was thermostated at 25 ± 0.1 °C. Antiracemization and racemization were followed at 554 and 552 nm, respectively for at least 2 half-lives in a usual manner.[10,11,22]

Registry No. cinchoH$^+$, 63296-30-0; cinchonidinium, 69847-14-9; cinchoninonium, 69847-15-0; acetylcinchoninium, 69847-16-1; *N*-Me-cinchoH$^+$, 69847-17-2; 10,11-H_2-cinchoH$^+$, 69847-18-3; 6′-MeO-cinchoH$^+$, 53264-66-7; *N,N,N′,N′*-tetramethyl-(*R*)-propylenediamine, 36366-15-1; Λ-$[Cr(ox)_3]^{3-}$, 34307-04-5; Δ-$[Cr(ox)_3]^{3-}$, 67486-80-0; $Co(ox)_3^{3-}$, 15053-34-6; Δ-$[Co(phen)_3]^{2+}$, 69880-68-8; Λ-$[Co(phen)_3]^{2+}$, 69880-69-9; $[Cr(ox)_3]^{3-}$, 15054-01-0; $[Co(phen)_3]^{2+}$, 16788-34-4.

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Synthesis and Structural Isomerism of Some (Silylamino)phosphinimines

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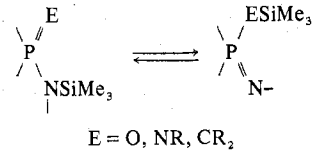
The synthesis and NMR (^1H and ^{13}C) spectroscopic characterization of several new (silylamino)phosphinimines including $(Me_3Si)_2NP(=NSiMe_3)PhX$ (**1**, X = Me; **2**, X = F), $(Me_3Si)_2NP[=N(t\text{-}Bu)]Me_2$ (**3**), $[Me(Me_3Si)N]_nP(=NSiMe_3)Me_{3-n}$ (**4**, n = 1; **5**, n = 2; **6**, n = 3), $Me_2SiCH_2CH_2SiMe_2NP(=NSiMe_3)Me_2$ (**7**), and $R(Me_3Si)NP[=NSiMe_2(t\text{-}Bu)]Me_2$ (**8**, R = Me_3Si; **9**, R = Me) are reported. The trisilylated compounds **1** and **2** exhibited reversible [1,3] silyl exchange with $\Delta G^{\ddagger}_{1,3}$ values of 14.2 and 18.3 kcal/mol, respectively. The other phosphinimines **3–9** exist as static structures which in some cases (**3**, **8**, and **9**) have resulted from irreversible silyl shifts.

Introduction

It is becoming increasingly apparent that an important feature of the chemistry of four-coordinate silicon–nitrogen–phosphorus compounds is the lability of silyl substituents toward intramolecular migrations.[2]

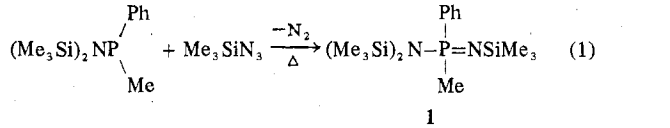


E = O, NR, CR_2

With few exceptions,[3] these rearrangements are irreversible for (silylamino)phosphine oxides (E = O)[4] and ylides (E = CR_2),[5,6] but the (silylamino)phosphinimines (E = NR)[7] offer greater possibilities for the study of reversible [1,3] silyl shifts. The steric and electronic factors which determine the ease of silyl migration in such compounds as well as their ground-state structures have not been fully elucidated. In this context, we report the synthesis and NMR (^1H and ^{13}C) spectroscopic properties of several new di-, tri-, and tetrasilylated phosphinimines.

Results and Discussion

Syntheses. There are two basic preparative routes available for the synthesis of (silylamino)phosphinimines. The first method is an adaptation of the well-known Staudinger reaction of organophosphines with azides.[8] The utility of this approach in Si–N–P chemistry has been broadened by the recent availability of the necessary (silylamino)phosphine reagents.[6] For example, when [bis(trimethylsilyl)amino]methylphenylphosphine was heated with a small excess of trimethylsilyl azide at ca. 100 °C for 20 h in the absence of solvent, the product isolated (eq 1) in 84% yield was *P*-



(1)

1

[bis(trimethylsilyl)amino]-*P*-methyl-*P*-phenyl-*N*-(trimethylsilyl)phosphinimine (**1**).

A second preparative method complements the first by allowing the synthesis of P-halogenated (silylamino)phosphinimines. Treatment of *P,P*-difluoro-*P*-phenyl-*N*-(tri-

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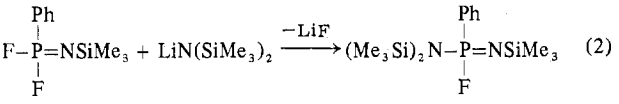
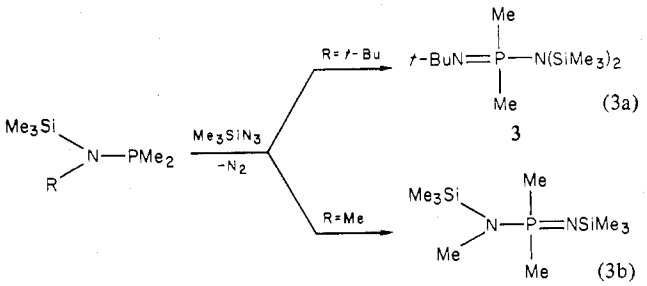
methylsilyl)phosphinimine[9] with an equimolar quantity of lithium bis(trimethylsilyl)amide (eq 2) afforded the *P*-fluoro analogue **2** in 56% yield.



(2)

2

In this study, we have also used the Staudinger reaction to prepare the trimethylsilyl azide derivatives (**3**–**7**) of the [alkyl(trimethylsilyl)amino]phosphines (eq 3), the bis- and tris[methyl(trimethylsilyl)amino]phosphines (eq 4) and the cyclic (disilylamino)phosphine (eq 5). As illustrated by eq 3a, the products of such reactions were sometimes found to have rearranged structures.



(3a)

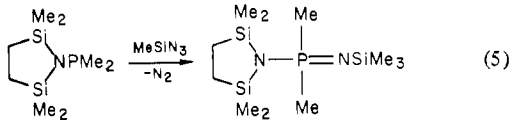
3

(3b)

4

(4)

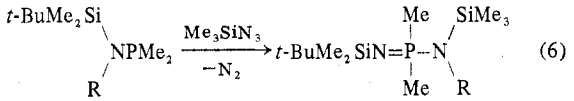
5: $n = 2$
6: $n = 3$



(5)

7

In a similar manner, aminophosphines containing the bulky *tert*-butyldimethylsilyl moiety also underwent reaction (eq 6)



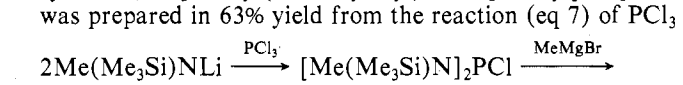
(6)

8: R = $SiMe_3$
9: R = Me

with Me_3SiN_3 to afford the somewhat unexpected products **8** and **9**. Compound **9** was also obtained in 64% yield from the reaction of $Me(Me_3Si)NPMe_2$ with *t*-$BuMe_2SiN_3$.

The reactions used to prepare compounds **1** and **3**–**9** were conveniently monitored by observing the evolution of N_2 through an oil bubbler or by periodically allowing the mixture to cool and recording its ^1H NMR spectrum. The P–C–H coupling constant of the PMe doublet characteristically[2,6] increased upon oxidation of the phosphine (P^{III}) to the phosphinimine (P^V). The approximate time needed for complete reaction (Table I) ranged from 4 to 72 h with the longer periods being required for the more sterically crowded phosphines.

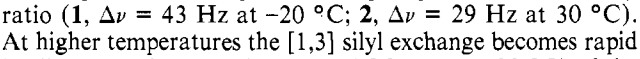
With the exception of the precursors to phosphinimines **5** and **6**, the (silylamino)phosphines utilized in these experiments have been previously reported.[6] In a similar "one-pot" synthesis, bis[methyl(trimethylsilyl)amino]methylphosphine was prepared in 63% yield from the reaction (eq 7) of PCl_3



(7)

with 2 equiv of $Me(Me_3Si)NLi$ followed by 1 equiv of a methyl Grignard reagent. Although it was not necessary to do so, the chlorophosphine intermediate could be isolated as a pale yellow liquid which decomposed upon attempted distillation.

Tris[methyl(trimethylsilyl)amino]phosphine was also prepared (eq 8) from PCl_3 and $Me(Me_3Si)NLi$ but only after

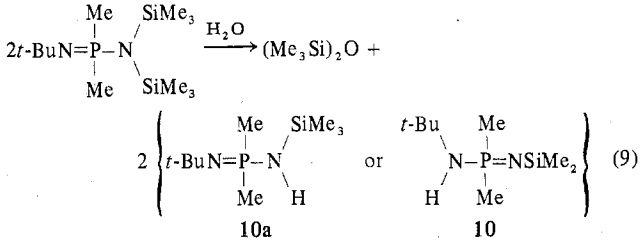


(8)

considerable experimentation with reaction conditions. The best yields (ca. 47%) were obtained when PCl_3 was slowly added at −78 °C to an ether solution containing 3 equiv of the lithium amide whose reactivity was enhanced by the addition of the complexing agent TMEDA (tetramethylethylenediamine). Contrary to an earlier report,[7] the bis- and tris(silylamino)phosphines were thermally stable compounds which were purified by fractional distillation. Their successful preparation now completes the homologous series of silylamino–group 5 element compounds:[7] $[Me(Me_3Si)N]_nEMe_{3-n}$ (E = P, As, Sb, Bi; n = 1, 2, 3).

Aside from compound **4** which was mentioned in a review by Scherer,[7] the (silylamino)phosphinimines **1**–**9** have not been previously reported. Their characterization is based primarily upon NMR (^1H and ^{13}C) spectroscopic data and elemental analysis (Table I). The IR spectra were complex and difficult to interpret although the characteristic ν(P=N) band at ca. 1300 cm^{-1} was always present.

The hydrolytic instability of these compounds was in some cases severe. For example, an analytically pure sample of the *tert*-butyl derivative **3** could not be obtained due to consistent contamination by its hydrolysis product. In a separate experiment it was shown that **3** reacted with atmospheric moisture according to eq 9 yielding an N–H derivative. It is



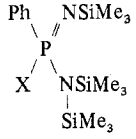
(9)

10a **10**

difficult to make a definite structural assignment of this product although isomer **10** is more consistent with the observed P–N–Si–C coupling constant,[2,6,10] the precedent for proton shifts in similar compounds,[7] and the expected higher basicity of a carbon-substituted relative to a silicon-substituted nitrogen function.[11]

Structural Isomerism. During our studies of the synthesis and characterization of (silylamino)phosphinimines **1**–**9** and the previously reported compound $(Me_3Si)_2NPMe_2NSiMe_3$,[2,7] two problems of stereochemical interest arose. The first is the kinetic (dynamic) phenomenon of reversible [1,3] silyl migration between the two nitrogen sites in the molecule. Second, there is the thermodynamic (static) problem of which isomeric form is the preferred structure for a given compound.

Examples of reversible [1,3] silyl shifts are provided by the trisilylated compounds which at low temperatures give ^1H



1: X = Me, $\Delta G^{\ddagger}_{1,3}$ = 14.2 kcal/mol
2: X = F, $\Delta G^{\ddagger}_{1,3}$ = 18.3 kcal/mol

NMR spectra consisting of two sharp singlets in a 2:1 intensity ratio (**1**, $\Delta\nu$ = 43 Hz at −20 °C; **2**, $\Delta\nu$ = 29 Hz at 30 °C). At higher temperatures the [1,3] silyl exchange becomes rapid leading to coalescence (**1**, T_c = 14 °C; **2**, T_c = 88 °C) of the

Table I. Preparative, Analytical, and NMR Spectroscopic Data for (Silylamino)phosphinimines (1-9)

compd	NMR spectra[a] signal obsd	$\delta(^1H)$	J_{PH}	$\delta(^{13}C)$	J_{PC}	reacn time, h	reacn temp, °C	% yield	bp, °C (torr)	anal.[b] % C	% H
$Me(Ph)P(=NSiMe_3)N(SiMe_3)_2$ (1)	$-NSiMe_3$	0.10[c]		4.96[c]		20	100	84	88-93 (0.01)	52.10	9.64
	$=NSiMe_3$									(51.84)	(9.52)
	PMe	1.78	13.3	22.15	82.4						
$F(Ph)P(=NSiMe_3)N(SiMe_3)_2$ (2)	$-NSiMe_3$	0.23		4.27	2.4[d]			56	143 (5)	47.98	8.45
	$=NSiMe_3$	−0.12		3.21	4.0[d]					(48.09)	(8.61)
$Me_2P(=N(t\text{-}Bu))N(SiMe_3)_2$ (3)	$NSiMe_3$	0.18		6.78		48	100	41	80-85 (0.5)		
	CMe_3	1.40		33.75	4.9						
	CMe_3			32.30	4.3						
	PMe_2	1.57	13.0	26.11	72.0						
$Me_2P(=NSiMe_3)N(Me)SiMe_3$ (4)	$-NSiMe_3$	0.20		2.07		24	95	74	100-106 (13.5)		
	$=NSiMe_3$	−0.07		3.74	3.7						
	PMe_2	1.30	13.0	18.76	78.1						
	NMe	2.45	12.0	30.46	2.4						
$[Me(Me_3Si)N]_2P(=NSiMe_3)Me$ (5)	$-NSiMe_3$	0.24		1.99		21	105	72	50-53 (0.5)	42.95	10.90
	$=NSiMe_3$	−0.04		3.82	3.7					(42.68)	(10.75)
	PMe	1.40	14.0	17.71	100.1						
	NMe	2.46	12.0	30.13							
$[Me(Me_3Si)N]_3P{=}NSiMe_3$ (6)	$-NSiMe_3$	0.22		1.50		72	120	70	89-90 (0.01)	42.89	11.05
	$=NSiMe_3$	−0.04		4.16	3.1					(42.40)	(10.68)
	NMe	2.45	14.0	32.16							
$Me_2P(=NSiMe_3)N(SiMe_2)SiMe_2$ (7)	$SiMe_2$	0.14		2.03		4	105	77	57-58 (0.01)	43.33	10.11
	$SiMe_3$	−0.17		4.00	3.1					(43.09)	(10.19)
	CH_2	0.62		9.28	13.7						
	PMe_2	1.29	13.2	23.92	76.9						
$Me_2P(=NSiMe_2(t\text{-}Bu))N(SiMe_3)_2$ (8)	$SiMe_3$	0.21		5.89	1.2	26	95	45	50-54 (0.01)	47.95	11.17
	$SiMe_3$	−0.17		0.89	2.5					(47.95)	(11.21)
	CMe_3	0.78		27.13							
	CMe_3			19.11	4.3						
	PMe_2	1.45	13.0	25.14	77.5						
$Me_2P(=NSiMe_2(t\text{-}Bu))N(Me)SiMe_3$ (9)	$SiMe_3$	0.25		2.56		18	105	78	50-54 (0.01)	49.39	11.14
	$SiMe_2$	−0.03		−0.89	2.2	(16)[e]	(105)[e]	(64)[e]		(49.27)	(11.37)
	CMe_3	0.70		27.05							
	CMe_3			18.99	4.2						
	PMe_2	1.35	10.4	19.17	77.9						
	NMe	2.48	11.6	31.07	2.7						

[a] Chemical shifts in ppm downfield from external Me_4Si; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C, $CDCl_3$. [b] Calculated values in parentheses. [c] Broad singlet (see text). [d] J(FP-NSiC) = 2.4 Hz; J(FP=NSiC) = 1.1 Hz. [e] Values in parentheses are from the reaction involving t-$BuMe_2SiN_3$ (see text).

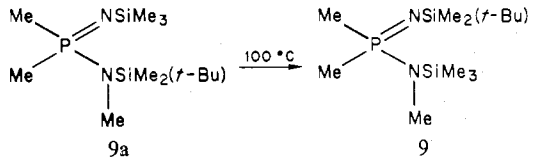
signals and permitting an estimate[12] of the exchange barrier ($\Delta G^{\ddagger}_{1,3}$). The *P*-dimethyl analogue of **1** is also fluxional at room temperature[2,7] and presumably has a similarly low-exchange barrier. In contrast, the *P*-dimethoxy derivative $(Me_3Si)_2NP(OMe)_2NSiMe_3$, which shows separate amino- and imino-$SiMe_3$ resonances in the ^1H NMR spectrum at ambient temperature, has a high $\Delta G^{\ddagger}_{1,3}$ value of 19.6 kcal/mol.[13] Moreover, other compounds of this type which contain electron-withdrawing substituents at phosphorus such as $(Me_3Si)_2NPX_2NSiMe_3$ (X = F,[9,14] Cl,[14] Br[14]) do not exhibit fluxional behavior at room temperature. It is concluded that *electron-releasing groups (e.g., Me) on phosphorus lower the [1,3] silyl exchange barrier* probably by inductively increasing the nucleophilicity of the imino nitrogen thereby facilitating its attack on the amino-$SiMe_3$ group. Similar arguments have been suggested in regard to silyl shifts in amides[15] and sulfinamides.[7]

The remaining (silylamino)phosphinimines (**3**–**9**) prepared in this study all gave ^1H and ^{13}C NMR spectra which are consistent with the existence of a single static structure in each case. Since the preparative reactions involved prolonged periods at high temperatures, it is very likely that the products obtained are the thermodynamically more stable isomers.

Each of the [methyl(trimethylsilyl)amino]phosphines reacted (eq 3b and 4) in a straightforward manner with trimethylsilyl azide to give the expected silylimino derivatives **4**–**6** which show separate ^1H and ^{13}C NMR signals (Table I) for the amino- and imino-$SiMe_3$ groups in the appropriate ratios. As in related compounds,[2,4,6,10] the imino-$SiMe_3$ carbons appear as a doublet with J(P=N—Si—C) ≈ 3–4 Hz. The ^1H NMR spectra of compounds **4**–**6** were unchanged at 115 °C indicating that the barrier to [1,3] silyl migration is quite high ($\Delta G^{\ddagger}_{1,3}$ > ca. 20 kcal/mol). It appears, therefore, that the $Me(Me_3Si)N$-substituted phosphinimines **4**–**6** are both

thermodynamically stable and kinetically nonfluxional.

When substituents more bulky than $SiMe_3$ are present on nitrogen in the (silylamino)phosphine reagent, however, the situation is quite different. Thus the reactions depicted by eq 3a and 6 give the structurally rearranged products **3**, **8**, and **9** in which *the sterically more demanding group (t-Bu or t-BuMe$_2$Si) occupies the less hindered imino position.* Structural assignments are based upon the observation of a single Me_3Si resonance in the NMR (^1H and ^{13}C) spectra of **3** and **8** and upon the marked similarity of the ^{13}C NMR parameters of the *t*-$BuMe_2Si$ moiety of **8** and **9** to those of other compounds containing the *t*-$BuMe_2SiN{=}P$ linkage.[16] The formation of compound **9** according to eq 6 presumably occurs via the intermediacy of isomer **9a** which logically should



9a 9

have been the initial product of the Me_3SiN_3 reaction. The silyl groups may exchange positions by undergoing [1,3] shifts to yield the more stable isomer **9**. The thermodynamic predominance of **9** over **9a** is further evidenced by the formation of a spectroscopically identical product from the reaction of *t*-$BuMe_2SiN_3$ with $Me(Me_3Si)NPMe_2$. In this case, no detectable quantity of the "reversed" isomer **9a** was obtained under the conditions of the reaction (Table I).

Finally, it is noted that the reaction of Me_3SiN_3 with the cyclic (silylamino)phosphine (eq 5) proceeded without rearrangement indicating that the five-membered ring is stable enough to prevent silyl migration. In a related study,[6] treatment of the methiodide salt of the same phosphine with a strong base gave only the ring-expanded product $Me_2SiCH_2CH_2SiMe_2CH_2PMe_2{=}N$ rather than the isomeric ylide $Me_2SiCH_2CH_2SiMe_2NP(=CH_2)Me_2$. This difference may be attributed to the greater nucleophilicity of the ylide function.[17]

Experimental Section

Materials. The following reagents were obtained from commercial sources: PCl_3, MeMgBr, *n*-BuLi, $(Me_3Si)_2NH$, Me_3SiN_3, and TMEDA. Methyl(trimethylsilyl)amine was prepared by addition of Me_3SiCl to an excess of $MeNH_2$ in xylene at −78 °C and was identified by its ^1H NMR spectrum.[18] A procedure similar to that described by Washburne and Peterson[19] was used to prepare *t*-$BuMe_2SiN_3$ which was identified by ^1H NMR and IR spectroscopy [δ 0.20 (Me_2Si), 0.93 (*t*-Bu); $\nu(N_3)$ = 2150 cm^{-1}]. Except for those described below, the (silylamino)phosphines were prepared as reported elsewhere.[6]

General Procedures. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen. Ethyl ether and hexane were distilled from calcium hydride prior to use. Other solvents were dried over molecular sieves. Proton and ^{13}C NMR spectra were recorded on JEOL MH-100 and FX-60 spectrometers, respectively. Infrared spectra were recorded on a Perkin-Elmer 297 spectrophotometer. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY.

The dynamic ^1H NMR studies utilized the MH-100 spectrometer equipped with a standard JEOL temperature controller which was calibrated with standard reference samples. Coalescence temperatures are accurate to within ±2 °C giving an uncertainty in the calculated[12] $\Delta G^{\ddagger}_{1,3}$ values of ca. ±0.2 kcal/mol. Compound **1** was studied as a 10% solution in CH_2Cl_2 while high-temperature runs used neat samples of **2** and **4**–**6**.

Physical, analytical, and spectroscopic data for the new (silylamino)phosphinimines are summarized in Table I.

Preparation of Bis[methyl(trimethylsilyl)amino]methylphosphine. Phosphorus trichloride (50 mmol) was added via syringe to a stirred solution of lithium methyl(trimethylsilyl)amide, prepared from $Me(Me_3Si)NH$ (100 mmol) and *n*-BuLi (107 mmol, hexane solution), in Et_2O (75 mL) at −78 °C. After stirring for 15 min, the mixture was allowed to warm to 0 °C and was stirred for another 15 min. The mixture was then recooled to −78 °C, and MeMgBr (50 mmol, ether solution) was added dropwise. After stirring for 2 h at −78 °C and 30 min at room temperature, the mixture was filtered under N_2, and solvents were removed under reduced pressure. Distillation afforded the phosphine as a colorless liquid (7.91 g, 63% yield, bp 65–68 °C (0.5 torr)). ^1H NMR (CH_2Cl_2 solution): δ 0.09 (J_{PH} = 1.0 Hz, $SiMe_3$), 1.20 (J_{PH} = 9.0 Hz, PMe), 2.60 (J_{PH} = 5.0 Hz, NMe). ^{13}C NMR ($CDCl_3$ solution): δ 0.42 (J_{PC} = 9.8, $SiMe_3$), 11.7 (J_{PC} = 19.5 Hz, PMe), 29.8 (J_{PC} = 5.5 Hz, NMe). IR (neat liquid): 2960 (s), 2900 (m), 2810 (w), 1435 (w), 1410 (w), 1280 (w), 1255 (s), 1180 (w), 1075 (s), 910 (s), 850 (vs), 750 (m), 690 (m), 640 (w) cm^{-1}. Anal. Calcd: C, 43.16; H, 10.87. Found: C, 43.38; H, 11.01.

Preparation of Tris[methyl(trimethylsilyl)amino]phosphine. *n*-Butyllithium (130 mmol, hexane solution) was added with stirring to a solution of $Me(Me_3Si)NH$ (140 mmol) in ether (150 mL) at 0 °C. The solution was allowed to warm to room temperature and was stirred for 20 min. The solvents and excess amine were removed under vacuum leaving $Me(Me_3Si)NLi$ (ca. 130 mmol) as a white solid. The solid was dissolved in Et_2O (150 mL) and TMEDA (133 mmol), and the solution was cooled to −78 °C. A solution of PCl_3 (43.3 mmol) in Et_2O (50 mL) was then added slowly with stirring. The reaction mixture was then stirred at −78 °C for 3 h and overnight at room temperature. Workup as described above gave the tris(amino)phosphine as a colorless liquid (6.89 g, 47% yield, bp 52–56 °C (0.01 torr)). ^1H NMR (CH_2Cl_2 solution): δ 0.12 (J_{PH} = 1.3 Hz, $SiMe_3$), 2.48 (J_{PH} = 5.5 Hz, NMe). ^{13}C NMR ($CDCl_3$ solution): δ 0.43 (J_{PC} = 9.2 Hz, $SiMe_3$), 30.2 (NMe). IR (neat liquid): 2960 (s), 2900 (m), 2805 (w), 1455 (w), 1410 (w), 1260 (s), 1175 (w), 1100 (s), 1080 (s), 910 (m), 850 (vs), 750 (m), 685 (m), 640 (w) cm^{-1}. Anal. Calcd: C, 42.68; H, 10.75. Found: C, 42.86; H, 10.81.

Preparation of *P*-[Bis(trimethylsilyl)amino]-*P*-methyl-*P*-phenyl-*N*-(trimethylsilyl)phosphinimine (1). Trimethylsilyl azide (40 mmol) and $(Me_3Si)_2NP(Ph)Me$ (32.8 mmol) were combined in a N_2-filled flask equipped with a magnetic stirrer and a reflux condenser, the top of which was connected to an oil bubbler. By means of an oil bath, the mixture was heated at 100 °C for 20 h during which a gas (presumably N_2) was evolved. Fractional distillation afforded **1** as a colorless liquid (Table I).

The same procedure was used to prepare other (silylamino)phosphinimines (**3**–**9**), and the reaction conditions are listed in Table I.

Preparation of *P*-[Bis(trimethylsilyl)amino]-*P*-fluoro-*P*-phenyl-*N*-(trimethylsilyl)phosphinimine (2). A solution of $(Me_3Si)_2NLi$ was prepared by the addition of *n*-BuLi (40 mmol) to $(Me_3Si)_2NH$ (40 mmol) in hexane (100 mL). Then $F_2(Ph)PNSiMe_3$[9] (40 mmol) was added via syringe, and the mixture was refluxed overnight. After filtration and solvent removal, fractional distillation gave unreacted $F_2(Ph)PNSiMe_3$ (ca. 1 mL, bp 68 °C (5 torr)) and compound **2** as a colorless higher boiling fraction (Table I).

Hydrolysis of *P*-[Bis(trimethylsilyl)amino]-*N*-*tert*-butyl-*P*,*P*-dimethylphosphinimine (3). In several preparations of **3** (according to the procedure described above for **1**) it was always found to be contaminated with a small amount of a lower-boiling impurity which could not be completely removed by distillation. A small amount of **3** was dissolved in $CHCl_3$ (5 mL) and exposed to the air for 4 h with stirring. The solvent and a volatile product, identified as $Me_3SiOSiMe_3$ by comparison of its IR spectrum to that of an authentic sample, were removed under vacuum leaving compound **10** as a white solid (mp 34.5–37 °C, bp 59–61 °C (0.8 torr)). ^1H NMR (CH_2Cl_2 solution): δ −0.10 ($SiMe_3$), 1.21 (*t*-Bu), 1.35 (J_{PH} = 14.0 Hz, PMe_2), 1.90 (NH). ^{13}C NMR ($CDCl_3$ solution): δ 3.49 (J_{PC} = 3.7 Hz, $SiMe_3$), 31.67 (J_{PC} = 3.7 Hz, CMe_3), 50.74 (J_{PC} = 3.1 Hz, CMe_3), 21.97 (J_{PC} = 84.2 Hz, PMe_2). Anal. Calcd: C, 49.05; H, 11.44. Found: C, 49.30; H, 11.49.

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Registry No. **1**, 69687-06-5; **2**, 69687-07-6; **3**, 69687-08-7; **4**, 69687-09-8; **5**, 69687-10-1; **6**, 69687-11-2; **7**, 69687-12-3; **8**,

69687-13-4; **9**, 69687-14-5; **10**, 69687-15-6; $[Me(Me_3Si)N]_2PMe$, 69687-16-7; $[Me(Me_3Si)N]_3P$, 69687-17-8; Me_3SiN_3, 4648-54-8; $(Me_3Si)_2NP(Ph)Me$, 68437-87-6; $(Me_3Si)_2NLi$, 4039-32-1; $F_2(Ph)PNSiMe_3$, 61701-83-5; $(t\text{-Bu})(Me_3Si)NPMe_2$, 68437-82-1; $Me(Me_3Si)NPMe_2$, 68437-84-3; $SiMe_2CH_2CH_2SiMe_2NPMe_2$, 68437-96-7; $(Me_3Si)(t\text{-BuMe}_2Si)NPMe_2$, 68437-90-1; $Me(t\text{-BuMe}_2Si)NPMe_2$, 68437-93-4; $Me(Me_3Si)NLi$, 10568-44-2; PCl_3, 7719-12-2; $[Me(Me_3Si)N]_2PCl$, 69687-18-9.

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Preparation and Characterization of Magnesium Tetrahydridozincate, $MgZnH_4$

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Magnesium tetrahydridozincate, $MgZnH_4$, has been prepared by the following synthetic routes: (1) $2MgH_2 + 2Me_2Zn \xrightarrow{THF} MgZnH_4 + MgZnMe_4$; (2) $2Me_2Mg + 2ZnH_2 \xrightarrow{THF} MgZnH_4 + MgZnMe_4$; (3) $2MgH_2 + Me_2Zn \xrightarrow{THF} MgZnH_4 + Me_2Mg$; (4) $2MgH_2 + 4Me_2Zn \xrightarrow{THF} MgZnH_4 + [Mg(ZnMe_3)_2 + Me_2Zn]$; (5) $2MeMg + 4ZnH_2 \xrightarrow{THF} MgZnH_4 + MgZnMe_4 + 2ZnH_2$; (6) $Me_2Mg + Me_2Zn \xrightarrow{THF} MgZnMe_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAlH_2Me_2$ (or $\xrightarrow{2MgH_2} MgZnH_4 + 2Me_2Mg$). Highly reactive magnesium hydride used in these reactions was prepared by the reaction of diethyl- or diphenylmagnesium with lithium aluminum hydride. Similarly, zinc hydride was prepared by the reaction of lithium aluminum hydride with either diphenylzinc, dimethylzinc, or zinc bromide in diethyl ether. Zinc hydride in active form was also prepared by the reaction of zinc bromide with magnesium hydride slurried in THF. Magnesium tetrahydridozincate was characterized by complete elemental analysis, X-ray powder diffraction, and DTA–TGA studies. The X-ray powder diffraction patterns of $MgZnH_4$, prepared by all of the above methods, were found to be identical.

Introduction

Since complex metal hydrides of aluminum and boron have become invaluable reagents in synthetic organic chemistry, it would seem important to evaluate complex metal hydrides of other main-group elements for possible usefulness as soluble chemical reducing agents. In this connection, we have reported the preparation of $KMgH_3$,[1] Li_2ZnH_4,[2] $LiCuH_2$,[3] and several other complex metal hydrides by the reaction of the corresponding "ate" complex with $LiAlH_4$. Very recently, we reported the preparation of magnesium zinc hydrides[4] by the reaction of magnesium zinc "ate" complexes with lithium aluminum hydride in diethyl ether. The product $MgZnH_4$ was reported to be prepared by two different methods (eq 1 and 2). In that report, we discussed a possible doubt about the

$$Me_2Mg + Me_2Zn \xrightarrow{Et_2O} MgZnMe_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAlH_2Me_2 \quad (1)$$

$$Li_2ZnMe_4 + MgBr_2 \rightarrow 2LiBr + MgZnMe_4 \xrightarrow{2LiAlH_4} MgZnH_4 + 2LiAlH_2Me_2 \quad (2)$$

existence of $MgZnH_4$ being a single and pure product or a physical mixture of MgH_2 and ZnH_2. The reason behind the doubt was that the so-called "ate" complex $MeZnMe_4$ was shown to exist in equilibrium with Me_2Mg and Me_2Zn. Therefore, the reaction of this product mixture with $LiAlH_4$ would probably give a mixture of products (eq 3). Furthermore, the X-ray powder diffraction patterns of the Mg/Zn

$$\begin{bmatrix} Me_2Mg \\ + \\ Me_2Zn \\ \uparrow\downarrow \\ MgZnMe_4 \end{bmatrix} \xrightarrow{2LiAlH_4} \begin{bmatrix} MgH_2 \\ + \\ ZnH_2 \\ + \\ MgZnH_4 \end{bmatrix} + 2LiAlMe_2H_2 \quad (3)$$

products of reactions 1 and 2 were found to be different. Of course, if only $MgZnH_4$ was formed in each reaction, the Mg/Zn product should exhibit the same X-ray powder diffraction pattern.

In order to resolve this discrepancy, it was decided to explore the preparation of $MgZnH_4$ by several other methods and to characterize the reaction products by X-ray powder diffraction and DTA–TGA studies. In this paper, we report several new synthetic routes to $MgZnH_4$ and attempts to prepare $Mg(ZnH_3)_2$.

Experimental Section

Apparatus. Reactions were performed under dry nitrogen by using Schlenk-tube techniques.[5] Filtration and other manipulations were carried out in a glovebox equipped with a recirculating system.[6]

X-ray powder diffraction data were obtained on a Philips-Norelco X-ray unit with a 114.6-mm camera with nickel-filtered Cu Kα radiation. Samples were sealed in 0.5-mm capillaries and exposed to X-rays for 6 h. *d* spacings were read on a precalibrated scale

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