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N,N,N′,N′,N″-Pentamethyl-*N″*-[(trifluorosilyl)methyl] phosphoric triamide. First example of the existence of intramolecular P=O→Si coordination bond in the Si-containing phosphoric triamides

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The *N,N,N′,N′,N″*-pentamethyl-*N″*-(trifluorosilylmethyl)phosphoric triamide $O{=}P(NMe_2)_2N(Me)CH_2SiF_3$ with intramolecular P=O→Si coordination was formed by the reaction of *N,N,N′,N′,N″*-pentamethyl-*N″*[(triethoxysilyl)methyl]phosphoric triamide with $BF_3{\cdot}Et_2O$. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: Si-containing phosphoric triamides; intramolecular P=O→Si coordination bond

INTRODUCTION

Compounds with hypervalent silicon attract considerable attention because of their structural aspects, unexpected reactivity and their key role in the chemical transformation of tetracoordihate organosilicon compounds.[1–7] Obtained from Si-substituted lactames (A), ethers (B) and amides (C) (Scheme 1) are typical and well investigated pentacoordinate organosilicon compounds with an intramolecular C=O→Si bond.[3,5,7–10]

However, only a few examples for intramolecularly coordinated compounds involving the interaction P=O→M (M = Si, Ge, Sn) are known.[11–17] They are either derivatives of phosphine oxides or phosphoric acids. The phosphoryl group of hexamethylphosphoric triamide (HMPA) has high donor properties,[18,19] which account for the solvating ability $O{=}P(NMe_2)_3$.[20–22] The amides of the phosphoric acids are widely used as monodentate ligands in the synthesis of coordination compounds of main groups elements (Al, Sn, Pb).[23–28] The ability of the phosphoryl group of amides of phosphoric acid to form intramolecular P=O→M coordination bonds, where M is an element of group 14 (Si, Ge, Sn), is less known. The reaction of *in situ* generated $LiCH_2NMeP(O)(NMe_2)_2$ with $H\text{-}GeR_3$ resulted in the production of a compound with an intramolecular P=O→Ge coordination bond.[29] In contrast, the first attempt of the synthesis of a phosphoric triamide adduct with intramolecular P=O→Si coordination bond gave rise to an unexpected result.[30] It was anticipated, that the reaction of the *N,N,N′,N′*-tetraethyl-*N″*-*tert*-butylphosphoric triamide with BuLi and the subsequent interaction with $ClCH_2SiMe_2Cl$ would result in the formation of a ring with the intramolecular P=O→Si coordination bond (Scheme 2). However, the product of this reaction is 2-phospha-4-silaoxazolidine with a Cl→Si coordination bond. It is interesting to note that the interaction of RR′R″SiLi (R,R′, R″ = Alk, Ar) with *N*-phosphinyl imines $Ph_2P(O)N{=}CHX$ or $(EtO)_2P(O)N{=}CHX$ produced the corresponding *N*-silylmethylamides of phosphoric acids $Ph_2P(O)NHCHXSiRR'R''$ or $(EtO)_2P(O)NHCHXSiRR'R''$.[31]

Our interest in investigating the reactivity and the new syntheses using α-silylamines has led us to study their interaction with $(Me_2N)_nP(O)Cl_{3-n}$. These investigations are based on our earlier method of acylation of α-silylamines.[32] Recently we synthesized a series of Si-containing phosphoric triamide $O{=}P(NMeCH_2SiMe_2X)_3$ with X = OEt, Cl, F.[33] We expected that the silicon atom in the compounds (X = F, Cl) would be

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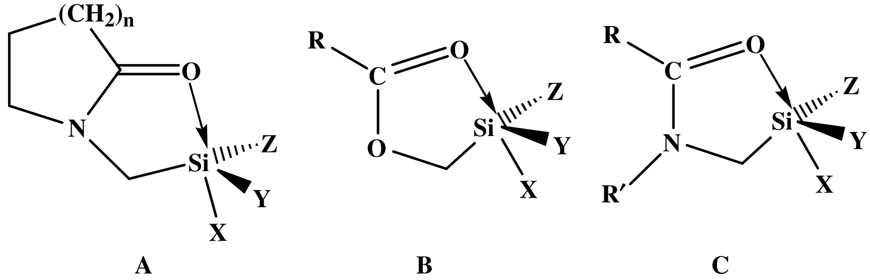
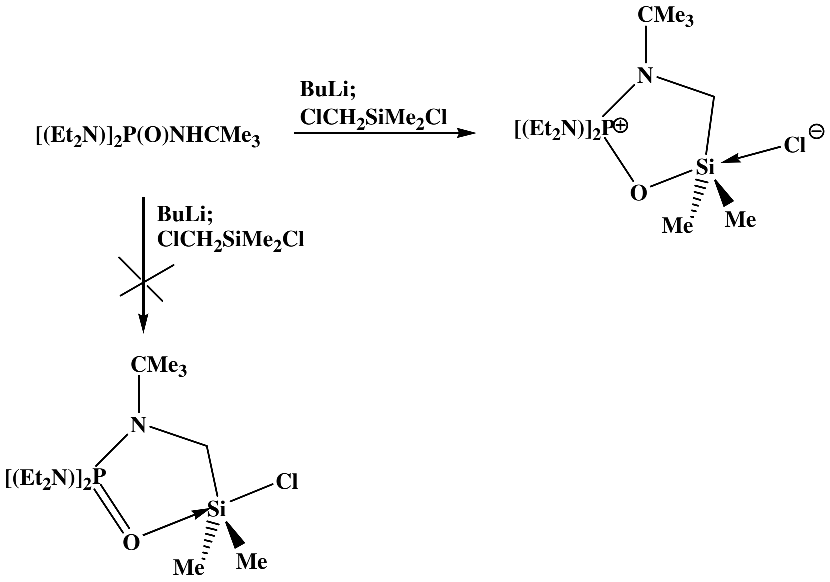


Scheme 1. The typical pentacoordinate organosilicon compounds: (**A**), (**B**) and (**C**).



Scheme 2. The reaction of the *N*,*N*,*N*′,*N*′-tetraethyl-*N*″-*tert*-butylphosphoric triamide with BuLi and the subsequent interaction with $ClCH_2SiMe_2Cl$.

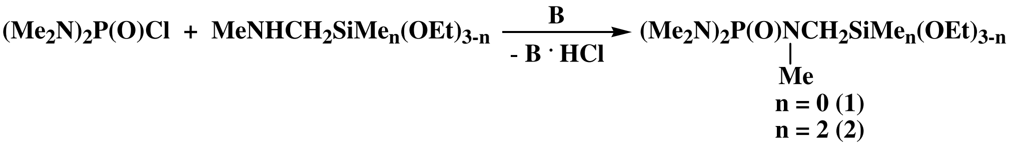
pentacoordinate owing to an intramolecular P=O→Si coordination. However, the spectral data show that the silicon atom is tetracoordinate in all synthesized compounds.

Herein, we report the results obtained for the synthesis and identification by NMR spectroscopy of some *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-silylmethyl phosphoric triamides.

RESULTS AND DISCUSSION

The reaction of the amines RR′NH with XYP(O)Cl is a classical method for the preparation of the amides corresponding acids XYP(O)NRR′.[34,35] Previously unknown *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-[(triethoxysilyl)methyl]phosphoric triamide **1** and *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-[(ethoxy)dimethylsilylmethyl]phosphoric triamide **2** were synthesized according to Scheme 3, starting from the α-silylmethylamines and $(Me_2N)_2P(O)Cl$ in the presence of hydrogen chloride acceptors.

We preferred to conduct these reactions in anhydrous Et_2O or THF under dry argon. The 15-fold excess of base (triethylamine or pyridine) was added to a solution of the α-silylmethylamine. It is necessary to avoid the interaction of



$$(Me_2N)_2P(O)Cl + MeNHCH_2SiMe_n(OEt)_{3-n} \xrightarrow[- B \cdot HCl]{B} (Me_2N)_2P(O)N(Me)CH_2SiMe_n(OEt)_{3-n}$$

n = 0 (**1**)
n = 2 (**2**)

Scheme 3. Synthesis of *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-[(triethoxysilyl)methyl]phosphoric triamide **1** and *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-[(ethoxy)dimethylsilylmethyl]phosphoric triamide **2**.

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Table 1. ^{1}H NMR parameters for **1–4** ($CDCl_3$, $t = 25\,^\circ C$)

			$\delta\ ^1H$		
No.	MeSi	CH3–C	NCH_2Si	NMe	CH_2O
1		1.19 (t)	2.56	2.56 m	3.81 (q)
2	0.15	1.19 (t, $^3J = 6.9$)	2.5 (d, $^3J_{PH} = 7.6$ Hz)	2.66 (d., NMe_2 $^3J_{PH} = 10.1$ Hz); 2.70 (d, 11.4 Hz)	3.70 (q)
3			2.68 (m)	2.64 (d, NMe_2 $^3J_{PH} = 10.5$ Hz); 2.59 (d, NMe, $^3J_{PH} = 8{,}0$ Hz)	
4	0.34		2.53 (d; $^3J_{PH} = 8.8$ Hz)	2.63 (d, NMe_2 $^3J_{PH} = 10.4$ Hz); 2.73 (d, NMe, $^3J_{PH} = 10.6$ Hz)	

Table 2. ^{13}C NMR parameters for **1**–**4** ($CDCl_3$, $t = 25\,^\circ C$)

			$\delta\ ^{13}C$		
No.	MeSi	CH_3–C	NCH_2Si	NMe	–CH_2O
1		18.06	36.05 ($^2J_{CP} = 3.8$ Hz)	33.27(NMe); 36.72(NMe_2)	58.5
2	−3.12	18.26	43.81	36.66 36.82 ($^2J_{CP} = 3.8$ Hz)	58.3
3			39.93($^2J_{CF} = 28.4$ Hz; $^2J_{CP} = 8.1$ Hz)	33.92 (NMe; $^2J_{CP} = 3.1$ Hz); 36.22 (NMe_2; $^2J_{CP} = 3.7$ Hz)	
4	−0.25		41.18 ($^2J_{CP} = 4.2$ Hz)	36.47 (NMe_2; $^2J_{CP} = 3.1$ Hz); 36.87 (NMe; $^2J_{CP} = 3.9$ Hz)	

Table 3. ^{29}Si, ^{31}P, ^{19}F NMR parameters for **1–4** and their model compounds ($CDCl_3$, 25 °C)

Compound	^{29}Si	^{31}P	^{19}F
1	−53.25 ($^3J_{SiP} = 15.1$ Hz)	27.2	
2	14.1 ($^3J_{SiP} = 8.02$ Hz)	26.91	
3	−111.6 ($^1J_{SiF} = 213$ Hz; $^3J_{SiP} = 23.3$ Hz)	32.8	−129.71
4	30.51 ($^1J_{SiF} = 286$ Hz; $^3J_{SiP} = 8.8$ Hz)	28.24	−159.42
$ClCH_2SiF_3$	−71.3 ($^1J_{SiF} = 267$ Hz)		−143.99
$ClCH_2SiMe_2F$	24.8 ($^1J_{SiF} = 287$ Hz)		−161.56

the last with hydrogen chloride. Treatment of the solution of this mixture with solution of equimolar amount of $(Me_2N)_2P(O)Cl$ at −25 to +10 °C led to the formation of the corresponding amide. The results show that the nature of a solvent and base has no influence on the yield of **1, 2**: the yield depends on the change of the temperature. Phosphorus halides give rise to cleavage of the Si–O–C bond[36] and the reaction of α-silylmethylamine with $(Me_2N)_2P(O)Cl$ can be complicated by side processes, which run sluggishly at low temperature. When the reaction temperature was decreased, a maximum yield was reached at −8 °C. A further decrease of temperature has little effect on the yield of these products. The amides **1** and **2** are oily liquids with a weak odour. The structures of **1** and **2** were confirmed by multinuclear NMR spectroscopy (Tables 1–3).

The compounds **1** and **2** reacted easily with $BF_3{\cdot}Et_2O$ with formation of the N,N,N',N',N''-pentamethyl-N''-[(trifluorosilyl)methyl]phosphoric triamide **3** and N,N,N',N', N''-pentamethyl-N''-[(fluorodimethylsilyl)methyl]phosphoric triamide **4** (Scheme 4).

These reactions were performed initially at −10 °C in order to avoid a possible formation of by-products. Products **3** and **4** are viscous oils* which decompose easily above 30 °C. Compounds **3** and **4** were studied by ^{1}H, ^{13}C, ^{29}Si, ^{31}P, ^{19}F NMR spectroscopy (Tables 1–3). The ^{29}Si chemical shift for **3** ($\delta = -111.6$ ppm in $CDCl_3$ solution) is 40.3 ppm higher than the related tetracoordinate organosilicon compound $ClCH_2SiF_3$ ($\delta = -71.3$ ppm).[37,38] The ^{19}F–^{29}Si coupling ($J_{Si-F} = 213.3$ Hz) in **3** is significantly lower when compared with $ClCH_2SiF_3$ ($J_{Si-F} = 267$ Hz). At ambient temperature, the ^{19}F chemical shift for **3** is −129.71 ppm (one broad triplet). A decrease of temperature of the solution to −90 °C (CD_2Cl_2) for compound **3** leads to the transformation the ^{19}F resonance into a triplet (−132.5 ppm) and a doublet (−121.9 ppm) the downfield triplet signal corresponds to the axial.

The downfield triplet signal corresponds to the axial fluorine atom and the upfield doublet signal corresponds to the two equatorial fluorine atoms. The value of the $^{19}F_{ax}$–$^{19}F_e$ coupling constant is 35.8 Hz. The value of the ^{1}J(Si–F_a) for compounds **3** is higher than that of ^{1}J(Si–F_e) (227.8 and 199.2 Hz, respectively). These results show that the silicon atom in **3** is pentacoordinate with an intramolecular P=O→Si coordination bond and agree well with the similar data for the pentacoordinate trifluorosilanes **B** and **C**.[9,32] At room temperature, a rapid intramolecular F_a–F_e exchange (on the NMR time scale) occurs, due to the cleavage of the P=O→Si bond or to a pseudorotation. The value of activation free energies for this process was measured ($\Delta G^{\neq} = 10.2$ kcal/mol) at the coalescence temperature (−8 °C).

However, the ^{29}Si chemical shift in **4** is downfield by 5.81 ppm as compared with its model compound $ClCH_2SiMe_2F$ (30.51 and 24.8 ppm accordingly) and the ^{19}F–^{29}Si spin–spin couplings for **4** and $ClCH_2SiMe_2F$ are almost equal (286.4 and 287 Hz accordingly). The ^{31}P

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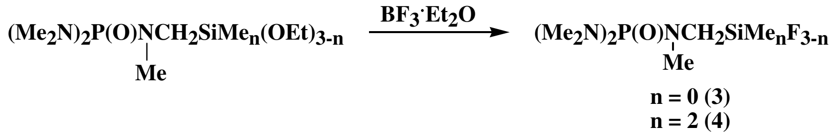
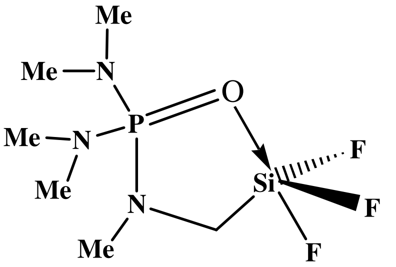
* Unfortunately, we failed to obtain reliable crystal for X-ray analysis.



Scheme 4. Synthesis of *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-[(trifluorosilyl)methyl]phosphoric triamide **3** and *N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-[(fluorodimethylsilyl)methyl]phosphoric triamide **4**.



D

Scheme 5. The compound **3** exists in an (O–Si)chelate form with an intramolecular P=O→Si coordination bond.

resonance of P=O (32.8 ppm) in the spectrum **3** is shifted downfield by 5.6 ppm as compared with **1** (27.2 ppm) while for **4** the downfield shift is only 1.33 ppm from with **2** (28.24 and 26.91 ppm accordingly). Apparently, the cause of this downfield shift is the transfer of electronic density from the oxygen atom of the P=O group onto the silicon atom and this displacement is higher in **3**.

These facts indicate that the structures of **3** and **4** differ. Compound **3** exists as **D** (Scheme 5) with the pentacoordinate silicon due to an intramolecular P=O→Si interaction; similarly, *N*-methyl-*N*-(trifluorosilylmethyl)acetamide has a pentacoordinate silicon atom due to an intramolecular C=O→Si interaction.[32]

The Lewis acidity of the silane is increased with increasing of the number of fluorine atoms at silicon.[39] Similarly, the number of fluorine atoms at silicon in the series of (O–Si)chelated amides of carboxylic acids (**C**) influences significantly the amount of the intramolecular C=O→Si bond formation.[32]

An intramolecular P=O→Si interaction in compound **4** is absent, showing that the Lewis acidity of silicon is less important. This is consistent with results obtained by us earlier for $O = P[N(Me)CH_2SiMe_2F]_3$.[33]

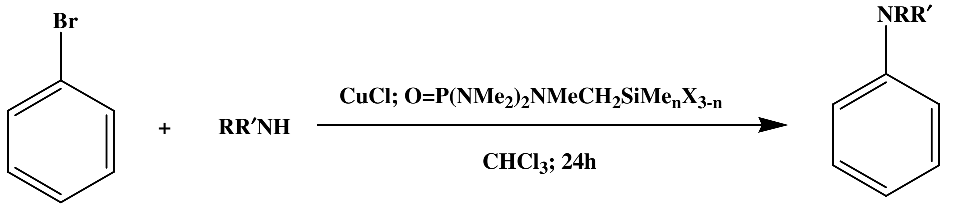
The amides of phosphoric acids are used as ligands in the metallocomplex catalysis.[40–44] The silyl groups, incorporated into an organic structure, were used widely in organic synthesis to control the stereochemistry of the reaction.[45,46] It is possible that a Si-containing phosphoric triamides will have unique properties. In particular, we expected that these compounds can be used as catalysts. Thus we have discovered that the addition of amides **1–4** as ligands could promote the Ullmann arylation of amines.

Despite the fact that this reaction was very well studied,[47,48] important problems remain. In particular, the search for milder and more efficient ligands for the formation of a classic copper-containing system, which catalyzes a reaction of amines and amides with ArHal, has been the subject of recent investigation.[49–51]

These first results demonstrate that the coupling reaction of PhBr with various amines was carried out using the catalyst systems **1–4** and the desired amination products were obtained in moderate yields (Scheme 6). The data

Table 4. Results of the arylation reaction of amines with **1–4**

Phosphoric triamide	Amine	*T*, °C	Product	Yield, %
1	$PhNH_2$	50	Ph_2NH	43
1	$O(CH_2CH_2)_2NH$	35	$O(CH_2CH_2)_2NPh$	59
1	$HN(CH_2CH_2OH)_2$	35	$PhN(CH_2CH_2OH)_2$	60
2	$PhNH_2$	50	Ph_2NH	45
2	$O(CH_2CH_2)_2NH$	35	$O(CH_2CH_2)_2NPh$	65
2	$HN(CH_2CH_2OH)_2$	35	$PhN(CH_2CH_2OH)_2$	57
3	$PhNH_2$	20	Ph_2NH	38
3	$O(CH_2CH_2)_2NH$	20	$O(CH_2CH_2)_2NPh$	43
3	$HN(CH_2CH_2OH)_2$	20	$PhN(CH_2CH_2OH)_2$	29
4	$PhNH_2$	20	Ph_2NH	41
4	$O(CH_2CH_2)_2NH$	20	$O(CH_2CH_2)_2NPh$	56
4	$HN(CH_2CH_2OH)_2$	20	$PhN(CH_2CH_2OH)_2$	41



Scheme 6. Compounds **1** and **4** are ligands for the Ullmann coupling reaction of amines with PhBr.

of Table 4 show little difference between **1–4.** However, future investigations of properties of **1–4** are necessary to understand the mechanism of formation and the influence of these new catalytic systems.

CONCLUSION

We have synthesized previously unknown *N,N,N′,N′,N″*-pentamethyl-*N″*-silylmethylphosphoric triamides. The degree of the intramolecular coordination interaction P=O→Si depends on the number of fluorine atoms at silicon. The increase in the value of the $\Delta\delta$ ^{29}Si shift in a series of the (O–Si)chelated **A, B** and **C** derivatives of carboxylic acids [$\Delta\delta = \delta \mathrm{Si}^{\mathrm{V}} - \delta \mathrm{Si}(\mathrm{ClCH_2SiXYZ})$] indicates that the degree of the intramolecular C=O→Si coordination interaction increases.[10] The strongest intramolecular X=O→Si coordination interaction among known (O–Si)chelated trifluorosilanes is observed in compound **3** (Table 5). The value of the activation free energies $\Delta G^{\neq}$ of the intramolecular exchange F$_a$—F$_e$ process indicates about a stereodynamic stability and the degree of the intramolecular coordination interaction of trifluorosilanes **B**.[53] The comparison of $\Delta G^{\neq}$ for **3** with $\Delta G^{\neq}$ for PhC(O)OCH$_2$SiF$_3$ and MeOC(O)N(Me)CH$_2$SiF$_3$ (Table 5) shows a larger stereodynamic stability and, consequently, a stronger coordination interaction in **3**.

It is provided by the high donor ability of the (Me$_2$N)$_2$P=O group. Further investigations on the structure and synthetic utility of these unique compounds are underway in our laboratory and will be reported in due course.

EXPERIMENTAL

^{1}H, ^{13}C, ^{29}Si, ^{31}P and ^{19}F spectra of CDCl$_3$ solutions of the compounds were recorded on a Bruker 400 MHz spectrometer. All solvents and amines were purified and carefully dried before use, according to literature procedures.[55,56] The α-silylmethylamines MeNHCH$_2$Si(OEt)$_3$ and MeNHCH$_2$SiMe$_2$(OEt) were synthesized by the method of Noll *et al.*[57] (Me$_2$N)$_2$P(O)Cl is commercially available from Acros. All experiments were performed under an inert dry argon.

Synthesis *N,N,N′,N′,N″*-pentamethyl-*N″*-[(triethoxysilyl)methyl]phosphoric triamide 1

A solution of 0.01 mol MeNHCH$_2$Si(OEt)$_3$ in 200 cm^3 of dry Et$_2$O was added to the 0.015 mol Et$_3$N. The mixture was cooled to $-8 \pm 0.5\,^\circ$C and 0.01 mol of (Me$_2$N)$_2$P(O)Cl in 150 cm^3 of dry Et$_2$O added slowly with stirring. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm up to room temperature and stirred for 24 h. The triethylamine hydrochloride was filtered, washed with Et$_2$O (3 × 50 cm^3) and this ether solution was added to the filtrate. The ether was removed in vacuum to afford a yellow oil. *N,N,N′,N′,N″*-pentamethyl-*N″*-[(triethoxysilyl)methyl]phosphoric triamide **1**, was purified by vacuum distillation. B.p.: 153–156 °C/1 mmHg; $n_D^{20} = 1.4479$. Elemental analysis (%) calculated for C$_{12}$H$_{32}$N$_3$O$_4$PSi: C 42.21, H 9.45, N 12.31; found: C 42.39, H 9.63, N 12.44.

Synthesis *N,N,N′,N′,N″*-pentamethyl-*N″*-[(ethoxy)dimethylsilylmethyl]phosphoric triamide 2

This compound was prepared from MeNHCH$_2$SiMe$_2$(OEt) following the above procedure. B.p.: 126–127 °C/1 mmHg; $n_D^{20} = 1.4568$. Elemental analysis (%) calculated for C$_{10}$H$_{28}$N$_3$O$_2$PSi: C 42.68, H 10.03, N 14.93; found: C 42.73, H 10.41, N 15.07.

Table 5. The data of ^{29}Si and $\Delta\delta = \delta\mathrm{Si}^{\mathrm{V}} - (-71.3\ \mathrm{ppm})^a$ for (O–Si)chelated trifluorsilanes

Compound	^{29}Si, ppm	Δ ^{29}Si, ppm	$\Delta G^{\neq}$(F$_a$—F$_e$), kcal/mol	Reference
MeC(O)SCH$_2$SiF$_3$	−82.1	−10.8		52
PhC(O)OCH$_2$SiF$_3$	−94.8	−23.5	8.4	53
MeC(O)N(Me)CH$_2$SiF$_3$	−102.7	−31.4		32
MeOC(O)N(Me)CH$_2$SiF$_3$	−103.4	−32.1	9.5	54
(Me$_2$N)$_2$P(O)N(Me)CH$_2$SiF$_3$	−111.6	−40.3	10.2	This work

[a] −71.3 ppm is the chemical shift ^{29}Si for ClCH$_2$SiF$_3$.

General procedure for the synthesis of 3 and 4

An equimolar amount $BF_3 \cdot Et_2O$ was dissolved in 20 cm^3 of dry Et_2O and added dropwise with stirring to a solution of 0.001 mol of **1** or **2** in 75 cm^3 of dry Et_2O at −10 °C. The reaction mixture was stirred for 12 h at this temperature. Afterwards the reaction mixture was warmed up to room temperature (<30 °C) and stirred for a further 24 h. Both Et_2O and $B(OEt)_3$ were removed in vacuum to afford a yellowish oil. The crude product was dissolved in Et_2O–pentane (4 : 1) at room temperature, the solution was cooled to approximately −5–10 °C and left this temperature for 48 h. The mixture of solvents was decanted and the residue washed with cold 4 : 1 Et_2O–pentane and then dried in vacuum.

The yield of **3** was 62%; $n_D^{20} = 1.4368$. Elemental analysis (%) calculated for $C_6H_{17}F_3N_3OPSi$: C 27.37, H 6.51, N 15.96;.found: C 27.02; H 6.19, N 16.11.

The yield of **4** was 77%; $n_D^{20} = 1.4472$. Elemental analysis (%) calculated for $C_8H_{23}FN_3OPSi$: C 37.63, H 9.08, N 16.46;.found: C 37.32, H 8.87, N 16.27.

General procedure of catalysis with 1–4

A mixture of 0.01 mol of PhBr, 0. 011 mol amine, $CHCl_3$ 30 ml, 0.001 mol corresponding phophoric triamide **1–4** was degased. The dry argon was entered in the reaction vessel. Then 0.001 mol CuCl was added. The mixture was stirred at the indicated temperature (Table 4) for 24 h. The reaction mixture was cooled to room temperature, the solution was decanted and the solid residue was washed by Et_2O (25 ml × 2). Et_2O was added to the solution and the solvents were removed under vacuum. The solid residue was purified.

Diphenylamine was purified by recrystallization from 6 : 1 H_2O : EtOH. White solid, m.p. = 53–54 °C (lit 54 °C). NMR ($CDCl_3$) δ ^1H: 6.93 (2H); 7.08 (m 4H), 7.24–7.29 (m, 4H); δ ^{13}C 118.0, 121.2, 129.2, 142.8.

N-Phenylmorpholine was purified by vacuum distillation. B.p. = 128–130 °C/12 mmHg. Brown solid. NMR ($CDCl_3$) δ ^1H: 3.2 (t, 4H), 3.91 (t, 4H), 6.91–7.05 (3H), 7.31 (2H); δ ^{13}C: 49.8, 67.2, 115.8, 120.6, 130.1, 151.5.

N-Phenyl(diethanol)amine was purified by vacuum distillation. B.p. = 112–116 °C/8 mmHg. Yellow solid. NMR ($CDCl_3$) δ ^1H: 3.63 (t, 4H); 3.95 (t, 4H); 6.87 (m, 3H); 7.18 (m, 2H); δ ^{13}C ($CDCl_3$) 55.58; 60.98; 113.0; 117.3; 129.9; 148.5.

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