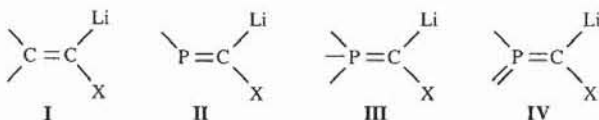


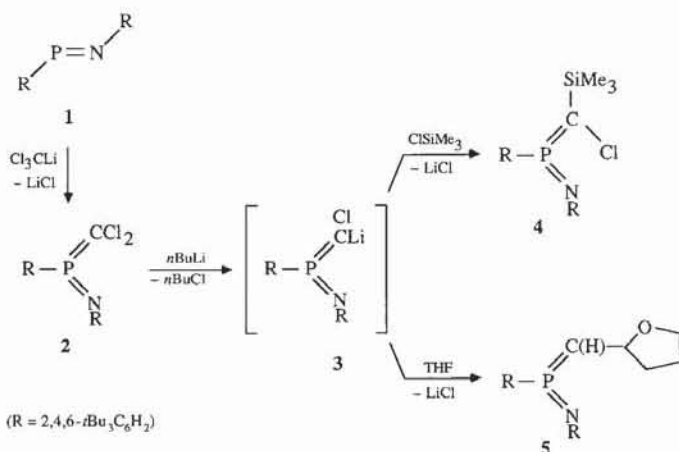
Reactions of an Iminophosphoranylidene Carbenoid**

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Vinylidene carbenoids **I** are of major significance as synthetic building blocks in organoelement chemistry.^[1] However, little is known about this type of carbenoids with phosphorus as heteroatom (**II–IV**). Only for the phosphanylidene carbenoid system **II** have several experimental investigations been made.^[2] Here we report on the synthesis and reactivity of an iminophosphoranylidene carbenoid of type **IV**, in which the phosphorus atom is in a trigonal-planar coordination environment.



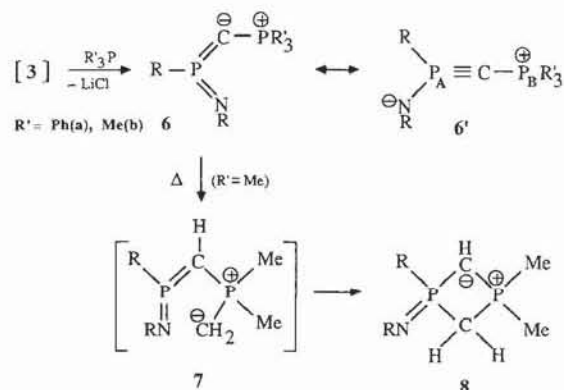
Bis(aryl)iminophosphane^[3] (**1**) reacts easily with trichloromethylithium to give imino(dichloromethylene)phosphorane (**2**); subsequent reaction with *n*-butyllithium in THF at -105°C results in a deepening of the color of the solution, suggestive of the formation of a carbenoid **3** as an intermediate (³¹P NMR: $\delta = 83.2$; $J_{\text{PLi}} = 25$ Hz). This intermediate can be trapped as the



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thermally stable, C-silylated substitution product **4** by the subsequent addition of chlorotrimethylsilane. In the absence of an electrophile, **3** reacts with the solvent to give the imino(tetrahydrofuran-2-yl-methylene)phosphorane **5**, which can formally be regarded as an insertion product of an iminophosphorylidene carbene with tetrahydrofuran. Reaction of intermediate **3** and triphenylphosphane yields the "phosphane-adduct" phosphonio(iminophosphoranylidene)methanide (**6a**) as a stable final product. The compound **6b** obtainable by the corresponding route with trimethylphosphane is, however, not stable in solution but isomerizes^[5] by 1,3-H-shift (**7**), followed by ring closure to give the 1,2-dihydro-1,3-diphosphete **8**. Nitrogen derivatives isoelectronic to **6** and **8** are known, a *N*-silylated bis(imino)phosphorane^[6] and a 1,2-dihydro-1,2,3λ⁵,4λ⁵-diazadiphosphete,^[7] respectively.



The compositions of compounds **2**, **4**, **5**, **6a**, and **8** are confirmed by elemental analyses and mass spectra. Their constitution in solution is verified by NMR spectra and, in case of compounds **2** and **4** by X-ray structure analysis.^[8] In the low-field region of the NMR spectrum the imino(methylene)phosphoranes **2**, **4**, and **5** show the characteristic resonances for the P=C structural unit^[8b] (δ (³¹P) = 70.1 (**2**), 86.2 (**4**), 75.0 (**5**); δ (¹³C) = 99.9 ($J_{\text{CP}} = 245.9$ Hz) (**2**), 93.7 ($J_{\text{CP}} = 119.8$ Hz) (**4**), 93.9 ($J_{\text{CP}} = 184.0$ Hz) (**5**)). In the phosphoranes **6a**, **b** the signal (split by the phosphonio group) for the three-coordinate phosphorus atom is shifted drastically to higher field ($\delta = 20.4$ (**6a**), 36.8 (**6b**)); the observed shift lies in the expected range for bis(imino)phosphoranes.^[9c, 10] The position of the signal of the phosphonio group and the value of $^2J_{\text{PP}}$ correspond with the values reported for carbodiphosphoranes^[11] ($\delta = -12.4$, $^2J_{\text{PP}} = 111.8$ Hz (**6a**); $\delta = -21.0$, $^2J_{\text{PP}} = 63.3$ Hz (**6b**)). The position of the signal for the two-coordinate carbon atom ($\delta = 90.8$ (**6a**) at low field in comparison to carbodiphosphoranes,^[12] and the relatively large coupling constants $^1J_{\text{CP}}$ (219.7 Hz [P_A], 162.1 Hz [P_B] (**6a**)) can be interpreted in terms of participation of the limiting dipolar structure **6'** and are also indicative of the formal relationship with alkylidene phosphoranes,^[9d] especially the phosphonium salt [(*i*-Pr₂N)₂P=C=PH(*i*-Pr₂N)₂]⁺[F₃CSO₃]⁻.^[13]

The composition and constitution of **8** can be deduced from the high-resolution mass spectrum (molecule peak) and from the results of NMR measurements. The four-membered ring structure is verified by the observation of resonance signals for one CH and one CH₂ unit, in which each of the carbon atoms (CH: $\delta = 41.7$, $^1J_{\text{CP}} = 89, 84$ Hz; CH₂: $\delta = 40.3$, $^1J_{\text{CP}} = 60, 51$ Hz) shows direct coupling to each of the two phosphorus atoms. In contrast to the NMR data obtained for **6a**, the chemical shifts for the ylidic carbon atom and for the proton bonded to it, as

well as the value of the $^2J_{pp}$ coupling constant (25.8 Hz), are quite typical. The unusual steric strain of the molecule hinders rotation of both aryl ligands, this gives rise to temperature-dependent coalescence phenomena in the ^1H and ^{13}C NMR spectra for the signals of the neighboring and non-neighboring substituents. Below temperatures of -50°C the rotation is completely "frozen" on the NMR timescale.

Figure 1 shows the structure of compound **4** in the crystal. As in all bis(ylene)phosphoranes that have been structurally investigated, the central phosphorus atom is in a trigonal-planar

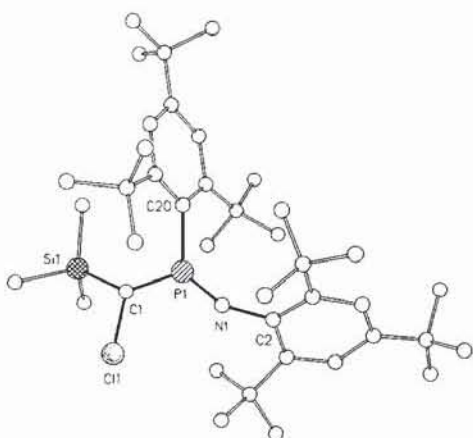


Fig. 1. Structure of imino(methylene)phosphorane **4** in the crystal. Selected bond lengths [pm] and angles [$^\circ$] (in parentheses the data for **2**): P1=C 167.0(3) [165.5(3)], P1-C_{aryl} 182.5(3) [181.1(6)], P1=N 152.0(2) [152.3(3)], C_{aryl}-P1-C 108.1(1) [107.7(2)], C_{aryl}-P1-N 128.1(1) [128.9(2)], C-P1-N 122.6(1) [121.8(3)].

coordination environment (Σ 358.8 $^\circ$). The atoms Cl1 and Si1 are approximately coplanar with the N1-P1-C1 plane (the angle between the planes P1-C1-Cl1-Si1 and C20-P1-N1-C1 is 15 $^\circ$), whereas the C2 atom is positioned out-of-plane (dihedral angle C20-P1-N1-C2 -58 $^\circ$; C1-P1-N1-C2 137 $^\circ$). In contrast to those in **1**, the two aryl substituents in **4** are *Z*-configured and orthogonal. The sterically more demanding methylene substituent (SiMe₃) occupies the favored *exo* position. The P1-N1 (150.0(2) pm) and P1-C1 distance (167.0(3) pm), and the C1-P1-N1 (122.6(1) $^\circ$) and C2-N1-P1 angles (145.8(2) $^\circ$) correspond with typical structural features found for imino(methylene)phosphoranes.^[9b] All important parameters for compound **2** deviate only slightly from those of **4**.

Experimental Procedure

2: To a solution of chloroform (1.67 g, 14 mmol) in THF (50 mL) and ether (10 mL), an equimolar amount of *n*BuLi in *n*-hexane was added at -105°C . After the mixture had been stirred for 1 h, **1** (4.3 g, 8 mmol) in ether (20 mL) was added dropwise. After warming the solution to 25°C the volatile constituents were removed under vacuum and the remaining residue was taken up in hexane, and the insoluble material (LiCl) was separated by filtration. Compound **2** crystallized from the concentrated filtrate at -30°C . Yield: 45%; m.p. 174 – 176°C ; MS (70 eV) *m/e* (%): 617 (12) [M^+], 57 (100) [*t*Bu $^+$].

4: At -105°C , *n*BuLi (0.63 mL, 1.6 M solution in *n*-hexane) was added to a solution of **2** (620 mg, 1 mmol) in THF (10 mL) and Et₂O (1 mL). After the mixture had been stirred for 1 h, Me₃SiCl (200 mg, 1.8 mmol) was added; the solution was then allowed to warm to room temperature. The volatile constituents were removed under vacuum, the residue was taken up in *n*-hexane, and the LiCl that had formed was filtered off. From the concentrated filtrate **4** crystallized at -30°C as a pale yellow solid. Yield: 69%; m.p. 175 – 177°C . Compound **5** is obtained in a similar fashion in the absence of Me₃SiCl. Yield: 52%. M.p. 148 – 150°C .

4: NMR (without aryl) ^1H (CDCl₃): δ = -0.19 (s, SiMe₃); ^{13}C (CDCl₃): δ = 93.7 (d, J_{CP} = 119.8 Hz, P=C), -0.8 (d, $^3J_{CP}$ = 3.6 Hz, PCSiC₃); MS (70 eV) *m/e* (%): 619 (2) [M^+], 57 (100) [*t*Bu $^+$].

5: NMR (without aryl) ^1H (CDCl₃): δ = 5.26 (ddt, $^3J_{HP}$ = 2.0, $^3J_{HM}$ = 7.0, 10.3 Hz, PCH), 3.92 ("q", $^2J_{HM}$ = $^3J_{HM}$ = 7.2 Hz), 3.57 (dd, $^2J_{HP}$ = 32.4, $^3J_{HM}$ = 10.3 Hz, PCH), 2.21 (m, OCCCH₂), 1.95 (m, OCCCH₂); ^{13}C (CDCl₃): δ = 93.9 (d, J_{CP} = 184.0 Hz, P=C), 75.2 (d, $^2P_{CP}$ = 1.8 Hz, PCCO), 67.3, 34.2, 26.5 (s, C₄O framework); MS (70 eV) *m/e* (%): 619 (<1) [M^+], 100 (100) [*t*Bu $^+$].

6, **7**: Reaction of **2** (620 mg, 1 mmol) with *n*BuLi (0.63 mL, 1.6 M in hexane) at -105°C yielded quantitatively (^{31}P NMR control) the stable phosphorane **6a**, which, following removal of LiCl, was obtained as a pale yellow solid. In contrast, reactions with PMe₃ yielded the unstable intermediate **6b**, which isomerized to **8** during workup of the reaction solution. **6a**: Yield: 83%, m.p. 154°C (decomp.); MS (70 eV) *m/e* (%): 809 (35) [M^+], 752 (100) [M^+ - *t*Bu $^+$]; **8**: MS (70 eV) *m/e* (%): 623 (0.4) [M^+], 566 (100) [M^+ - *t*Bu $^+$], 608 (3) [M^+ - CH₃].

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- [8] a) X-ray structure analysis for **2** [**4**] C₃₇H₃₉Cl₂NP [C₃₀H₃₆-CINPSi-1/2 toluene]; orange [yellow] crystals, crystal dimensions 0.25 × 0.40 × 0.40 [0.40 × 0.50 × 0.70] mm; M_r = 618.7 [702.5 with solvent]; space group C2/c (no. 15) [P2₁/n], a = 36.605(4) [9.994(1)], b = 10.684(1) [26.039(2)], c = 22.571(2) [17.034(2)] Å, β = 120.77(1) $^\circ$ [90.19(1) $^\circ$], V = 7.585(1) [4.433(1)] nm³, Z = 8 [4], ρ_{calcd} = 1.08 [1.05] g cm⁻³, $\mu(\text{CuK}\alpha)$ = 2.10 [1.55] mm⁻¹; 5607 [6581] symmetry-independent reflections ($2\theta_{\text{max}}$ = 120 $^\circ$ [120 $^\circ$], T = 293 [193] K), of which 3473 [6158] reflections with $F > p\sigma(F)$ (p = 3 [4]) were used for structure solution (direct methods) and refinement (368 [434] parameters), non-hydrogen atoms anisotropic, H atoms refined with a "riding" model; R = 0.067 [0.062] (R_w = 0.068 [0.071]), w^{-1} = $\sigma^2(F) = gF^2$, g = 0.0008 [0.0001]. Extinction correction (for **4**) and empirical absorption correction (for **2**) was applied by using the program DIFABS. In **2** a *p*-*tert*-butyl group is disordered (s.o.f. C31, C32, C33 = 0.62(1)). In **4** a toluene molecule is disordered over an inversion center. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-58059. b) N. Walker, D. Stuart, *Acta Crystallogr. Sect. A* **1993**, 39, 158–166.
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