Inorganic Chemistry
Article
pubs.acs.org/IC

Controlled Oxidation of an NHC-Stabilized Phosphinoaminosilylene with Dioxygen

Haiyan Cui,*[†] Jianying Zhang,[‡] Yunwen Tao,[§] and Chunming Cui*[‡]

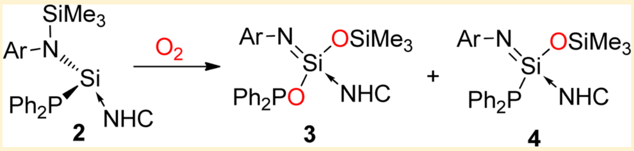
[†]Jiangsu Key Laboratory of Pesticide Science, College of Sciences, Nanjing Agricultural University, Nanjing 210095, People's Republic of China

[‡]State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

[§]Department of Chemistry, Southern Methodist University, 3215 Daniel Avenue, Dallas, Texas 75275-0314, United States

Supporting Information

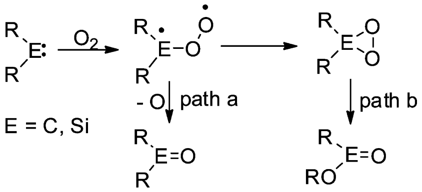
ABSTRACT: Reaction of the N-heterocyclic carbene-stabilized phosphinoaminosilylene $ArN(SiMe_3)Si(I^iPr)PPh_2$ (Ar = 2,6-$^iPr_2C_6H_3$, I^iPr = 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene) (**2**) with dioxygen resulted in the formation of the two products ArN = $Si(I^iPr)(OSiMe_3)(OPPh_2)$ (**3**) and ArN = $Si(I^iPr)(OSiMe_3)PPh_2$ (**4**), and the ratios of the two products can be controlled by the reaction temperatures and dioxygen concentrations.



INTRODUCTION

Controlled oxidation of organic and main group elemental compounds by dioxygen presents the most environmentally benign and atom-economic method for the synthesis of desired oxygen-containing products.[1,2] Particularly, the oxidation of reactive intermediates can lead to the discovery of new catalytic processes for the controlled oxidation of organic and organometallic substrates.[1] Over the past few decades, extensive experimental and theoretical studies on the reaction of dioxygen with carbenes have been conducted. It has been generally accepted that the reaction may involve the initial trapping of carbene by O_2 to give highly photolabile carbonyl oxides (diradical),[3] which may undergo photolytic decomposition via two pathways (Scheme 1): (a) loss of single oxygen atom resulting in the corresponding carbonyl compounds and (b) rearrangement via dioxiranes to esters.

Scheme 1. Known Mechanisms for the Reactions of Carbenes and Silylenes with Dioxygen



Although the analogous studies on the reactions of silylenes,[4] the silicon carbene analogues, with dioxygen have received much less attention, the mechanism has been proposed to be very similar to that of carbenes.[4] The great successes on the synthesis of stable silylenes including donor-stabilized silylenes[5] have stimulated the renewed interest in the reactions of silylenes with dioxygen[4] and other small molecules containing oxygen.[6] However, only a few well-characterized products from oxygenation of silylenes with dioxygen have been reported by several groups[7] (Figure 1). This is probably because the oxidation by dioxygen cannot be easily controlled. Theoretical studies on the reaction of silylenes with oxidants have been conducted.[8] Thus, the investigation of the factors that control the oxidation reactions by dioxygen is of great interest and crucial to the understanding the reaction mechanism.

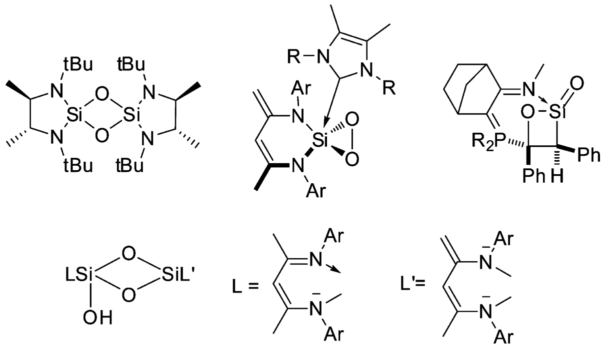


Figure 1. Known isolated products from reactions of silylenes with dioxygen.

RESULTS AND DISCUSSION

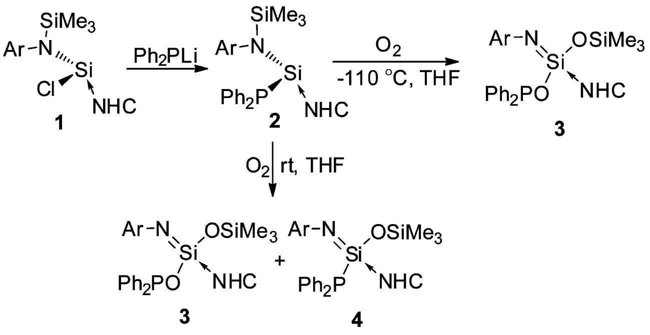
Herein, we report on the reaction of the N-heterocyclic carbene (NHC)-stabilized silylene $ArN(SiMe_3)Si(I^iPr)PPh_2$ (**2**, Ar = 2,6-$^iPr_2C_6H_3$, I^iPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) with dioxygen, leading to the formation of the two products $ArN{=}Si(I^iPr)(OSiMe_3)OPPh_2$ (**3**) and ArN=Si-

Received: July 30, 2015

DOI: 10.1021/acs.inorgchem.5b02580

$(\mathrm{I}^i\mathrm{Pr})(\mathrm{OSiMe}_3)\mathrm{PPh}_2$ (**4**). Interestingly, the product distributions can be controlled by the reaction temperature and dioxygen concentration. The phosphinoaminosilylene **2** was obtained as red crystals in high yield by the reaction of the aminochlorosilylene $\mathrm{ArN(SiMe_3)Si(I^iPr)Cl}$ (**1**)[9] with $\mathrm{LiPPh_2}$ (Scheme 2) and has been fully characterized by ^{1}H, ^{31}P, ^{13}C, and ^{29}Si NMR spectroscopy, elemental analysis, and an X-ray single-crystal analysis.

Scheme 2. Reaction of 2 with Dioxygen at Different Temperatures



Ar = 2,6-$^i\mathrm{Pr_2C_6H_3}$, NHC = 1,3-$^i\mathrm{Pr_2}$-4,5-$\mathrm{Me_2}$-imidazol-2-ylidene

The ^{29}Si resonance for the central silicon atom (δ = 4.23 ppm, doublet, $^1J_{\mathrm{SiP}}$ = 78.37 Hz) is comparable to most observed for the known NHC-supported silylenes (−8.78 to 10.9 ppm).[10] The ^{13}C NMR signal for the NHC central carbon atom in **2** appears at 166.25 ppm, consistent with those found in the NHC → Si donor−acceptor complexes.[10,11] The ^{31}P NMR spectrum of **2** exhibits at δ −33.6 ppm. The structure of **2**, shown in Figure 2, features a trigonal-pyramidal silicon center, revealing the presence of a stereochemically active lone pair of electrons at the Si(II) atom (the sum of angles at the Si2 atom = 309.5°), which is very similar to that of **1**. The Si2−C16 bond length (1.9909(18) Å) is in the reported range for NHC-stabilized halosilylenes (1.980(3) and 2.0023(19) Å)[10] but longer than those in the NHC → :$\mathrm{Si(Si^tBu_3)(R)}$ [R = $^t\mathrm{Bu_3Si}$ (1.933(4) Å), R = H (1.942(3) Å)][11b,c] and silacyclopentadienylidenes.[11a] The Si2−P1 bond length (2.3748(7) Å) is comparable to a Si−P single bond (2.27−2.31 Å).[12]

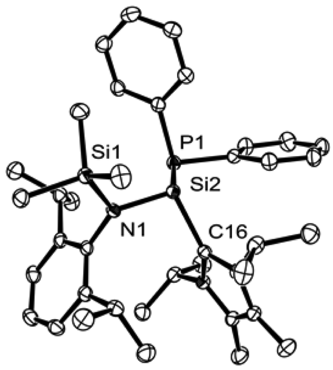


Figure 2. Ortep drawing of **2** with ellipsoids given at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−Si2 2.3748(7), Si1−N1 1.7518(15), Si2−N1 1.8132(15), Si2−C16 1.9909(18); N1−Si2−C16 101.58(7), N1−Si2−P1 108.47(5), C16−Si2−P1 99.47(5).

Compound **2** exhibits high thermal stability in solutions, but it is extremely air and moisture sensitive. Exposure of the red solution of **2** in tetrahydrofuran (THF) to $\mathrm{O_2}$ at −110 °C resulted in an immediate decoloration. Colorless crystals of **3** were obtained in 64% yield by crystallization from *n*-hexane at room temperature (Scheme 2). Compound **3** was fully characterized by multinuclear NMR, IR spectroscopy, and elemental analysis. The ^{31}P NMR exhibits at δ 103.8 ppm. The ^{29}Si NMR spectra for the central silicon atom of **3** exhibits a doublet signal at δ −104.00 ppm (Si═N, $^2J_{\mathrm{SiP}}$ = 14.51 Hz). The X-ray crystal-structure analysis confirmed compound **3** to be an NHC-stabilized 1-siloxy-1-phosphinoxysilaimine, consisting of a four-coordinated silicon atom attached to two oxygen atoms (Figure 3). The Si1−N1 bond length (1.596(2) Å) is in the range of reported free- and donor-stabilized silaimines (1.568−1.620 Å);[13] Si1−C13 bond length is 1.929(3) Å, which is very similar to C−Si coordinate bond length.[10,11] Compound **3** represents a rare example of donor-stabilized dioxysilaimine.

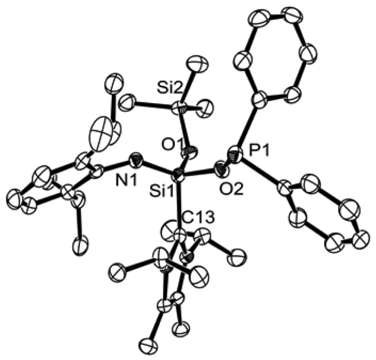


Figure 3. Ortep drawing of **3** with ellipsoids given at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): P1−O2 1.619(2), Si1−N1 1.596(2), Si1−O1 1.643(2), Si1−O2 1.661(2), Si1−C13 1.929(3), Si2−O1 1.646(2), N1−C1 1.369(4), N1−Si1−O1 115.36(12), N1−Si1−O2 118.61(12), O1−Si1−O2 102.20(11), N1−Si1−C13 112.00(13), O1−Si1−C13 107.10(12), O2−Si1−C13 99.85(11), Si1−O1−Si2 133.50(13), P1−O2−Si1 135.49(14).

Interestingly, the exposure of a solution of **2** in THF to $\mathrm{O_2}$ at room temperature led to the isolation of the new compound **4** as light yellow crystals in 23% yield from *n*-hexane extract. The subsequent crystallization also resulted in the isolation of **3** in ca. 50% yield (Scheme 2). Compound **4** is air and moisture sensitive and was fully characterized by multinuclear NMR, IR spectroscopy, and elemental analysis. The ^{31}P NMR exhibits at δ −35.40 ppm. The ^{29}Si NMR spectra for the central silicon atom of **4** exhibits a doublet signal at δ −84.94 (Si−P, $^1J_{\mathrm{SiP}}$ = 38.26 Hz) ppm. The X-ray crystal-structure analysis confirmed compound **4** to be an NHC-stabilized 1-siloxysilaimine, consisting of a four-coordinated silicon atom attached to one oxygen atom (Figure 4). The Si1−N1 bond length is 1.6021(12) Å, in line with the value found for Si═N double bond length (1.568−1.620 Å);[13] Si1−C13 bond length (1.9471(16) Å) is a typical coordinate bond length.[10,11]

The formation of **3** and **4** at room temperature prompted us to investigate the effects of temperature on the product distributions. Thus, the reaction of **2** with dioxygen were conducted from −80 to 40 °C with the fixed concentration and pressure of dioxygen in 1 min. It was found that the amount of **3** decreased with the elevation of temperatures (Table 1, entries

DOI: 10.1021/acs.inorgchem.5b02580
Inorg. Chem. XXXX, XXX, XXX−XXX

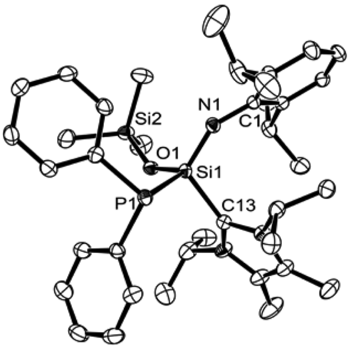


Figure 4. Ortep drawing of **4** with ellipsoids given at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–Si1 2.2687(7), O1–Si1 1.6411(10), O1–Si2 1.6482(11), Si1–N1 1.6021(12), Si1–C13 1.9471(16), N1–C1 1.3654(18), Si1–O1–Si2 141.03(6), N1–Si1–O1 116.42(6), N1–Si1–C13 113.31(6), O1–Si1–C13 106.33(6), N1–Si1–P1 110.84(5), O1–Si1–P1 108.22(4), C13–Si1–P1 100.42(5), C1–N1–Si1 148.72(11).

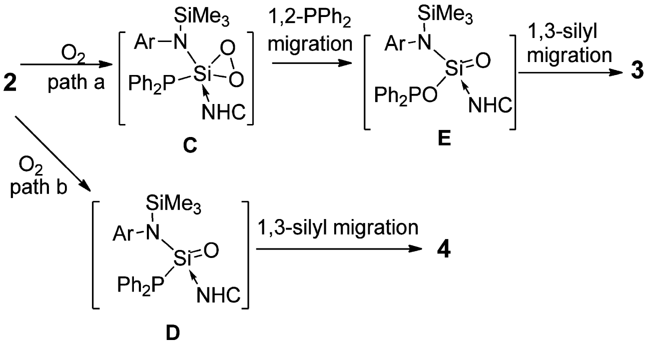
Table 1. Product Distributions of the Reaction of 2[a] with Dioxygen under Different Conditions

entry	temperature (°C)	O_2 pressure[b]	product ratios[c] (3:4)	actual yield (%, 3:4)
1	−80	1	1:0.05	85.5:4.3
2	−60	1	1:0.08	79.4:6.3
3	−40	1	1:0.14	71.4:10.0
4	−20	1	1:0.21	63.7:13.4
5	0	1	1:0.29	62.9:18.2
6	40	1	1:0.71	30.4:21.6
7	0	0.5	1:0.38	57.1:21.7
8	0	0.1	1:0.74	50.8:37.6

[a] Conditions: 1 min, 40 mg of **2** in 5 mL of THF. [b] The partial pressure relative to that of argon under normal pressure. [c] Determined by ^{1}H NMR spectra.

1–6). However, above 40 °C, a significant amount of impurities were also formed. Since the temperature is related to the solubility of dioxygen, the effects of the partial pressure of dioxygen were also studied by mixing of oxygen with argon at 0 °C under the normal pressure. It can be seen from Table 1 (entries 5, 7, and 8) that, with the decrease of dioxygen pressure, the amount of **4** increased substantially. In addition, the exposure of **4** to dioxygen did not lead to the formation of **3**. These experiments indicated that **3** and **4** are formed via different mechanisms and that dioxygen concentration has significant effects on the ratios of the two products.

Scheme 3. Proposed Pathways for the Dioxygen Reactions with 2



On the basis of these experiments, we proposed the formation of **3** and **4** are from two pathways. The pathway for the reaction from **2** to **3** was explored theoretically by density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level of theory (Scheme 3, path a). The reaction of **2** and O_2 initially gives dioxasilirane **C**,[7c,d] which underwent first 1,2-PPh_2 migration through transition state **TS1** to give silaester **E**, then 1,3-silyl migration from the nitrogen atom to the oxygen to afford final product **3** via transition state **TS2** (Figure 5). And the reaction step from **C** to **E** has a barrier (free energy) of 18.56 kcal/mol. And the barrier from **E** to **3** is 14.57 kcal/mol. The energy difference between geometry **C** with the total energy of geometry **2** and a triplet oxygen molecule as G(**C**) − [G(**2**) + G($^{3}O_2$)], which is −67.141 kcal/mol. However, the energy difference G(**E**) − G(**C**) equals −104.617 kcal/mol, while G(**3**) − G(**E**) is −12.049 kcal/mol. From the calculations, we proved that this reaction pathway is valid in each step. And the calculated free energy data indicated that the whole pathway could proceed spontaneously. However, the pathway for the reaction from **2** to **4** is unclear until now. We assumed the reaction may proceed through the intermediate silanone **D** under low concentration of dioxygen, followed by 1,3-silyl migration to give **4** (Scheme 3, path b). Since the reactions are rapid even at very low temperature, attempts to detect the possible intermediates are not possible under the current conditions.

■ CONCLUSIONS

In summary, we have shown that the reaction of the NHC-stabilized silylene **2** with dioxygen resulted in the formation of the two products **3** and **4** with different ratios under different temperatures and dioxygen concentrations. The results indicated that **3** and **4** are formed via different reaction mechanisms. This is the first observation that the reaction product distributions of a silylene with dioxygen are dependent on the concentrations of dioxygen and temperatures. Further studies on the reactions of various silylenes with dioxygen under controlled manner may lead to the discovery of green routes for the synthesis of oxygen-containing materials such as silicones by the oxidation of silylene intermediates with dioxygen.

■ EXPERIMENTAL SECTION

General Considerations. All operations were performed under an atmosphere of dry argon or nitrogen by using modified Schlenck line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. Elemental analyses were performed on an Elemental Vario EL analyzer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data were recorded on Bruker Mercury Plus 300, 400, and 600 MHz NMR spectrometers. Infrared spectra were recorded on a Bio-Rad FTS 6000 spectrometer. The UV–vis spectra were recorded on a Shimadzu UV-2450 spectrometer, and emission spectra were recorded on an Edinburgh Analytical Instruments FL900CD spectrometer. $ArN(SiMe_3)Si(I^iPr)Cl$ (**1**)[9] (Ar = 2,6-$^iPr_2C_6H_3$, I^iPr = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) was synthesized according to published procedure.

Synthesis of $Ph_2PLi·1.5THF$. Lithium crumbs (0.35 g, 50 mmol) was added to a stirred solution of Ph_2PCl (4.41 g, 20 mmol) in THF (50 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight, whereupon the solution became dark red. The volatiles were removed under vacuum. The residue was extracted with toluene (40 mL). After filtration and removal of solvents, the remaining residue was washed with *n*-hexane (25 mL × 2) to afford a yellow powder of $Ph_2PLi·1.5THF$ (5.0 g, 83.3%). ^{1}H

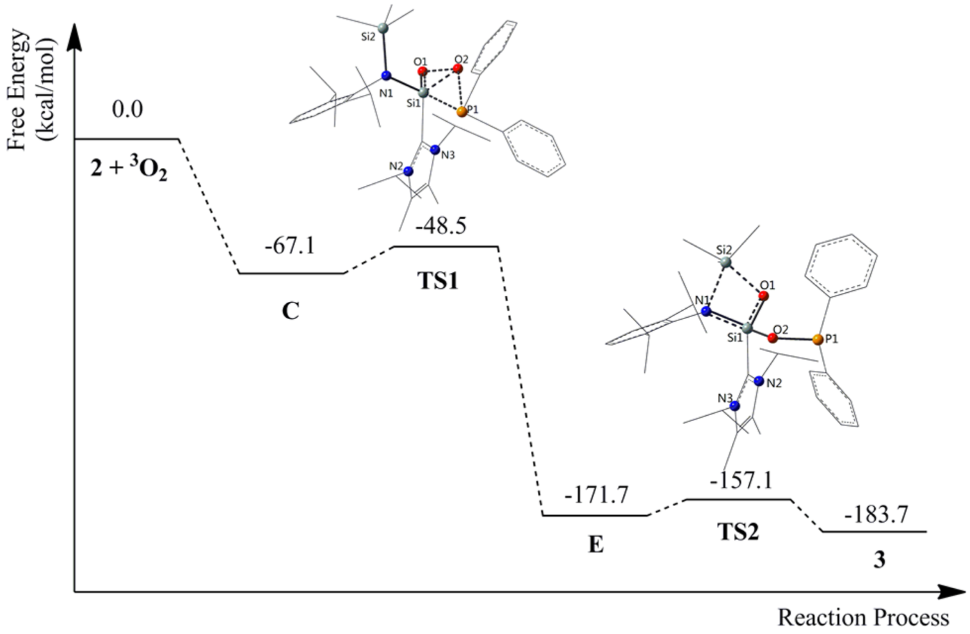


Figure 5. DFT-calculated free energy profile for synthesis of **3**.

NMR (400 MHz, C_6D_6): δ 1.17 (m, 6 H,CH_2CH_2O), 3.41 (m, 6H, CH_2CH_2O), 6.95 (m, 2H, Ar-*H*), 7.17 (m, 4H, Ar-*H*), 7.89 (m, 4H, Ar-*H*). ^{31}P NMR (161.97 MHz, C_6D_6): δ −25.03.

*Synthesis of ArN(SiMe$_3$)Si(I^{i}Pr)PPh$_2$ (**2**).* A solution of $Ph_2PLi\cdot 1.5THF$ (0.30 g, 1 mmol) in THF (5 mL) was added to a stirred solution of **1** (0.49 g, 1 mmol) in THF (10 mL) at −78 °C. The mixture was slowly warmed to room temperature and stirred overnight. The volatiles were removed under vacuum. The residue was extracted with toluene (30 mL × 2). After filtration and removal of solvents, the remaining residue was washed with *n*-hexane (20 mL × 2) to afford a red powder of **2** (0.29 g, 45.2%). mp 206−207 °C. ^1H NMR (400 MHz, C_6D_6): δ 0.15 (s, 9H, $Si(CH_3)_3$), 0.24 (d, 3H, $CH(CH_3)_2$), 0.33 (d, 3H, $CH(CH_3)_2$), 1.17 (d, 3H, $CH(CH_3)_2$), 1.24 (dd, 6H, $CH(CH_3)_2$), 1.33 (m, 9H, $CH(CH_3)_2$, $=CCH_3$), 1.53 (s, 3H, $=CCH_3$), 1.82 (d, 3H, $CH(CH_3)_2$), 3.27 (m, 1H, $CH(CH_3)_2$), 4.21 (m, 1H, $CH(CH_3)_2$), 5.65 (m, 1H, $CH(CH_3)_2$), 6.92−7.04 (m, 5H, Ar-*H*), 7.28−7.40 (m, 5H, Ar-*H*), 7.70 (m, 1H, Ar-*H*), 8.33 (s, 2H, Ar-*H*). ^{31}P NMR (161.97 MHz, C_6D_6): δ −33.66. ^{13}C NMR (100.61 MHz, d_8-THF): δ 3.44 ($Si(CH_3)_3$), 10.08, 10.45 (=CCH3), 19.61, 20.54, 21.21, 23.01, 24.23, 25.78, 26.10, 27.71, 28.81, 52.43, 55.46 ($CH(CH_3)_2$), 123.75, 124.56, 124.73, 125.85, 127.67, 127.77, 128.76, 134.60, 138.07, 145.27, 147.54, 149.99 (Ar-*C*), 166.25 (d, $^2J_{CP}$ = 14.68 Hz, carbene-*C*). ^{29}Si NMR (79.49 MHz, C_6D_6): δ 4.23 (d, Si−P, $^1J_{SiP}$ = 78.37 Hz), 1.45 (*Si*$(CH_3)_3$). Anal. Calcd for $C_{38}H_{56}N_3PSi_2$: C, 71.09; H, 8.79; N, 6.55. Found: C, 71.54; H, 7.88; N, 6.95%. UV−vis (THF): $\varepsilon = 5.35 \times 10^4$ L·mol^{-1}·cm^{-1}.

*Synthesis of ArN═Si(I^{i}Pr)(OSiMe$_3$)OPPh$_2$ (**3**).* A solution of **2** (0.15 g, 0.23 mmol) in THF (5 mL) was cooled to 110 °C. The flask was evacuated and placed under an atmosphere of O_2. The color of the solution soon changed from red to colorless. Removal of the solvents afforded light yellow oil. The mixture was extracted with hexane (30 mL). Concentration to ca. 2 mL and storage at room temperature overnight afforded colorless crystals of **3** (0.10 g, 63.5%). mp 108−110 °C. ^1H NMR (400 MHz, C_6D_6): δ 0.25 (s, 9H, $Si(CH_3)_3$), 1.02 (dd, 12H, $CH(CH_3)_2$), 1.33 (s, 6H, $=CCH_3$), 1.37 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.52 (d, *J* = 7.0 Hz, 6H, $CH(CH_3)_2$), 4.16 (m, 2H, Ar−$CH(CH_3)_2$), 6.03 (m, 2H, carbene−$CH(CH_3)_2$), 6.96−7.20 (m, 7H, Ar-*H*), 7.36 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.76 (m, 2H, Ar-*H*), 7.86 (m, 2H, Ar-*H*). ^{31}P NMR (161.97 MHz, C_6D_6): δ 103.88. ^{13}C NMR (100.61 MHz, C_6D_6): δ 2.17 ($Si(CH_3)_3$), 10.02 ($=CCH_3$), 21.39, 21.51, 24.14, 24.43 ($CH(CH_3)_2$), 28.52 (Ar-$CH(CH_3)_2$), 51.12 (carbene-$CH(CH_3)_2$), 113.69 ($=CCH_3$), 122.35, 126.40, 128.36, 128.43, 128.50, 128.86, 129.08, 130.13, 130.31, 130.35, 130.54, 139.01, 145.77, 146.00, 146.22, 149.29 (Ar-*C*), 153.62 (carbene-*C*) ppm; ^{29}Si NMR (79.49 MHz, C_6D_6): δ −104.00 (d, Si═N, $^2J_{SiP}$ = 14.51 Hz), 8.54 (*Si*$(CH_3)_3$). Anal. Calcd for $C_{38}H_{56}N_3O_2PSi_2$: C, 67.71; H, 8.37; N, 6.23. Found: C, 67.25; H, 8.72; N, 6.44%.

*Synthesis of ArN═Si(I^{i}Pr) (OSiMe$_3$)PPh$_2$ (**4**).* A solution of **2** (0.15 g, 0.23 mmol) in THF (5 mL) was placed in a 100 mL Schlenk flask. The flask was evacuated and placed under an atmosphere of O_2. The color of the solution soon changed from red to light yellow. Removal of the solvents afforded light yellow oil. The mixture was extracted with hexane (30 mL). Concentration to ca. 2 mL and storage at room temperature overnight afforded light yellow crystals of **4** (0.035 g, 23.1%). Concentration of the filtrates to ca. 1 mL and storage at ambient temperature overnight afforded colorless crystals of **3** (0.078 g, 50.3%). mp 212−213 °C. ^1H NMR (400 MHz, C_6D_6): δ 0.25 (s, 9H, $Si(CH_3)_3$), 0.69 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.16 (d, *J* = 6.7 Hz, 6H, $CH(CH_3)_2$), 1.25 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.34 (s, 6H, $=CCH_3$), 1.46 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 4.11 (m, 2H, Ar−$CH(CH_3)_2$), 6.13 (m, 2H, carbene−$CH(CH_3)_2$), 6.93−7.05 (m, 5H, Ar-*H*), 7.18−7.23 (m, 2H, Ar-*H*), 7.30 (d, *J* = 7.4 Hz, 2H, Ar-*H*), 7.72 (s, 2H, Ar-*H*), 8.09 (s, 2H, Ar-*H*). ^{31}P NMR (161.97 MHz, C_6D_6): δ −35.40. ^{13}C NMR (100.61 MHz, C_6D_6): δ 2.55 ($Si(CH_3)_3$), 10.15 ($=CCH_3$), 21.18, 22.31, 22.35, 24.48, 25.55 ($CH(CH_3)_2$), 28.22 (Ar-$CH(CH_3)_2$), 50.87, 50.91 (carbene-$CH(CH_3)_2$), 114.24, 122.78, 126.68, 133.57, 136.49, 139.74, 149.39 (Ar-C), 152.64 (d,, $^2J_{CP}$ = 44.21 Hz, carbene-C). ^{29}Si NMR (79.49 MHz, C_6D_6): δ −84.94 (d, Si−P, $^1J_{SiP}$ = 38.26 Hz), 8.81 (*Si*$(CH_3)_3$). Anal. Calcd for $C_{38}H_{56}N_3OPSi_2$: C, 69.36; H, 8.58; N, 6.39. Found: C, 69.35; H, 8.95; N, 6.28%. UV−vis (THF): $\varepsilon_{226} = 1.0244 \times 10^4$ L·mol^{-1}·cm^{-1}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02580.

Text giving NMR spectra, X-ray structural characterization data for **2−4**, computational details, optimized geometries, and additional references. (PDF)

Crystallographic data for compounds **2−4** and computational details. (CIF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: haiyancui555@163.com.
*E-mail: cmcui@nankai.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China and the 973 Program (Grant No. 2012CB821600), the Fundamental Research Funds for the Central Universities (Grant No. KJQN201551), the National Natural Science Foundation of China (Grant No. 21402094), and the Natural Science Foundation of Jiangsu Province (Grant No. BK20140678).

REFERENCES

(1) (a) Vedernikov, A. N. *Acc. Chem. Res.* **2012**, *45*, 803. (b) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013. (c) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047. (d) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737. (e) Stahl, S. S. *Science* **2005**, *309*, 1824. (f) Stahl, S. S. *Angew. Chem.* **2004**, *116*, 3480; *Angew. Chem., Int. Ed.* **2004**, *43*, 3400. (g) Sawwan, N.; Greer, A. *Chem. Rev.* **2007**, *107*, 3247.

(2) (a) Yuan, F.-Q.; Han, F.-S. *Org. Lett.* **2012**, *14*, 1218. (b) Zhang, P.; Wang, Y.; Li, H.; Antonietti, M. *Green Chem.* **2012**, *14*, 1904. (c) Liu, C.; Wang, J.; Meng, L.; Deng, Y.; Li, Y.; Lei, A. *Angew. Chem.* **2011**, *123*, 5250; *Angew. Chem., Int. Ed.* **2011**, *50*, 5144. (d) Dondoni, A.; Massi, A. *Angew. Chem.* **2008**, *120*, 4716; *Angew. Chem., Int. Ed.* **2008**, *47*, 4638. (e) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993. (f) Subramaniam, B. *Coord. Chem. Rev.* **2010**, *254*, 1843. (g) Yao, Z.; Hu, X.; Mao, J.; Li, H. *Green Chem.* **2009**, *11*, 2013. (h) Apeloig, Y. *Nat. Chem.* **2015**, *7*, 468. (i) Wang, Y.; Chen, M.; Xie, Y.; Wei, P.; Schaefer, H. F.; Schleyer, P. V.; Robinson, G. H. *Nat. Chem.* **2015**, *7*, 509.

(3) (a) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583. (b) Sander, W.; Schroeder, K.; Muthusamy, S.; Kirschfeld, A.; Kappert, W.; Boese, R.; Kraka, E.; Sosa, C.; Cremer, D. *J. Am. Chem. Soc.* **1997**, *119*, 7265. (c) Sander, W.; Kirschfeld, A.; Kappert, W.; Muthusamy, S.; Kiselewsky, M. *J. Am. Chem. Soc.* **1996**, *118*, 6508. (d) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J.-P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021. (e) Kirschfeld, A.; Muthusamy, S.; Sander, W. *Angew. Chem.* **1994**, *106*, 2261; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2212. (f) Sander, W. *Angew. Chem.* **1990**, *102*, 362; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. (g) Ganzer, G. A.; Sheridan, R. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1986**, *108*, 1517. (h) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213. (i) Lorberth, J.; Krapf, H.; Noeth, H. *Chem. Ber.* **1967**, *100*, 3511.

(4) (a) Akasaka, T.; Nagase, S.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1988**, *110*, 6270. (b) Patyk, A.; Sander, W.; Gauss, J.; Cremer, D. *Angew. Chem.* **1989**, *101*, 920; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 898. (c) Patyk, A.; Sander, W.; Gauss, J.; Cremer, D. *Chem. Ber.* **1990**, *123*, 89. (d) Bornemann, H.; Sander, W. *J. Am. Chem. Soc.* **2000**, *122*, 6727. (e) Moiseev, A. G.; Leigh, W. J. *Organometallics* **2007**, *26*, 6277. (f) Haaf, M.; Schmiedl, A.; Schmedake, T. A.; Powell, D. R.; Millevolte, A. J.; Denk, M.; West, R. *J. Am. Chem. Soc.* **1998**, *120*, 12714. (g) Xiong, Y.; Yao, S.; Driess, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 4302.

(5) For leading reviews on silylenes and NHC-stabilized silylenes, see: (a) Ghadwal, R. S.; Azhakar, R.; Roesky, H. W. *Acc. Chem. Res.* **2013**, *46*, 444. (b) Sen, S. S.; Khan, S.; Samuel, P. P.; Roesky, H. W. *Chem. Sci.* **2012**, *3*, 659. (c) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479. (d) Kira, M. *J. Organomet. Chem.* **2004**, *689*, 4475. (e) Gehrhus, B.; Lappert, M. F. *J. Organomet. Chem.* **2001**, *617–618*, 209. (f) Haaf, M.; Schmedake, T. A.; West, R. *Acc. Chem. Res.* **2000**, *33*, 704.

(6) (a) Ahmad, S. U.; Szilvási, T.; Irran, E.; Inoue, S. *J. Am. Chem. Soc.* **2015**, *137*, 5828. (b) Filippou, A. C.; Baars, B.; Chernov, O.; Lebedev, Y. N.; Schnakenburg, G. *Angew. Chem.* **2014**, *126*, 576−581; *Angew. Chem., Int. Ed.* **2014**, *53*, 565. (c) Rodriguez, R.; Troadec, T.; Gau, D.; Saffon-Merceron, N.; Hashizume, D.; Miqueu, K.; Sotiropoulos, J.-M.; Baceiredo, A.; Kato, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 4426. (d) Ghadwal, R. S.; Azhakar, R.; Propper, K.; Dittrich, B.; John, M. *Chem. Commun.* **2013**, *49*, 5987. (e) Ghadwal, R. S.; Azhakar, R.; Roesky, H. W.; Propper, K.; Dittrich, B.; Goedecke, C.; Frenking, G. *Chem. Commun.* **2012**, *48*, 8186. (f) Khan, S.; Michel, R.; Koley, D.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2011**, *50*, 10878.

(7) (a) Li, W.; Hill, N. J.; Tomasik, A. C.; Bikzhanova, G.; West, R. *Organometallics* **2006**, *25*, 3802. (b) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *J. Am. Chem. Soc.* **2007**, *129*, 7268. (c) Xiong, Y.; Yao, S.; Müller, R.; Kaupp, M.; Driess, M. *Nat. Chem.* **2010**, *2*, 577. (d) Rodriguez, R.; Gau, D.; Troadec, T.; Saffon-Merceron, N.; Branchadell, V.; Baceiredo, A.; Kato, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 8980.

(8) (a) Su, M.-D.; Chu, S.-Y. *J. Phys. Chem. A* **1999**, *103*, 11011. (b) Su, M.-D. *J. Phys. Chem. A* **2002**, *106*, 9563.

(9) Cui, H.; Cui, C. *Dalton Trans.* **2011**, *40*, 11937.

(10) NHC-stabilized halosilylenes: (a) Agou, T.; Hayakawa, N.; Sasamori, T.; Matsuo, T.; Hashizume, D.; Tokitoh, N. *Chem. - Eur. J.* **2014**, *20*, 9246. (b) Filippou, A. C.; Lebedev, Y. N.; Chernov, O.; Straßmann, M.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2013**, *52*, 6974. (c) Al-Rafia, S. M. I.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Chem. - Eur. J.* **2012**, *18*, 13810. (d) Filippou, A. C.; Chernov, O.; Blom, B.; Stumpf, K. W.; Schnakenburg, G. *Chem. - Eur. J.* **2010**, *16*, 2866. (e) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 5683. (f) Filippou, A. C.; Chernov, O.; Schnakenburg, G. *Angew. Chem., Int. Ed.* **2009**, *48*, 5687.

(11) (a) Gao, Y.; Zhang, J.; Hu, H.; Cui, C. *Organometallics* **2010**, *29*, 3063. (b) Tanaka, H.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2012**, *134*, 5540. (c) Inoue, S.; Eisenhut, C. *J. Am. Chem. Soc.* **2013**, *135*, 18315. (d) Cui, H.; Zhang, J.; Cui, C. *Organometallics* **2013**, *32*, 1.

(12) (a) Karsch, H. H.; Keller, U.; Gamper, S.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 295. (b) Inoue, S.; Wang, W.; Präsang, C.; Asay, M.; Irran, E.; Driess, M. *J. Am. Chem. Soc.* **2011**, *133*, 2868. (c) So, C.-W.; Roesky, H. W.; Gurubasavaraj, P. M.; Oswald, R. B.; Gamer, M. T.; Jones, P. G.; Blaurock, S. *J. Am. Chem. Soc.* **2007**, *129*, 12049.

(13) (a) Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813. (b) Lerner, H. W.; Bolte, M.; Schurz, K.; Wiberg, N.; Baum, G.; Fenske, D.; Bats, J. W.; Wagner, M. *Eur. J. Inorg. Chem.* **2006**, *2006*, 4998. (c) Klingebiel, U.; Noltemyer, M.; Schmidt, H. G.; Schmidt-Bäse, D. *Chem. Ber.* **1997**, *130*, 753. (d) Junge, K.; Popowski, E.; Michalik, M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1532. (e) Lerner, H. W.; Scholz, S.; Bolte, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1638. (f) Niesmann, J.; Klingebiel, U.; Schäfer, M.; Boese, R. *Organometallics* **1998**, *17*, 947. (g) Wiberg, N.; Schurz, K.; Reber, G.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1986**, 591. (h) Hesse, M.; Klingebiel, U. *Angew. Chem.* **1986**, *98*, 638; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 649. (i) Cui, H.; Cui, C. *Dalton Trans.* **2015**, *44*, 20326.