# ORGANOMETALLICS

# N-P Bond Cleavage Induced Ring Formation of Cyclosilazanes from Reactions of Aryl(phosphanyl)aminotrichlorosilanes with Lithium Alkynyls

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Supporting Information

ABSTRACT: The aryl(silyl)aminotrichlorosilane 2,6*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>2</sub>Ph)SiCl<sub>3</sub> (1) and aryl(phosphanyl)aminotrichlorosilane ArN(PPh<sub>2</sub>)SiCl<sub>3</sub> (Ar =  $2,6-iPr_2C_6H_3$ (2), 4-MeC<sub>6</sub>H<sub>4</sub> (3), 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> (4)) were prepared and utilized for investigation in reactions with freshly prepared lithium alkynyls. Reaction of 1 with PhC=CLi resulted in the compounds PhMe<sub>2</sub>SiC=CPh and  $2_{6}-iPr_{2}C_{6}H_{3}N[Li(THF)_{3}]$ -Si(C $\equiv$ CPh)<sub>3</sub> (5), while 2 reacted with R'C $\equiv$ CLi to produce



the compounds  $Ph_2PC \equiv CR'$  and  $[2,6-iPr_2C_6H_3NSi(C \equiv CR')_2]_2$  (R' = Ph (6), tBu (7), CH<sub>2</sub>CH<sub>2</sub>Ph (8)). Reaction of 3 with PhC $\equiv$ CLi led to the formation of Ph<sub>2</sub>PC $\equiv$ CPh and [4-MeC<sub>6</sub>H<sub>4</sub>NSi(C $\equiv$ CPh)<sub>2</sub>]<sub>3</sub> (9a) as a major product and {4- $MeC_6H_4NSi(C \equiv CPh)[N(4-MeC_6H_4)Si(C \equiv CPh)_3]$ , (9b) as a minor product. When 4 was reacted with PhC = CLi, [2,4,6- $Me_3C_6H_2NSi(C \equiv CPh)_2]_2$  (10a) was isolated as the major product while  $[(2,4,6-Me_3C_6H_2)_3N_3Si_2(C \equiv CPh)_4Li(THF)]^-[Li-CPh)_4Li(THF)]^ (THF)_4]^+$  (10b) was the minor product. The formation of Ph<sub>2</sub>PC=CPh was also detected. All reported compounds were characterized by multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and/or <sup>31</sup>P) and/or IR spectroscopy, and compounds 2, 5-8, 9a, and 10b were further distinguished by single-crystal X-ray crystallography. These results exhibit a route to the  $Si_2N_2$ - or  $Si_3N_3$ -based cyclosilazanes 6-8, 9a, 9b, and 10a via the N–P bond cleavage of the aryl(phosphanyl)aminotrichlorosilanes during multiple metathesis reactions.

# INTRODUCTION

Cyclosilazanes are Si- and N-based cyclic compounds and are often used as single-source precursors for the preparation of silicon nitride, an important valuable refractory material.<sup>1</sup> This combination constitutes a special class of compounds with rich Si-N bonds without any carbon atoms in the ring skeletons.<sup>2</sup> Cyclosilazanes with alternating silicon and nitrogen centers are normally prepared by the reaction of primary amines with dihalosilanes. Alternatively, they are also synthesized by a number of other routes (Chart 1).<sup>2a,3-5</sup> They consist of a variety of ring or cage structures which largely depend on the size of the substituents at either the Si or N atom. By taking advantage of the sterically demanding groups, acyclic types of  $R_2SiNR'$  ( $R_2$ , R' = organic substituent(s)) have also been obtained.<sup>6</sup> The latter compound is known as a silaimine, which contains a Si=N double bond with strongly polar character and thus is prone to undergo cycloaddition reactions. They are often considered as intermediates which finally resulted in the preparation of cyclosilazane.<sup>5</sup> Nevertheless, the ring formation via inter- or intramolecular salt elimination leading to cyclosilazanes has also been suggested.<sup>4b,c</sup> It is noted that the various R'-substituted primary amines can be provided for

synthesis of cyclosilazanes having different ring or cage structures. However, cyclosilazanes which are tuned at the Si atom usually require additional metathesis reactions when silicon halide is utilized as the precursor. There are also reports on metathesis reactions at the Si atoms of the preformed Si<sub>2</sub>N<sub>2</sub> ring.<sup>4j</sup> Herein, we report a direct synthetic route to Sialkynylated cyclosilazanes by reacting N-silyl and -phosphanyl group substituted arylaminotrichlorosilanes, ArN(R)SiCl<sub>3</sub> (Ar  $= 2_{6} - i \Pr_{2}C_{6}H_{3}$ , R = SiMe<sub>2</sub>Ph (1), PPh<sub>2</sub> (2); Ar = 4-MeC\_{6}H\_{4}, R =  $PPh_2$  (3); Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, R =  $PPh_2$  (4)), as precursors with several lithium alkynyls. A series of Si<sub>2</sub>N<sub>2</sub> ring compounds  $[2,6-i\Pr_2C_6H_3NSi(C\equiv CR')_2]_2$  (R' = Ph ( $\tilde{6}$ ), tBu (7),  $CH_2CH_2Ph$  (8)) and  $\{4-MeC_6H_4NSi(C\equiv CPh)[N(4 MeC_6H_4$ )Si(C=CPh)<sub>3</sub>] $_2$  (9b) and the cyclic Si<sub>3</sub>N<sub>3</sub> compound  $[4-MeC_6H_4NSi(C \equiv CPh)_2]_3$  (9a) were produced and structurally characterized together with the lithium derivatives 2,6 $iPr_2C_6H_3N[Li(THF)_3]Si(C \equiv CPh)_3$  (5) and [(2,4,6- $Me_3C_6H_2)_3N_3Si_2(C \equiv CPh)_4Li(THF)]^{-}[Li(THF)_4]^+$  (10).

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Chart 1. Some Examples of Cyclosilazanes Prepared from Chlorosilanes



These results show the formation of a variety of cyclosilazanes originated by multiple metathesis reactions.

# RESULTS AND DISCUSSION

The N-silyl or -phosphanyl group bonded arylaminotrichlorosilanes ArN(R)SiCl<sub>3</sub> (Ar =  $2,6-iPr_2C_6H_3$ , R = SiMe<sub>2</sub>Ph (1),  $PPh_2$  (2); Ar = 4-MeC<sub>6</sub>H<sub>4</sub>, R =  $PPh_2$  (3); Ar = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>,  $R = PPh_2(4)$  were prepared by using a consecutive route. The monosubstituted aryl amine ArNH(R) was prepared from ArNH<sub>2</sub> in situ with *n*BuLi and then treated with chlorodimethylphenylsilane (PhMe<sub>2</sub>SiCl) or chlorodiphenylphosphine (Ph<sub>2</sub>PCl). The deprotonation of ArNH(R) using *n*BuLi resulted in Ar(R)NLi. The latter was further employed for the reaction with SiCl<sub>4</sub>. By removal of insoluble LiCl and all volatiles, washing with cold *n*-hexane, and crystallization of the *n*-hexane washing solution at -20 °C, the target compounds were obtained as off-white solids together with colorless crystals in good yield (1, 81%; 2, 89%; 3, 74%; 4, 88%). A general preparative procedure of these compounds is shown in Scheme 1. Compounds 1-4 were characterized by multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and/or <sup>31</sup>P) spectroscopy and elemental analysis, and compound 2 was further confirmed by X-ray crystallog-

Scheme 1. Consecutive Route Synthesis of Combounds 1	Scheme	1.	Consecutive	Route	Synthesis	of	Compounds	1-	_4
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raphy. The <sup>29</sup>Si NMR spectrum of 1 exhibits a resonance at  $\delta$  1.83 ppm corresponding to the silicon atom of the SiMe<sub>2</sub>Ph group. The resonance at  $\delta$  –27.1 ppm is assigned to the silicon atom for the SiCl<sub>3</sub> group, which can be compared with those observed in silyltrichloride Ar'N(SiMe<sub>3</sub>)SiCl<sub>3</sub> (Ar' = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>,  $\delta_{SiCl_3}$  –28.2 ppm; 2-*i*Pr-6-MeC<sub>6</sub>H<sub>3</sub>,  $\delta_{SiCl_3}$  –27.9 ppm; 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>,  $\delta_{SiCl_3}$  –28.3 ppm).<sup>7</sup> The <sup>29</sup>Si NMR spectra of **2**–4 display a resonance of the SiCl<sub>3</sub> group ( $\delta$  –28.90 ppm and  $J_{PSi}$  = 24.10 Hz for **2**, –26.65 ppm and 48.90 Hz for **3**, and –28.61 ppm and 48.90 Hz for **4**). These resonances each split into a doublet due to the coupling with the <sup>31</sup>P nucleus of PPh<sub>2</sub>. The <sup>31</sup>P NMR spectra exhibit each a resonance at  $\delta$  55.69 ppm for **2**, 54.73 ppm for **3**, and 42.73 ppm for **4**, respectively.

Reaction of 1 with freshly prepared PhC=CLi<sup>8</sup> in a molar ratio of 1:4 was carried out in a mixture of solvents (Et<sub>2</sub>O/THF). The reaction was performed initially at -78 °C, and the temperature was slowly raised to room temperature. The compound 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N[Li(THF)<sub>3</sub>]Si(C=CPh)<sub>3</sub> (5) was isolated as the major product. The formation of PhMe<sub>2</sub>SiC=CPh<sup>9</sup> as a side product was also detected, which was concluded by NMR (<sup>1</sup>H and <sup>13</sup>C) and IR spectral analysis (Scheme 2).

Scheme 2. Reaction of 1 with PhC≡CLi To Give Compound 5 and PhMe<sub>2</sub>SiC≡CPh



Under similar conditions, the reaction of **2** with PhC=CLi in a 1:3 molar ratio yielded compound  $[2,6-iPr_2C_6H_3NSi(C=CPh)_2]_2$  (**6**) with a Si<sub>2</sub>N<sub>2</sub> four-membered ring. By replacing PhC=CLi with *t*BuC=CLi and PhCH<sub>2</sub>CH<sub>2</sub>C=CLi, similar products  $[2,6-iPr_2C_6H_3NSi(C=CtBu)_2]_2$  (**7**) and  $[2,6-iPr_2C_6H_3NSi(C=CCH_2CH_2Ph)_2]_2$  (**8**) were obtained (Scheme 3). In the last three reactions, the respective

Scheme 3. Reactions of 2 with R'C $\equiv$ CLi To Give Compounds 6–8 and the Corresponding Ph<sub>2</sub>PC $\equiv$ CR'



compound  $Ph_2PC \equiv CR'$  (R' = Ph during the formation of 6, *t*Bu for 7, and  $CH_2CH_2Ph$  for 8) was also produced, as evidenced by the <sup>31</sup>P resonance.<sup>10</sup>

The formation of **5** indicates the substitution of all chlorine atoms at the Si atom of **1** by three phenylethynyl groups with PhC $\equiv$ CLi. The compound 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>2</sub>Ph)Si(C $\equiv$  CPh)<sub>3</sub> (C) probably forms and further reacts by metathesis with PhC $\equiv$ CLi to give **5** and PhMe<sub>2</sub>SiC $\equiv$ CPh (Scheme 4). Comparable examples have only been observed for reactions of

Scheme 4. Plausible Formation of Compound 5



 $R^1C \equiv CSi(SiMe_3)_3$  ( $R^1 = H$ , Me, Ph, SiMe\_3, Si(SiMe\_3)\_3) with KOtBu to give R<sup>1</sup>C≡CSi(SiMe<sub>3</sub>)<sub>2</sub>K and Me<sub>3</sub>SiOtBu.<sup>11</sup> We performed the reactions of 1 with PhC=CLi in a molar ratio of 1:3 or even 1:2 under the same conditions in an attempt to isolate C, but failed. Compound 5 and PhMe<sub>2</sub>SiC≡CPh were always formed, although in a relatively low yield. Moreover, the starting material 1 was found unreacted on the basis of <sup>29</sup>Si NMR measurements. The formation of 6-8 might involve an initial production of the lithium amide 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(Li)SiCl<sub>3</sub> (A) with release of  $Ph_2PC \equiv CR'$ . A reacts with elimination of LiCl to give **B**, and **B** is then transferred to 6–8 through further metathesis with R'C CLi (Scheme 5). The lithium amide A can be compared with 5, which is well-known as an intermediate for the formation of cyclosilazanes.<sup>4b,c</sup> B has been isolated as a stable compound by treatment of in situ formed  $2_{,6}$ -*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(H)SiCl<sub>3</sub> with *n*BuLi or Et<sub>3</sub>N (see the synthesis and characterization in the Supporting Information). Obviously, the formation of 6-8 is different from that of 5, probably because the N-bonded group is SiMe<sub>2</sub>Ph in 1 while in **2** it is the  $PPh_2$  substituent.<sup>12</sup>

Compounds 5–8 were isolated as colorless crystals in moderate to good yields (72% for 5, 62% for 6, 55% for 7, and 68% for 8). All reported compounds are moisture sensitive. Compound 5 is thermally unstable and decomposes at 108 °C. Compounds 6–8 appear stable up to the melting points of 224, 165, and 198 °C, respectively. They have been fully characterized by NMR (<sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si) and IR spectroscopy, elemental analysis, and X-ray crystallography.

The crystal structure of **5** is shown in Figure 1s (see the Supporting Information), which clearly reveals that three phenylethynyl groups are bound to the Si atom. Moreover,  $\text{Li}(\text{THF})_3$  is coordinated to the N atom. NMR and IR spectroscopy shows the <sup>13</sup>C resonances ( $\delta$  97.04 and 101.80 ppm) and the corresponding IR band ( $\nu$  2152.8 cm<sup>-1</sup>) for the phenylethynyl C $\equiv$ C functionality. The presence of the coordinated THF molecules is evidenced from the characteristic <sup>1</sup>H ( $\delta$  1.34 and 3.52 ppm) and <sup>13</sup>C ( $\delta$  25.30 and 68.05 ppm) NMR data. The <sup>29</sup>Si NMR spectrum displays the silicon resonance ( $\delta$  –93.59 ppm), which is comparable to those found in alkynylsilanes (RC $\equiv$ C)<sub>4</sub>Si (R = 4-MeC<sub>6</sub>H<sub>4</sub>,  $\delta$  –92.63 ppm; R = 4-tBuC<sub>6</sub>H<sub>4</sub>, -92.52 ppm; R = 4-PhC<sub>6</sub>H<sub>4</sub>, -92.52 ppm).

The crystal structures of 6-8 are displayed in Figures 1-3 with selected bond distances and angles. All compounds



**Figure 1.** X-ray single-crystal structure (50% probability level of the thermal ellipsoids) of **6** with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) (data in brackets are for another independent molecule): Si(1)–N(1) 1.724(2) [1.721(2)], Si(2)–N(1) 1.722(2) [1.719(2)], C(1)–C(2) 1.198(3) [1.201(3)], C(11)–C(12) 1.199(3) [1.210(3)]; N(1)–Si(1)–N(1A) 86.38(13) [86.60(12)], Si(1)–N(1)–Si(2) 93.55(10) [93.47(9)], Si(1)–C(1)–C(2) 174.3(2) [175.1(2)], Si(2)–C(11)–C(12) 173.4(2) [169.8(2)]. Symmetry code: (A) –*x*, *y*, –*z* +  $^{1}/_{2}$ .



**Figure 2.** X-ray single-crystal structure (50% probability level of the thermal ellipsoids) of 7 with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)-N(1) 1.706(4), Si(1)-N(1A) 1.660(3), C(1)-C(2) 1.239(6), C(11)-C(12) 1.249(6); N(1)-Si(1)-N(1A) 79.06(16), Si(1)-N(1)-Si(2) 100.94(16), Si(1)-C(1)-C(2) 172.4(5), Si(1)-C(11)-C(12) 171.9(4). Symmetry code: (A) -x + 2, -y, -z + 1.

Scheme 5. Reasonable Reaction Pathway to Compounds 6–8





Figure 3. X-ray single-crystal structure (50% probability level of the thermal ellipsoids) of 8 with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) (data in brackets are for another independent molecule): Si(1)–N(1) 1.718(2) [1.725(2)], Si(1)–N(1A) 1.715(5) [1.720(2)], C(1)–C(2) 1.194(4) [1.199(4)], C(11)–C(12) 1.203(4) [1.204(4)]; N(1)–Si(1)–N(1A) 86.68(11) [86.52(11)], Si(1)–N(1)–Si(1A) 93.32(11) [93.48(11)], Si(1)–C(1)–C(2) 178.3(3) [175.9(3)], Si(1)–C(11)–C(12) 178.0(3) [174.9(3)]. Symmetry code: (A) -x, -y + 2, -z.

contain an ideal N<sub>2</sub>Si<sub>2</sub> planar four-membered ring with a *centro* symmetry (the  $\Delta$  values of the least-square planes of Si(1)N(1)Si(2)N(1A) and Si(3)N(2)Si(4)N(2A) in 6, Si(1)-N(1)Si(1A)N(1A) in 7, and Si(1)N(1)Si(1A)N(1A) and Si(2)N(2)Si(2A)N(2A) in 8 are all calculated to be 0.0000 Å). This structural feature appears common in (RNSiMe<sub>2</sub>)<sub>2</sub> (R = *s*IMe<sub>3</sub>, Mes, SiH(SiMe<sub>3</sub>)<sub>2</sub>, SiMetBu<sub>2</sub>),<sup>4k</sup> and (RNSiCl<sub>2</sub>)<sub>2</sub> (R = *t*Bu,<sup>4h</sup> 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Exceptional examples are found in the nonplanar ring compounds  $[(tBu<sub>2</sub>ClSi)NSiCl(NH<sub>2</sub>)]_2$ ,<sup>4i</sup> (MesNSiClMes)<sub>2</sub>,<sup>4f</sup> and MesNSi(*t*Bu)(X)N(Mes)Si(*t*Bu)-(NHMes) (X = H, Cl; Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>),<sup>4g</sup> probably due to the two different groups attached at the Si atoms of the ring. In these planes the *N*-aryls are perpendicularly arranged while two alkynyl groups are located up and down at each Si

atom. The Si–N bond lengths (1.719(2)-1.724(2) Å in 6, 1.660(3)-1.706(4) Å in 7, and 1.715(5)-1.725(2) Å in 8) are comparable to those of the previously reported ring compounds  $(1.713(1)-1.756(6) \text{ Å})^{4f,g,i,k}$  but longer than those in 5 (1.640(1) Å) as well as in silaimines having Si–N double bonds  $(1.5329(16)-1.6209(13) \text{ Å}).^{6d-g}$  The <sup>29</sup>Si NMR spectra exhibit resonances at  $\delta$  –88.33 for 6, –63.12 for 7, and –61.96 ppm for 8, respectively.

We further carried out the reaction of 3 with 3 equiv of PhC $\equiv$ CLi and the isolated compound [4-MeC<sub>6</sub>H<sub>4</sub>NSi(C $\equiv$  $(CPh)_2]_3$  (9a) as colorless square blocks in 52% yield. To our surprise, another compound  $\{4-MeC_6H_4NSi(C \equiv CPh)[N(4 MeC_6H_4$ )Si(C $\equiv$ CPh)<sub>3</sub>] $_2$  (9b) was also obtained as colorless plates in a very low yield (8%, Scheme 6). Similarly, the reaction of 4 with 3 equiv of PhC=CLi was completed and compound  $[2,4,6-Me_3C_6H_2NSi(C \equiv CPh)_2]_2$  (10a) was obtained as colorless needles of the major part (66%), while  $[(2,4,6-\text{Me}_3C_6H_2)_3\text{N}_3\text{Si}_2(C \equiv CPh)_4\text{Li}(THF)]^-[\text{Li}(THF)_4]^+$ (10b) was produced as colorless arris-piece crystals as the minor part (8%, Scheme 7). In both reactions  $Ph_2PC \equiv CPh$ was formed. The formation of 9a or 10a follows the reaction pathway similarly to those of 6-8. The production of 9b might undergo an additional metathesis reaction involving the intermediate 4-MeC<sub>6</sub>H<sub>4</sub>NLi[Si(C $\equiv$ CPh)<sub>3</sub>], like that of compound 5. However, compound 10b could be considered as a result of the further reaction of 10a with the possibly in situ formed dilithium amide 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NLi<sub>2</sub>, a known type species that can be produced from the reaction of primary amine with *n*BuLi.<sup>14</sup> Nonetheless, due to the very low yield of 9b and 10b, the detailed mechanism for the formation of these two compounds still needs further investigation.

Compounds 9a,b and 10a,b are moisture sensitive. Compound 9a melts at 216 °C, while 9b has a melting point at 257 °C. Correspondingly, 10a has a clear melting point at 242 °C, whereas 10b decomposes when heated to 178 °C, as indicated by a color change from colorless to yellow and finally to black. Compounds 9a and 10b have been confirmed by NMR and IR spectroscopy and elemental analysis as well as by single-crystal X-ray structures. Compounds 9b and 10a have been characterized by NMR and IR spectroscopy and elemental analysis, and their composition and structure have been further supported by a preliminary structural analysis from X-ray diffraction studies.<sup>15</sup> The crystal structure of 9a is shown in Figure 4 and that of 10b in Figure 2s in the Supporting Information. Compound 9a features a Si<sub>3</sub>N<sub>3</sub> six-membered ring  $(\Delta_{Si(1)N(1)Si(2)N(2)Si(3)N(3)} = 0.0638$  Å), which deviates slightly from the ideal plane in comparison to those of 6-8. In the similar compounds (ArNSiMe<sub>2</sub>)<sub>3</sub> (Ar = o-MeC<sub>6</sub>H<sub>4</sub>, m-MeC<sub>6</sub>H<sub>4</sub>,

Scheme 6. Reaction of 3 and PhC=CLi To Give Compounds 9a,b and Ph<sub>2</sub>PC=CPh



# Scheme 7. Reaction of 4 with PhC≡CLi To Give Compounds 10a,b and Ph<sub>2</sub>PC≡CPh





Figure 4. X-ray single-crystal structure (50% probability level of the thermal ellipsoids) of 9a with H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)-N(1) 1.717(4), N(1)-Si(2) 1.724(4), Si(2)-N(2) 1.721(4), N(2)-Si(3) 1.722(4), Si(3)-N(3) 1.719(3), N(3)-Si(1) 1.724(3), C(1)-C(2) 1.166(8), C(11)-C(12) 1.231(8), C(21)-C(22) 1.200(7), C(31)-C(32) 1.215(7), C(41)-C(42) 1.199(7), C(51)-C(52) 1.204(7); N(1)-Si(1)-N(3) 108.98(17), Si(1)-N(3)-Si(3) 130.5(2), N(3)-Si(3)-N(2) 108.86(18), Si(3)-N(2)-Si(2) 128.4(2), N(2)-Si(2)-N(1) 108.91(18), Si(2)-N(1)-Si(1) 130.4(2).

 $p\text{-MeC}_6H_4)$  the boatlike  $\mathrm{Si}_3\mathrm{N}_3$  ring conformations were indicated.  $^{16}$  Inside the ring, Si–N bond lengths (1.717(4)– 1.724(4) Å) can be compared to those in the  $Si_2N_2$  fourmembered rings of 6 and 8, but the N-Si-N (108.86(18)- $108.93(17)^{\circ}$ ) and Si-N-Si bond angles  $(128.4(2)-130.5(2)^{\circ})$ become wider (in 6 and 8, N-Si-N 86.38(13)-88.08(5)° and Si-N-Si 91.92(5)-93.55(10)°). Compound 10b is an ion pair with the anionic part of the Si<sub>2</sub>N<sub>3</sub>Li-fused six-membered ring and cationic part of  $[Li(THF)_4]^+$ . The N-Li bond lengths are 1.913(6) and 1.941(6) Å and are shorter in comparison to that in 5 (2.005(3) Å), probably due to the ring restriction and the lower coordination around the Li atom. The N(1)-Si(1)(1.638(3) Å) and N(2)-Si(2) (1.654(3) Å) bond lengths are remarkably shorter than the N(3)-Si(1) (1.729(2) Å) and N(3)-Si(2) bond lengths (1.745(2) Å) because of the coordination of both N(1) and N(2) atoms to the Li. The first two distances are close to that found in 5, while the last two are comparable to those of the cyclosilazanes 6, 8, and 9a, respectively.

# CONCLUSION

In summary, we have prepared the aryl(silyl)aminotrichlorosilane  $2,6-iPr_2C_6H_3N(SiMe_2Ph)SiCl_3$  (1) and aryl(phosphanyl)aminotrichlorosilane ArN(PPh<sub>2</sub>)SiCl<sub>3</sub> (Ar =  $2,6-iPr_2C_6H_3$  (2),  $4-MeC_6H_4$  (3),  $2,4,6-Me_3C_6H_2$  (4)) and carried out the reactions of these compounds with several lithium alkynyls. The reaction of **1** with PhC≡CLi underwent the substitution of all the chlorine atoms at the silicon center with phenylethynyls and moreover a cleavage of the N-Si<sub>SiMe,Ph</sub> bond, leading to the formation of the compounds 2,6 $iPr_2C_6H_3N[Li(THF)_3]Si(C \equiv CPh)_3$  (5) and PhMe\_SiC = CPh. The reactions of 2-4 with R'C≡CLi, however, resulted in the cleavage of the  $N-P_{PPh_2}$  bond and the substitution of the chlorides with alkynyls, producing the cyclosilazanes [2,6 $i Pr_2 C_6 H_3 NSi(C \equiv CR')_2]_2 (R' = Ph (6), tBu (7), CH_2 CH_2 Ph$ (8)),  $[4-MeC_6H_4NSi(C \equiv CPh)_2]_3$  (9a),  $\{4-MeC_6H_4NSi(C \equiv CPh)_2\}_3$  $CPh)[N(4-MeC_6H_4)Si(C \equiv CPh)_3]\}_2$  (9b), and [2,4,6- $Me_{3}C_{6}H_{2}NSi(C\equiv CPh)_{2}]_{2}$  (10a) and the ionic lithium salt derivative  $[(2,4,6-Me_3C_6H_2)_3N_3Si_2(C \equiv CPh)_4Li(THF)]^-[Li (THF)_4]^+$  (10b). In all cases  $Ph_2PC \equiv CR'$  (R' = Ph in the reactions of 2-4 with PhC $\equiv$ CLi, R = *t*Bu in the reaction of 2 with *t*BuC $\equiv$ CLi, and R = CH<sub>2</sub>CH<sub>2</sub>Ph in the reaction of **2** with PhCH<sub>2</sub>CH<sub>2</sub>C≡CLi) was formed. These results reveal a novel synthetic route for the formation of cyclosilazanes via the N-P<sub>PPh2</sub> bond cleavage by multiple metathesis reactions when aryl(phosphanyl)aminotrichlorosilanes were utilized as the starting material and reacted with the lithium alkynyls.

# EXPERIMENTAL SECTION

**Materials and Methods.** All manipulations were carried out under a dry argon or nitrogen atmosphere by using Schlenk line and glovebox techniques. The organic solvents toluene, *n*-hexane, diethyl ether, and tetrahydrofuran were dried by refluxing with sodium/ potassium benzophenone under N<sub>2</sub> prior to use. The NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, and <sup>31</sup>P) spectra were recorded on a Bruker Avance II 400 or 500 MHz spectrometer. Infrared spectra were obtained on a Nicolet FT-IR 330 spectrometer. Melting points of compounds were measured in a sealed glass tube using a Büchi-540 instrument. Elemental analysis was performed on a Thermo Quest Italia SPA EA 1110 instrument. Commercial reagents were purchased from Aldrich, Acros, or Alfa-Aesar Chemical Co. and used as received.

Synthesis of 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>2</sub>Ph)SiCl<sub>3</sub> (1). At  $-78 \degree C nBuLi$  (20.83 mL, 2.4 M solution in *n*-hexane, 50 mmol) was added dropwise to a solution of 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> (9.43 mL, 50 mmol) in diethyl ether (150 mL). The mixture was warmed to room temperature and stirred for 12 h to form the lithium salt 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHL*i*. This solution was again cooled to  $-78 \degree C$ , and to it was added neat PhMe<sub>2</sub>SiCl (8.27 mL, 50 mmol). The mixture was warmed to room temperature and stirred for 12 h to give 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH(SiMe<sub>2</sub>Ph), which was directly used for further reaction without isolation. This suspension was cooled again to  $-78 \degree C$ , and to it was added *n*BuLi (20.83 mL, 2.4 M solution

in n-hexane, 50 mmol). After the mixture was warmed to room temperature over 24 h, the lithium salt 2,6-iPr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(SiMe<sub>2</sub>Ph)Li was formed, which was cooled to -78 °C and to it was added neat SiCl<sub>4</sub> (5.75 mL, 50 mmol). The mixture reacted by naturally warming to room temperature. After additional stirring for 12 h, all of the insoluble solids were filtered off and the filtrate was evaporated to dryness under reduced pressure. The remaining residue was washed with cold *n*-hexane  $(2 \times 5 \text{ mL})$  to give an off-white solid of 1 (15.63) g). The *n*-hexane washing solution was kept at -20 °C for 2 days to give a second crop of 1 as colorless crystals (2.39 g). Total yield: 18.02 g, 81%. Mp: 86 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 0.63 (s, 6 H, SiMe<sub>2</sub>Ph), 1.26 (d, 6 H,  ${}^{3}J_{HH} = 6.8$  Hz, CHMe<sub>2</sub>), 1.39 (d, 6 H,  ${}^{3}J_{\rm HH}$  = 6.8 Hz, CHMe<sub>2</sub>), 3.63 (sept, 2 H,  ${}^{3}J_{\rm HH}$  = 6.8 Hz, CHMe<sub>2</sub>), 7.14–7.24 (m), 7.32 (m), 7.70 (m) (8 H,  $C_6H_3$  and Ph). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  –0.18 (SiMe<sub>2</sub>Ph), 24.25, 25.45, 28.31 (CHMe2), 124.65, 127.09, 127.88, 130.17, 134.81, 135.67, 138.01, 147.38 (C<sub>6</sub>H<sub>3</sub> and Ph). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  -27.06 (SiCl<sub>3</sub>), 1.83 (SiMe<sub>2</sub>Ph). Anal. Calcd for  $C_{20}H_{28}Cl_3NSi_2$  ( $M_r = 444.97$ ): C, 53.98; H, 6.34; N, 3.15. Found: C, 53.90; H, 6.29; N, 3.32.

Synthesis of ArN(PPh<sub>2</sub>)SiCl<sub>3</sub>. The synthetic procedure on the same scale was similar to that of 1, in which in addition to 2,6- $iPr_2C_6H_3NH_2$  two other primary arylamines were used (4-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, 5.40 g, 50 mmol; 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NH<sub>2</sub>, 7.02 mL, 50 mmol), and Ph<sub>2</sub>PCl (8.27 mL, 50 mmol) was used instead of PhMe<sub>2</sub>SiCl.

**2,6-***i***Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N(PPh<sub>2</sub>)SiCl<sub>3</sub> (2).** Yield: 22.02 g, 89%. Mp: 99 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  0.56 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 1.23 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 3.36 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 1.23 (d, 6 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 3.36 (sept, 2 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 6.97–7.16 (m), 7.65 (m) (13 H, C<sub>6</sub>H<sub>3</sub> and Ph). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  23.28, 25.52, 29.35 (CHMe<sub>2</sub>), 124.96, 128.35 (d, J<sub>CP</sub> = 8.1 Hz), 130.25, 135.14, 135.34, 135.50 (d, J<sub>CP</sub> = 25.1 Hz), 138.64 (d, J<sub>CP</sub> = 2.8 Hz), 148.04 (C<sub>6</sub>H<sub>3</sub> and Ph). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  –28.90 (d, J<sub>SIP</sub> = 24.1 Hz, *si*Cl<sub>3</sub>). <sup>31</sup>P NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  54.73. Anal. Calcd for C<sub>24</sub>H<sub>27</sub>Cl<sub>3</sub>NPSi (M<sub>r</sub> = 494.90): C, 58.25; H, 5.50; N, 2.83. Found: C, 58.32; H, 5.53; N, 2.85.

**4-MeC<sub>6</sub>H<sub>4</sub>N(PPh<sub>2</sub>)SiCl<sub>3</sub> (3).** Yield: 15.62 g, 74%. Mp: 141 °C. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 298 K, ppm): δ 1.87 (s, 3 H, 4-MeC<sub>6</sub>H<sub>4</sub>), 6.54 (dd, 2 H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz,  $J_{PH}$  = 2.0 Hz,  $C_6H_4$ ), 6.65 (d, 2 H, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz,  $C_6H_4$ ), 7.03 (m), 7.44 (m) (10 H, Ph). <sup>13</sup>C NMR (100 MHz,  $C_6D_6$ , 298 K, ppm): δ 20.49 (4-MeC<sub>6</sub>H<sub>4</sub>), 128.21 (d,  $J_{CP}$  = 6.5 Hz), 129.48 (d,  $J_{CP}$  = 21.3 Hz), 129.99, 133.65 (d,  $J_{CP}$  = 21.5 Hz), 135.89, 136.06, 136.30, 137.80 (d,  $J_{CP}$  = 3.6 Hz) ( $C_6H_4$  and Ph). <sup>29</sup>Si NMR (99 MHz,  $C_6D_6$ , 298 K, ppm): δ = -26.65 (d,  $J_{SIP}$  = 48.9 Hz, SiCl<sub>3</sub>). <sup>31</sup>P NMR (160 MHz,  $C_6D_6$ , 298 K, ppm): δ 55.69. Anal. Calcd for  $C_{19}H_{17}Cl_3NPSi$  ( $M_r$  = 424.76): C, 53.72; H, 4.03; N, 3.30. Found: C, 53.55; H, 4.01; N, 3.25.

**2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>N(PPh<sub>2</sub>)SiCl<sub>3</sub> (4).** Yield: 19.92 g, 88%. Mp: 115 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  1.71 (s, 6 H, 2,6-*Me*<sub>2</sub>C<sub>6</sub>H<sub>2</sub>), 2.05 (s, 3 H, 4-*Me*C<sub>6</sub>H<sub>2</sub>), 6.61 (s, 2 H, C<sub>6</sub>H<sub>2</sub>), 6.66–7.07 (m), 7.66 (m) (10 H, *Ph*). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  19.72 (2,6-*Me*<sub>2</sub>C<sub>6</sub>H<sub>2</sub>), 20.59 (4-*Me*C<sub>6</sub>H<sub>2</sub>), 128.15 (d, *J*<sub>CP</sub> = 20.0 Hz), 130.01 (d, *J*<sub>CP</sub> = 60.6 Hz), 135.14, 135.29, 135.33 (d, *J*<sub>CP</sub> = 26.3 Hz), 136.20, 137.53 (d, *J*<sub>CP</sub> = 2.2 Hz), 138.10 (C<sub>6</sub>H<sub>2</sub> and *Ph*). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  -28.61 (d, *J*<sub>SiP</sub> = 44.5 Hz, *Si*Cl<sub>3</sub>). <sup>31</sup>P NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  42.73. Anal. Calcd for C<sub>21</sub>H<sub>21</sub>Cl<sub>3</sub>NPSi (*M*<sub>r</sub> = 452.82): C, 55.70; H, 4.67; N, 3.09. Found: C, 55.67; H, 4.71; N, 3.08.

Synthesis of 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N[Li(THF)<sub>3</sub>]Si(C=CPh)<sub>3</sub> (5). PhC= CLi was freshly prepared by reacting PhC=CH (0.49 g, 4.8 mmol) and *n*BuLi (2.0 mL, 2.4 M in *n*-hexane, 4.8 mmol) in Et<sub>2</sub>O (50 mL) from -30 °C to room temperature within 3 h and adding this mixture to a solution of 1 (0.53 g, 1.2 mmol) in THF (6 mL) at -78 °C. The mixture reacted on warming to room temperature. After the mixture was stirred for an additional 12 h, the insoluble solid was removed by filtration and then the filtrate was evaporated to dryness under reduced pressure. The remaining residue was washed with *n*-hexane (10 mL) followed by extraction with a THF/*n*-hexane (2 mL/4 mL) mixture. The *n*-hexane washing solution was dried to give a viscous oil, of which

compound PhMe₂SiC≡CPh was analyzed to be the major component by NMR (<sup>1</sup>H and <sup>13</sup>C) and IR spectral analysis. The extract was stored at -20 °C for 2 days to give colorless crystals of 5. Yield: 0.63 g, 72% (based on 1). Mp: 108 °C dec. Data for 5 are as follows. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 1.34 (m, 12 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 1.55 (d, 12 H,  ${}^{3}J_{\rm HH}$  = 6.8 Hz, CHMe<sub>2</sub>), 3.52 (m, 12 H, THF- $OCH_2CH_2$ ), 4.61 (sept, 2 H,  ${}^{3}J_{HH} = 6.8$  Hz,  $CHMe_2$ ), 6.91 (m), 7.09 (m), 7.30–7.50 (m) (18 H,  $C_6H_3$  and Ph). <sup>13</sup>C NMR (100 MHz,  $C_6 D_{62}$  298 K, ppm):  $\delta = 25.30$  (THF-OCH<sub>2</sub>CH<sub>2</sub>), 25.36, 28.00  $(CHMe_2)$ , 68.05  $(THF-OCH_2CH_2)$ , 97.04, 101.80  $(C \equiv C)$ , 117.57, 122.71, 124.44, 127.67, 127.89, 132.11, 143.28, 151.26 (C<sub>6</sub>H<sub>3</sub> and Ph). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  –93.59 (SiC=CPh). IR (KBr plate, cm<sup>-1</sup>):  $\nu$  2152.8 (C $\equiv$ C). Data for PhMe<sub>2</sub>SiC $\equiv$ CPh are as follows. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 298 K, ppm):  $\delta$  0.46 (s, 6 H, SiMe<sub>2</sub>), 6.80–7.54 (m) (10 H, Ph). <sup>13</sup>C NMR (100 MHz,  $C_6D_6$ , 298 K, ppm):  $\delta$  2.6 (SiMe<sub>2</sub>), 92.02, 106.80 (C=C), 123.45, 127.62, 127.84, 129.21, 129.34, 132.11, 133.57, 148.22 (*Ph*). IR (KBr plate, cm<sup>-1</sup>):  $\nu$ 2158.6 (C=C). Anal. Calcd for  $C_{48}H_{56}LiNO_3Si$  (5,  $M_r = 729.99$ ): C, 78.98; H, 7.73; N, 1.92. Found: C, 78.49; H, 7.96; N, 1.86. Note: the initial reaction was carried out between 1 and 3 equiv of PhC=CLi, and 5 was isolated as colorless crystals as well but in a relatively lower vield (48%) based on PhC≡CLi.

Synthesis of  $[2,6-iPr_2C_6H_3NSi(C \equiv CPh)_2]_2$  (6). PhC  $\equiv$  CLi (6) mmol in 50 mL of Et<sub>2</sub>O) was freshly prepared in a manner similar to that used in the synthesis of 5 and added to a solution of 2 (0.99 g, 2.0 mmol) in THF (6 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The insoluble solid was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was washed with n-hexane (8 mL) followed by extraction with a THF/n-hexane (2 mL/6 mL) mixture. The n-hexane washing solution was dried to give a viscous oil, of which compound  $Ph_2PC \equiv CPh$  was analyzed to be the major component by <sup>31</sup>P NMR. The extract was stored at -20 °C for 3 days to afford colorless crystals of 6. Yield: 0.50 g, 62% (based on 2). Mp: 224 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  1.61 (d, 24 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 4.68 (sept, 4 H,  ${}^{3}J_{HH}$  = 6.8 Hz, CHMe<sub>2</sub>), 6.86 (m), 7.29 (m), 7.39 (m) (26 H,  $C_6H_3$  and Ph). <sup>13</sup>C NMR (100 MHz,  $C_6D_6$ , 298 K, ppm):  $\delta$ 26.63, 28.91 (CHM $e_2$ ), 91.73, 108.37 (C $\equiv$ C), 122.24, 124.34, 125.69, 127.67, 128.19, 129.23, 132.37, 148.21 (C<sub>6</sub>H<sub>3</sub> and Ph). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ −88.33 (SiC≡CPh). IR (KBr plate, cm<sup>-1</sup>):  $\nu$  2154.4 (C=C). Anal. Calcd for C<sub>56</sub>H<sub>54</sub>N<sub>2</sub>Si<sub>2</sub> ( $M_r$  = 811.21): C, 82.91; H, 6.71; N, 3.45. Found: C, 82.98; H, 6.59; N, 3.47.

**Synthesis of [2,6-***i***Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NSi(C≡CtBu)<sub>2</sub>]<sub>2</sub> (7).** The preparation of 7 is similar to that of 6 on the same scale. *t*BuC≡CLi was freshly prepared by reacting *t*BuC≡CH (0.49 g, 6 mmol) with *n*BuLi (2.5 mL, 2.4 M in *n*-hexane, 6 mmol) in Et<sub>2</sub>O (50 mL) from -30 °C to room temperature within 3 h and was used instead of PhC≡CLi. Compound Ph<sub>2</sub>PC≡CtBu was characterized by <sup>31</sup>P NMR, and 7 was obtained as colorless crystals. Yield: 0.40 g, 55% (based on 2). Mp: 165 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 1.05 (s, 36 H, *tBu*), 1.58 (d, 24 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 4.36 (sept, 4 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 7.20–7.30 (m, 6 H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 27.09, 27.79, 28.20, 30.16 (*tBu* and CHMe<sub>2</sub>), 81.83, 118.62 (C≡C), 124.06, 125.23, 134.78, 148.04 (C<sub>6</sub>H<sub>3</sub>). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ –63.12 (SiC≡CtBu). IR (KBr plate, cm<sup>-1</sup>): ν 2149.4 (C≡C). Anal. Calcd for C<sub>48</sub>H<sub>70</sub>N<sub>2</sub>Si<sub>2</sub> (M<sub>r</sub> = 731.25): C, 78.84; H, 9.65; N, 3.83. Found: C, 78.95; H, 9.57; N, 3.70.

Synthesis of  $[2,6-iPr_2C_6H_3NSi(C \equiv CCH_2CH_2Ph)_2]_2$  (8). The preparation of 8 is similar to that of 6 on the same scale. PhCH<sub>2</sub>CH<sub>2</sub>C  $\equiv$  CLi was freshly prepared by reacting PhCH<sub>2</sub>CH<sub>2</sub>C  $\equiv$  CH (0.78 g, 6 mmol) with *n*BuLi (2.5 mL, 2.4 M in *n*-hexane, 6 mmol) in Et<sub>2</sub>O (50 mL) from -30 °C to room temperature within 3 h and was used instead of PhC  $\equiv$  CLi. Finally, compound Ph<sub>2</sub>PC  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>Ph was characterized by <sup>31</sup>P NMR, and 8 was obtained as colorless crystals. Yield: 0.63 g, 68% (based on 2). Mp: 198 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  1.52 (d, 24 H, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, CHMe<sub>2</sub>), 2.30 (t, 8 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, C  $\equiv$  CCH<sub>2</sub>CH<sub>2</sub>), 2.63 (t, 24 H, <sup>3</sup>J<sub>H</sub>

δ 22.47, 26.38, 28.43, 34.39 (CHMe<sub>2</sub> and C≡CCH<sub>2</sub>CH<sub>2</sub>), 83.41, 109.85 (C≡C), 124.15, 125.28, 126.35, 128.28, 128.44, 134.40, 140.26, 148.05 (C<sub>6</sub>H<sub>3</sub> and Ph). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ −61.96 (SiC≡CCH<sub>2</sub>CH<sub>2</sub>Ph). IR (KBr plate, cm<sup>-1</sup>): ν 2177.1 (C≡C). Anal. Calcd for C<sub>64</sub>H<sub>70</sub>N<sub>2</sub>Si<sub>2</sub> (M<sub>r</sub> = 923.40): C, 83.24; H, 7.64; N, 3.03. Found: C, 83.14; H, 7.74; N, 2.98.

Synthesis of  $[4-MeC_6H_4NSi(C\equiv CPh)_2]_3$  (9a) and  $\{4-MeC_6H_4NSi(C\equiv CPh)[N(4-MeC_6H_4)Si(C\equiv CPh)_3]\}_2$  (9b). PhC= CLi (6 mmol in 50 mL of Et<sub>2</sub>O) was freshly prepared in a manner similar to that used in the synthesis of 5 and added to a solution of 3 (0.85 g, 2.0 mmol) in THF (6 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The insoluble solid was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was washed with n-hexane (8 mL) followed by extraction with a THF/n-hexane (2 mL/6 mL)solvent mixture. The n-hexane washing solution was dried and analyzed to contain Ph₂PC≡CPh on the basis of <sup>31</sup>P NMR data. The extract was stored at -20 °C for 3 days to give colorless square-block crystals of 9a.2THF (0.40 g, 52% yield based on 3). The mother solution was decanted into another bottle and stored at -20 °C for another 3 days to afford colorless crystalline plates of 9b.THF (0.058 g, 8% yield based on 3). Data for 9a 2THF are as follows. Mp: 216 °C. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , 298 K, ppm):  $\delta$  1.42 (m, 8 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 2.07 (s, 9 H, 4-MeC<sub>6</sub>H<sub>4</sub>), 3.58 (m, 8 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 6.79-6.87 (m), 7.27 (m) (30 H, Ph), 7.07 (d, 6 H,  ${}^{3}J_{HH} = 6.4 \text{ Hz}, 4-\text{MeC}_{6}H_{4}$ , 8.13 (d, 6 H,  ${}^{3}J_{HH} = 6.4 \text{ Hz}, 4-\text{MeC}_{6}H_{4}$ ). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 25.44 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 31.57 (4-MeC<sub>6</sub>H<sub>4</sub>), 67.47 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 91.06, 106.84 ( $C \equiv C$ ), 122.78, 127.96, 128.51, 129.39, 131.14, 132.24, 134.60, 139.75 (4- $MeC_6H_4$  and Ph). <sup>29</sup>Si NMR (99 MHz,  $C_6D_6$ , 298 K, ppm):  $\delta$  -56.37 (SiC≡CPh). IR (KBr plate, cm<sup>-1</sup>):  $\nu$  = 2158.4 (C≡C). Anal. Calcd for C<sub>77</sub>H<sub>67</sub>N<sub>3</sub>O<sub>2</sub>Si<sub>3</sub> (9a·2THF, M<sub>r</sub> = 1150.63): C, 80.38; H, 5.87; N, 3.65. Found: C, 80.15; H, 5.96; N, 3.62. Data for 9b.THF are as follows. Mp: 257 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 1.42 (m, 4 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 1.87 (s, 6 H, 4-MeC<sub>6</sub>H<sub>4</sub>), 2.09 (s, 6 H, 4- $MeC_6H_4$ ), 3.58 (m, 4 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 6.72 (d, 2 H,  ${}^{3}J_{HH} = 6.4$  ${}^{3}J_{\rm HH} = 6.4$  Hz), 7.74 (d, 2 H,  ${}^{3}J_{\rm HH} = 6.4$  Hz), 8.11 (d, 2 H,  ${}^{3}J_{\rm HH} = 6.4$ Hz) (4-MeC<sub>6</sub>H<sub>4</sub>), 6.76–6.94 (m), 7.29 (m) (40 H, Ph). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 20.38, 20.47 (4-MeC<sub>6</sub>H<sub>4</sub>), 25.44 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 67.44 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 88.47, 90.21, 107.22, 108.23  $(C \equiv C)$ , 119.62, 122.47, 122.73, 127.96, 128.28, 128.33, 128.73, 128.87, 129.42, 130.19, 130.35, 132.33, 132.84, 134.17, 139.32, 142.28 (4-MeC<sub>6</sub>H<sub>4</sub> and Ph). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  –59.74, –59.61 (SiC=CPh). IR (KBr plate, cm<sup>-1</sup>):  $\nu$  2161.3 (C= C). Anal. Calcd for  $C_{96}H_{76}N_4OSi_4$  (9b·THF,  $M_r = 1414.00$ ): C, 81.54; H, 5.42; N, 3.96. Found: C, 81.22; H, 5.47; N, 3.71.

Synthesis of  $[2,4,6-Me_3C_6H_2NSi(C \equiv CPh)_2]_2$  (10a) and  $[(2,4,6-Me_3C_6H_2NSi(C \equiv CPh)_2]_2$  $Me_{3}C_{6}H_{2})_{3}N_{3}Si_{2}(C \equiv CPh)_{4}Li(THF)]^{-}[Li(THF)_{4}]^{++}$  (10b). PhC = CLi (6 mmol in 50 mL of Et<sub>2</sub>O) was freshly prepared in a manner similar to that used in the synthesis of 5 and added to a solution of 4 (0.91 g, 2.0 mmol) in THF (6 mL) at -78 °C. The mixture was warmed to room temperature and stirred for 12 h. The insoluble solid was removed by filtration. The filtrate was evaporated to dryness under reduced pressure. The residue was washed with n-hexane (8 mL) followed by extraction with a THF/n-hexane (2 mL/6 mL) mixture. The *n*-hexane washing solution was dried and analyzed to contain Ph₂PC≡CPh on the basis of <sup>31</sup>P NMR data. The extract was stored at -20 °C for 2 days to give colorless needle-shaped crystals of 10b. toluene (0.063 g, 8% yield based on 4). The mother solution was decanted into another bottle and kept at -20 °C for about 1 week, producing colorless arris-piece crystals of 10a (0.192 g, 66% yield based on 4). Data for 10a are as follows. Mp: 242 °C. <sup>1</sup>H NMR (400 MHz,  $C_6D_{62}$  298 K, ppm):  $\delta$  2.21 (s, 6 H, 4-Me $C_6H_2$ ), 3.20 (s, 12 H,  $2,6-Me_2C_6H_2$ , 6.95 (s, 4 H,  $C_6H_2$ ), 6.80–6.90 (m), 7.32 (m) (20 H, *Ph*). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 20.33, 20.69 (2,4,6- $Me_3C_6H_2$ ), 92.14, 107.39 (C=C), 122.15, 128.24, 129.19, 129.46, 132.22, 133.65, 135.34, 137.05 (C<sub>6</sub>H<sub>2</sub> and Ph). <sup>29</sup>Si NMR (99 MHz,  $C_6D_{62}$  298 K, ppm):  $\delta$  -65.09 (SiC=CPh). IR (KBr plate, cm<sup>-1</sup>):  $\nu$ 

2156.9 (C=C). Anal. Calcd for  $C_{50}H_{42}N_2Si_2$  ( $M_r = 727.05$ ): C, 82.60; H, 5.82; N, 3.85. Found: C, 82.55; H, 5.59; N, 3.72. Data for 10b. toluene are as follows. Mp: 178 °C (dec.). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  1.33 (m, 20 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 2.11 (s, 3 H, MePh), 2.20 (s, 6 H), 2.21 (s, 3 H), 2.27 (s, 6 H), 2.85 (s, 3 H), 3.14 (s, 3 H), 3.21 (s, 6 H) (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 3.49 (m, 20 H, THF-OCH<sub>2</sub>CH<sub>2</sub>), 6.77-7.49 (m, 26 H, C<sub>6</sub>H<sub>2</sub>, C≡CPh, and MePh). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm): δ 19.20, 20.42, 20.75, 20.84, 22.78, 31.70 (2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), 25.33 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 67.86 (THF-OCH<sub>2</sub>CH<sub>2</sub>), 89.98, 94.72, 101.16, 105.47 (C≡C), 122.31, 122.79, 123.42, 123.77, 124.49, 128.90, 129.24, 129.80, 129.08, 131.37, 132.01, 132.11, 132.19, 132.85, 133.26, 134.64, 136.17, 137.04, 137.71, 138.61 ( $C_6H_2$ , C= CPh, and MePh). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, ppm):  $\delta$  –51.15 (SiC=CPh). IR (KBr plate, cm<sup>-1</sup>):  $\nu$  2161.3 (C=C). Anal. Calcd for  $C_{86}H_{101}Li_2N_3O_5Si_2$  (10b·toluene,  $M_r = 1326.79$ ): C, 77.85; H, 7.67; N, 3.17. Found: C, 77.45; H, 7.39; N, 3.12.

#### ASSOCIATED CONTENT

## **S** Supporting Information

Text, tables, and CIF files giving crystal data and structure refinement details and crystal structures of compounds **2**, **5**, and **10b**·toluene and the synthesis, characterization, and crystal structure of  $(2,6-iPr_2C_6H_3NSiCl_2)_2$  (**B**). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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