Notes

Synthesis and Characterization of [(Trimethylsilyl)methyl]- and [Bis(trimethylsilyl)methyl]phosphines

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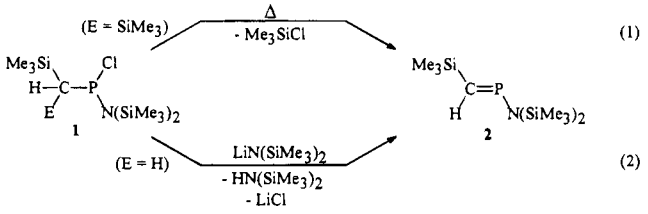
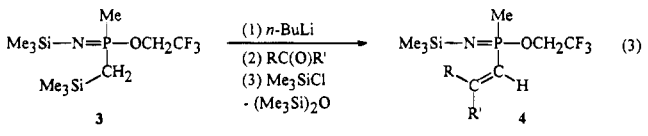
Introduction

Compounds which contain the silicon−carbon−phosphorus linkage are versatile synthetic reagents for at least two reasons. First, the electropositive nature of silicon relative to carbon makes the Si−C bond susceptible to cleavage by nucleophilic attack at silicon. This feature is often manifested in elimination reactions leading, for example, to methylenephosphines (e.g., **2**, eq 1).[1,2] Second, the π-accepting ability of silicon increases the acidity of protons bound to carbon in groups such as Me_3Si-CH_2-P. This can be used to synthetic advantage in a number of ways, such as base-induced dehydrohalogenation, again leading to methylenephosphines (e.g., **2**, eq 2)[3]



These two useful effects of silyl substitution can be combined in some processes, the most notable of which is the Peterson olefination reaction.[4] In this type of reaction, the anion derived from a Me_3Si-CH_2 moiety is treated with a carbonyl compound. After silyl migration to oxygen and elimination of Me_3SiOLi or $Me_3SiOSiMe_3$, the result is formation of a C=C double bond. The process is illustrated in eq 3 for the conversion of (silylmethyl)phosphoranimines (e.g., **3**) to *P*-vinyl-substituted *N*-silylphosphoranimines (**4**).[5]



Despite their synthetic utility, the known Si−C−P compounds are still relatively few in number. This is especially true of unsymmetrically substituted species and/or those that contain reactive functional groups (e.g., P−Cl) on phosphorus. Some important exceptions to this statement are the dichloro(silylmethyl)phosphines, $Me_3SiCH(R)PCl_2$ [R = H,[6] Ph,[6] $SiMe_3$[7]], and the trisilylmethyl analog, $(Me_3Si)_3CPCl_2$,[8] which have been used extensively as precursors to methylenephosphines.[2] Within the context of our continuing studies of the chemistry of novel low-coordinate phosphorus compounds and various types of phosphorus-based polymer systems, we have had many occasions to prepare new silicon−carbon−phosphorus reagents. Many of these compounds may also be of use as novel ligands in organometallic complexes. We report here the synthesis and characterization of a series of new (silylmethyl)phosphines bearing varied combinations of potentially reactive groups (e.g., Cl, OCH_2CF_3, NMe_2, etc.) on phosphorus.

Results and Discussion

Synthesis. The new compounds in this study were generally prepared by treatment of the appropriate silylmethyl Grignard reagents [derived from Me_3SiCH_2Cl or $(Me_3Si)_2CHCl$] or the alkyllithium derivative of Me_3SiCH_2Ph, with either PCl_3 or $PhPCl_2$ (eq 4). The remaining P−Cl bonds were then replaced by dimethylamino and/or trifluoroethoxy groups upon subsequent addition of Me_3SiNMe_2 and/or $LiOCH_2CF_3$ (eq 5). These new mono- and bis(silylmethyl)phosphines were obtained in ca. 40−80% yields as distillable liquids that were fully characterized by NMR spectroscopy and elemental analysis (Tables 1 and 2).

In the synthesis of the unsymmetrical derivatives that contain both OCH_2CF_3 and NMe_2 groups (**6**, **11**, and **14**), it was necessary to introduce the dimethylamino group first by treatment of the dichlorophosphine (eq 4) with 1 equiv of the silylamine, Me_3SiNMe_2 (eq 5). As is usually the case, these Si−N bond cleavage reactions proceeded smoothly and selectively to give the monosubstituted products, $Me_3SiCH(E)P(Cl)NMe_2$ (**7**: E = H, and **15**, E = Ph). The other member of this series (E = $SiMe_3$) has been previously prepared by a different procedure.[9] In all cases, the P−Cl derivatives were readily converted to the $P-OCH_2CF_3$ analogs by reaction with lithium trifluoroethoxide. It was not possible, however, to cleanly obtain monosubstituted trifluoroethoxy compounds such as $Me_3SiCH_2P(OCH_2CF_3)Cl$ by using only 1 equiv of $LiOCH_2CF_3$ with a dichlorophosphine.

In a somewhat different procedure, the silylmethyl Grignard reagent, Me_3SiCH_2MgCl, was also treated with chloro(dimethylamino)phosphines, $RP(NMe_2)Cl$ (R = Ph, *t*-Bu), to afford compounds **8** and **17** (eq 6) in over 80% yield. This reaction occurred smoothly even for the sterically congested *tert*-butylphosphine substrate. The unsymmetrical chlorophosphines **18**[6] and **19**, are then obtained by subsequent reaction of the $P-NMe_2$ intermediates with either PCl_3 or anhydrous HCl (eq 7). In this reaction sequence, the dimethylamino group essentially serves a protecting role on route to the P−Cl species. Further reaction, for example with $LiOCH_2CF_3$ (eq 8), is possible and leads to the fully substituted derivatives **9** and **20**, respectively.

(1) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585.
(2) For some general reviews of the field of low-coordinate phosphorus compounds, see, for example: (a) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 217. (b) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989**, *33*, 259. (c) Regitz, M. *Chem. Rev.* **1990**, *90*, 191. (d) Cowley, A. H. *Polyhedron* **1984**, *3*, 389. (e) Markovski, L. N.; Romanenko, V. D. *Tetrahedron* **1989**, *45*, 6019.
(3) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1969.
(4) (a) Peterson, D. J. *J. Org. Chem.* **1968**, *33*, 780. (b) For a general review, see: Ager, D. J. *Synthesis* **1984**, 384.
(5) Scheide, G. M.; Neilson, R. H. *Organometallics* **1989**, *8*, 1987.
(6) Corriu R. J. P.; Masse, J.; Samati, D. J. *J. Organomet. Chem.* **1975**, *93*, 71.
(7) Ford, R. R.; Neilson, R. H. *Polyhedron* **1986**, *5*, 643.
(8) Issleib, K.; Schmidt, H.; Wirkener, C. *Z. Chem.* **1980**, *20*, 419.
(9) Goldwhite, H.; Power, P. P. *Org. Magn. Reson.* **1978**, *11*, 10.

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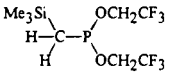
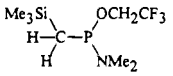
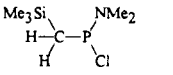
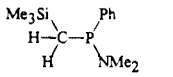
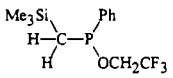
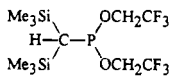
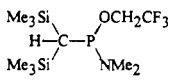
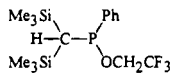
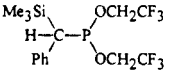
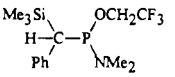
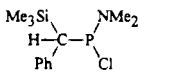
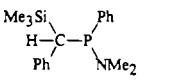
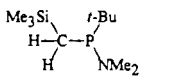
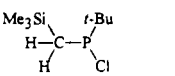
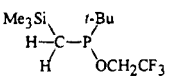
Table 1. NMR Spectral Data[a] for (Silylmethyl)phosphines

Compound	Signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 **5**	Me_3Si	0.13		0.13	3.9	206.1
	PCH_2	1.13	5.6	24.79	35.6	
	OCH_2	4.1[b]		64.27	11.7	
					(34.8)[c]	
	CF_3			123.85	7.0	
					(278.0)[c]	
 **6**	Me_3Si	0.06		- 0.17	5.1	187.5
	PCH_2	1.02	14.4	21.67	27.1	
	NMe_2	2.67	8.8	38.41	15.9	
	OCH_2	3.9[b]		65.40	19.5	
					(34.0)[c]	
	CF_3			124.50	8.2	
					(274.0)[c]	
 **7**	Me_3Si	0.11		- 0.15	5.1	162.9
	PCH_2	1.52	5.8	27.08	46.1	
	NMe_2	2.03	15.7	39.50	19.9	
 **8**	Me_3Si	0.13		0.07	5.1	54.7
	PCH_2	1.34[d]	0.2	24.79	29.0	
			[13.4][e]			
		1.06[d]	5.4			
	NMe_2	2.53	9.2	40.83	12.6	
	Ph	7.3-7.4[b]		127-130[b]		
 **9**	Me_3Si	0.03		0.02	5.5	136.4
	PCH_2	1.27[d]	5.9	24.93	31.4	
			[12.9][e]			
		1.53[d]	2.1			
	OCH_2	3.9[b]		66.31	9.9	
					(35.4)[c]	
	CF_3			124.50	9.9	
					(269.3)[c]	
	Ph	7.3-7.4[b]		127-130[b]		
 **10**	Me_3Si	0.13		2.12	3.5	228.5
	CH	0.52	3.5	27.35	39.0	
	OCH_2	4.1[b]		65.93	21.4	
					(35.0)[c]	
	CF_3			123.85	123.85	
					(278.0)[c]	
 **11**	Me_3Si[f]	0.06		1.40	6.5	165.2
		0.10		2.40	4.0	
	CH	1.00	3.1	21.78	49.2	
	NMe_2	2.62	7.5	39.01	16.7	
	OCH_2	3.8[b]		64.59	18.1	
					(35.2)[c]	
	CF_3			124.45	9.3	
					(277.8)[c]	
 **12**	Me_3Si[f]	0.03		1.60		146.8
		0.22		2.55	5.0	
	CH	1.15	1.0	24.13	47.7	
	OCH_2	3.8[b]		66.09	21.4	
					(35.3)[c]	
	CF_3			129.53	13.1	
					(277.7)[c]	
	Ph	7.4-7.7[b]		128-144[b]		
 **13**	Me_3Si	0.10		- 0.94	3.0	202.6
	CH	2.74		45.89	36.4	
	OCH_2[g]	4.18	2.4	65.82	16.7	
			(7.7)[c]		(35.4)[c]	
		3.93	3.5	53.80	10.6	
			(8.4)[c]		(35.4)[c]	
	CF_3			129.00	4.6	
					(288.6)[c]	
	Ph	7.1-7.3[b]		128-130[b]		
 **14**	Me_3Si	0.06		- 1.20	4.1	159.6[h]
	CH	2.75	9.7	43.20	31.0	151.0
	NMe_2	2.49	8.1	39.29	17.2	
	OCH_2	3.8[b]		66.49	20.1	
					(33.8)[c]	
	CF_3			129.65	5.8	
					(276.1)[c]	
	Ph	7.1-7.3[b]			128-129[b]	
 **15**	Me_3Si[h]	0.13		- 0.69	3.5	151.5[h]
		0.19		- 1.34	2.5	161.7
	CH	3.20	1.5	37-41[b]		
		3.22	3.0			
	NMe_2	2.80	12.4	45.59	49.5	
		2.57	12.9	44.63	51.4	
	Ph	7.1-7.6[b]		125-140[b]		
 **16**	Me_3Si[h]	- 0.06		- 1.08	3.8	59.7[h]
		0.23		- 1.25	3.8	63.8
	CH	2.88	9.2	36.28	35.0	
		2.77	9.4	34.84	27.6	
	NMe_2	2.43	8.7	40.78	13.0	
		2.61	9.1	41.72	15.3	
	Ph	7.3-7.8[b]		124-141[b]		
 **17**	Me_3Si	- 0.03		- 0.16	4.8	70.0
	PCH_2	0.14[d]	6.9	9.90	32.4	
			[14.2][e]			
		1.05[d]	13.2			
	Me_3C	0.86	12.2	27.05	16.3	
	Me_3C			34.53	22.4	
	NMe_2	2.53	7.5	42.05	14.9	
 **19**	Me_3Si	0.10		0.30	4.5	129.0
	PCH_2	0.97	8.6	17.33	53.7	
	Me_3C	1.04	13.4	25.02	18.0	
	Me_3C			33.35	32.0	
 **20**	Me_3Si	0.06		0.11	4.1	161.1
	PCH_2	0.44[d]	8.8	16.28	38.3	
			[14.0][e]			
		1.04[d]	1.5			
	Me_3C	0.94	12.4	24.74	15.8	
	Me_3C			33.61	18.9	
	OCH_2	3.9[b]		66.0	23.6	
					(34.7)[c]	
	CF_3			129.1	12.4	
					(278.5)[c]	

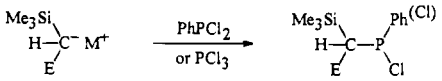
[a] Proton and ^{13}C chemical shifts downfield from Me_4Si; ^{31}P shifts downfield from H_3PO_4; $CDCl_3$ solvent. [b] Complex multiplet. [c] J_{FH} or J_{FC} values in parentheses. [d] Diastereotopic protons within CH_2 group. [e] J_{HH} values in brackets. [f] Diastereotopic Me_3Si groups. [g] Diastereotopic OCH_2CF_3 groups. [h] Diastereomers.

Characterization. In addition to satisfactory elemental analysis (Table 2), compounds **5**−**20** were fully characterized by multinuclear NMR spectral data (Table 1). For the most part, all of the chemical shifts, coupling constants, and integrated intensities were readily interpreted on the basis of the assigned structures. Several points about the NMR spectral data,

Table 2. Preparative and Analytical Data for (Silylmethyl)phosphines

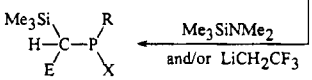
compd	yield, %	bp, °C/mmHg	analysis[a] C	analysis[a] H
5	46	32−35/0.02	29.72 (30.11)	4.96 (4.78)
6	46	35−41/0.02	37.12 (36.77)	7.58 (7.33)
7	50	41−44/0.02	36.28 (36.45)	8.74 (8.67)
8	83	44−45/0.01	60.24 (60.25)	9.17 (9.20)
9	56	55−60/0.02	49.00 (48.97)	6.12 (6.16)
10	59	51−52/0.03	34.25 (34.01)	6.05 (5.97)
11	63	52−55/0.02	39.04 (39.62)	8.32 (8.16)
12	36	85−90/0.10	49.38 (49.18)	7.64 (7.15)
13	50	75−76/0.02	43.02 (42.86)	4.91 (4.84)
14	61	85−88/0.02	49.86 (49.84)	7.02 (6.87)
15	69	90−92/0.02	52.49 (52.64)	7.64 (7.73)
16	36	135−140/0.02	68.33 (68.53)	8.11 (8.31)
17	85	52−53/1.7	54.54 (54.75)	11.98 (11.95)
19	87	53−54/2.1	45.44 (45.59)	9.53 (9.57)
20	79	49−50/2.1	43.60 (43.78)	8.00 (8.08)

[a] Calculated values in parentheses.



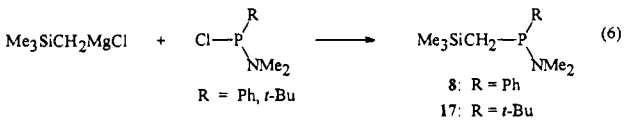
(4)

E = H, $SiMe_3$; M = MgCl
E = Ph; M = Li(TMEDA)



(5)

No.	E	R	X
5	H	OCH_2CF_3	OCH_2CF_3
6	H	OCH_2CF_3	NMe_2
7	H	Cl	NMe_2
8	H	Ph	NMe_2
9	H	Ph	OCH_2CF_3
10	$SiMe_3$	OCH_2CF_3	OCH_2CF_3
11	$SiMe_3$	OCH_2CF_3	NMe_2
12	$SiMe_3$	Ph	OCH_2CF_3
13	Ph	OCH_2CF_3	OCH_2CF_3
14	Ph	OCH_2CF_3	NMe_2
15	Ph	Cl	NMe_2
16	Ph	Ph	NMe_2



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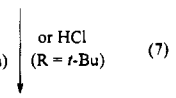

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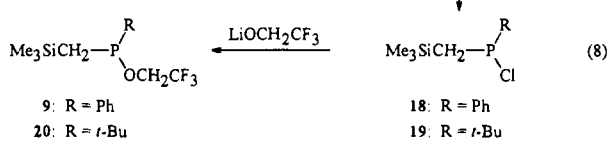

(8)

however, are noteworthy. First, the ^{31}P chemical shifts of these compounds span a very wide range due to the variety of substituents present. Other things being equal, the ^{31}P signal shifts downfield in the order: OCH_2CF_3 > Cl > NMe_2 [e.g., **20** (OCH_2CF_3) δ 161; **19** (Cl) δ 129; **18** (NMe_2) δ 70]. Second, the *C*-phenyl compounds **14**−**16** exist as mixtures of diastereomers due to the presence of chiral centers at both phosphorus and carbon. This is evidenced by the observation of two signals in the ^{31}P NMR spectra of these compounds and a doubling of the number of Me_3Si, CH, and NMe_2 signals in some ^1H and ^{13}C NMR spectra, especially for **15** and **16** (Table 1). Third, the unsymmetrical substitution pattern *at phosphorus* in several compounds leads to the observation of diastereotopic 1H NMR signals (for example, the CH_2 protons in **8** and **9** and the Me_3Si protons in **11** and **12**). Fourth, the unsymmetrical substitution pattern *at carbon* in **13** is reflected in the presence of two sets of signals in the ^1H and ^{13}C NMR spectra for the nonequivalent $POCH_2CF_3$ groups.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: PCl_3, $PhPCl_2$, Me_3SiCl, Me_3SiCH_2Cl, Me_3SiNMe_2, *n*-BuLi (hexane solution), *t*-BuLi (pentane solution), and CF_3CH_2OH. Hexane, ether, and CH_2Cl_2 were distilled from CaH_2 and stored over molecular sieves. THF was distilled from sodium benzophenone immediately prior to use. The following starting materials were prepared according to published procedures: $(Me_3Si)_2CHCl$,[10] $Me_3SiCH(R)PCl_2$ (R = H,[6] Ph,[6] Me_3Si[8]). The dichlorophosphine, *t*-$BuPCl_2$,[11] was prepared by slow addition of *t*-BuLi (pentane solution) to an excess of PCl_3 (1.5 equiv) in Et_2O (ca. 1 M solution) at −78 °C. The amino(chloro)phosphines, $Me_2NP(R)Cl$ (R = Ph,[12] *t*-Bu[13]), were prepared by addition of Me_3SiNMe_2 to an equimolar amount of $RPCl_2$ in CH_2Cl_2 at 0 °C. Proton, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-300 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are typical of those used for the preparation of the new compounds in this study. The physical, analytical, and NMR spectroscopic data for the new compounds are summarized in Tables 1 and 2.

Chloro(dimethylamino)[(trimethylsilyl)methyl]phosphine (7). A 100-mL, three-neck flask, equipped with a magnetic stirrer, a septum, and N_2 inlet adapter, was charged with CH_2Cl_2 (40 mL) and $Me_3SiCH_2PCl_2$ (5.7 g, 30 mmol). The solution was cooled to 0 °C, and Me_3SiNMe_2 (3.5 g, 30 mmol) was added via syringe. The mixture was allowed to warm to room temperature and was stirred for 30 min. The mixture was filtered under N_2 to remove a small amount of unidentified white solid. After the solvent was removed under reduced pressure, distillation afforded **7** as a colorless liquid.

(Dimethylamino)(2,2,2-trifluoroethoxy)[(trimethylsilyl)methyl]phosphine (6). A 100-mL, three-neck flask, equipped with a magnetic stirrer, a septum, and N_2 inlet adapter, was charged with Et_2O (25 mL) and CF_3CH_2OH (1.5 g, 15 mmol). The solution was cooled to 0 °C, and *n*-BuLi (5.6 mL, 2.6 M, 15 mmol) was added slowly via syringe. The mixture was allowed to stir for 30 min and was then cooled to −78 °C. The chlorophosphine **7** (2.9 g, 15 mmol) was added via syringe to the stirred solution of CF_3CH_2OLi at −78 °C. The mixture was then allowed to warm to room temperature and was stirred overnight. Following filtration and solvent removal, distillation gave **6** as a colorless liquid.

***tert*-Butyl(dimethylamino)[(trimethylsilyl)methyl]phosphine (17).** A 1-L, three-neck flask, equipped with a large addition funnel, magnetic stirrer, and N_2 inlet adapter, was charged with Et_2O (300 mL) and the chlorophosphine, *t*-$BuP(NMe_2)Cl$ (46.3 g, 255 mmol). In a separate flask, a solution of the Grignard reagent, Me_3SiCH_2MgCl (ca. 255 mmol), in Et_2O (300 mL) was prepared according to the published procedure.[14] The Grignard solution was transferred to the addition funnel under N_2 and was then added slowly to the stirred solution of *t*-$BuP(NMe_2)Cl$ at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 48 h to complete the reaction. Following filtration and solvent removal, distillation gave **17** as a colorless liquid.

***tert*-Butyl(chloro)[(trimethylsilyl)methyl]phosphine (18).** A 1-L, three-neck flask, equipped with a magnetic stirrer, a septum, and N_2

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atmosphere, was charged with hexane (300 mL) and the (dimethylamino)phosphine **17** (25.0 g, 114 mmol). The mixture was cooled to 0 °C, and a syringe needle attached to a cylinder of anhydrous HCl was inserted through the septum into the solution. Gaseous HCl was bubbled into the solution while it was stirred at 0 °C. Periodically, the stirring was stopped in order to observe formation of the salt, Me_2NH_2Cl, near the syringe needle. Addition of HCl was continued until this salt formation was no longer observed. The mixture was allowed to warm to room temperature while stirring. Following filtration and solvent removal, distillation afforded **18** as a colorless liquid.

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