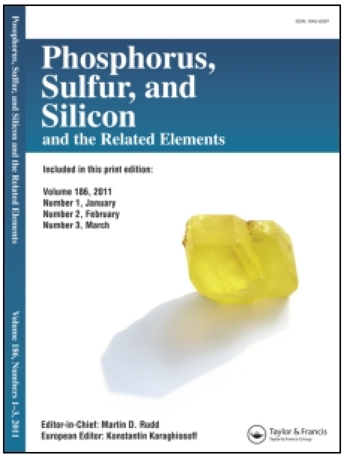

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STRUCTURAL ISOMERIZATION OF *P*-(*P'*-TRIMETHYLSILYLPHOSPHINO)-METHYLENEPHOSPHINE TO DIPHOSPHENE: A NEW APPROACH TO THE SYNTHESIS OF UNSYMMETRICAL DIPHOSPHENES

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STRUCTURAL ISOMERIZATION OF *P*-(*P'*-TRIMETHYLSILYLPHOSPHINO)-METHYLENEPHOSPHINE TO DIPHOSPHENE: A NEW APPROACH TO THE SYNTHESIS OF UNSYMMETRICAL DIPHOSPHENES

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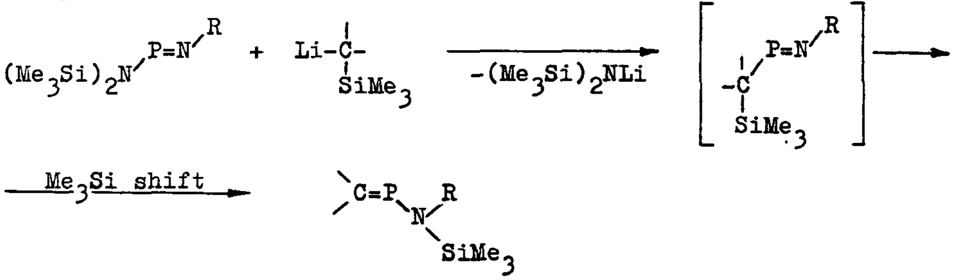
The reactions of *P*-chloro-bis(trimethylsilyl)methylenephosphine **1** with $LiP(SiMe_3)Bu^t$, $LiP(SiMe_3)Ar$ and $LiN(SiMe_3)Ar$ ($Ar = 2,4,6\text{-}Bu^t{}_3C_6H_2$) have been investigated. Depending upon the steric bulk of the phosphorus substituent in starting silylphosphine, the product was either *P*-(*P'*-trimethylsilylphosphino)methylenephosphine **3** or the structurally rearranged diphosphene **4**. The latter conversion constitutes the first example of *P*-phosphinomethylenephosphine → diphosphene isomerization. The product of the reaction of **1** with $LiN(SiMe_3)Ar$ exists in the form *P*-amino-methylenephosphine **6**.

Previously, we have shown that *N*,*N*-bis(trimethylsilyl)aminoiminophosphines react with sterically hindered C-silylated organolithium compounds to form the thermodynamically stable *P*-aminomethylenephosphines via nucleophilic displacement at the dicoordinated phosphorus atom with subsequent [1,3]silyl migration from carbon to nitrogen.[1,2]



In this communication we describe a new approach to the synthesis of unsymmetrical diphosphenes based on P → C [1,3]silyl migration in the —P—P=C< triad.

P-Chloro-bis(trimethylsilyl)methylenephosphine **1** reacts with lithium trimethylsilyl-tert-butylphosphide **2a** (ether, −78°C) to give thermostable compound, which was identified as the *P*-phosphinomethylenephosphine **3a**. The ^{31}P nmr spectrum of **3a** contains two types of signals at 477.5 and −29.3 ppm corresponding to the di- and three-coordinated phosphorus atoms. The ^{13}C (δ 226.5 ppm) signal for C=P

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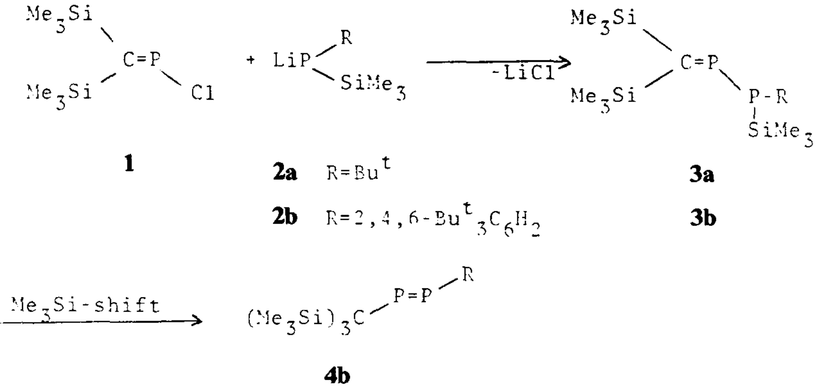
carbon occurs at low field as would be expected for an sp^2- rather than an sp^3-hybridized carbon. In accord with the methylene structure, the ^1H and ^{13}C nmr spectra show nonequivalence of the C-bonded Me_3Si groups.



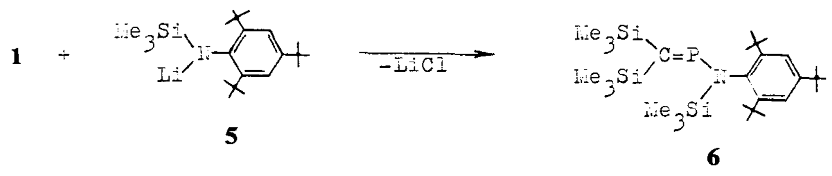
1 **2a** $R = Bu^t$ **3a**

2b $R = 2,4,6\text{-}Bu^t_3C_6H_2$ **3b**

4b

Methylenephosphine **3a** shows no signs of isomerization to the corresponding diphosphene on heating in benzene solution or under the influence of UV-radiation. However, when substituent more bulky than Bu^t is present on phosphorus in the silylphosphine reagent, the situation is quite different. The more sterically crowded lithium trimethylsilyl-2,4,6-tri-tert-butylphenylphosphide **2b** reacts with **1** to give in quantitative yield the structurally rearranged product **4b**. In this case the rate of formation of the diphosphene is so fast that the intermediate P-phosphino-methylenephosphine **3b** could not be observed by ^{31}P nmr spectroscopy. The spectral characteristics of compound **4b** correspond to those for P-tris(trimethylsilyl)methyl-P′-2,4,6-tri-tert-butylphenyldiphosphene obtained by other method.[3]

In contrast to **2b** the lithium *N*-trimethylsilyl 2,4,6-tri-tert-butylphenylamide **5** reacts with *P*-chloro-methylenephosphine **1** to give product which exists exclusively in the form of the *P*-amino-methylenephosphine **6**.



1 **5** **6**

The spectroscopic parameters of **6** are similar to those of the methylenephosphine $(Me_3Si)_2C{=}PN(SiMe_3)Bu^t$.[1] The compound **6** as well as its N-tert-butyl analogue do not isomerize to the corresponding iminophosphine even under drastic conditions (80°C, UV-radiation). Since the molecular crowding of the structure **6** is greater than that of **3b**, the absence of a tendency toward isomerization in the methylenephosphine **6**, in contrast to **3b** undoubtedly results from the energetic predominance of the C=P—N system bonds over the C—P=N system. The ready isomerization *P*-phosphino-methylenephosphine **3b** to the diphosphene **4b** enable us to presume that the difference in the bond energies of $\mathrm{Si{-}\overset{|}{P}{-}P{=}C{<}}$ and $\mathrm{{-}P{=}P{-}\overset{|}{\underset{|}{C}}{-}Si}$ systems is essentially lower than that in case of $\mathrm{Si{-}\overset{|}{N}{-}P{=}C{<}}$ and $\mathrm{{-}N{=}P{-}\overset{|}{\underset{|}{C}}{-}Si}$ groupings.

Further studies on the synthetic utility of new route to unsymmetrical diphosphenes are in progress.

EXPERIMENTAL

Known methods were used for the preparation of *P*-chloro-bis(trimethylsilyl)methylenephosphine,[4] trimethylsilyl-tert-butylphosphine[5] and 2,4,6-tri-tert-butylphenylphosphine.[6]

All reactions and other manipulations were carried out in an atmosphere of dry argon or under vacuum. Ether and THF were distilled from CaH_2, prior to use.

NMR spectra were recorded on a Bruker WP-200 spectrometer using TMS as internal standard (^1H,^{13}C) and 85% H_3PO_4 as external standard (^{31}P).

P-(P′-Trimethylsilyl-tert-butylphosphino)-bis(trimethylsilyl)methylenephosphine **3a**. A solution of **2a** (prepared from 20 mmol $Bu^t(Me_3Si)PH$ in 15 ml ether and 16.7 ml of a 1.2 M solution of MeLi in ether) was added with stirring over a 1 h period to an equimolar quantity of **1** in ether (30 ml) at −78°C. The solution was allowed to warm to room temperature and was stirred for 2 h. Filtration, solvent removal, and distillation gave **3a**, bp 101–103°C (0.02 torr); yield 89%. ^1H nmr ($CDCl_3$): δ 0.24 (d, $^4J_{PH}$ 2.40 Hz, Me_3SiC), 0.26 (d.d, $^3J_{PH}$ 3.79 Hz, $^4J_{PH}$ 0.48 Hz, Me_3SiP), 0.33 (d, $^4J_{PH}$ 0.70 Hz, Me_3SiC), 1.35 (d, $^3J_{PH}$ 11.80 Hz, Bu^t). ^{13}C nmr ($CDCl_3$): δ 1.67 (d.d, $^2J_{PC}$ 10.7 Hz, $^3J_{PC}$ 3.7 Hz, Me_3SiPP), 2.02 (d, $^3J_{PC}$ 2.0 Hz, Me_3SiC), 4.24 (d.d, $^3J_{PC}$ 8.8 Hz, $^4J_{PC}$ 3.3 Hz, Me_3SiC), 32.91 (d.d, $^2J_{PC}$ 12.1 Hz, $^3J_{PC}$ 5.2 Hz, Me_3C), 226.45 (d.d, $^1J_{PC}$ 100.1 Hz, $^2J_{PPC}$ 7.3 Hz, P=C). ^{31}P nmr (C_6D_6): δ − 29.3 (d, PSi), 477.5 (d, P=C); $^1J_{PP}$ 244 Hz. Calculated for $C_{14}H_{36}P_2Si_3$ (found): C 47.96% (47.97), H 10.35% (10.30), P 17.67% (17.73), Si 24.03% (24.00).

P-Trimethylsilyl-2,4,6-tri-tert-butylphenylphosphine. 16 ml (32 mmol) n-BuLi (2.0 M hexane solution) was dropped to a solution of 30 mmol $2,4,6\text{-}Bu^t_3C_6H_2PH_2$ in 170 ml THF at −78°C. After 1 h stirring at this temperature 32 mmol Me_3SiCl dissolved in 20 ml THF was added. The mixture was stirred at −78°C for 0.5 h and then was allowed to warm to room temperature. Filtration and evaporation of the solvent gave *P*-trimethylsilylphosphine as colourless, viscous liquid in almost quantitative yield (5% impurity by nmr-control). ^1H nmr (C_6D_6): δ −0.32 (d, $^3J_{PH}$ 3.5 Hz, Me_3Si), 1.30 (s, p-Bu^t), 1.62 (s, o-Bu^t), 4.36 (d, $^1J_{PH}$ 213.7 Hz, PH), 7.57 (d, $^4J_{PH}$ 2.2 Hz, arom.). ^{31}P nmr (C_6H_6): δ −129 (d), $^1J_{PH}$ 214 Hz. Calculated for $C_{21}H_{39}PSi$ (found): C 71.94% (71.65), H 11.21% (11.35).

P-Tris(trimethylsilyl)methyl-P′-(2,4,6-tri-tert-butylphenyl)diphosphen **4b**. A solution of **2b** (prepared from 20 mmol $2,4,6\text{-}Bu^t_3C_6H_2P(SiMe_3)H$ in 30 ml ether and 16.7 ml of a 1.2 M solution of MeLi in ether) was added with stirring over a 0.5 h period to an equimolar quantity of **1** in ether (25 ml) at −78°C. The mixture was stirred at −78°C for 1 h and then was allowed to warm to room temperature. Filtration and evaporation of the solvent leaves the crude product in almost quantitative yield. The remaining residue was taken up in little pentane and recrystallized at −30°C. This gave 7.8 g of pure 4: 72% yield, mp 172–175°C (dec.). ^1H nmr ($CDCl_3$): δ 0.30 (s, Me_3Si), 1.34 (s, p-Bu^t), 1.47 (s, o-Bu^t). ^{31}P nmr ($CDCl_3$): δ 533.0 (d, P^A), 530.3 (d, P^B); $^1J_{PP}$ 619.1 Hz.

N-(Trimethylsilyl)amino-2,4,6-tri-tert-butylbenzene. 26 ml (52 mmol) n-BuLi (2.0 M hexane solution) was dropped to a solution of 13.1 g (50 mmol) $2,4,6\text{-}Bu^t_3C_6H_2NH_2$ in 100 ml THF at room temperature with stirring. After cooling to 0°C 8.1 g (75 mmol) Me_3SiCl, dissolved in 25 ml THF was added. Filtration and evaporation of the solvent gave the crude product in almost quantitative yield, which was purified by crystallization from little hexane, 85% yield, mp 93–96°C. ^1H nmr ($CDCl_3$): δ 0.16 (s, Me_3Si), 1.28 (s, p-Bu^t), 1.46 (s, o-Bu^t), 7.28 (s, arom.). Calculated for $C_{21}H_{39}NSi$ (found): C 75.60% (75.34), H 11.78% (11.80), Si 8.42% (8.60).

P-(N-Trimethylsilyl-2,4,6-tri-tert-butylphenylamino)-bis(trimethylsilyl)methylenephosphine **6**. A solution of **5** (prepared from 20 mmol *N*-(trimethylsilyl)amino-2,4,6-tri-tert-butylbenzene in 25 ml THF and 10.0 ml of a 2.0 M solution of n-BuLi in hexane) was added dropwise at 20°C to a stirred solution of 1 (20 mmol) in 25 ml of THF. After stirring for 3 h at room temperature, filtration, and removal of solvent, the residue was purified by sublimation (130°C (bath) at 0.02 torr), yield 69%, mp 63–64°C. ^{1}H nmr (C_6D_6): δ 0.13 (s, Me_3SiC), 0.32 (s, Me_3SiN), 0.47 (d, $^4J_{PH}$ 2.8 Hz, Me_3SiC), 1.27 (s, p-Bu^t), 1.63 (s, o-Bu^t). ^{31}P nmr (THF): δ 329.3 (s). Calculated for $C_{28}H_{56}NPSi_3$ (found): C 64.42% (64.46), H 10.81% (10.84), P 5.93% (5.82), Si 16.14% (16.01).

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