

Synthesis, crystal structure and rearrangement of a methylene(ylene)-phosphorane containing a CH₂-moiety at an sp²-hybridized phosphorus(v) centre

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The reaction of the iminophosphane, (Me₃Si)₃C–P=N–Mes*, with Me₂S=CH₂ affords the first methylenephosphorane containing a CH₂ moiety at an sp²-hybridized phosphorus(v) centre; the crystal structure as well the rearrangement of which is reported.

Methylenephosphoranes **I**, which may be formally regarded as a phosphane stabilized methylene (CH₂), are well established¹ and their chemistry with respect to organic and organometallic syntheses has long been known.²

In contrast, only one kinetically stable derivative of a methylenephosphane,³ **II**, is known so far in which the CH₂ moiety is linked to a phosphinidene unit. Methylene(ylene)-phosphoranes **III**, which also contain an sp²-hybridized phosphorus centre as in **II** but with phosphorus(v) are known so far only as transient species, and their existence has only been inferred from trapping experiments.⁴ Here we report the synthesis and X-ray structure of the first example of a stable derivative of a methylenephosphorane of the type **III** (Fig. 1).

In a typical experiment, a THF solution of the iminophosphane, (Me₃Si)₃CP=NMe₃*, **1** [obtained by the treatment of ClP=NMe₃*⁵ with an equimolar quantity of LiC(SiMe₃)₃ in THF at –78 °C†] was added under stirring to an equimolar quantity of Me₂S=CH₂ in THF at –40 °C.

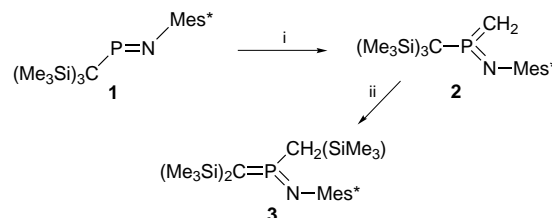
The solvent was removed under vacuum and the residue was taken up in 40 ml of hexane. The LiI present was removed by filtration and the filtrate concentrated and the resulting residue recrystallized from hexane to give **2** as pale colourless crystals (82.6% yield).

Compound **2** was shown to be a monomer from the observation of the molecular ion in the high-resolution mass spectrum at *m/z* 534 (6%). The formation of an imino(methylene)phosphorane and not of the valence isomeric azaphosphirane⁶ is readily demonstrated by the low field ³¹P NMR chemical shift (δ 157.8), while the lowest field signal in the ¹³C NMR spectrum (δ 64.2, ¹J_{CP} 108.2 Hz) manifests the existence of a methylene carbon atom attached to a phosphorus(v) centre. The direct proximity of two chemical inequivalent hydrogens attached to this atom (d δ 3.07; dd 3.38, ²J_{PH} 14.1, ²J_{HH} 7.7 Hz) unambiguously proves the presence of a >P=CH₂ moiety (Scheme 1).

The new methylenephosphorane **2** was conclusively characterized by X-ray crystallography‡ for which suitable crystals were obtained from hexane at room temperature (Fig. 2). As in all structurally investigated bis(ylene)phosphoranes,⁷ the central phosphorus atom exhibits a trigonal planar environment (sum of the angles at P = 360°). The methylene carbon atom, both the hydrogen atoms bonded to it, and the atoms P(1)–N(1)–C(12) are almost planar (mean deviation from plane = 0.005 Å). The

aryl substituent at N(1) is approximately orthogonal to the central π-bond system (the angle between the plane P(1)–N(1)–C(1)–C(2) and the aryl plane is 89°) and in an *E*-configuration relative to the (Me₃Si)₃C substituent at P(1), as is found in the iminophosphane **1** (Scheme 1). As compared to known imino(methylene)phosphoranes,⁸ the P(1)–N(1)-bond length [1.556(2) Å] in **2** is elongated which may be interpreted in terms of the small P(1)–N(1)–C(12) angle [121.2(2)°], whereas the P(1)–C(1) distance [1.612(3) Å] is significantly shorter. Other bond lengths and angles do not show any peculiarities.

While compound **2** is stable at ambient temperatures it easily isomerizes by heating a toluene solution of **2** at about 100 °C to give the corresponding imino(methylene)phosphorane **3**, which was isolated by recrystallization from non-polar solvents as a colourless powder (84.7% yield). The isomerization **2** → **3** by [1,3] silyl migration in the C–P=C triad results in chemical equivalence and the shielding of the two hydrogen atoms, as shown by ¹H NMR, (δ 2.0, ²J_{PH} 16.1 Hz), which reflects the change in hybridization from sp² to sp³. Furthermore the three equivalent silyl groups in **2** split into a set of three resonances in **3**. The tricoordinated phosphorus(v) centre maintains the characteristic low field shift in the ³¹P NMR spectrum (δ 129.5), whereby the chemical shift of the methylene carbon in the ¹³C NMR spectrum (δ 68.3, ¹J_{PC} 43.1 Hz) falls in the same spectral



Scheme 1 Reagents and conditions: i, Me₂SCH₂, THF, –40 °C, 82.6%; ii, toluene, 1 h, reflux, 84.7%

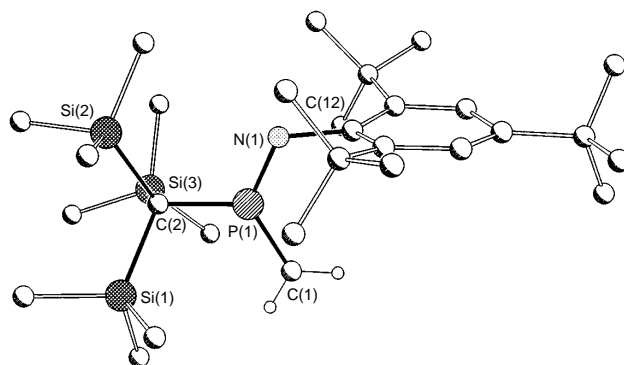


Fig. 2 Molecular structure of **2**. Disordered parts and methyl and aromatic hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.612(3), P(1)–N(1) 1.556(2), P(1)–C(2) 1.803(2); C(1)–P(1)–N(1) 124.8(1), C(1)–P(1)–C(2) 118.6(1), N(1)–P(1)–C(2) 116.7(1), P(1)–N(1)–C(12) 121.2(2), C(1)–P(1)–N(1)–C(12) 2.6(3), C(2)–P(1)–N(1)–C(12) –178.5(2).

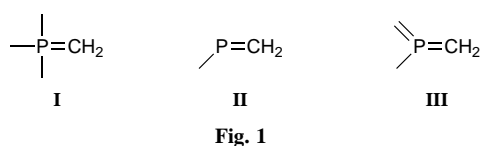


Fig. 1

region as in **2**. The composition of **3** was further deduced from the high-resolution mass spectrum.

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Footnotes

† *Spectroscopic data for 1*: Yield 76.1% mp 78–81 °C. ^{31}P NMR (C_6D_6): δ 500.4; ^1H NMR (C_6D_6): δ 0.53 (s, 27 H, SiMe_3), 1.50 (s, 9 H, *p*-Bu^t), 1.68 (s, 18 H, *o*-Bu^t), 7.67 (s, 2 H, C_6H_2); ^{13}C NMR (C_6D_6): δ 5.4 (d, $^3J_{\text{PC}}$ 4.4 Hz, SiMe_3), 32.2 (s, *o*-CCH₃), 34.6 (d, J_{PC} 2.6 Hz, *p*-CCH₃), 34.9 (s, *p*-CCH₃), 37.2 (s, *o*-CCH₃), 47.9 (d, $^1J_{\text{PC}}$ 100.3 Hz, *p*-CSi₃), 122.7 (s, *m*-Ar), 137.2 (d, $^3J_{\text{PC}}$ 11.7 Hz, *o*-Ar), 143.0 (s, *p*-Ar), 150.7 (d, $^2J_{\text{PC}}$ 15.7 Hz, *ipso*-Ar). MS (20 eV, EI) m/z (%) 521 (7%) [M^+], 290 (100) [PNMes*⁺]. For **2**: Yield 82.6%, mp 86–90 °C. ^{31}P NMR (C_6D_6): δ 157.8; ^1H NMR (C_6D_6): δ 0.56 (s, 27 H, SiMe_3), 1.51 (s, 9 H, *p*-Bu^t), 1.84 (s, 18 H, *o*-Bu^t), 3.10 (d, $^2J_{\text{HH}}$ 7.7 Hz, $^2J_{\text{PH}} < 1.0$ Hz, 1 H, P=CH₂), 3.38 (dd, $^2J_{\text{HH}}$ 7.7, $^2J_{\text{PH}}$ 14.1 Hz, 1 H, P=CH₂), 7.65 (d, $^6J_{\text{PH}}$ 2.2 Hz, 2 H, C_6H_2); ^{13}C NMR (C_6D_6): δ 6.0 (d, $^3J_{\text{PC}}$ 3.1 Hz, SiMe_3), 17.2 (d, $^1J_{\text{PC}}$ 28.5 Hz, P-CSi₃), 32.3 (d, $^7J_{\text{PC}}$ 1.7 Hz, *p*-CCH₃), 33.2 (d, $^5J_{\text{PC}}$ 1.4 Hz, *o*-CCH₃), 35.0 (d, $^6J_{\text{PH}}$ 1.9 Hz, *p*-CCH₃), 37.5 (d, $^4J_{\text{PH}}$ 2.3 Hz, *o*-CCH₃), 64.2 (d, $^1J_{\text{PC}}$ 108.2 Hz, P=CH₂), 123.0 (d, $^4J_{\text{PH}}$ 5.7 Hz, *m*-Ar), 141.5 (d, $^3J_{\text{PC}}$ 11.8 Hz, *o*-Ar), 142.2 (d, $^5J_{\text{PH}}$ 6.5 Hz, *p*-Ar), 146.2 (d, $^2J_{\text{PC}}$ 13.4 Hz, *ipso*-Ar). The CH₂ group is confirmed by a DEPT 135 experiment. MS (20 eV, EI) m/z (%) 535 (4) [M^+], 73 (100) [(CH₃)₃Si⁺] (Found: M^+ , 535.3614. $\text{C}_{29}\text{H}_{58}\text{N}_1\text{:Si}_3\text{P}_1$ requires 535.3620). For **3**: Yield 84.7%, mp 82–84 °C. ^{31}P NMR (C_6D_6): δ 129.5; ^1H NMR (C_6D_6): δ 0.29 (s, 9 H, SiMe_3), 0.31 (s, 9 H, SiMe_3), 0.39 (s, 9 H, SiMe_3), 1.51 (s, 9 H, *p*-Bu^t), 1.74 (s, 18 H, *o*-Bu^t), 2.0 (d, $^2J_{\text{PH}}$ 16.1 Hz, 2 H, SiMe_3CH_2), 7.55 (d, $^6J_{\text{PH}}$ 2.2 Hz, 2 H, C_6H_2); ^{13}C NMR (C_6D_6): δ 1.14 (d, $^3J_{\text{PC}}$ 3.4 Hz, P=CSiMe₃), 4.37 (d, $^3J_{\text{PC}}$ 4.9 Hz, P=CSiMe₃), 5.6 (d, $^3J_{\text{PC}}$ 5.0 Hz, SiMe_3CH_2), 21.7 (d, $^1J_{\text{PC}}$ 62.3 Hz, P-C(SiMe₃)H₂), 32.1 (d, $^7J_{\text{PC}}$ 1.2 Hz, *p*-CCH₃), 32.3 (d, $^5J_{\text{PC}}$ 1.7 Hz, *o*-CCH₃), 35.0 (d, $^6J_{\text{PH}}$ 1.5 Hz, *p*-CCH₃), 37.0 (d, $^4J_{\text{PH}}$ 1.9 Hz, *o*-CCH₃), 68.3 [d, $^1J_{\text{PC}}$ 43.1 Hz, P=C(SiMe₃)₂], 122.5 (d, $^4J_{\text{PH}}$ 4.2 Hz, *m*-Ar), 140.0 (d, $^3J_{\text{PC}}$ 10.3 Hz, *o*-Ar), 142.2 (d, $^5J_{\text{PH}}$ 5.0 Hz, *p*-Ar), 144.7 (d, $^2J_{\text{PC}}$ 10.3 Hz, *ipso*-Ar). MS (20 eV, EI) m/z (%) 535(3) [M^+], 73 (100) [(CH₃)₃Si⁺].

‡ *Crystal data for 1*: $\text{C}_{28}\text{H}_{56}\text{NPSi}_3$, $M = 522.0$, triclinic space group $P\bar{1}$ (no. 2), red crystals, dimensions $0.10 \times 0.20 \times 0.38$ mm³, $a = 9.814(3)$, $b = 13.580(5)$, $c = 14.113(4)$ Å, $\alpha = 64.38(3)$, $\beta = 82.94(2)$, $\gamma = 79.20(3)^\circ$, $U = 1664(1)$ Å³, $D_c = 1.04$ mg m⁻³, $Z = 2$, $\mu(\text{CuK}\alpha) = 1.87$ mm⁻¹, $T = 200(2)$ K, $F(000) = 576.5647$ symmetry independent reflections were used for the structure solution (direct methods) and refinement (full-matrix least-squares on F^2 , 316 parameters). Non-

hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a 'riding' model. $wR2 = 0.136$ ($R_1 = 0.049$ [$I > 2\sigma(I)$]). An empirical absorption correction on the basis of Ψ -scans was applied. Selected bond lengths (Å) and angles (°): P(1)–N(1) 1.566(3), P(1)–C(19) 1.837(3), N(1)–C(1) 1.429(4); P(1)–N(1)–C(1) 120.2(2), C(19)–P(1)–N(1) 110.4(2), C(1)–N(1)–P(1)–C(19)–178.7(2). For **2**: $\text{C}_{29}\text{H}_{58}\text{NPSi}_3$, $M = 536.0$, triclinic, space group $P\bar{1}$ (no. 2), yellow crystals, dimensions $0.60 \times 0.70 \times 0.80$ mm³, $a = 9.182(3)$, $b = 13.539(5)$, $c = 15.247(5)$ Å, $\alpha = 65.59(3)$, $\beta = 84.94(3)$, $\gamma = 82.42(3)^\circ$, $U = 1710(1)$ Å³, $D_c = 1.04$ mg m⁻³, $Z = 2$, $\mu(\text{MoK}\alpha) = 0.20$ mm⁻¹, $T = 293(2)$ K, $F(000) = 592.6025$ symmetry independent reflections were used for the structure solution (direct methods) and refinement (full-matrix least-squares on F^2 , 444 parameters, 540 restraints). Non-hydrogen atoms were refined anisotropically, H atoms localized by difference electron density and refined using a 'riding' model. $wR2 = 0.184$ ($R_1 = 0.062$ [$I > 2\sigma(I)$]). The *p*-Bu^t and the C(SiMe₃)₃ group were disordered. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/318.

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