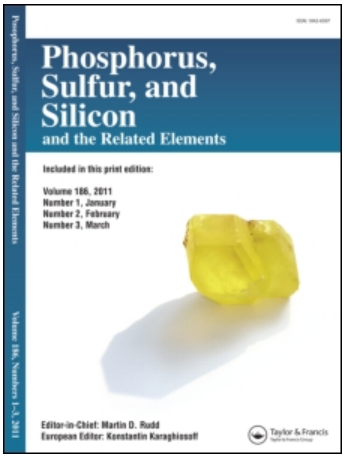

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INTERACTION OF λ³-AMINOIMINOPHOSPHINES WITH TRIS(TRIMETHYLSILYL)METHYL- AND BIS(TRIMETHYLSILYL)METHYL-LITHIUM: A New Approach to the Synthesis of Aminomethylenephosphines

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INTERACTION OF λ^3-AMINOIMINOPHOSPHINES WITH TRIS(TRIMETHYLSILYL)METHYL- AND BIS(TRIMETHYLSILYL)METHYL-LITHIUM: A New Approach to the Synthesis of Aminomethylenephosphines

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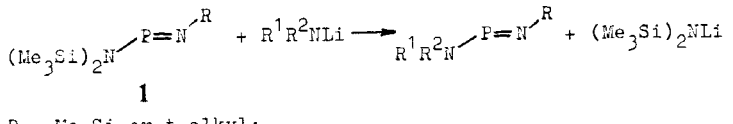
N,N-Bis(trimethylsilyl)aminoiminophosphines **1** react with $(Me_3Si)_3CLi$ and $(Me_3Si)_2CHLi$ to form the stable aminomethylenephosphines **3** via nucleophilic displacement at the dicoordinated phosphorus atom with subsequent C → N silyl migration. This reaction is a new synthetic route to *N*-trimethylsilyl functionalized aminomethylenephosphines. Proton, ^{13}C and ^{31}P nmr spectroscopic data for the compounds **3** are reported.

INTRODUCTION

In previous publications[1,2] we have shown that aminoiminophosphines **1** undergo nucleophilic transamination with the retention of phosphorus coordination when treated with sterically highly hindered lithium amides.



1

R = Me_3Si or t-alkyl;
R^1 = R^2 = alkyl or R^1 = alkyl, R^2 = Me_3Si (1)

In addition to being significant from a theoretical viewpoint, the reaction described offers a considerable potential for the preparation of new compounds of two-coordinate phosphorus. Thus, the application of this principle to the reaction of aminoiminophosphines with sterically hindered organolithium compounds provides a pathway to derivatives of dicoordinated phosphorus, involving the skeleton C—P=N.[2,3] In order to extend this approach to the synthesis of different types of compounds of dicoordinated phosphorus we have begun a study of the reactions of aminoiminophosphines with functionalized organometallic species. This paper describes the results obtained in the reactions of tris(trimethylsilyl)methyl- and bis(trimethylsilyl)methyl-lithium with *N,N*-bis(trimethylsilyl)aminoiminophosphines.

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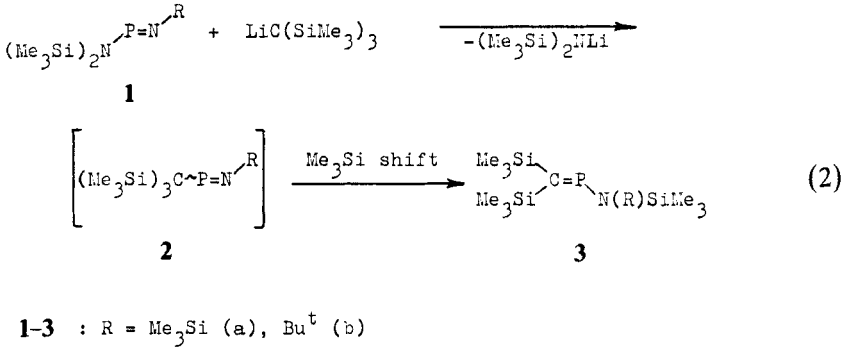
RESULTS AND DISCUSSION

Treatment of tris(trimethylsilyl)aminoiminophosphine **1a** with an equimolar quantity of $(Me_3Si)_3CLi$ in tetrahydrofuran (THF) at $-78°C$, followed by warming to room temperature, resulted in a red-brown solution. The ^{31}P nmr spectrum of this solution consists solely of a signal at 383 ppm, which falls in the region observed for compounds of two-coordinate phosphorus, and represents an appreciable downfield shift from the starting material (325.5 ppm). Analogously, addition of $(Me_3Si)_3CLi$ to *N*,*N*-bis(trimethylsilyl)amino-*N'*-tert-butyliminophosphine **1b** in THF results in the formation of a compound the ^{31}P nmr spectrum of which consists of a singlet at 391 ppm. Simple workup of the reaction mixture gave a practically pure product in good yield.



(2)

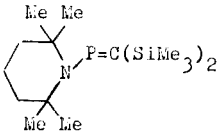
1–3 : R = Me_3Si (a), Bu^t (b)

According to the formal scheme of nucleophilic displacement at the two-coordinate phosphorus atom the compounds obtained must have the structure of iminophosphines **2**. However, the spectroscopic studies indicate that they are based on structure **3**, rather than **2**. This conclusion is supported by at least three lines of evidence. First, the ^{31}P nmr spectra of the products do not contain peaks in the region where resonance is observed for λ^3-iminophosphines (δ_P 400 ppm).[2,4] The observed ^{31}P chemical shifts are in good agreement with the values reported for compounds containing the structural element $—P{=}C(SiMe_3)_2$.[5,6] A second piece of spectroscopic evidence in favor of the methylene structure for the compounds obtained is the observation of a peak in the ^{13}C nmr spectra at 187.8 ppm (for **3a**) and 182.8 ppm (for **3b**) indicative of sp^2-hybridized carbon. The resonance is split into a doublet with the coupling constant $^1J(PC)$, of ca. 95 Hz being especially characteristic of the P=C bond.[5] In accord with the methylene structure, the ^1H nmr spectra show nonequivalence of the C-bonded Me_3Si groups, arising from the different position of these groups, relative to the free electron pair on the phosphorus atom. Conversely, the Me_3Si groups attached to nitrogen are equivalent and exhibit coupling constants, $^3J_{PC}$ and $^4J_{PH}$ typical of the PNSiCH grouping (see Table I).

Further proof of the formulation of the compounds obtained from reactions of aminoiminophosphines **1a** and **1b** with $(Me_3Si)_3CLi$ as methylenephosphines stems from the comparison of nmr data of compounds **3a**, **3b** with those of methylenephos-

TABLE I

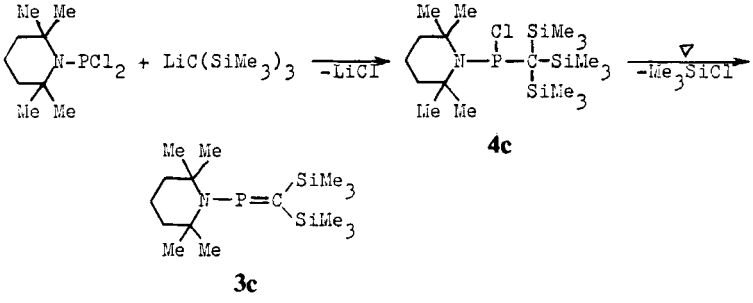
Proton, ^{13}C and ^{31}P nmr[a] data for aminomethylenephosphines **3a–c**

Compound	Signal	^1H nmr δ	^1H nmr J_{PH}	^{13}C nmr δ	^{13}C nmr J_{PC}	^{31}P nmr
$(Me_3Si)_2N-P=C(SiMe_3)(E)(SiMe_3)(Z)$	Me_3SiN	0.28	0.6	4.0	4.3	383.4
	Me_3SiC (Z)[b]	0.35		3.8	3.3	
	Me_3SiC (E)	0.37	2.5	3.5	8.5	
(3a)	P=C			187.5	98.0	
$Me_3Si(Bu^t)N-P=C(SiMe_3)_2$	Me_3SiN	0.30	0.3	6.2	3.0	391.3
	Me_3SiC (Z)	0.38	0.25	3.9	2.0	
	Me_3SiC (E)	0.41	2.5	3.5	9.5	
	Me_3CN	1.38		33.2	8.6	
	Me_3CN			56.7	5.2	
(3b)	P=C			182.8	93.7	
	Me_3Si (E)	0.24	2.35	3.7	15.0	406.8
	Me_3Si (Z)	0.28		3.6	3.5	
	Me_2C	1.20		31.9	16.3	
(3c)	P=C			193.6	75.0	

[a] Chemical shifts in ppm downfield from Me_4Si for ^1H and ^{13}C nmr spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvent: C_6D_6.

[b] Assignment for C-bonded Me_3Si groups is based on the ^4J(P = CSiCH) and ^3J(P = CSiC) values, see Ref. 12.

phine **3c**, obtained by the thermal decomposition of 2,2,6,6,-tetramethylpiperidino-tris(trimethylsilyl)methyl-chlorophosphine **4c**.



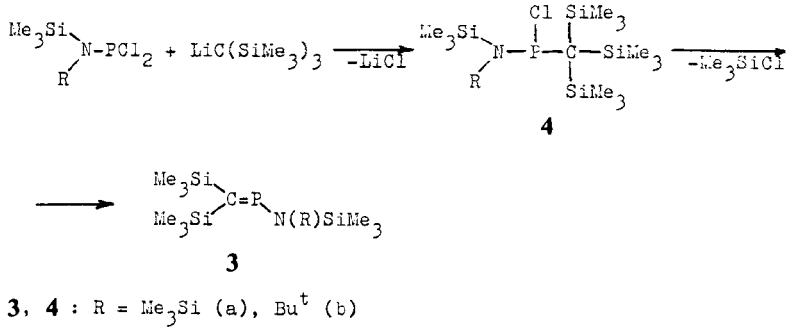
4c

3c (3)

The spectroscopic parameters of methylenephosphine **3c** are very similar to those of **3a** and **3b**. This compound shows a peak in the ^{31}P spectrum at 406.8 ppm; the ^{13}C chemical shift of the methylene carbon and the $^1J_{PC}$ values are in the same range as observed for compounds **3a** and **3b**.

The formation of aminomethylenephosphines **3** in the reactions of aminoiminophosphines **1** with $(Me_3Si)_3CLi$ presumably involves [1, 3] silyl migration from carbon to nitrogen in the initially formed λ^3-iminophosphines **2**, although no direct

evidence for such intermediate products has been obtained. NMR spectra recorded as the reaction proceeds consist only of peaks assignable to the starting aminoiminophosphine and the rearranged product. The thermodynamic predominance of the methylene structure, C=P—N over the imino structure, C—P=N is further proved by the formation of aminomethylenephosphines **3a** and **3b** via the thermal elimination of Me_3SiCl from aminochlorophosphines **4**, which are obtainable from aminodichlorophosphines and tris(trimethylsilyl)methyl-lithium.



4

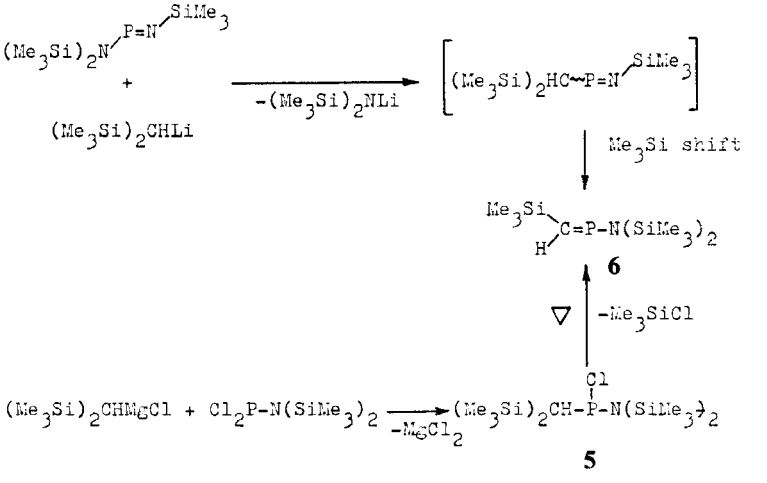
3

(4)

3, **4** : R = Me_3Si (a), Bu^t (b)

The structure of products was confirmed by comparison of the ^1H, ^{31}P nmr and ir spectra with those of methylenephosphines obtained according to Eq. (2).

The success of the novel synthetic route to aminomethylenephosphines prompted us to attempt a similar reaction with $(Me_3Si)_2CHLi$. Earlier, E. Niecke and his co-workers have reported that bis(trimethylsilyl)amino-bis(trimethylsilyl)methylchlorophosphine **5** decomposes thermally by Me_3SiCl elimination, forming methylenephosphine **6**.[7] We report here the preparation of compound **6** by a nucleophilic displacement reaction between aminoiminophosphine **1a** and $(Me_3Si)_2CHLi$. Addition of $(Me_3Si)_2CHLi$ (1 equiv.) to **1a** in THF at $-78°C$ resulted in the formation of aminomethylenephosphine **6**. The conversion is virtually quantitative on the basis of ^{31}P nmr spectroscopy. The spectral data of the compound **6** are in agreement with those described in the literature.



5

(5)

Reactions according to Eqs. (2) and (5) are thus a method for converting the readily available bis(trimethylsilyl)aminoiminophosphines into aminomethylenephosphines. Evidently, the electrophilic character of the phosphine centre in aminoiminophosphines and the lability of silyl substituents in the —N=P—C(H)—$SiMe_3$ system toward intramolecular migration can be utilized to effect the synthesis of a variety of *N*-silyl functionalized aminomethylenephosphines.

EXPERIMENTAL

Known methods were used for the preparation of *N,N*-bis(trimethylsilyl)amino-*N'*-trimethylsililiminophosphine,[8] *N,N*-bis(trimethylsilyl)amino-*N'*-(*t*-butyl)iminophosphine,[9] tris(trimethylsilyl)methyllithium[10] and bis(trimethylsilyl)methyl-lithium.[11] Ether and THF were distilled from CaH_2, prior to use.

Proton and ^{31}P nmr spectra were recorded on a Bruker WP-200 spectrometer; ^{13}C nmr spectra were obtained on a Bruker WH-90 instrument. Infrared spectra were obtained on a Specord 75 IR spectrophotometer.

All reactions and other manipulations were carried out in an atmosphere of dry argon or under vacuum.

Preparation of amino-bis(trimethylsilyl)methylenephosphines **3a** *and* **3b**

(*a*) *From N,N-bis(trimethylsilyl)aminoiminophosphines* **1** *and* $(Me_3Si)_3CLi$. In a typical preparation, a solution of $(Me_3Si)_3CCl$ (prepared from 52 mmol $(Me_3Si)_3CH$ in 120 ml THF and 43.3 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 aminoiminophosphine **1** in THF (50 ml) at −78°C. The solution was stirred at room temperature for 2 h and then recooled to −60°C. 2,2,6,6-Tetramethylpiperidine hydrochloride (50 mmol) was added and the mixture was allowed to warm to room temperature. After 2 h of stirring the mixture was filtered and solvents were removed under vacuum. The residue thus remaining was distilled to give a yellow liquid, identified as **3**.

N,N-Bis(trimethylsilyl)amino-bis(trimethylsilyl)methylene **3a**. Yield: 49%, bp 80–82°C (0.02 torr). Anal. Calcd. for $C_{13}H_{36}NPSi_4$: C, 44.64; H, 10.37. Found: C, 44.65; H 10.47.

N-Trimethylsilyl-tert-butylamino-bis(trimethylsilyl)methylenephosphine **3b**. Yield: 46%, bp 86–90°C (0.02 torr). Anal. Calcd. for $C_{14}H_{36}NPSi_3$: C, 50.39; H, 10.87; P, 9.28; Si 25.25. Found: C, 50.10; H, 11.21; P, 9.25; Si, 24.80. Spectroscopic data of the compounds **3a** and **3b** are compiled in Table I.

(*b*) *From aminodichlorophosphines and* $(Me_3Si)_3CLi$. Tris(trimethylsilyl)methyl-lithium (prepared from 95 mmol $(Me_3Si)_3CH$ in 200 ml of THF and 79.2 ml of a 1.2 M solution of MeLi in ether) was added with stirring to a solution of aminodichlorophosphine (92 mmol) in ether (200 ml) at −78°C. The solution was allowed to warm to room temperature and was stirred for 10 h. Filtration, solvent removal, and distillation gave **3**. The yield of **3a** was 14.5 g (41.4 mmol, 45%), bp 80–82°C (0.02 torr). Aminomethylenephosphine **3b** was obtained in 49% yield, bp 85–90°C (0.02 torr). The ^1H and ^{31}P nmr spectra of the two compounds were identical with those of the samples of **3a** and **3b** mentioned previously.

2,2,6,6,-Tetramethylpiperidino-bis(trimethylsilyl)methylene-phosphine **3c**. Yield: 15.8 g (52%), bp 110–115°C (0.04 torr). Anal. Calcd. for $C_{16}H_{36}NPSi_2$: C, 58.29; H, 11.01; P, 9.40; Si, 17.04. Found: C, 58.20; H, 11.01; P, 9.29; Si, 16.78. Spectroscopic data are given in Table I.

N,N-Bis(trimethylsilyl)amino-trimethylsilylmethylenephosphine **6**. Use of the procedure described above for compounds **3a** and **3b**, treatment of aminoiminophosphine **1a** with $(Me_3Si)_2CHLi$ gave the product which was identified as **6**:[7] yield 55%, bp 60–62°C (0.1 torr); ^{31}P nmr (in C_6D_6): δ 309 ppm.

REFERENCES AND NOTES

1. V. D. Romanenko, A. V. Ruban and L. N. Markovski, *Zh. Obshch. Khim.* **53**, 678 (1983).
2. V. D. Romanenko, A. V. Ruban and L. N. Markovski, *J. Chem. Soc. Chem. Commun.*, 187 (1983).
3. V. D. Romanenko, A. V. Ruban and L. N. Markovski, *Zh. Obshch. Khim.*, **53**, 778 (1983).
4. E. Niecke, R. Rüger and W. Schoeller, *Angew. Chem.*, **93**, 1100 (1981).
5. K. Issleib, H. Schmidt and Chr. Wirkner, *Z. anorg. allg. Chem.*, **473**, 85 (1981).
6. R. Appel, J. Peters and A. Westerhaus, *Tetrahedron Lett.*, **22**, 4957 (1981).
7. E. Niecke, W. W. Schoeller and D.-A. Wildbredt, *Angew. Chem.*, **93**, 119 (1981). The synthesis of compound (6) via dehydrohalogenation of the chlorophosphine, $(Me_3Si)_2N—P(Cl)—CH_2SiMe_3$, using $LiN(SiMe_3)_2$ as the base has been described by J. C. Wilburn, P. Wisian-Neilson and R. H. Neilson, *Inorg. Chem.*, **20**, 1679 (1981).
8. O. J. Scherer and N. Kuhn, *Chem. Ber.*, **107**, 2123 (1974).
9. O. J. Scherer and N. Kuhn, *J. Organometal. Chem.*, **82**, C3 (1974).
10. M. A. Cook, C. Eaborn, A. G. Jukes and D. R. M. Walton, *J. Organometal. Chem.*, **24**, 529 (1970).
11. P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc. Dalton Trans.*, 2268 (1976).
12. R. Appel, F. Knoll and I. Ruppert, *Angew. Chem.*, **93**, 771 (1981).