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Registry No. *trans*-$PdCl_2(P(t\text{-}Bu)_2CH_2\overline{CHCH_2CH_2})_2$, 85318-43-0; $[\overline{PdCl(P(t\text{-}Bu)_2CH{=}C(CH_3)CH_2)}]_2$, 85318-44-1.

Supplementary Material Available: Table III, the thermal parameters, Table IV, a listing of parameters for the hydrogen atoms, and Table VI, a listing of $10|F_o|$ and $10|F_c|$ (13 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Some *P*-Mesityl-Substituted Phosphorus Compounds

Ze-Min Xie and Robert H. Neilson*

Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

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The preparation and characterization of a series of *P*-mesityl-substituted phosphorus compouds containing the Si–N–P and/or Si–C–P linkages are described. The reaction of $RPCl_2$ (R = 2,4,6-$Me_3C_6H_2$) with 1 equiv of $(Me_3Si)_2NLi$ affords the thermally unstable chlorophosphine $(Me_3Si)_2NP(R)Cl$ (**1**) in nearly quantitative yield. Substitution reactions of **1** are used to prepare the stable derivatives $(Me_3Si)_2NP(R)X$ (**2**, X = Me; **3**, X = H; **4**, X = CH_2SiMe_3), while treatment with Me_3SiN_3 yields the unstable azidophosphine $(Me_3Si)_2NP(R)N_3$ (**5**). The methylphosphine **2** reacts smoothly with CCl_4 via elimination of $CHCl_3$ and a [1,3]-silyl shift to form the chlorophosphinimine $Me_3SiN{=}P(R)(CH_2SiMe_3)Cl$ (**6**), which is readily converted to the P–Me analogue **7** by reaction with MeLi. Depending on the reaction stoichiometry, treatment of $RPCl_2$ with Me_3SiCH_2MgCl gives either the chlorophosphine $Me_3SiCH_2P(R)Cl$ (**8**) as an unstable product from which **4** is produced by reaction with $(Me_3Si)_2NLi$ or the stable disubstituted phosphine $(Me_3SiCH_2)_2PR$ (**9**). Decomposition of the azidophosphine **5** proceeds with elimination of nitrogen and formation of the dimeric forms of the bis(imino)phosphorane $RP(=NSiMe_3)_2$ (**5a**). Either the cis (**10**) or trans (**11**) four-membered ring dimer can be isolated under appropriate conditions. Proton, ^{13}C, and ^{31}P NMR data are reported for the new compounds.

Introduction

Currently, there is considerable interest in the chemistry of "low-coordinate" phoshorus compounds such as the two-coordinate phosphines[1] R—P=E and the three-coordinate phosphoranes[2] $R—P(=E)_2$ where E = NR′ or CR'_2. Several examples of stable compounds of each type now exist, and some reports of their derivative chemistry[3] have appeared recently. Our interest in such compounds stems mainly from the possibility that they might be useful precursors to new classes of phosphorus-containing polymers or cyclic oligomers. It seems reasonable that systems suited to this purpose should contain: (1) a sterically bulky, unreactive group on phosphorus to provide kinetic stability and (2) functional linkages such as Si–N–P and/or Si–C–P which could serve as sites for condensation–polymerization reactions.[4,5]

As the initial phase of this project, we report here on the synthesis and reactivity of a series of silylated, *P*-mesityl-substituted compounds. The potential uses of some of these reagents in the preparation of low-coordinate species and new oligomers will be described in subsequent papers.

Results and Discussion

Mesityldichlorophosphine $RPCl_2$ (R = 2,4,6-$Me_3C_6H_2$) was selected as the starting material in this study for essentially two reasons: (1) it provides an unreactive P–C bond with a substantial amount of steric hinderance around phosphorus and (2) it is easily prepared in relatively large quantity (~100 g) and good yield (~80%) from PCl_3 and mesityl Grignard reagent. The reactions described herein were primarily intended to introduce Si–N–P or Si–C–P linkages in various arrangements for the purpose outlined above.

Treatment of $RPCl_2$ (R = mesityl) with 1 equiv of lithium bis(trimethylsilyl)amide (eq 1) in ether solution gave the important reagent [bis(trimethylsilyl)amino]chloromesitylphosphine (**1**). Compound **1** was obtained in ca.

(1) See for example: (a) Appel, R.; Kündgen, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 219. (b) Appel, R.; Knoll, F.; Ruppert, I. *Ibid.* **1981**, *20*, 731. (c) Neilson, R. H. *Inorg. Chem* **1981**, *20*, 1679. (d) Becker, G.; Rössler, M. Uhl, W. *Z. Anorg. Allg. Chem.* **1981**, *473*, 7. (e) Becker, G.; Uhl, W.; Wessely, H.-J. *Ibid.* **1981**, *479*, 41. (f) Issleib, K.; Schmidt, H.; Wirkner, Ch. *Ibid.* **1981**, *473*, 85. (g) Scherer, O. J.; Conrad, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *B36*, 515. (h) Niecke, E.; Rüger, R.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1034. (i) Scherer, O. J.; Kuhn, N. *Ibid.* **1974**, *13*, 811. (j) Niecke, E.; Flick, W. *Ibid.* **1973**, *12*, 585.

(2) See for example: (a) Appel, R.; Peters, J.; Westerhaus, A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 80. (b) Appel, R.; Westerhaus, A. *Tetrahedron Lett.* **1982**, *23*, (c) Niecke, E.; Schäfer, H.-G. *Chem. Ber.* **1982**, *115*, 185. (d) Niecke, E.; Wildbredt, D.-A. *J. Chem. Soc., Chem. Commun.* **1981**, 72. (e) Scherer, O. J.; Kuhn, N. *Chem. Ber.* **1974**, *107*, 2123.

(3) See for example: (a) Scherer, O. J.; Konrad, R.; Guggolz, E.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 297. (b) Scherer, O. J.; Konrad, R.; Krüger, C.; Tsay, Yi.-H. *Chem. Ber.* **1982**, *115*, 414. (c) Cowley, A. H.; Kemp, R. A. *J. Chem. Soc., Chem. Commun.* **1982**, 319. (d) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. *Polyhedron* **1982**, *1*, 89. (e) Knaap, Th. A.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 2037. (f) Knaap, Th. A.; Bickelhaupt, F.; Poel, H.; Koten, G.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 1756. (g) Cowley, A. H.; Kilduff, J. E.; Wilburn, J. C. *Ibid.* **1981**, *103*, 1575. (h) Keim, W.; Appel, R.; Storeck, A., Krüger, C.; Goddard, R. *Angew Chem., Int. Ed. Engl.* **1981**, *20*, 116. (i) Niecke, E.; Kroeher, R. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34*, 837. (j) Röschenthaler, G.-V.; Sauerbrey, K.; Schmutzler, R. *Chem. Ber.* **1978**, *111*, 3105.

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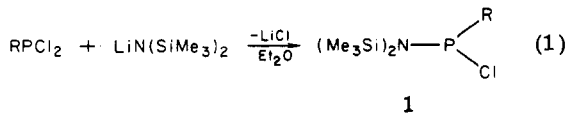

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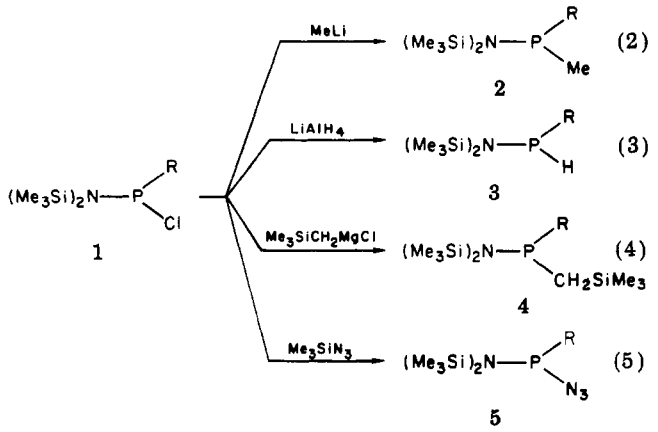
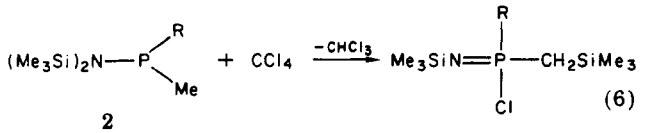
90% yield as a viscous orange-brown liquid which was characterized by NMR (^1H, ^{13}C, ^{31}P) spectroscopy (Table I) and by its derivative chemistry. Even when traces of LiCl were tediously removed from **1**, however, it could not be distilled without substantial thermal decomposition to Me_3SiCl and a complex mixture of unidentified nonvolatile products. Undistilled samples of **1**, nevertheless, were of sufficient purity to provide good NMR spectra and to be used in subsequent reactions.

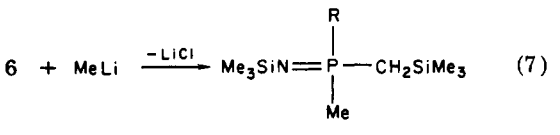
The chlorophosphine **1** reacted smoothly with MeLi (eq 2), $LiAlH_4$ (eq 3), and Me_3SiCH_2MgCl (eq 4) to yield the



distillable liquid products **2**, **3**, and **4**, respectively. These derivatives were characterized by elemental analysis (Table II) in addition to NMR spectroscopy. The azidophosphine **5** was obtained as an unstable species (see below) from the slow, but eventually quantitative reaction of **1** with trimethylsilyl azide (eq 5).

In addition to providing chemical confirmation of the P–Cl reagent **1**, derivatives **2**–**5** are synthetically useful compounds themselves. For example, the CCl_4 reaction (eq 6) of the methylphosphine **2** proceeded with elimina-

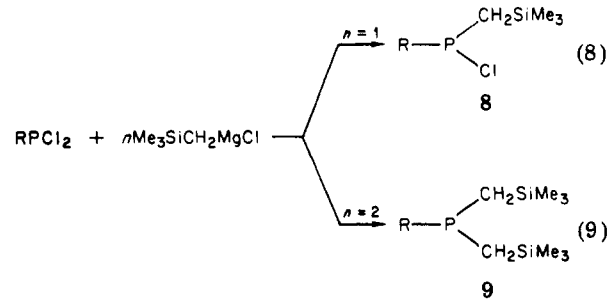




7

tion of $CHCl_3$ and silyl group migration from nitrogen to carbon[6,7] affording the *P*-chlorophosphinimine **6** in high yield. Compound **6** gave the *P*-methyl analogue **7** upon treatment with MeLi (eq 7).

As part of this study, we were also interested in preparing *P*-mesityl systems containing the Si–C–P linkage alone (i.e., without silylamino substituents). The reaction of $RPCl_2$ with 1 equiv of the (trimethylsilyl)methyl Grignard reagent (eq 8) was, unfortunately, not entirely successful in that regard. The desired monochlorophosphine



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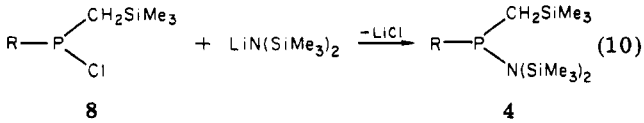
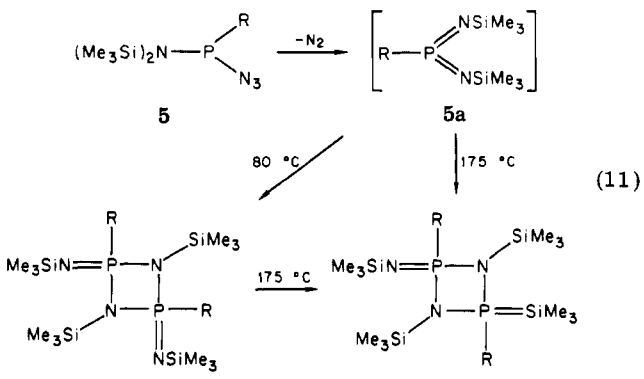
8 was obtained but only as an impure product which could not be distilled without extensive decomposition. Its characterization is therefore based on ^1H and ^{31}P NMR data; a satisfactory ^{13}C spectrum was not obtained due to its insufficient purity and ease of decomposition. The NMR spectra of the residue after Me_3SiCl elimination indicate the formation of P–CH_2–P condensation products, but no specific compounds could be identified. The use of excess Grignard reagent (eq 9) did allow the preparation of the disubstituted product **9** as a well-characterized, thermally stable derivative. Compound **9** was, in fact, usually observed as a hard-to-separate impurity in the preparation of **8**. Additional chemical evidence for the chlorophosphine **8** was found in its reaction with LiN($SiMe_3$)$_2$ which gave **4** in about 50% yield (eq 10).



As mentioned above, the azidophosphine **5** was thermally unstable, decomposing with loss of N_2 even at room temperature. Its thermolysis was studied under a variety of conditions in an effort to isolate the likely decomposition product, bis[(trimethylsilyl)imino]mesitylphosphorane (**5a**). Although the three-coordinate phosphorane **5a** could not be directly observed, its dimerization products **10** and **11** were each obtained as pure crystalline solids (eq 11).



10, cis 11, trans

When **5** was heated either in refluxing CH_2Cl_2 or neat at 80 °C, the cis isomer **10** was formed. Decomposition under more vigorous conditions (neat, 175 °C) gave the trans isomer **11** which was also produced when **10** was heated at the same temperature. The dimers were characterized by elemental analysis, NMR spectroscopy, and molecular weight measurements (by mass spectroscopy and cryoscopically in benzene). The structures of the isomers are assigned on the basis of their relative formation temperatures, melting points, and ^{31}P chemical shifts.[1c]

One of the main goals of this study was to compare the thermal stability and chemical reactivity of the *P*-mesityl compounds with the previously reported P–N($SiMe_3$)$_2$

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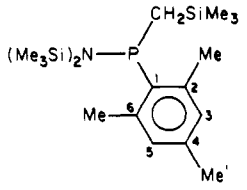
Table I. NMR Spectroscopic Data[a]

compd (R = mesityl)	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
$(Me_3Si)_2N-P(R)Cl$ **1**	Me_3Si	0.31	1.8	4.00	8.8	151.1
	o-Me	2.60	2.5	23.85	13.7	
	p-Me	2.28	1.8	20.99		
	C_6H_2	6.80	3.6	131-141		
$(Me_3Si)_2N-P(R)Me$ **2**	Me_3Si	0.24		4.15	6.8	47.8
	PMe	1.88	8.2	22.29	52.7	
	o-Me	2.52		22.74	15.6	
	p-Me	2.28		20.40		
	C_6H_2	6.74	2.7	130-140		
$(Me_3Si)_2N-P(R)H$ **3**	Me_3Si	0.21	1.2	3.15	6.9	−10.4
	PH	6.28	228.0			
	o-Me	2.40	2.3	22.68	5.9	
	p-Me	2.25	1.8	21.05		
	C_6H_2	6.75	2.4	129-140		
$(Me_3Si)_2N-P(R)CH_2SiMe_3$ **4**	$(Me_3Si)_2N$	0.21		5.13	5.9	50.9
	Me_3SiC	0.01		0.16	4.9	
	PCH_2 [b]	1.81	8.7	22.87	42.7	
		2.29	1.2			
	o-Me	2.60		23.19	18.3	
	p-Me	2.23		21.07		
	C_6H_2	2.0		130-142		
$(Me_3Si)_2N-P(R)N_3$ **5**	Me_3Si	0.31	1.8	3.87	6.8	124.8
	o-Me	2.60	2.5	23.49	10.7	
	p-Me	2.28	2.2	20.86		
	C_6H_2	6.80	3.6	131-141		
$Me_3SiN=P(R)(Cl)CH_2SiMe_3$ **6**	Me_3SiN	0.25		3.20	4.9	13.2
	Me_3SiC	0.21		0.00	3.9	
	CH_2 [b]	2.01	26.5	33.75	69.3	
		2.29	7.9			
	o-Me	2.83	0.9	24.65	2.9	
	p-Me	2.35		20.98		
	C_6H_2	6.94	4.8	131-142		
$Me_3SiN=P(R)(Me)CH_2SiMe_3$ **7**	Me_3SiN	0.07		3.68	3.9	3.8
	Me_3SiC	−0.04		0.13	1.1	
	PMe	1.84	12.6	26.02	75.2	
	CH_2 [b]	1.35	25.1	25.76	67.4	
		1.65	10.6			
	o-Me	2.63		24.17	6.1	
	p-Me	2.26		20.57		
	C_6H_2	6.81	3.3	131-143		
$R-P(CH_2SiMe_3)Cl$ **8**	Me_3Si	0.03				88.2
	CH_2	2.32	13.8			
	o-Me	2.70	2.4			
	p-Me	2.28				
	C_6H_2	6.78	2.7			
$R-P(CH_2SiMe_3)CH_2SiMe_3$ **9**	Me_3Si	−0.06		−0.18	5.8	26.9
	CH_2 [b]	1.02	2.1	18.74	71.3	
		1.50	0.7			
	o-Me	2.60		23.27	21.5	
	p-Me	2.24		18.52		
	C_6H_2	6.76	1.8	129-145		
$[Me_3SiN-P(=NSiMe_3)-R]_2$ **10**, cis	Me_3Si	0.07		3.31	4.3	−19.7
		0.43		3.51	5.5	
	o-Me	2.46		25.42	4.9	
				25.42	0.0	
	p-Me	2.18		20.95		
	C_6H_2	6.66	4.2	130-140		
11, trans	Me_3Si	−0.02		0.97		−24.7
		0.04		3.53		
	o-Me	2.86		26.19	0.0	
				26.21	5.5	
	p-Me	2.24		20.83		
	C_6H_2	6.86	4.2	131-141		

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Analysis of ABX pattern yields $^2J_{HH'}$ values: 4, 13.5; 6, 14.4; 7, 14.7; 9, 13.8.

systems. Several differences as well as some similarities are noteworthy. First, the chlorophosphines **1** and $[(Me_3Si)_2N]_2PCl$ are both unstable with respect to elimination of Me_3SiCl. The mesityl compound **1** yields an uninterpretable mixture of phosphorus products, whereas the latter gives the stable two-coordinate phosphine $(Me_3Si)_2NP{=}NSiMe_3$.[1i] Second, the P–H derivatives **3** and $[(Me_3Si)_2N]_2PH$ are both stable, distillable compounds as are a number of other recently prepared (silylamino)-phosphines with P–H bonds.[8-10] Third, the chloro[(trimethylsilyl)methyl]phosphines **8** and $(Me_3Si)_2NP(Cl)CH_2SiMe_3$ show different modes of reactivity toward bases such as $LiN(SiMe_3)_2$. While **8** yields the simple nucleophillic substitution product **4**, the $(Me_3Si)_2N$ derivative is dehydrohalogenated and the novel (methylene)phosphine $(Me_3Si)_2NP{=}CHSiMe_3$ is obtained in high yield.[1c] Finally, the azidophosphines **5** and $[(Me_3Si)_2N]_2PN_3$ both decompose with elimination of N_2 and [1,3]-silyl migration, but **5** affords only the dimers **10** and **11**, whereas the stable monomeric phosphorane $(Me_3Si)_2NP{=}NSiMe_3$ is obtained from the persilylated system.[2e] The formation of dimeric products from the decomposition of **5** is similar to the behavior of other compounds including $(Me_3Si)_2NP(N_3)R$ (R = CH_2SiMe_3[1c] and Ph[11]). Viewed in total, these results suggest that *the mesityl group is somewhat less effective than $(Me_3Si)_2N$ in its ability to kinetically stabilize low-coordinate phosphorus compounds.*

Finally, some features of the ^{13}C NMR spectra of these *P*-mesityl compounds are worthy of note. Although compounds **1–11** all have chiral phosphorus centers, the planarity of the mesityl group renders the ortho methyl groups magnetically equivalent unless rotation about the P–C bond is restricted on the NMR time scale. Such hindered rotation was noted by Bickelhaupt[12] for the *two-coordinate* (sp^2) phosphine $Mes{-}P{=}CPh_2$. However, with the exception of the sterically congested dimers **10** and **11**, the ^1H and ^{13}C NMR data (Table I) reported here for the *three-coordinate* (sp^3) phosphines are consistent with free rotation about the P–C bond. For example, the mesityl portions of the ^{13}C NMR spectrum of **4** are completely assigned as follows. The observation of three peaks in the methyl region is interpreted as a doublet due to the equivalent ortho-methyl groups with spin coupling to phosphorus and a singlet due to the more remote para-methyl substituent. When the ^{13}C spectrum of **4** was recorded in different solvents, the splitting of 18.3 Hz remained constant, indicating that it is reasonably assigned as a coupling constant ($^3J_{PC}$) rather than a chemical shift difference. The magnitude of this $^3J_{PC}$ (18.3 Hz) is well within the range of values obtained on related P^{III} systems.[10,11] The ^{13}C spectra of the other compounds are similar, although, in some cases, overlap of the resonances for the ring carbons (C_1–C_6) made individual peak assignments difficult. Consequently, only ranges of δ values are listed for these carbons in Table I.



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	$\delta(^{13}C)$	J_{PC}, Hz
Me	23.19	18.3
Me'	21.07	
C_1	137.26	42.0
$C_{2,6}$	142.13	16.6
$C_{3,5}$	130.53	
C_4	138.14	

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: mesityl bromide, $(Me_3Si)_2NH$, PCl_3, Me_3SiCH_2Cl, Me_3SiN_3, *n*-BuLi (hexane solution), and ether solutions of MeLi, MeMgBr, and $LiAlH_4$. Ether and THF were distilled from CaH_2 prior to use; other solvents were dried over molecular sieves. The Grignard reagent Me_3SiCH_2MgCl was prepared according to the published procedure.[13] Mesityldichlorophosphine[14] was prepared in 85% yield from $MesMgBr$[15] and PCl_3 by a procedure similar to that used by Clark[16] for the synthesis of $(o\text{-tolyl})_2PCl$. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Mass spectral data were obtained on a Finnagin GC-MS system. 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 procedures described herein are typical of those used for the preparation of the new compounds in this study.

[Bis(trimethylsilyl)amino]chloromesitylphosphine (1). A solution of $(Me_3Si)_2NLi$, prepared from $(Me_3Si)_2NH$ (7.5 mL, 36 mmol) and *n*-BuLi (20.6 mL, 1.7 M), in Et_2O (30 mL) was added at 0 °C to a stirred solution of $MesPCl_2$ (8.0 g, 36 mmol) in Et_2O (30 mL). The mixture was allowed to warm to room temperature and was stirred for 3 h. Ether was removed under vacuum, and hexane (~60 mL) was added to extract the product from the lithium salts. After being stirred for 2 h, the mixture was filtered under nitrogen and the filtrate was kept at −15 °C overnight. An additional small amount of solid was separated by decanting the solution, and the solvent was removed from the decantate, leaving **1** as an orange liquid (11.2 g, 90% yield, purity estimated to be ~95% by ^1H and ^{31}P NMR). On attempted distillation, the compound decomposed rapidly above 100 °C giving Me_3SiCl and unidentified nonvolatile products.

[Bis(trimethylsilyl)amino]mesitylmethylphosphine (2). Methyllithium (65 mL, 1.6 M) was added slowly at 0 °C to a stirred solution of **1**, (34 g, 0.1 mol) prepared as above, in Et_2O (150 mL). After the mixture was warmed to room temperature and stirred for 1 h, Et_2O was removed and hexane (200 mL) was added. The mixture was filtered, allowed to stand at −15 °C, decanted, and freed of solvent. Compound **2** (Table II) was isolated as a colorless liquid by vacuum distillation.

[Bis(trimethylsilyl)amino]mesitylphosphine (3). In the same manner, the chlorophosphine **1** (22.7 g, 66 mmol) in Et_2O (100 mL was treated with $LiAlH_4$ (18 mL, 1.0 M) at 0 °C. After being stirred overnight at room temperature, the mixture was filtered and the solvent was removed under vacuum. Distillation gave the P–H derivative **3** (Table II) as a colorless liquid.

[Bis(trimethylsilyl)amino]mesityl[(trimethylsilyl)methyl]phosphine (4). From 1. A solution of Me_3SiCH_2MgCl (ca. 100 mmol in 100 mL of Et_2O) was added at 0 °C to a stirred solution of **1** (33.5 g, 96 mmol) in Et_2O (100 mL). After the mixture was stirred for 4 h at room temperature, compound **4** (Table II) was obtained as a colorless liquid by using the procedure described above for **2**. **From 8.** The chlorophosphine **8** (22 g, 81 mmol), prepared as described below, was added at 0 °C to a stirred

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Table II. Preparative and Analytical Data

compd	preparative		analytical[a]	
	% yield	bp, °C (mm)	% C	% H
2	68	106-108 (0.05)	59.60 (59.03)	10.30 (9.91)
3	63	98 (0.1)	58.00 (57.82)	9.46 (9.71)
4	62 (50)[b]	124-126 (0.04)	57.95 (57.37)	10.15 (10.14)
6	89	117-119 (0.03)	53.41 (53.39)	8.62 (8.69)
7	56	96-99 (0.03)	59.73 (60.12)	10.01 (10.09)
9	51	93-95 (0.03)	62.25 (62.91)	10.27 (10.25)
10	50	mp 170-171	54.49 (55.51)	8.93 (9.00)
11	42	mp 230	54.44 (55.51)	8.86 (9.00)

[a] Calculated values in parentheses. [b] Yield of 4 obtained by treatment of 8 with $(Me_3Si)_2NLi$ (eq 10) is given in parentheses.

solution of $LiN(SiMe_3)_2$ (ca. 90 mmol, prepared from $(Me_3Si)_2NH$ and *n*-BuLi) in THF (50 mL) at 0 °C. The mixture was stirred overnight at room temperature. Filtration, solvent removal, and distillation gave **4** as a colorless liquid (16 g, 50% yield).

Azido[bis(trimethylsilyl)amino]mesitylphosphine (5). A freshly prepared sample of **1** (5.0 g, 14.5 mmol) was treated with Me_3SiN_3 (2.5 g 21.7 mmol) at 0 °C. After being stirred for 2 h, the mixture was allowed to stand at −15 °C for 72 h in order to complete the reaction with minimal decomposition of the azidophosphine product. The excess azidosilane and Me_3SiCl were removed under vacuum leaving compound **5** which was found to be of high purity by NMR spectroscopy. Attempted distillation caused elimination of N_2 and dimerization as described below.

***P*-Chloro-*P*-mesityl-*P*-[(trimethylsilyl)methyl]-*N*-(trimethylsilyl)phoshinimine (6).** The *P*-methylphosphine **2** (22.0 g, 67.6 mmol) was treated with CCl_4 (13.8 mL, 143 mmol) at 0 °C. After the mixture was stirred overnight at room temperature, distillation gave **6** as colorless liquid (Table II).

***P*-[Bis(trimethylsilyl)amino]-*P*-mesityl-*P*-methyl-*N*-(trimethylsilyl)phosphinimine (7).** Methyllithium (33 mL, 1.6 M) was added at −40 °C to a stirred solution of the chlorophosphinimine **6** (18.0 g, 50 mmol) in Et_2O (50 mL). After being stirred for 1 h at −40 °C, the mixture was allowed to warm to room temperature with stirring overnight. Filtration, solvent removal, and distillation gave **7** as a colorless liquid (Table II).

Chloro[(trimethylsilyl)methyl]mesitylphosphine (8). A solution of Me_3SiCH_2MgCl (ca. 100 mmol in 40 mL of Et_2O) was added at −78 °C over 30 min to a stirred solution of $MesPCl_2$ (22.5 g, 100 mmol) in Et_2O (50 mL). After the mixture was stirred overnight at room temperature, the Et_2O was removed and hexane (150 mL) was added. The mixture was then filtered, and the filtrate was allowed to stand at −15 °C overnight, during which time some additional solids were precipitated. The supernatant liquid was decanted and solvent removal gave **8** as an orange liquid (22 g, ca. 80% yield) which was 85–90% pure as indicated by ^1H and ^{31}P NMR (Table I). The compound evolved Me_3SiCl slowly on standing at room temperature or rapidly on attempted distillation to yield unidentified nonvolatile products.

Bis[(trimethylsilyl)methyl]mesitylphosphine (9). In a similar manner, $MesPCl_2$ (18.8 g, 85 mmol) in Et_2O (80 mL) was treated at 0 °C with Me_3SiCH_2MgCl (ca. 200 mmol in 80 mL of Et_2O). The same workup procedure as described for **8** afforded compound **9** as a stable, colorless liquid after vacuum distillation (Table II).

Preparation of the Dimers (10 and 11) of Bis[(trimethylsilyl)imino]mesitylphosphorane (5a). A freshly prepared sample of the azidophosphine **5** (5.0 g, 14.4 mmol) was heated without a solvent at 80–85 °C for 30 min. Gas evolution and formation of yellow solid was observed. Slow crystallization from hexane (5 mL) at −15 °C gave white crystals of the cis dimer **10** (2.27 g, 50% yield, mp 171 °C). When the decomposition of **5** was conducted in refluxing CH_2Cl_2 solution and monitored by ^1H and ^{31}P NMR, **10** was the only observable product; no evidence of the monomer **5a** was obtained. The trans isomer **11** (mp 230 °C) was prepared in 42% yield by heating a neat sample of **10** at 175 °C for 1 h, followed by recrystallization from hexane at −15 °C. Alternatively, the trans dimer **11** was obtained directly from the rapid decomposition of the azidophosphine **5** at 175 °C. Mass spectra of both **10** and **11** contained a significant parent ion peak at *m/e* 648 and a large peak corresponding to the monomer **5a**. Major fragments in mass spectrum of **10**: *m/e* (relative intensity) 648 (2), 633 (5), 325 (11), 324 (4), 310 (12), 309 (47), 146 (13), 130 (21), 74 (22), 73 (100), 45 (20). Molecular weights were also determined by freezing point depression measurements in benzene solution: **10**, 638; **11**, 586 (calcd 648).

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Registry No. **1**, 85336-20-5; **2**, 85336-30-7; **3**, 85336-21-6; **4**, 85336-22-7; **5**, 85336-23-8; **6**, 85336-24-9; **7**, 85336-25-0; **8**, 85336-26-1; **9**, 85336-29-4; **10**, 85336-27-2; **11**, 85336-28-3; $(Me_3Si)_2NLi$, 4039-32-1; $(Me_3Si)_2NH$, 999-97-3; Me_5PCl_2, 6781-96-0; Me_3SiCH_2Cl, 2344-80-1; Me_3SiN_3, 4648-54-8.