Synthesis and Crystal Structures of *P*-Halogeno(imino)methylenephosphoranes $X{-}P(=NtBu_3C_6H_2)=C(SiMe_3)_2$ (X = Cl, Br, I)

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The iminophosphane $(Me_3Si)_3C{-}P{=}N{-}Mes^*$ (**1**) reacts with iodine to form the imino(methylene)phosphorane $I{-}P({=}N{-}Mes^*){=}C(SiMe_3)_2$ (**2**). Upon subsequent treatment with AgCl, the corresponding chloro derivative **3** is obtained. Chlorine/bromine exchange in **3** with bromotrimethylsilane affords the bromo analogue **4**. The structures of **2**, **3** and **4** were confirmed by X-ray crystal structure analysis; each of the compounds features a trigonal-planar phosphorus atom.

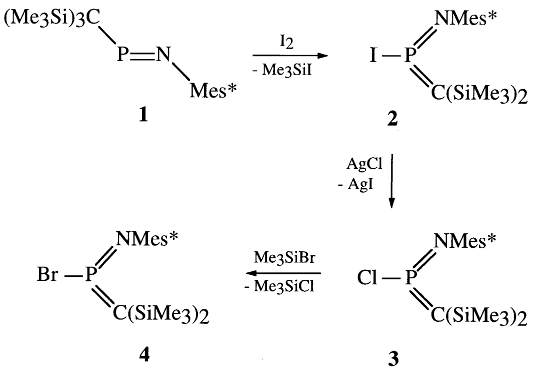
Introduction

The discovery of the first stable compound containing a trigonal-planar phosphorus(V) center in 1974[1] represents a landmark in organophosphorus chemistry. It opened the door to a rapid development of the chemistry of such compounds and structurally related derivatives[2 . Among these, bis(imino)-[3a] and bis(methylene)phosphoranes[3b] have attracted considerable attention, not only because they are valuable building blocks in organophosphorus and organometallic chemistry[4], but also because they are suitable precursors for monomeric metaphosphate analogues[5] and have found application in the catalysis of olefin polymerization[6]. In contrast, information concerning imino(methylene)phosphoranes, which feature both P−N- and P−C-pπ bonds, is comparatively sparse[3c]. Herein, we report on the synthesis and crystal structure analysis of the first *P*-halogeno(imino)methylenephosphoranes.

Results and Discussion

Treatment of the iminophosphane $(Me_3Si)_3C{-}P{=}N{-}Mes^*$ (**1**)[7], with iodine in THF at −40°C cleanly afforded the *P*-iodo(imino)methylenephosphorane **2**. Further reaction with AgCl in CH_2Cl_2 at 25°C resulted in I/Cl exchange of **2**, yielding the chloro derivative **3**. Subsequent reaction of **3** with Me_3SiBr led smoothly to the bromo derivative **4**. By crystallization from small volumes of *n*-hexane, compounds **2**−**4** were isolated as highly air- and moisture-sensitive, red (**2**), light-yellow (**3**), or orange (**4**) crystals (Scheme 1).

Scheme 1



Mes* = 2,4,6-$tBu_3C_6H_2$

The *P*-halogeno(imino)methylenephosphoranes **2**−**4** have been characterized on the basis of their elemental analyses and ^1H-, ^{13}C-, ^{31}P-NMR and mass-spectrometric data. Furthermore, the solid-state structures of compounds **2**−**4** have been determined by X-ray crystallography.

The ^{31}P-NMR chemical shifts of compounds **2**−**4** are observed at relatively low field values, which is typical for bis(ylene)phosphoranes[8]. The deshielding of the phosphorus nuclei on going from the iodo derivative **2** to the chloro analogue **3** [^{31}P: $\delta = 53.3$ (**2**) $<$ 65.2 (**4**) $<$ 72.5 (**3**)] is a characteristic feature of tetracoordinated P^V compounds[9].

The ^{13}C-NMR signals of the methylene carbon atoms, which are observed at lower fields than in "classical" methylenephosphoranes, show the inverse trend. A stronger carbon shielding is found on going from compound **2** to **4** to **3**, i.e. on increasing the electronegativities of the substituents [^{13}C: $\delta = 68.0$ (**2**) $>$ 58.2 (**4**) $>$ 51.7 (**3**)]. At the same time, a significant increase in the magnitude of $^1J(C,P)$ from 34.1 Hz (**2**) through 50.6 Hz (**4**) to 65.3 Hz (**3**) is observed. An inverse electronegativity effect on both ^{31}P- and ^{13}C-chemical shifts was also observed for substitution at the methylene carbon atom in imino(methylene)phosphoranes and was attributed to a polarization effect[10]. Similar trends in the $\delta^{31}P$, $\delta^{13}C$ and $^1J(C,P)$ values were observed in the corresponding *P*-halogenobis(methylene)phosphoranes[3a] and *P*-halogenobis(imino)phosphoranes ($\delta^{31}P$)[11]. As compared to compounds **2**−**4**, the ^{31}P nuclei in the former are less shielded by 30 to 65 ppm, while those in the latter appear more shielded by 30 to 70 ppm com-

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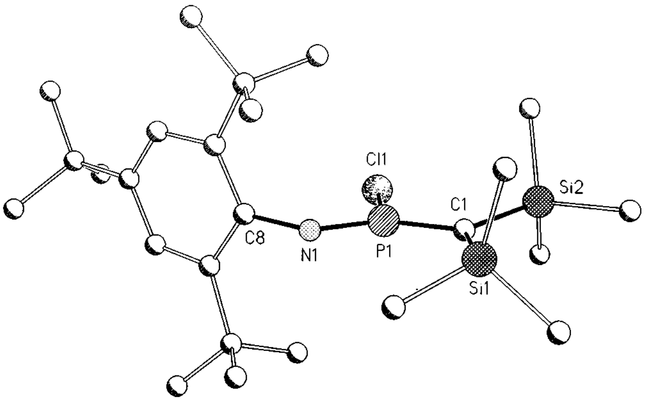
pared to the corresponding nuclei in the imino(methylene)phosphoranes. Furthermore, a detailed experimental and quantum-chemical study on the influence of phosphorus substituents on ^{15}N-NMR shifts in bis(imino)phosphoranes led to the conclusion that the substituent effects were transmitted by both inductive and mesomeric interactions, and revealed a correlation between increased shielding and higher ylidic character of the ylene bond[12].

Table 1. Representative NMR data of *P*-halogenobis(ylidene)phosphoranes X−P(=A)=B

	δ^{31}P	δ^{13}C(P=C)	$^1J_{PC}$ [Hz]
X = Cl; A = B = N	−18.5	−	−
X = Br; A = B = N	−30.2	−	−
X = I; A = B = N	−42.9	−	−
X = Cl; A = N; B = C	72.5	51.7	65.3
X = Br; A = N; B = C	65.2	58.2	50.6
X = I; A = N; B = C	53.3	68.0	34.1
X = Cl; A = B = C	136.8	83.3	38.6
X = Br; A = B = C	122.5	91.3	30.8
X = I; A = B = C	84.7	102.9	23.5

The constitutions of compounds **2−4** were further corroborated by single-crystal X-ray diffraction studies. The phosphorus and carbon atoms of the imino(methylene) moieties exhibit the expected trigonal-planar geometries (Figure 1). The atoms of the CSi_2 and P−N−C$_{ipso}$ moieties are almost coplanar (dihedral angle 4.4−5.6°), while the aryl substituent is approximately orthogonal to the central π-bond system (angle between the plane P−N−C$_{ipso}$ and the aryl plane: 88.8−91.7°). The P−N double bond adopts a (*Z*) configuration, as is observed in *P*-halogeno(imino)phosphanes[13]. The P−halogen distances [**3**: 206.9(2), **4**: 223.1(1), **2**: 242.9(1) pm] are shortened in comparison with the corresponding bond lengths in bis(imino)phosphoranes[11], but are longer than those in bis(methylene)phosphoranes[14]. The P−N [151.8(3)−153.1(4) pm] and P−C [162.4(4)−164.2(4) pm] distances, as well as the central C−P−N valence angles [129.2(2)−130.5(2)°] represent typical structural features common to both bis(imino)- and bis(methylene)phosphoranes[3a][3b]. The other bond lengths and angles show no peculiarities.

Figure 1. Crystal structure of the imino(methylene)phosphorane **3**[a]



[a] Selected bond lengths [pm] and bond angles [°]: **3**: P(1)−Cl(1) 206.9(2), P(1)−N(1) 152.7(4), P(1)−C(1) 162.4(4), N(1)−C(8) 142.6(5); Cl(1)−P(1)−N(1) 113.1(1), Cl(1)−P(1)−C(1) 116.3(2), N(1)−P(1)−C(1) 130.5(2), P(1)−N(1)−C(8) 127.0(3). − **2**: P(1)−I(1) 242.9(1), P(1)−N(1) 153.1(4), P(1)−C(1) 164.2(4), N(1)−C(8) 142.3(5), I(1)−P(1)−N(1) 112.0(2), I(1)−P(1)−C(1) 118.8(2), N(1)−P(1)−C(1) 129.2(2), P(1)−N(1)−C(8) 125.6(3). − **4**: P(1)−Br(1) 223.1(1), P(1)−N(1) 151.8(3), P(1)−C(1) 162.7(4), N(1)−C(8) 140.8(5); Br(1)−P(1)−N(1) 112.1(1), Br(1)−P(1)−C(1) 117.5(2), N(1)−P(1)−C(1) 130.4(2), P(1)−N(1)−C(8) 127.8(3).

Regarding the potential synthetic utility of these halogeno(imino)methylenephosphoranes, one can expect them to undergo nucleophilic displacement reactions as well as thermally induced β eliminations of silyl halide. Both of these strategies are currently under investigation.

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Experimental Section

All experiments were carried out with the exclusion of air and moisture under argon. Solvents were purified and dried according to standard methods. Compound **1** was prepared according to a literature procedure[7]. − NMR: Bruker AMX 300 (^{31}P: 121.5 MHz, external standard 85% H_3PO_4; ^{1}H: 300.1 MHz, external standard TMS; ^{13}C: 75.5 MHz, external standard TMS). − MS: Kratos Instruments Concept 1 H, Kratos Instruments MS 50, VG Instruments VG 12-250. − Elemental analyses: Analytisches Laboratorium Pascher. − Melting points were determined in sealed glass capillaries and are uncorrected.

Iodo[(2,4,6-tri-tert-butylphenyl)imino][bis(trimethylsilyl)methylene]phosphorane (**2**): To a solution of iminophosphane **1** (2.61 g, 5 mmol) in 20 ml of THF, an equimolar amount of iodine, dissolved in 20 ml of THF, was added at −40°C. The reaction mixture was then allowed to warm to room temp. under stirring. The solvent and all volatile components were removed in vacuo and the remaining residue was taken up in 30 ml of *n*-hexane. Storage of the resulting solution at 0°C led to the deposition of **2** in the form of red crystals, which were found to be suitable for X-ray structural analysis. − Yield 2.57 g (89.3%), m.p. 111−113°C. − ^{31}P NMR (C_6D_6): δ = 53.3. − ^{1}H NMR (C_6D_6): δ = 0.57 (s, 18 H, $SiMe_3$), 1.47 (s, 9 H, *p*-*t*Bu), 1.72 (s, 18 H, *o*-*t*Bu), 7.61 (d, $^5J_{HP}$ = 5.8 Hz, 2 H, C_6H_2). − ^{13}C NMR (C_6D_6): δ = 5.0 (d, $^3J_{PC}$ = 5.8 Hz, $SiMe_3$), 32.1 (d, J_{PC} = 4.2 Hz, *p*-CCH_3), 32.9 (d, $^5J_{PC}$ = 2.7 Hz, *o*-CCH_3), 35.3 (d, J_{PC} = 4.4 Hz, *p*-CCH_3), 37.2 (d, $^4J_{PC}$ = 4.7 Hz, *o*-CCH_3), 68.0 (d, $^1J_{PC}$ = 34.3 Hz, P=C), 123.0 (d, $^4J_{PC}$ = 11.8 Hz, *m*-Ar), 143.7 (d, $^3J_{PC}$ = 19.1 Hz, *o*-Ar), 145.7 (d, $^5J_{PC}$ = 14.1 Hz, *p*-Ar), 145.8 (d, $^2J_{PC}$ = 24.1 Hz, *ipso*-Ar). − MS (70 eV); *m*/*z* (%): 574 (49) [M^+], 290 (100) [$t\mathrm{Bu}_3C_6H_2NP^+$]. − $C_{25}H_{47}INPSi_2$ (594.7): calcd. C 52.15, H 8.22; found C 52.28, H 8.26.

Chloro[(2,4,6-tri-tert-butylphenyl)imino][bis(trimethylsilyl)methylene]phosphorane (**3**): To a solution of imino(methylene)phosphorane **2** (1.44 g, 2.5 mmol) in 10 ml of CH_2Cl_2, AgCl (0.39 g, 2.7 mmol) was added at room temp. and the suspension was stirred for 12 h. The solvent and the volatiles were then removed in vacuo and the remaining residue was taken up in 20 ml of *n*-hexane. The insoluble silver salt (AgI) was separated by filtration. Storage of the filtrate at 0°C resulted in the deposition of **3** in the form of yellow crystals. − Yield: 1.05 g (86.7%), m.p. 81−82°C. − ^{31}P NMR (C_6D_6): δ = 72.5. − ^{1}H NMR (C_6D_6): δ = 0.40 (s, 9 H, $SiMe_3$), 0.60 (s, 9 H, $SiMe_3$), 1.45 (s, 9 H, *p*-*t*Bu), 1.73 (s, 18 H, *o*-*t*Bu), 7.63 (d, $^5J_{PH}$ = 3.3 Hz, 2 H, C_6H_2). − ^{13}C NMR (C_6D_6): δ = 4.2 (d, $^3J_{PC}$ = 7.0 Hz, $SiMe_3$), 4.6 (d, $^3J_{PC}$ = 2.0 Hz, $SiMe_3$), 32.1 (d, J_{PC} = 3.0, *p*-CCH_3), 32.2 (d, $^5J_{PC}$ = 2.3 Hz, *o*-CCH_3), 35.2 (d, J_{PC} = 3.4 Hz, *p*-CCH_3), 36.9 (d, $^4J_{PC}$ = 3.8 Hz, *o*-CCH_3), 51.7

(d, $^1J_{PC}$ = 65.3 Hz, P=C), 122.7 (d, $^4J_{PC}$ = 8.9 Hz, *m*-Ar), 140.8 (d, $^2J_{PC}$ = 23.3 Hz, *ipso*-Ar), 142.9 (d, $^3J_{PC}$ = 15.7 Hz, *o*-Ar), 145.0 (d, $^5J_{PC}$ = 10.7 Hz, *p*-Ar). − MS (70 eV); *m*/*z* (%): 483 (11) [M$^+$], 290 (100) [tBu$_3$C$_6$H$_2$NP$^+$]. − $C_{25}H_{47}ClNPSi_2$ (484.2): calcd. C 62.01, H 9.78; found C 62.22, H 9.84.

Bromo[(2,4,6-tri-tert-butylphenyl)imino][bis(trimethylsilyl)-methylene]phosphorane (**4**): To a solution of **3** (1.21 g, 2.5 mmol) in 10 ml of THF was added an equimolar amount of Me_3SiBr and the reaction mixture was stirred for 2 h at room temp. The solvent and the halosilanes were then removed in vacuo and the residue was crystallized from a small volume of *n*-hexane. The product was obtained as an orange, crystalline solid. − Yield 1.16 g (87.5%), m.p. 99−101°C. − ^{31}P NMR (C_6D_6): δ = 65.2. − ^{1}H NMR (C_6D_6): δ = 0.40 (s, 9 H, SiMe$_3$), 0.60 (s, 9 H, SiMe$_3$), 1.45 (s, 9 H, *p*-*t*Bu), 1.73 (s, 18 H, *o*-*t*Bu), 7.62 (d, $^5J_{PH}$ = 3.6 Hz, 2 H, C_6H_2). − ^{13}C NMR (C_6D_6): δ = 4.6 (s, SiMe$_3$), 5.0 (d, $^3J_{PC}$ = 5.7 Hz, SiMe$_3$), 32.1 (d, J_{PC} = 6.1 Hz, *p*-C*C*H$_3$), 32.5 (d, $^5J_{PC}$ = 2.6 Hz, *o*-C*C*H$_3$), 35.2 (d, J_{PC} = 3.8 Hz, *p*-*C*CH$_3$), 37.0 (d, $^4J_{PC}$ = 3.8 Hz, *o*-*C*CH$_3$), 58.2 (d, $^1J_{PC}$ = 50.6 Hz, P=C), 122.8 (d, $^4J_{PC}$ = 10.2 Hz, *m*-Ar), 142.0 (d, $^2J_{PC}$ = 24.4 Hz, *ipso*-Ar), 143.2 (d, $^3J_{PC}$ = 17.1 Hz, *o*-Ar), 145.3 (d, $^5J_{PC}$ = 12.2 Hz, *p*-Ar). − MS (70 eV); *m*/*z* (%): 527 (52) [M$^+$], 290 (100) [tBu$_3$C$_6$H$_2$NP$^+$]. − $C_{25}H_{47}BrNPSi_2$ (528.7): calcd. C 56.79, H 8.96; found C 56.98, H 9.04.

Crystal-Structure Analyses. − Crystal Data: **2**: $C_{25}H_{47}INPSi_2$, M_r = 575.7, red tablets, 0.60 × 0.50 × 0.35 mm; monoclinic, space group $P2_1/c$ (No. 14), a = 8.853(3), b = 33.25(1), c = 10.666(4) Å, β = 99.75(3)°, V = 3094(2) Å^3, Z = 4, D_x = 1.24 Mg m^{-3}, μ(Mo-K_α) = 1.18 mm^{-1}, T = 293(2) K, F(000) = 1200, number of reflections: 7843 (7145 independent, R_{int} = 0.025), $R(F)$ = 0.054, $wR(F^2$ all data) = 0.153 (266 parameters, 50 restraints). − **3**: $C_{25}H_{47}ClNPSi_2$, M_r = 484.2, yellow blocks, 0.40 × 0.30 × 0.20 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 8.902(2), b = 32.825(5), c = 10.516(1) Å, β = 98.95(1)°, V = 3035.4(9) Å^3, Z = 4, D_x = 1.06 Mg m^{-3}, μ(Cu-K_α) = 2.44 mm^{-1}, T = 293(2) K, F(000) = 1056, number of reflections: 4845 (4442 independent, R_{int} = 0.096), $R(F)$ = 0.075, $wR(F^2$ all data) = 0.232 (266 parameters, 62 restraints). − **4**: $C_{25}H_{47}BrNPSi_2$, M_r = 528.7, orange blocks, 0.80 × 0.70 × 0.50 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 8.851(2), b = 32.87(1), c = 10.556(4) Å, β = 99.15(3)°, V = 3032(2) Å^3, Z = 4, D_x = 1.16 Mg m^{-3}, μ(Mo-K_α) = 1.50 mm^{-1}, T = 293(2) K, F(000) = 1128, number of reflections: 5622 (5325 independent, R_{int} = 0.053), $R(F)$ = 0.055, $wR(F^2$ all data) = 0.151 (266 parameters, 62 restraints). An absorption correction on the basis of Ψ scans was applied.

Structure Solution and Refinement: The structures were solved by direct methods and refined anisotropically on F^2 (program system: SHELXTL-Plus[15], SHELXL-93[16]). Non-hydrogen atoms were refined anisotropically; H atoms were refined using a riding model; the *tert*-butyl groups were found to be disordered. Full details of the crystal structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100474 (**2**, **3**, **4**). Copies may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44(0)1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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