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1,3-Dipolarophile Character of an Extremely Bulky Phosphaalkyne Mes*C≡P (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$) Leading to the Formation of 1,2,4-Diazaphospholes with Unique Hydrogen Bonding Properties

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2-(2,4,6-Tri-*tert*-butylphenyl)-1-phosphaethyne was allowed to react with trimethylsilyldiazomethane derivatives to afford the corresponding 1,2,4-diazaphospholes via [2+3] cycloaddition followed by H/SiMe$_3$ migration, in spite of the steric encumbrance of the substrates. The aromatic character of 1,2,4-diazaphosphole is indicated by the NMR spectroscopic data and the X-ray structure analysis as well as by theoretical calculation to confirm the planar delocalized ring skeleton. The crystal structure of the obtained 1,2,4-diazaphospholes showed remarkable hydrogen bonding character in relation to molecular aggregation due to the presence of bulky aryl groups.

Introduction

Phosphaalkynes [R–C≡P] are only stable if protected by bulky substituents such as the *tert*-butyl or 2,4,6-tri-*tert*-butylphenyl (Mes*) group. Cycloaddition reactions of such phosphaalkynes have extensively been developed to provide a number of P-heterocyclic compounds which have widely been utilized especially in coordination and organometallic chemistry.[1] Throughout the investigation of phosphaalkynes, *tert*-butylphosphaacetylene [*t*BuC≡P] has played a principal role in the synthesis of P-heterocyclic compounds because of its moderate stability and desirable reactivity,[1,2] and a number of [2+1], [2+2], [2+3], and [2+4] cycloadditions have been observed so far. On the contrary, a phosphaalkyne bearing an extremely bulky Mes* group (**1**, [Mes*C≡P])[3] showed considerably low reactivity in comparison with *t*BuC≡P. Whereas *t*BuC≡P reacts with a diene to afford the corresponding [2+4] adduct,[1] compound **1** gave no six-membered ring compound as a result of Diels–Alder cycloaddition.[4] In addition to the low reactivity and high stability of **1**, the presence of the Mes* group often causes unusual reactions. In the [2+1] cycloaddition with compound **1**, expulsion of the P atom from the initially formed three-membered phosphirene intermediate leads to the formation of the corresponding acetylene derivative **2**,[5,6] probably because of the congestion around the phosphorus, whereas *t*BuC≡P reacts with a carbene (or its heavier congener) to afford the corresponding three-membered phosphirene.[1] Although the presence of bulky substituents in **1** induces such unexpected conversion as to give **3**[6] and **4**[7] in an attempted synthesis of P-heterocyclic compounds, we have utilized **1** for investigations of unique P-heterocyclic diradicals **5**[8] and a monoradical **6**,[8e] which shows the advantage of the introduced Mes* group (Figure 1). Thus, these individual properties of the bulky phosphaalkyne **1** prompted us to explore its unique character, leading to novel findings in the chemistry of P-heterocycles.

In this paper we describe [2+3] additions of compound **1** and trimethylsilyldiazomethane derivatives as dipolar CN$_2$ reagents to demonstrate the ordinary reaction mode of phosphaalkynes[1] leading to important results on novel extremely bulky 1,2,4-diazaphospholes. In these reactions, diazoalkanes overcome the shielding effect of the Mes* group, leading to regioselective cycloaddition for 1,2,4-diazaphospholes, and the formal control of silyl and hydrogen migrations has been accomplished by employing neutral and lithiated trimethylsilyldiazomethanes.[9] Structures of the newly synthesized 1,2,4-diazaphospholes, one of which carries substantial aromatic character,[1,10,11] are discussed in terms of hydrogen-bonding control of molecular aggregation in the presence of the Mes* group. Several 1,2,4-diazaphosphole nucleosides **7** are known, and even the X-ray structures have been reported for **7A** and **7C**. Furthermore, thiocarboxamide **7C** shows antitumor activity against L1210 in vivo,[12] and therefore the newly obtained 1,2,4-diazaphospholes might be available for drug design (Figure 2).

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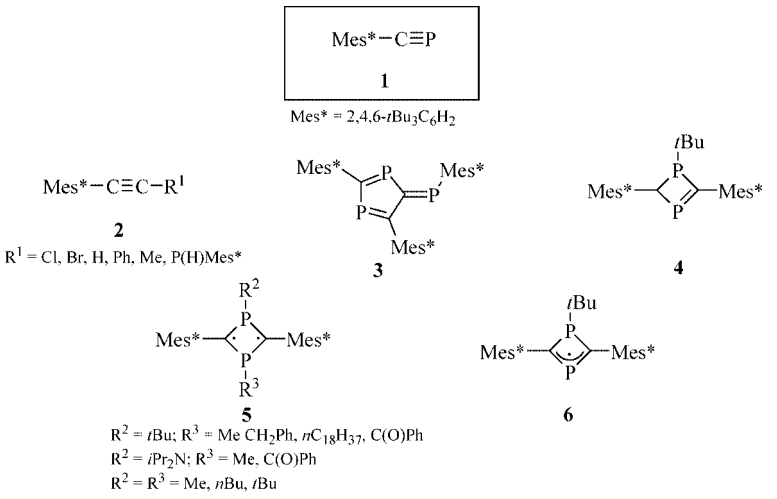


Figure 1. Selected products from phosphaalkyne **1**.

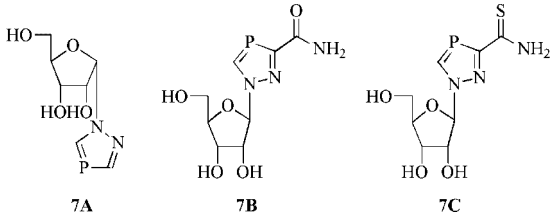


Figure 2. 1,2,4-Diazaphosphole nucleosides **7**.

Results and Discussion

1,3-Dipolar Cycloaddition of Mes*C≡P (1) with $Me_3Si(CN_2)H$

Phosphaalkyne **1**, prepared according to our previous reports,[8a,8b] was allowed to react with trimethylsilyldiazomethane in a similar manner to the reported procedures,[13] and 1-trimethylsilyl-1,2,4-diazaphosphole **9** was formed through intermediate **8** almost quantitatively after the solvent was removed (Scheme 1). ^1H and ^{13}C NMR spectroscopic data of **9** confirm the presence of $NSiMe_3$ and =*C*H groups as well as a 1*H*-1,2,4-diazaphosphole structure. The migration of the silyl group has been observed in previous studies.[13,14] Actually, the total energy of theoretically optimized structures for model compounds **8x**, **9x**, and **9xx** suggested facile conversion from **8** to **9** as well as the migratory aptitude of the silyl group (Figure 3).[15–17] In the ^{13}C NMR spectroscopic data of **9**, the H-substituted carbon atom C(sp^2)-3 has a slightly smaller $^1J_{PC}$ constant ($^1J_{PC}$ = 53.7 Hz, *C*H) than the C-5 ($^1J_{PC}$ = 59.7 Hz, *C*Mes*), which might represent a 5-substituted 1*H*-1,2,4-diazaphosphole.[18–20] The exclusive formation of **9** without a 1,2,3-diazaphosphole isomer indicates that regioselective [2+3] cycloaddition of **1** with the CN_2 moiety proceeds under kinetic control by the bulky Mes* group[21] followed by subsequent silyl group migration[13,14,16] to gain higher aromatic stabilization. The N–Si bond in **9** is sensitive to alcohol and moisture, and desilylation took place to afford **10** by addition of ethanol (Scheme 1).[13,22] In the ^1H NMR spectrum, the *o-tert*-butyl groups in both **9** and **10** showed a shift to a higher field, because of the aromatic character of the 1,2,4-diazaphosphole ring. A more detailed discussion about structures in relation to aggregation in solution is in progress.

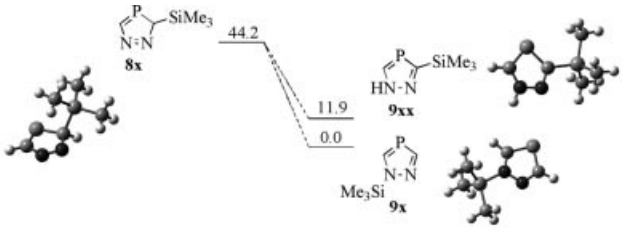
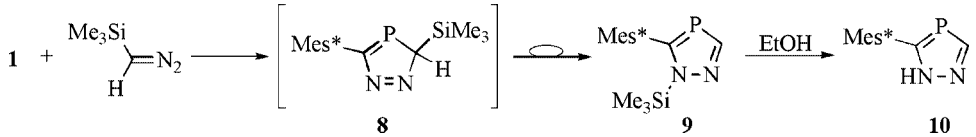


Figure 3. Energy profile (kcal mol^{-1}) for the optimized structures **8x**, **9x**, and **9xx** at the B3LYP/6-31+G(d) level.

Molecular and Crystal Structure of a Bulky 1,2,4-Diazaphosphole 10

The structure of **10** was confirmed by X-ray crystallography. Figure 4a shows one of the three independent molecules of **10** (molecule A) in the unit cell. Table 1 shows se-



Scheme 1. Reaction of **1** with trimethylsilyldiazomethane.

lected bond lengths and angles of **10**, indicating that the parameters are similar to the previously reported 1,2,4-diazaphospholes.[12,23–25] The parameters indicate a relatively large contribution of a 5-substituted 1*H*-1,2,4-diazaphosphole structure: the P1–C1 bonds are longer than the P1–C2 distances, and correspondingly the N1–C1 lengths are shorter than the N2–C2 values. Such bonding properties are almost equal to the previously analyzed structures of nonsubstituted or 3,5-disubstituted 1,2,4-diazaphospholes.[23] The diazaphosphole ring is almost planar [Θ(P–C1–N1–N2) = 0.3–0.7°, Θ(P–C2–N1–N2) = 0.6–1.0°], and the Mes* ring is perpendicular to the five-membered ring (dihedral angle: 89.8–90.0°) in order to reduce the steric congestion. As displayed in Figure 4b, three molecules (A, B, and C) form a trimer structure connected by three N–H···N hydrogen bonds (H···N 1.945–1.971 Å; N···N 2.861–2.867 Å). Such a trimer structure of 1,2,4-diazaphospholes has never been reported so far, whereas pyrazoles, a carbon congener of diazaphospholes, show several aggregation modes.[26] The trimer seems to be additionally stabilized by C–H···π_{Mes*} interactions, with H···π_{Mes*} distances of 2.763, 2.788, and 2.804 Å.[26] Therefore, the first characterized trimer structure[27] of 1,2,4-diazaphosphole **10** in the crystalline state reflects the effect of the Mes* group in determining the position of the atoms as a result of CH–π interaction.[28]

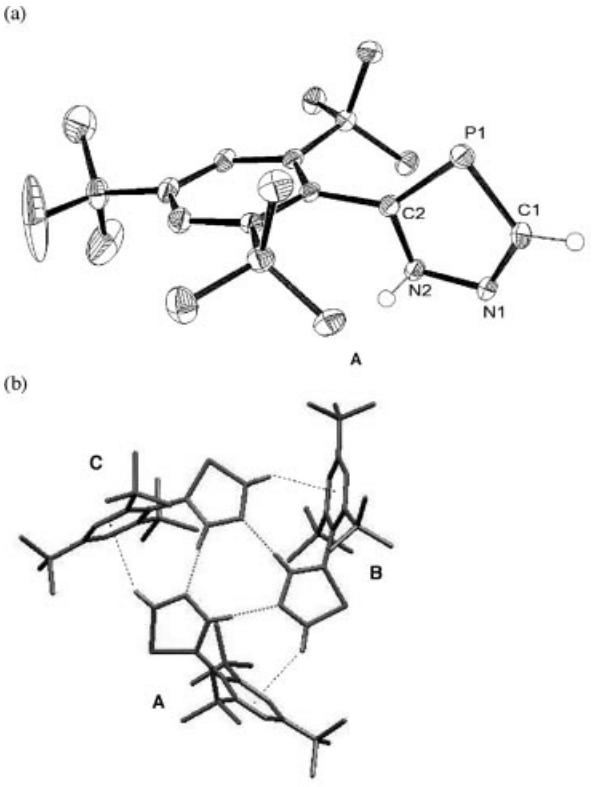


Figure 4. (a) An ORTEP drawing for **10** (50% probability ellipsoids). One of the three independent molecules (**A**) is displayed. Hydrogen atoms in the Mes* group are omitted for clarity. Atom numbering is independent of the nomenclature of 1,2,4-diazaphosphole. (b) Hydrogen-bonded trimer structure of **10** in the crystalline state. ····· NH···N interaction. - - - CH···π_{Mes*} interaction.

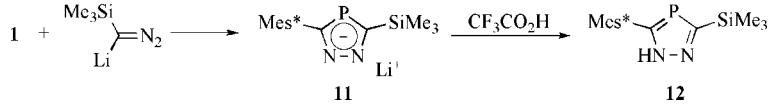
Table 1. Selected bond lengths [Å] and angles [°] of **10**.

Parameter	Molecule A	Molecule B	Molecule C
P1–C1	1.753(2)	1752(2)	1.754(2)
P1–C2	1.740(2)	1.742(2)	1.745(2)
N1–N2	1.350(2)	1.344(2)	1.349(2)
N1–C1	1.324(3)	1.329(3)	1.328(3)
N2–C2	1.344(2)	1.340(2)	1.343(3)
C2–C_{Mes*}	1.499(3)	1.498(3)	1.493(3)
C1–P1–C2	86.45(9)	86.36(9)	86.61(9)
N2–N1–C1	108.4(2)	108.0(2)	108.4(2)
N1–N2–C2	117.7(2)	117.8(2)	118.1(2)
P1–C1–N1	116.6(2)	116.8(1)	116.4(2)
P1–C2–N2	110.9(1)	111.0(1)	110.6(1)
P1–C2–C_{Mes*}	135.0(1)	134.7(1)	134.9(1)
N2–C2–C_{Mes*}	114.1(2)	114.3(2)	114.5(2)

Preparation and Structure of Bulky 3-Trimethylsilyl-1,2,4-diazaphosphole 12

The reaction of **1** with lithiated trimethylsilyldiazomethane [$Me_3Si(CN_2)Li$] (Scheme 2) gave a different result from that described above. Compound **1** was allowed to react with freshly prepared $Me_3Si(CN_2)Li$ to generate diazaphospholido anion **11**, which was observed by ^{31}P NMR (δ_P = 135.0 ppm), at a value close to that of a fundamental 1,2,4-diazaphospholido anion.[23,29] The anion **11** was then treated with trifluoroacetic acid to afford 3-trimethylsilyl-1,2,4-diazaphosphole **12** in a moderate yield together with a small amount of **10**. The formation of **10** would also have been possible by using nonlithiated trimethylsilyldiazomethane (Scheme 1).

The crystal structure of **12** (Figure 5) is a dimer connected by two N–H···N hydrogen bonds (H···N 2.105 Å; N···N 2.817 Å). A similar dimer structure was known for 3,5-di-*tert*-butyl-1,2,4-diazaphosphole,[23] and the silyl group appears to be effective in constructing the dimer structure of 1,2,4-diazaphosphole. The P–C1 bond is longer than the P–C2 distance, indicating the predominance of the 5-substituted 1*H*-1,2,4-diazaphosphole structure. On the other hand, almost the same bond lengths were observed for N1–C1 and N2–C2, probably because of the π-accepting effect of the silyl group to stabilize the polarized N^-H^+ structure.[30] In the ^{13}C NMR spectrum, the C(sp^2) atoms in the five-membered ring did not give sharp signals because of signal broadening, probably indicating effects of



Scheme 2. Reaction of **1** with lithiated trimethylsilyldiazomethane.

the dimer structure of **12** in solution. The five-membered ring is planar [Θ(P–C1–N1–N2) = 0.1(4)°, Θ(P–C2–N1–N2) = 0.3(4)°], and the Mes* ring is perpendicular to the five-membered ring (dihedral angle: 90.0°). Compound **12** is an isomer of **9**, and the silyl- and hydrogen rearrangements of **8** can be formally controlled by the reaction conditions.[9] In contrast to the observed predominant migratory aptitude of the silyl group in the rearrangement from **8** to **9** (Scheme 1), the Si–C bond was tolerant to alcoholysis with wet thf in ethanol.

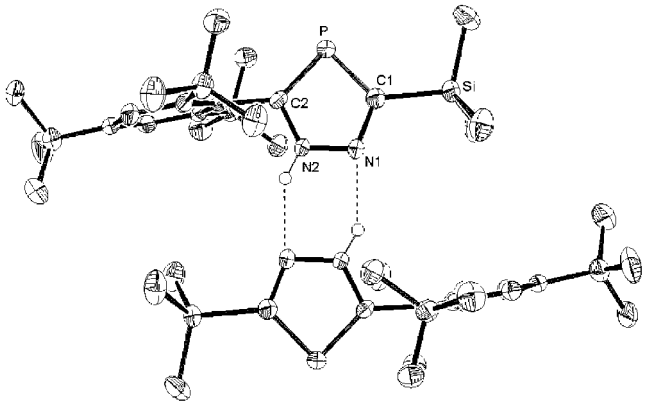


Figure 5. An ORTEP drawing for **12** with dimer structure (50% probability ellipsoids). Hydrogen atoms in the Mes* and the $SiMe_3$ groups are omitted for clarity. Atom numbering is independent from the nomenclature of 1,2,4-diazaphosphole. Typical bond lengths [Å] and angles [°]: P–C1 1.763(4), P–C2 1.744(3), Si–C1 1.886(4), N1–N2 1.349(4), N1–C1 1.340(4), N2–C2 1.337(4), C2–C_{Mes*} 1.500(5), C1–P–C2 87.8(2), N2–N1–C1 109.2(3), N1–N2–C2 118.7(3), P–C1–Si 129.2(2), P–C1–N1 114.4(3), Si–C1–N1 116.4(3), P–C2–N2 109.9(3), P–C2–C_{Mes*} 136.5(3), N2–C2–C_{Mes*} 113.6(3).

Conclusions

We have demonstrated ordinary [2+3] cycloadditions of phosphaalkyne **1** with diazomethane derivatives affording 1,2,4-diazaphospholes in spite of the presence of an extremely bulky Mes* group. Neutral or lithiated trimethylsilyldiazomethane operated on the structure of the [2+3] adduct to give almost selectively **10** or **12**, respectively. The crystal structure of **10** exhibits the first example of a trimer structure of 1,2,4-diazaphosphole resulting from the presence of the bulky aryl substituent, whereas **12** forms a dimer structure. Although 1,2,4-diazaphosphole is an inherently stable compound and does not require kinetic stabilization, the Mes* group might be effective in discovering novel characteristics of 1,2,4-diazaphospholes which operate molecular assemblies. Attempts to utilize **9**–**12** as unique P-heterocyclic reagents for coordination chemistry are in progress.[1,12,24,31]

Experimental Section

General Methods: All manipulations were carried out under an argon atmosphere by means of standard Schlenk techniques or in a glove box. All solvents employed were dried by appropriate methods. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker Avance 400 spectrometer with Me_4Si (^1H, ^{13}C) and H_3PO_4 (^{31}P) as internal or external standards. Mass spectra were recorded with a Bruker APEX3 spectrometer. Compound **1** was prepared by the procedures described in the literature.[8a,8b]

Reaction of 1 with $Me_3Si(CN_2)H$: To a solution of **1** (91.4 mg, 0.317 mmol) in thf (5 mL) was added trimethylsilyldiazomethane (0.38 mmol, 2.0 M solution in hexane,) at room temperature. After stirring for 30 min, volatiles were removed, and the residual amorphous solid **9** was characterized by NMR spectroscopy. Ethanol (2 mL) was added to **9**, and the volatiles were removed. The residual solid containing **10** was dissolved in chloroform (20 mL), and insoluble materials were filtered off. The chloroform solution was concentrated, and the residue was washed with hexane to obtain **10** as colorless crystals. Compound **10** was purified by silica-gel column chromatography (hexane/EtOAc = 1:1) (total 77.4 mg, 74%). **9**: Colorless amorphous solid: $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6): δ = 116.6 ppm. ^1H NMR (400 MHz, C_6D_6): δ = 0.19 (s, 9 H, $SiMe_3$), 1.25 (s, 18 H, *o*-*t*Bu), 1.32 (s, 9 H, *p*-*t*Bu), 7.65 (s, 2 H, Mes*), 8.42 (d, $^2J_{PH}$ = 39.5 Hz, 1 H, CH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ = –0.63 (s, $SiMe_3$), 31.9 (s, *p*-C*Me*$_3$), 34.2 (d, $^5J_{PC}$ = 3.5 Hz, *o*-C*Me*$_3$), 35.3 (s, *p*-*C*Me$_3$), 38.3 (s, *o*-*C*Me$_3$), 122.6 (s, *m*-Mes*), 133.2 (d, $^2J_{PC}$ = 21.3 Hz, *ipso*-Mes*), 149.3 (s, *p*-Mes*), 149.6 (d, $^3J_{PC}$ = 3.0 Hz, *o*-Mes*), 162.1 (d, $^1J_{PC}$ = 53.7 Hz, *C*H), 182.0 (d, $^1J_{PC}$ = 59.7 Hz, *C*Mes*) ppm. ESI-MS: calcd. for $[M + Na]^+$ ($C_{23}H_{39}N_2PSi$ + Na) 425.2512; found 425.2511. **10**: Colorless prisms (hexane), m.p. 255–256 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 106.7 ppm. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.12 (s, 18 H, *o*-*t*Bu), 1.38 (s, 9 H, *p*-*t*Bu), 7.56 (s, 2 H, Mes*), 8.32 (d, $^2J_{PH}$ = 45.3 Hz, 1 H, CH), 12.0 (brs, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 31.8 (s, *p*-C*Me*$_3$), 33.4 (d, $^5J_{PC}$ = 3.7 Hz, *o*-C*Me*$_3$), 35.6 (s, *p*-*C*Me$_3$), 38.1 (s, *o*-*C*Me$_3$), 122.7 (s, *m*-Mes*), 127.7 (d, $^2J_{PC}$ = 16.2 Hz, *ipso*-Mes*), 150.7 (d, $^3J_{PC}$ = 3.6 Hz, *o*-Mes*), 151.0 (s, *p*-Mes*), 162.5 (d, $^1J_{PC}$ = 68.5 Hz, *C*Mes*), 174.7 (d, $^1J_{PC}$ = 49.3 Hz, *C*H) ppm. ESI-MS: calcd. for $[M + Na]^+$ ($C_{20}H_{31}N_2P$ + Na) 353.2117, found 353.2116. $C_{20}H_{31}N_2P$ (330.45): calcd. C 72.69, H 9.46, N 8.48; found C 72.52, H 9.46, N 8.50.

Reaction of 1 with $Me_3Si(CN_2)Li$: To a solution of trimethylsilyldiazomethane (0.10 mmol) in thf (2 mL) was added butyllithium (0.10 mmol, 1.6 M solution in hexane) at –78 °C and stirred for 5 min. To the mixture was added **1** (30 mg, 0.10 mmol) in thf (1 mL) at –78 °C and stirred for 5 min. The reaction mixture was warmed to room temperature and an aliquot was removed via syringe to observe **11** by ^{31}P NMR (δ_P = 135.0). The mixture was treated with trifluoroacetic acid (0.20 mmol) and volatiles were removed in vacuo. The residual materials were purified by silica-gel column chromatography (hexane/EtOAc = 1:1) to afford **12** (28 mg, 66%) and **10** (3 mg, 9%). Pure **12** was obtained by dissolving in hexane (**10** is less soluble in hexane). **12**: Colorless prisms (hexane), m.p. 251–253 °C; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 141.2 (br) ppm. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.39 (s, 9 H, $SiMe_3$), 1.13 (s, 18 H, *o*-*t*Bu), 1.37 (s, 9 H, *p*-*t*Bu), 7.53 (s, 2 H, Mes*), 11.2 (brs, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 0.04 (s, $SiMe_3$), 31.8 (s, *p*-C*Me*$_3$), 33.8 (d, $^5J_{PC}$ = 2.9 Hz, *o*-C*Me*$_3$), 35.4 (s, *p*-*C*Me$_3$), 38.1 (s, *o*-*C*Me$_3$), 122.6 (s, *m*-Mes*), 149.7 (s, *p*-Mes*), 149.9 (s, *o*-Mes*, *ipso*-Mes*, 3- and 5-C atoms were unclear) ppm. ESI-MS: calcd. for $[M + Na]^+$ ($C_{23}H_{39}N_2PSi$ + Na) 425.2512; found 425.2513. $C_{23}H_{39}N_2PSi$ (402.63): calcd. C 68.61, H 9.76, N 6.96; found C 68.62, H 9.62, N 7.00.

X-ray Crystallography: A Rigaku RAXIS-IV imaging plate detector with graphite-monochromated Mo-K_α radiation (λ = 0.71070 Å) was used. The structure was solved by direct methods

(SIR92),[32] expanded using Fourier techniques (DIRDIF94).[33] A symmetry-related absorption correction using the program ABSCOR[34] was applied for **10**. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The data were corrected for the Lorentz polarization effect. Structure solution, refinement, and graphical representation were carried out with the teXsan package.[35] The data are summarized in Table 2. CCDC-635494 (**10**) and CCDC-635495 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Table 2. X-ray data for compounds **10** and **12**.

Compound	**10**	**12**
Formula	$C_{20}H_{31}N_2P$	$C_{23}H_{39}N_2PSi$
Fw /g mol^{-1}	330.45	402.63
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a /Å	15.3082(2)	12.583(1)
b /Å	17.4576(3)	10.1014(9)
c /Å	15.2989(5)	20.1680(9)
α /°	112.328(2)	90
β /°	106.479(1)	90.087(3)
γ /°	112.335(2)	90
V /Å^3	3029.0(2)	2563.4(3)
Z	6	4
T /K	140	150
ρ_{calc} /g cm^{-3}	1.087	1.043
μ /mm^{-1}	0.138	0.163
$2\theta_{max}$ /°	55	55
Observed reflections	23356	19885
Unique reflections	12523	5612
R_{int}	0.031	0.067
R_1 [$I > 2\sigma(I)$]	0.052	0.054
R_w (all data)	0.162	0.077
Parameters	622	361
GOF	1.124	1.020

Theoretical Calculation: A Gaussian 03 (Revision D.01) was used for DFT calculations for **8x**, **9x**, **9xx**, **9meA**, and **9meB**.[36]

Supporting Information (see footnote on the first page of this article): Cartesian coordinates and total energies of the calculated structures and an energy diagram of the [1,5] rearrangements.

Acknowledgments

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[18] In Scheme 1, the 5-substituted isomer is shown as the structure of **9** although tautomerism might occur between the 5- and 3-substituted forms with trimethylsilyl group shift. Note, however, that 5-methyl-1-trimethylsilyl-1*H*-1,2,4-diazaphosphole (**9meA**) is less stable than the corresponding 3-methyl-1-trimethylsilyl-1*H*-1,2,4-diazaphosphole (**9meB**) by 3.9 kcal mol^{-1} at the B3LYP/6-31+G(d) level of calculation because of the steric repulsion between methyl and trimethylsilyl groups.

[19] 3-Trimethylsilyl-1*H*-1,2,4-diazaphosphole, a tautomeric isomer of **9xx**, possesses lower total energy by 1.4 kcal mol^{-1} at the B3LYP/6-31+G(d) level. See Supporting Information.

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