in pentane (10 ml) at room temperature is added dropwise the phosphaalkene 7 (2.38 g, 7.0 mmol) in pentane (5 ml). After 24 h the mixture is filtered under suction and the residue washed with pentane to leave the colourless, analytically pure product 11; yield: 1.83 g (77%); m.p. 120°C (decomp.).

Method B, from 8 and 9: To a stirred solution of mesityl nitrile oxide[29] (9; 338 mg, 2.1 mmol) in pentane (5 ml) at room temperature is added dropwise the phosphaalkyne 8 (374 mg, 2.1 mmol) in pentane (2 ml). The mixture is worked up as described under Method A; yield: 606 mg (85%); m.p. 120°C (decomp.).

$C_{21}H_{16}NOP$ calc. C 74.31 H 7.72 N 4.13
(339.4) found 74.2 7.65 4.2

I.R. (KBr): $v = 2900$ (CH); 1445 cm^{-1} (phosphole ring).

^{1}H-N.M.R. (C_6D_6): $\delta = 1.5–2.1$ (m, 15 H$_{adamantyl}$); 2.17 (s, 3 H, 4-H$_3$C—C_6H_2); 2.27 [s, 6 H, 2,6-(H$_3$C)$_2$C$_6$H$_2$]; 6.81 ppm (s, 2 H$_{arom}$).

^{13}C-N.M.R. (C_6D_6): $\delta = 21.6$, 21.8 [s, 2,4,6-(H$_3$C)$_3$C$_6$H$_2$]; 29.4 (s, C-3, C-5, C-7); 37.3 (s, C-4, C-6, C-10); 41.0 (d, $^2J_{C,P} = 10.8$ Hz, C-1); 43.5 (d, $^3J_{C,P} = 7.1$ Hz, C-2, C-8, C-9); 129.3, 129.4, 130.0, 137.8, 139.5 (C$_{arom}$); 181.0 (d, $^1J_{C,P} = 61.0$ Hz, C-3$_{phosphole}$); 228.0 ppm (d, $^1J_{C,P} = 65.0$ Hz, C-5$_{phosphole}$).

^{31}P-N.M.R.(C_6D_6): $\delta = 74.4$ ppm.

5-(Adamant-1-yl)-3-t-butyl-5-trimethylsiloxy-4,5-dihydro-3H-1,2,4-diazaphosphole (13):

To a stirred solution of the diazoalkane 12a[30] (1.47 g, 15.0 mmol) in diethyl ether (20 ml) at room temperature is added dropwise the phosphaalkene 7 (2.74 g, 8.0 mmol) in diethyl ether (5 ml). After 24 h the mixture is evaporated at 20°C/15 torr and the residue allowed to stand for 5 h at 20°C/10^{-2} torr. The residue is recrystallised from pentane to give the not completely analytically pure product 13 as yellow crystals; yield: 2.68 g (76%); m.p. 50°C (decomp.).

I.R. (toluene): $v = 2840$ (CH); 1250 cm^{-1} (Si—CH$_3$).

^{1}H-N.M.R. (C_6D_6): $\delta = 0.23$ [s, 9 H, OSi(CH$_3$)$_3$]; 0.30 [d, $^3J_{H,P} = 4.8$ Hz, PSi(CH$_3$)$_3$]; 1.25 (s, 9 H, t-C$_4$H$_9$); 1.6–2.3 (m, 15 H$_{adamantyl}$); 4.95 ppm (d, $^2J_{H,P} = 5.2$ Hz, 1 H, H-3).

^{13}C-N.M.R.(C_6D_6): $\delta = 1.4$ (d, $^2J_{C,P} = 13.3$ Hz, P—Si—CH$_3$); 3.8 (s, O—Si—CH$_3$); 29.7 (s, C-3, C-5, C-7); 29.8 (s, C—CH$_3$); 36.2 (d, $^2J_{C,P} = 18.3$ Hz, C—CH$_3$); 38.1 (s, C-4, C-6, C-10); 40.2 (d, $^3J_{C,P} = 10.7$ Hz, C-2, C-8, C-9); 42.8 (d, $^2J_{C,P} = 24.2$ Hz, C-1); 100.4 (d, $^1J_{C,P} = 29.0$ Hz, C-3); 136.6 ppm (d, $^1J_{C,P} = 38.2$ Hz, C-5$_{phosphole}$).

^{31}P-N.M.R. (C_6D_6): $\delta = 105.1$ ppm.

5-(Adamant-1-yl)-3-t-butyl-1H-1,2,4-diazaphosphole (14a):

Method A, from 13 using sodium hydroxide as catalyst: To a stirred solution of 13 (2.68 g, 6.1 mmol) in diethyl ether (10 ml) at room temperature is added a catalytic amount of powdered sodium hydroxide (~ 10 mg). After 24 h the mixture is evaporated at 20°C/15 torr. The residue is sublimed in a kugelrohr apparatus at 220°C (oven temperature)/10^{-2} torr to give the colourless product 14a; yield: 1.56 g (93%); m.p. 234°C.

Method B, from 8 and 12a[30]: To a stirred solution of the diazoalkane 12a (294 mg, 3.0 mmol) in diethyl ether (5 ml) at room temperature is added dropwise the phosphaalkyne 8 (400 mg, 2.2 mmol) in diethyl ether (2 ml). After 24 h the mixture is evaporated at 20°C/15 torr and worked up as described under Method A; yield: 563 mg (91%); m.p. 234°C. The I.R. spectrum is superimposable with that of a sample prepared according to Method A.

$C_{16}H_{25}N_2P$ calc. C 69.54 H 9.12 N 10.14
(276.4) found 69.7 9.23 10.3

I.R. (KBr): $v = 3200$ (NH); 2900 (CH); 1450 cm^{-1} (phosphole ring).

^{1}H-N.M.R. (CDCl$_3$): $\delta = 1.35$ (d, $^4J_{H,P} = 1.1$ Hz, 9 H, t-C$_4$H$_9$); 1.6–2.1 (m, 15 H$_{adamantyl}$); 10.3 ppm (s, 1 H, NH).

^{31}P-N.M.R. (CDCl$_3$): $\delta = 67.0$ ppm.

Because of its poor solubility in the usual solvents, a ^{13}C-N.M.R. spectrum of 14a could not be recorded.

Methyl 5-(Adamant-1-yl)-1H-1,2,4-diazaphosphole-3-carboxylate (14b):

To a stirred solution of the α-diazo ester 12b[31] (140 mg, 1.4 mmol) in diethyl ether (5 ml) at room temperature is added dropwise the phosphaalkyne 8 (255 mg, 1.4 mmol) in diethyl ether (2 ml). After 24 h the mixture is filtered under suction and the residue is washed with a small amount of pentane to leave the product 14b as a colourless, crystalline powder; yield: 370 mg (93%); m.p. 191°C.

$C_{14}H_{19}N_2O_2P$ calc. C 60.42 H 6.88 N 10.07
(278.3) found 60.2 6.74 9.9

I.R. (KBr): $v = 3160$ (NH); 2900 (CH); 1720 (C=O); 1430 cm^{-1} (phosphole ring).

^{1}H-N.M.R. (CDCl$_3$): $\delta = 1.6–2.2$ (m, 15 H$_{adamantyl}$); 3.78 (s, 3 H, OCH$_3$); 11.3 ppm (s, 1 H, NH).

^{13}C-N.M.R. (CDCl$_3$): $\delta = 28.5$ (s, C-3, C-5, C-7); 36.2 (s, C-4, C-6, C-10); 37.2 (d, $^2J_{C,P} = 13.1$ Hz, C-1); 43.8 (d, $^3J_{C,P} = 6.8$ Hz, C-2, C-8, C-9); 52.2 (s, OCH$_3$); 164.0 (d, $^2J_{C,P} = 22.9$ Hz, C=O); 165.0 (d, $^1J_{C,P} = 56.0$ Hz, C-3$_{phosphole}$); 192.8 ppm (d, $^1J_{C,P} = 59.8$ Hz, C-5$_{phosphole}$).

^{31}P-N.M.R. (CDCl$_3$): $\delta = 95.1$ ppm.

5-(Adamant-1-yl)-3-benzoyl-1H-1,2,4-diazaphosphole (14c):

Prepared from the diazo ketone 12c[32] (210 mg, 1.4 mmol) and the phosphaalkyne 8 (255 mg, 1.4 mmol) following the procedure described for 14b above and obtained as a colourless crystalline powder; yield: 422 mg (91%); m.p. 160°C (decomp.).

$C_{19}H_{21}N_2OP$ calc. C 70.36 H 6.52 N 8.64
(324.4) found 70.3 6.54 8.7

I.R. (KBr): $v = 3200$ (NH); 2900 (CH); 1635 (C=O); 1445 cm^{-1} (phosphole ring).

^{1}H-N.M.R. (CDCl$_3$): $\delta = 1.6–2.2$ (m, 15 H$_{adamantyl}$); 7.3–8.3 (m, 5 H$_{arom}$); 11.8 ppm (s, 1 H, NH).

^{13}C-N.M.R. (1/5 C_6D_6/CH_2Cl_2): δ = 28.9 (s, C-3, C-5, C-7); 36.5 (s, C-4, C-6, C-10); 37.7 (d, $^2J_{C,P}$ = 13.5 Hz, C-1); 44.2 (d, $^3J_{C,P}$ = 6.9 Hz, C-2, C-8, C-9); 130.2, 130.3, 133.3, 138.0 (C_{arom}); 167.8 (d, $^1J_{C,P}$ = 59.5 Hz, C-3$_{phosphole}$); 187.3 (d, $^2J_{C,P}$ = 19.0 Hz, C=O); 193.8 ppm (d, $^1J_{C,P}$ = 64.3 Hz, C-5$_{phosphole}$).

^{31}P-N.M.R. (C_6D_6): δ = 103.7 ppm.

5-(Adamant-1-yl)-3-methyl-1,2,3,4-triazaphosphole (16):

To a stirred solution of the azide 15^{33} (96 mg, 1.7 mmol) in pentane (5 ml) at room temperature is added dropwise the phosphaalkyne 8 (200 mg, 1.1 mmol) in pentane (2 ml). After 1 h the mixture is evaporated at 30°C/15 torr. The oily residue is distilled in a kugelrohr apparatus at 150°C (oven temperature/10^{-2} torr to give the product 16 which solidifies on cooling; yield: 235 mg (89 %); m.p. 76°C.

$C_{12}H_{18}N_3P$ calc.   C 61.26   H 7.71   N 17.86
(235.3)   found   61.3   7.89   17.7

I.R. (KBr): v = 2900 (CH); 1445 cm^{-1} (phosphole ring).

^{1}H-N.M.R. (C_6D_6): δ = 1.6–2.3 (m, 15 $H_{adamantyl}$); 3.58 ppm (d, $^3J_{H,P}$ = 7.2 Hz, 3 H, N—CH_3).

^{13}C-N.M.R. (C_6D_6): δ = 29.8 (s, C-3, C-5, C-7); 37.7 (s, C-4, C-6, C-10, and N—CH_3); 38.6 (d, $^2J_{C,P}$ = 15.3 Hz, C-1); 45.4 (d, $^3J_{C,P}$ = 7.6 Hz, C-2, C-8, C-9); 200.4 ppm (d, $^1J_{C,P}$ = 54.1 Hz, C-5$_{phosphole}$).

^{31}P-N.M.R. (C_6D_6): δ = 174.4 ppm.

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