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Synthesis and reactivity of P-acetylenic (silylamino)phosphines

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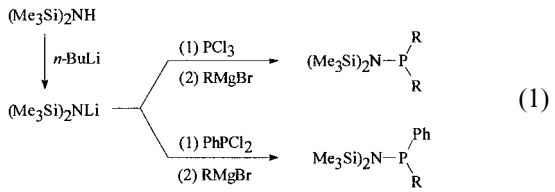
Abstract

The title compounds, $(Me_3Si)_2NP(C{\equiv}CR)_2$ (**1**: R = $SiMe_3$; **2**: R = *n*-Bu; **3**: R = CH_2OCH_3), $(Me_3Si)_2NP(Ph)C{\equiv}CSiMe_3$ (**4**), and $(Me_3Si)_2NP(R)C{\equiv}CCH_2OCH_3$ (**5**: R = *i*-Pr; **6**: R = CH_2SiMe_3; **7**: R = *n*-Bu) were obtained from the reactions of C-lithiated acetylenes LiC≡CR with either mono- or dichloro substituted (silylamino)phosphines. Similar reactions involving HC≡CMgCl gave the parent P-ethynyl derivatives, $(Me_3Si)_2NP(R)C{\equiv}CH$ (**12**: R = CH_2SiMe_3; **13**: R = Ph). Deprotonation–substitution at the terminal C–H group of **12** readily afforded the Me_3Si derivative, $(Me_3Si)_2NP(CH_2SiMe_3)C{\equiv}CSiMe_3$ (**14**). Oxidative bromination of **7** gave the P-bromophosphoranimine, $Me_3SiN{=}P(n\text{-Bu})(C{\equiv}CCH_2OCH_3)Br$ (**8**). The P-trifluoroethoxy analogs, $Me_3SiN{=}P(CH_2SiMe_3)(C{\equiv}CCH_2OCH_3)OCH_2CF_3$ (**10**) and $Me_3SiN{=}P(C{\equiv}CSiMe_3)_2OCH_2CF_3$ (**11**), were prepared from phosphines **6** and **1**, respectively, via bromination followed by substitution with CF_3CH_2OH–Et_3N. The diphosphinoacetylenes, $(Me_3Si)_2N(R)P{-}C{\equiv}C{-}P(R)N(SiMe_3)_2$ (**15**: R = *n*-Pr; **16**: R = CH_2SiMe_3), were obtained by treating appropriate P-chloro(silylamino)phosphines with the carbide reagent LiC≡CMgCl. All of these P-acetylenic derivatives were thermally stable, distillable liquids that were characterized by NMR spectroscopy. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphines; P-acetylenic; Acetylenes; Phosphoranimines

1. Introduction

Compounds containing the silicon–nitrogen–phosphorus linkage have a rich derivative chemistry and considerable synthetic utility. Depending on the oxidation state of phosphorus and the nature and reactivity of the substituents, such compounds are useful as precursors to cyclic and polymeric phosphazenes, $[R_2P{=}N]_n$ [1], and low-coordinate phosphorus systems, e.g. $R_2NP{=}ER$ (R = $SiMe_3$, E = N, CH) [2]. The most general and convenient synthetic route to Si–N–P compounds involves the initial preparation of (silylamino)phosphines via the Wilburn method [3]. This process utilizes sequential substitution reactions of either PCl_3 or $PhPCl_2$ in a one-pot synthesis (Eq. (1)).



(1)

R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, CH_2Ph, $CH{=}CH_2$, $CH_2CH{=}CH_2$, CH_2SiMe_3, etc.

We report here on a useful variation of this approach that allows for the incorporation of acetylenic functional groups (–C≡CR, R = H, Ph, $SiMe_3$, etc.) at phosphorus. In addition, some representative examples of the derivative chemistry, including oxidative halogenation at phosphorus and deprotonation–substitution of the terminal –C≡CH moiety, are described.

Other types of acetylenic phosphorus compounds (i.e. without the Si–N functionality) have been previously reported. These include the parent ethynylphosphines, $H_2PC{\equiv}CH$ [4] and $P(C{\equiv}CH)_3$ [5], as well as various alkylamino derivatives, e.g. $R_2NP(C{\equiv}CPh)_2$ and $R_2NP(Cl)C{\equiv}CPh$ [6]. Some terminal acetylenes, e.g. $Ph_2PC{\equiv}CH$, have been converted via deprotonation–substitution to silylated derivatives, e.g. $Ph_2PC{\equiv}CSiMe_3$ [7]. Some acetylenic derivatives containing two-coordinate phosphorus centers, e.g. $RC{\equiv}C{-}P{=}C(SiMe_3)_2$ [8] have also been prepared. Finally, we have reported a series of novel P(III) and P(V) compounds containing P-acetylene or allene linkages from the reactions of terminal acetylenes with two- or three-coordinate (silylamino) phosphines [9].

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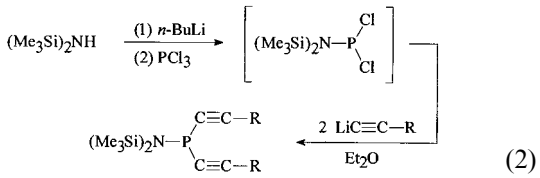
2. Results and discussion

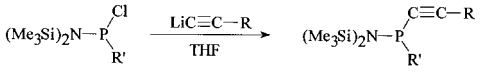
In this study, we initially used the Wilburn method to prepare the symmetrically substituted diacetylenic (silylamino)phosphines **1**–**3** (Eq. (2)). In this process, the intermediate dichlorophosphine was not isolated but was simply treated at 0 °C with two equivalents of an appropriate C-lithiated acetylene. The latter reagents were prepared by treating trimethylsilylacetylene, phenylacetylene, or methyl propargyl ether with *n*-BuLi in THF solution at −78 °C.



(2)

1: R = $SiMe_3$
2: R = *n*-Bu
3: R = CH_2OCH_3

Similarly, the reactions of stable mono-chlorophosphines [10,11] with one equivalent of the lithium acetylide were used to prepare the series of mono-acetylene derivatives **4**–**7** (Eq. (3)).



(3)

4: R = $SiMe_3$; R' = Ph
5: R = CH_2OCH_3; R' = *i*-Pr
6: R = CH_2OCH_3; R' = CH_2SiMe_3

The acetylenic phosphines **1**–**7** were obtained in moderate to good yields (42–83%) as colorless, distillable liquids that were fully characterized by NMR (^1H, ^{13}C, and ^{31}P) spectroscopy (Table 1) and elemental analysis (Table 2). The yields of these acetylenic phosphines were quite dependent on the reaction conditions employed. Optimal yields were obtained when deprotonation of the terminal alkyne was performed in THF solution at −78 °C. By allowing the acetylide solution to warm slowly to room temperature, formation of unidentified tar-like residues was reduced. In contrast, when the deprotonation was carried out at 0 °C, lower yields of the final product and much larger amounts of black, gummy material in the crude product were observed.

The structures of **1**–**7** were readily confirmed by the NMR spectroscopic data. Most notably, in the ^{13}C-NMR spectra, two doublets are consistently observed (in the range ca. 80–115 ppm) for the sp-hybridized, acetylenic carbon centers. The ^{31}P chemical shifts of these compounds are significantly upfield of their alkyl- or aryl-substituted analogs, consistent with the increased shielding provided by the electron-rich –C≡C– substituent. For example, the ^{31}P resonance moves dramatically upfield in the following series (R = $SiMe_3$):

Table 1
NMR spectroscopic data for P-acetylenic Si–N–P compounds

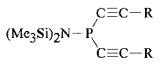
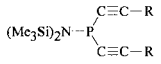
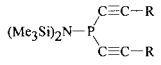
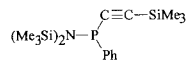
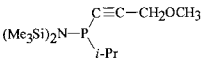
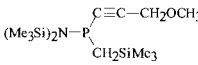
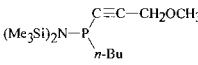
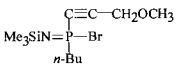
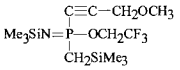
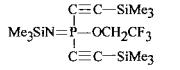
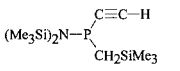
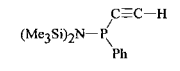
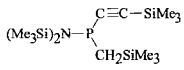
Compound	Signal	^1H NMR δ	^1H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
	P-*C*≡C			107.4	23.0	- 10.4
	P-C≡*C*			114.7	1.5	
	C-Si*Me*$_3$	0.18		- 0.2		
1: R = $SiMe_3$	N-Si*Me*$_3$	0.30	1.0	3.7	7.6	
	P-*C*≡C			81.1	11.8	- 9.5
	P-C≡*C*			108.3	9.0	
	-C≡C-*CH*$_2$	2.31	2.8	30.6	2.3	
2: R = *n*-Bu			(7.0)[b]			
	-CH_2-*C*H_2-	1.45	3.4	22.2		
			[c]	20.2		
	-C_2H_4-*CH*$_3$	0.90	(7.1)[b]	13.8		
	N-Si*Me*$_3$	0.27	1.1	3.7	7.8	
	P-*C*≡C			87.4	19.0	- 11.4
	P-C≡*C*			103.1	7.7	
	-*CH*$_2$-O	4.20	2.2	60.7		
3: R = CH_2OCH_3	-O-*CH*$_3$	2.28		57.8		
	N-Si*Me*$_3$	0.29	1.1	3.6	7.6	
	P-*C*≡C			109.1	33.6	22.8
	P-C≡*C*			116.9	2.4	
	C-Si*Me*$_3$	0.25		- 0.1		
4	N-Si*Me*$_3$	0.22		3.9	7.1	
	Ph	7.2-7.5		143.2 (C^1)	11.4	
				129.0 (C^2)	17.8	
				128.3 (C^3)	3.7	
				127.6 (C^4)	2.0	
	P-*C*≡C			90.1	37.5	29.3
	P-C≡*C*			103.4	2.2	
	-*CH*$_2$-O	4.17		60.8		
5	-O-*CH*$_3$	3.34		57.6		
	-*CH*(CH$_3$)$_2$	2.26	8.8	29.4	8.8	
			(7.0)[b]			
	-CH(*CH*$_3$)$_2$	1.02	3.1	18.1	28.4	
			(7.0)[b]			
		0.95	(7.0)[b]	18.7	23.9	
	N-Si*Me*$_3$	0.02		4.2	7.0	
	P-*C*≡C			92.4	36.3	14.8
	P-C≡*C*			103.7		
	-*CH*$_2$-O	4.18	2.1	60.8		
6	-O-*CH*$_3$	3.37		57.7		
	-*CH*$_2$-Si	1.69	1.4	23.8	33.4	
			(13.3)[b]			
		0.90	1.1			
			(13.3)[b]			
	-CH_2Si*Me*$_3$	0.10	0.9	0.0	4.5	
	N-Si*Me*$_3$	0.24	1.1	4.2	7.9	
	P-*C*≡C			90.6	36.2	18.0
	P-C≡*C*			103.7		
	-*CH*$_2$-O	4.18	1.9	60.8		
7	-O-*CH*$_3$	3.36		57.7		
	P-*CH*$_2$-	1.7-1.8[c]		33.5	12.3	
	P-CH_2*CH*$_2$-	1.3-1.4[c]		27.4	20.4	
	-*CH*$_2$-CH_3	1.3-1.4[c]		24.1	14.8	
	-CH_2-*CH*$_3$	0.90	(6.8)[b]	14.1		
	N-Si*Me*$_3$	0.23	1.1	4.2	7.3	

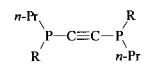
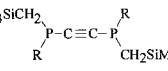
Table 1 (*Continued*)

 **8**	P-C≡C			82.8	156.7	- 28.3
	P-C≡*C*			97.4	26.6	
	-*CH*$_2$-O	4.22	3.0	59.9	2.9	
	-O-*CH*$_3$	3.39		58.3		
	P-*CH*$_2$-	2.2-2.3[c]		42.7	105.8	
	P-CH$_2$*CH*$_2$-	1.6-1.8[c]		25.1	5.7	
	-*CH*$_2$-CH$_3$	1.4-1.5[c]		23.2	22.3	
	-CH$_2$-*CH*$_3$	0.92	(7.3)[b]	13.8		
	N-Si*Me*$_3$	0.08		2.3	6.7	
 **10**	P-C≡C			82.8	169.2	- 1.6
	P-C≡*C*			95.3	29.8	
	-*CH*$_2$-O	4.17	2.9	60.0	2.9	
	-O-*CH*$_3$	3.38		58.2		
	-*CH*$_2$-Si	1.3-1.4[c]		23.9	116.2	
	-CH$_2$Si*Me*$_3$	0.05		0.0	4.1	
	-O*CH*$_2$CF$_3$	4.16	8.4	60.2	5.9	
			(20.1)[d]		(36.9)[e]	
	-OCH$_2$*CF*$_3$			123.7	11.9	
					(277.4)[e]	
	N-Si*Me*$_3$	0.17		3.1	4.1	
 **11**	P-C≡C			98.8	229.0	- 41.4
	P-C≡*C*			109.8	33.4	
	C-Si*Me*$_3$	0.08		2.7		
	-O*CH*$_2$CF$_3$	4.22	10.0	60.7	4.2	
			(8.3)[d]		(37.6)[e]	
	-OCH$_2$*CF*$_3$			123.2	11.9	
					(277.6)[e]	
	N-Si*Me*$_3$	0.22		0.9		
 **12**	P-C≡C			90.7	39.3	16.3
	P-C≡*CH*	3.17	1.9	95.1	29.8	
	-*CH*$_2$-Si	1.71	1.2	23.7	33.5	
			(13.3)[b]			
		0.91	1.4			
			(13.3)[b]			
	-CH$_2$Si*Me*$_3$	0.12		0.1	5.5	
	N-Si*Me*$_3$	0.26	1.1	4.2	8.1	
 **13**	P-C≡C			87.0	34.5	24.2
	P-C≡*CH*	3.43	1.7	96.9	3.8	
	N-Si*Me*$_3$	0.25		3.9	6.7	
	Ph	7.3-7.7[c]		128-130[c]		
 **14**	P-C≡C			113.0	36.8	15.0
	P-C≡*C*			115.0		
	≡C-Si*Me*$_3$	0.16		- 0.2		
	-*CH*$_2$-Si	1.68	1.2	24.2	34.0	
			(13.2)[b]			
		0.89	1.9			
			(13.2)[b]			
	-CH$_2$Si*Me*$_3$	0.12	0.9	0.1	5.3	
	N-Si*Me*$_3$	0.25	1.1	4.3	7.9	

R_2NPPh_2 (48.1 ppm) [12], $R_2NP(Ph)C{\equiv}CR$ (**4**: 22.8 ppm), and $R_2NP(C{\equiv}CR)_2$ (**1**: − 10.4 ppm).

Like most (silylamino)phosphines [13], these P-acetylenic derivatives underwent facile oxidative halogenation reactions to yield *N*-silyl-P-halophosphoranimines. Bromine, for example, reacted exclusively at the P(III) center with no sign of addition to the C≡C triple bond. In the case of phosphine **7**, the P-bromophosphoranimine **8** (Eq. (4)) was isolated as a distillable liquid but it could not be purified sufficiently for elemental analysis. Nevertheless, it did provide some interesting NMR spectroscopic data. As was observed for the P(III) systems above, the ^{31}P chemical shift (− 28.3 ppm) lies ca. 40 ppm upfield of the dialkyl analogs [13]. Compound **8** also exhibits a very large

Table 1 (*Continued*)

 **15**: R = N(SiMe$_3$)$_2$	P-C≡			113.2	38.4	13.9[f]
					2.4	
	P-C≡			112.7	38.4	12.3[f]
					2.6	
	P-*CH*$_2$-	1.5-1.8[c]		36.0	13.9	
				35.8	12.5	
	-*CH*$_2$CH$_3$	1.5-1.8[c]		18.8	21.0	
				18.9	22.4	
	-CH$_2$-*CH*$_3$	1.01	7.7	15.8	17.5	
				15.8	17.5	
	N-Si*Me*$_3$	0.25		4.2		
 **16**: R = N(SiMe$_3$)$_2$	P-C≡			114.2	40.7	16.0[f]
						15.1[f]
	-*CH*$_2$SiMe$_3$	1.69	(13.2)[b]	23.1	35.3	
		1.66	(13.2)[b]		3.5	
		0.92	(13.2)[b]	23.0	33.7	
		0.90	(13.2)[b]			
	-CH$_2$Si*Me*$_3$	0.10	0.8	0.1		
	N-Si*Me*$_3$	0.25		4.2		

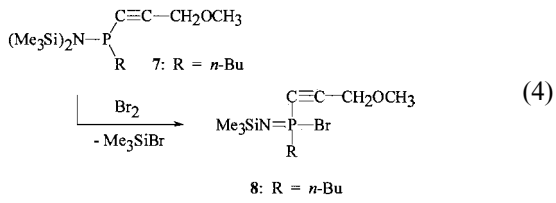
[a] Proton and ^{13}C chemical shifts downfield from Me_4Si; ^{31}P shifts downfield from H_3PO_4. Solvent: $CDCl_3$. [b] J_{HH} values in parentheses. [c] Complex multiplet. [d] J_{HF} values in parentheses. [e] J_{CF} values in parentheses. [f] Two signals due to diastereomers.

Table 2
Preparative and analytical data for P-acetylenic Si–N–P compounds

Compound	Yield (%)	bp (°C/mmHg)	Analysis [a]	
			%C	%H
1	76	88–90/0.01	49.43 (49.81)	9.28 (9.41)
2	42	112–114/0.01	60.85 (61.14)	10.45 (10.26)
3	44	109–110/0.01	50.87 (51.03)	9.01 (8.56)
4	56	110–112/0.01	55.92 (55.84)	8.86 (8.82)
5	83	71–78/0.01	51.01 (51.44)	9.91 (9.96)
6	53	78–79/0.01	49.15 (48.37)	10.21 (9.86)
7	50	81–82/0.01	52.72 (52.95)	10.03 (10.16)
8	52	95–99/0.01	[b]	[b]
10	63	63–66/0.01	41.83 (41.81)	7.47 (7.29)
11	49	73–74/0.01	43.91 (43.77)	7.26 (7.10)
12	52	56–57/0.01	47.51 (47.47)	10.35 (9.96)
14	82	75–76/0.01	47.36 (47.94)	10.46 (10.19)
15	57	140–141/0.01	48.82 (48.73)	10.15 (10.22)
16	33	154–156/0.01	49.50 (49.40)	10.32 (10.47)

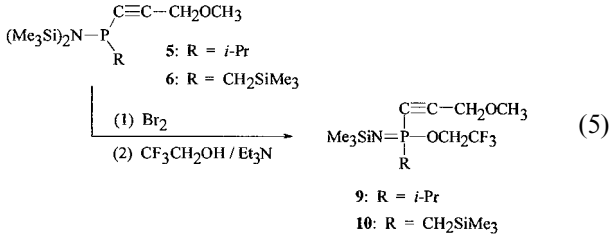
[a] Calculated values in parentheses.
[b] Inseparable impurity precluded elemental analysis.

one-bond $^1J_{PC}$ coupling constant (157 Hz) as compared with values of 80–100 Hz that are typically observed for P-alkylphosphoranimines [13]. Similar differences in the $^1J_{PC}$ values in P(III) and P(V) analogs have been observed [6].



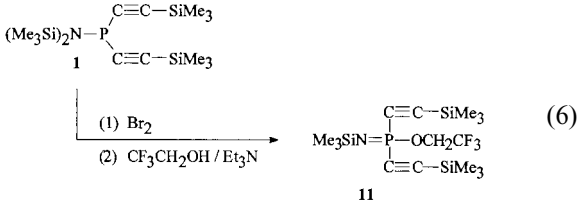
(4)

Instead of isolating the P-bromo intermediates, it was also possible to convert the P–C≡C– substituted (silylamino)phosphines directly to their P-trifluoroethoxy derivatives such as **9** and **10** in a one-pot synthesis (Eq. (5)) using CF_3CH_2OH and Et_3N. These compounds also exhibit large one-bond $^1J_{PC}$ coupling constants (ca. 170 Hz) and relatively high-field ^{31}P chemical shifts. In the case of the P-*iso*-propyl derivative **9**, an inseparable impurity precluded elemental analysis and complete assignment of the NMR signals.



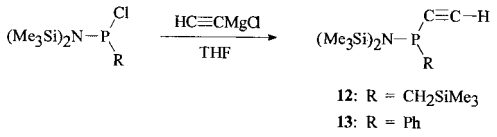
(5)

In similar fashion (Eq. (6)), the diacetylenic (silylamino)phosphine **1** was readily converted to its P-trifluoroethoxy derivative **11** in 49% isolated yield. Consistent with the presence of two acetylenic side groups, the ^{31}P-NMR resonance of **11** is observed at very high field (-41.4 ppm) and the one-bond $^1J_{PC}$ coupling constant (229 Hz) is extremely large.



(6)

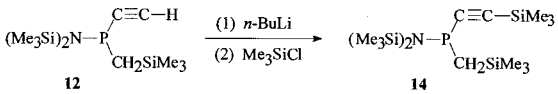
The synthesis of P-ethynyl functionalized (silylamino)phosphines was also of interest in this study due to the additional potential for reactivity of the terminal C–H bond. Treatment of appropriate P-chlorophosphines with one equivalent of the commercially available Grignard reagent, ethynylmagnesium chloride, did afford the desired P-ethynylphosphines **12** and **13** in ca. 50% yield (Eq. (7)). While only **12** could be sufficiently purified for elemental analysis, both derivatives were readily characterized by NMR spectroscopy. Most of the spectral features were similar to those of the C-substituted analogs **1**–**7**, however, the appearance of a doublet at ca. 3.1 ppm in the ^{1}H-NMR spectra confirmed the presence of the terminal C–H moiety.



(7)

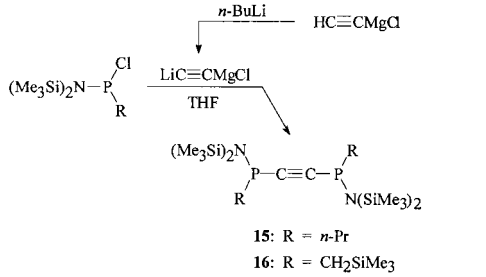
Several unsuccessful attempts were made to prepare the symmetrically substituted bis(ethynyl)phosphine, $(Me_3Si)_2NP(C{\equiv}CH)_2$, from the dichloro intermediate (as in Eq. (1)). Although ^{31}P-NMR spectroscopy (major peak at -9.7 ppm) indicated that the target compound was probably present in the crude reaction mixture, only black tar-like residues were obtained upon attempted isolation of the product.

In terms of derivative chemistry, we observed that deprotonation–substitution reactions occurred selectively at the terminal C–H center in these ethynylphosphines. Thus, treatment of the (trimethylsilyl)methyl derivative **12** with *n*-BuLi in THF solution, followed by Me_3SiCl, gave the expected product **14** in 82% yield. Although other examples were not investigated in this study, this type of derivative chemistry is likely to be quite general (Eq. (8)).



(8)

In addition to studying the reactivity of monometallic acetylene reagents (i.e. RC≡CLi and HC≡CMgCl) toward P-chloro(silylamino)phosphines, we also investigated the use of the pseudo carbide species LiC≡CMgCl. A slurry of this insoluble species was produced by adding *n*-BuLi to an equimolar quantity of the ethynyl Grignard reagent in THF solution (Eq. (9)). Subsequent addition of two equivalents of appropriate P-chlorophosphines gave the diphosphinoacetylenes **15** and **16**. Similar reactions with more sterically hindered phosphines (e.g. R = *i*-Pr, *t*-Bu) were not successful. Compounds **15** and **16** were obtained as pale yellow, viscous, high-boiling liquids in yields of 57 and 33%, respectively, and were fully characterized by NMR spectroscopy and elemental analyses.



(9)

Because of the presence of two asymmetric phosphorus centers, **15** and **16** were formed as mixtures of diastereomers in ca. 1:1 ratios. This is confirmed by the appearance of two signals of similar intensity in their ^{31}P-NMR spectra. Moreover, two sets of doubled-doublets are clearly seen for the acetylenic carbons of **15** and two distinct, 8-line, ABX patterns are observed for the diastereotopic P–CH_2–Si protons of **16**.

3. Experimental

3.1. Materials and general procedures

The following reagents were obtained from commercial sources and used without further purification: Me_3SiCl, *n*-BuLi, PCl_3, $PhPCl_2$, $(Me_3Si)_2NH$, $Me_3SiC{\equiv}CH$, $HC{\equiv}CMgCl$, $CH_3OCH_2C{\equiv}CH$, and 1-hexyne. Hexane, THF, ether, and benzene were distilled from CaH_2 and stored over molecular sieves. The following reagents were prepared according to published procedures: $(Me_3Si)_2NP(CH_2SiMe_3)Cl$ [10] and $(Me_3Si)_2NP(R)Cl$ (R = *n*-Pr, *i*-Pr, *n*-Bu) [11]. Proton, ^{13}C-, and ^{31}P-NMR spectra were recorded on a Varian XL-300 spectrometer in $CDCl_3$ solution. Elemental analysis were performed by E&R Microanalytical Services, Corona, NY. All reactions were carried out under an inert atmosphere of dry nitrogen or under vacuum.

3.2. Preparation of diacetylenic (silylamino)phosphines, $(Me_3Si)_2NP(C{\equiv}CR)_2$ (1–3)

In a typical preparation, a 500 ml, 3-necked flask was equipped with a magnetic stir bar, an addition funnel, and a N_2 inlet adapter and charged with $(Me_3Si)_2NH$ (10.6 ml, 50 mmol) and Et_2O (100 ml. This solution was cooled to 0 °C and *n*-BuLi (20 ml, 50 mmol, 2.5 M hexane solution) was added slowly. After warming to room temperature (r.t.), the solution was cooled to −78 °C. Next, PCl_3 (4.4 ml, 50 mmol) was added slowly via the addition funnel that had first been washed with hexane (ca. 5 ml). This solution was allowed to warm slowly to r.t. (during which time the reaction between PCl_3 and $LiN(SiMe_3)_2$ occurs) while stirring for about 1 h. A separate 250 ml, 3-necked flask was equipped with a magnetic stirrer bar, an addition funnel, and a N_2 inlet adapter and charged with $HC{\equiv}CSiMe_3$ (9.8 ml, 100 mmol) and THF (100 ml). This solution was cooled to −78 °C and *n*-BuLi (40 ml, 100 mmol, 2.5 M hexane solution) was added dropwise. This solution of the lithiated trimethylsilylacetylene was allowed to warm to r.t., transferred via cannula to the other addition funnel, and then added slowly to the dichlorophosphine solution at 0 °C. The mixture was then allowed to warm to r.t. The solvent was removed under reduced pressure and dry hexane (ca. 150 ml) was added to extract the product from the salts. Filtration and solvent removal under reduced pressure left a viscous brown liquid. Subsequent distillation through a 3-cm column afforded the product **1** as a colorless liquid (Tables 1 and 2). Compounds **2** and **3** were prepared in a similar manner from the respective alkynes, $HC{\equiv}CR$ (R = *n*-Bu, CH_2OCH_3).

3.3. Preparation of acetylenic (silylamino)phosphine, $(Me_3Si)_2NP(Ph)C{\equiv}CSiMe_3$ (4)

By using $PhPCl_2$ instead of PCl_3 in the above procedure, the intermediate chloro(phenyl)phosphine, $(Me_3Si)_2NP(Ph)Cl$, was prepared on a 50-mmol scale. Subsequent addition of one equivalent of $LiC{\equiv}CSiMe_3$, prepared as described above, followed by a similar work-up procedure, afforded **4** as a colorless liquid (Tables 1 and 2).

3.4. Preparation of acetylenic (silylamino)phosphines, $(Me_3Si)_2NP(R)C{\equiv}CCH_2OCH_3$ (5–7)

In a typical preparation, a 500 ml, 3-necked flask was equipped with a magnetic stirrer bar, an N_2 inlet, and an addition funnel and then charged with methyl propargyl ether, $HC{\equiv}C–CH_2OCH_3$ (12.6 ml, 150 mmol) and THF (150 ml). This solution was cooled to −78 °C and *n*-BuLi (60 ml, 150 mmol, 2.5 M hexane solution) was added dropwise. The solution was allowed to warm to r.t. while stirring and was then cooled to 0 °C. The chlorophosphine, $(Me_3Si)_2NP(i\text{-}Pr)Cl$ (40.4 g, 150 mmol) was then added slowly via the addition funnel. The mixture was then allowed to warm to r.t. The solvent was removed under reduced pressure and dry hexane (ca. 250 ml) was added to extract the product from the salts. Filtration and solvent removal under reduced pressure left a viscous brown liquid. Subsequent distillation through a 3-cm column afforded the product **5** as a colorless liquid (Tables 1 and 2). Compounds **6** and **7** were prepared in a similar manner from the respective P-chloro(silylamino)-phosphines, $(Me_3Si)_2NP(R)Cl$ (R = CH_2SiMe_3, *n*-Bu).

3.5. Preparation of the P-bromophosphoranimine, $Me_3SiN{=}P(n\text{-}Bu)(C{\equiv}CCH_2OCH_3)\text{-}Br$ (8)

A 100 ml, 3-necked flask was equipped with a magnetic stirrer bar, an addition funnel, and a N_2 inlet and then charged with the phosphine **7** (13.5 g, 43 mmol) and benzene (50 ml). The solution was cooled to 0 °C and a solution of bromine (2.2 ml, 20% excess) in benzene (6 ml) was added slowly from the addition funnel. Addition of the bromine solution was stopped when the endpoint (a slight, persistent yellow color) was reached. The solvent and Me_3SiBr were removed under reduced pressure. Distillation through a 3-cm

column afforded the product **8** as a clear colorless liquid (Tables 1 and 2).

3.6. Preparation of P-trifluoroethoxyphosphoranimines, $Me_3SiN{=}P(R)(C{\equiv}CCH_2OCH_3)$-$OCH_2CF_3$ (10–11)

A 250 ml, 3-necked flask was equipped with a magnetic stirrer, a N_2 inlet, and an addition funnel and then charged with the phosphine **6** (9.6 g, 27.0 mmol) and benzene (30 ml). The solution was cooled to 0 °C and a solution of bromine (1.8 ml, 30 mmol) in benzene (6 ml) was added slowly until the solution turned slightly yellow as noted above. The solvent and Me_3SiBr were then removed under reduced pressure leaving the crude P-bromo compound as a yellow liquid. Ether (30 ml) was then added along with Et_3N (3.8 ml, 27 mmol). The mixture was cooled to 0 °C and CF_3CH_2OH (1.9 ml, 27 mmol) was added slowly via syringe. The ice bath was removed and the solution was stirred for 1 h. The salts were removed by filtration and washed with hexane. After solvent removal, distillation afforded **10** as a colorless liquid (Tables 1 and 2). Compound **11** was prepared in a similar manner from the phosphine **1**.

3.7. Preparation of the P-ethynylphosphine, $(Me_3Si)_2NP(CH_2SiMe_3)C{\equiv}CH$ (12)

A 250 ml, 3-necked flask was equipped with a N_2 inlet, an addition funnel, and a magnetic stirrer and then charged with ethynyl magnesium chloride (100 ml, 50 mmol, 0.5 M THF solution). After the reaction vessel was cooled to 0 °C, the chlorophosphine $(Me_3Si)_2NP(CH_2SiMe_3)Cl$ (16.0 g, 51 mmol) was added slowly via the addition funnel. The mixture was allowed to warm to r.t. and was stirred overnight. The solvent was removed under reduced pressure and dry hexane (ca. 100 ml) was added to extract the product from the salts. Filtration and solvent removal under reduced pressure left a viscous brown liquid. Subsequent distillation through a 3-cm column afforded the product **12** as a colorless liquid (Tables 1 and 2). Compound **13** was prepared in a similar manner from the phosphine, $(Me_3Si)_2NP(Ph)Cl$, but it could not be purified sufficiently for elemental analysis.

3.8. Preparation of $(Me_3Si)_2NP(CH_2SiMe_3)C{\equiv}CSiMe_3$ (14) via deprotonation of 12

A 250 ml, 3-necked flask was equipped as above and charged with compound **12** (5.7 g, 19 mmol) and THF (50 ml). The reaction mixture was cooled to −78 °C and *n*-BuLi (7.5 ml, 19 mmol, 2.5 M hexane solution) was added slowly. The mixture was stirred 1 h at −78 °C and then Me_3SiCl (2.4 ml, 19 mmol) was added slowly. The mixture was then allowed to warm to r.t. while stirring. The solvent was removed under reduced pressure and dry hexane (ca. 100 ml) was added to extract the product from the salts. Filtration and solvent removal under reduced pressure left a viscous brown liquid. Subsequent distillation through a 3-cm column afforded the product **14** as a colorless liquid (Tables 1 and 2).

3.9. Preparation of the diphosphinoacetylenes, $(Me_3Si)_2NP(R)C{\equiv}CP(R)N(SiMe_3)_2$ (15–16)

A 250 ml, 3-necked flask was equipped as above and charged with ethynyl magnesium chloride (30 ml, 15 mmol, 0.5 M TFIF solution). The reaction vessel was cooled to 0 °C and then *n*-BuLi (6 ml, 15 mmol, 2.5 M hexane solution) was added slowly via syringe. The mixture was stirred until it formed a thick slurry. At this point, THF (30 ml) was added to yield a more smoothly dispersed suspension. With the reaction mixture at 0 °C, the chlorophosphine $(Me_3Si)_2NP(n\text{-}Pr)Cl$ (8.1 g, 30 mmol) was added via syringe. The ice bath was removed and the mixture was stirred overnight. The solvent was removed under reduced pressure and dry hexane (ca. 100 ml) was added to extract the product from the salts. Filtration and solvent removal under reduced pressure left a very viscous brown liquid. Subsequent distillation through a 3-cm column afforded the product **15** as a slightly yellow liquid (Tables 1 and 2). Compound **16** was prepared in a similar manner from $(Me_3Si)_2NP(CH_2SiMe_3)Cl$.

Acknowledgements

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