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Synthesis and Characterization of *N*-Heterocyclic Carbene-Coordinated Silicon Compounds Bearing a Fused-Ring Bulky Eind Group

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Abstract: The reactions of the fused-ring bulky Eind-substituted 1,2-dibromodisilene, (Eind)BrSi=SiBr(Eind) (**1a**) (Eind = 1,1,3,3,5,5,7,7-octaethyl-*s*-hydrindacen-4-yl (**a**)), with *N*-heterocyclic carbenes (NHCs) (Im-Me_4 = 1,3,4,5-tetramethylimidazol-2-ylidene and Im-$^i Pr_2 Me_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) are reported. While the reaction of **1a** with the sterically more demanding Im-$^i Pr_2 Me_2$ led to the formation of the mono-NHC adduct of arylbromosilylene, (Im-$^i Pr_2 Me_2$)$\rightarrow$SiBr(Eind) (**2a′**), a similar reaction using the less bulky Im-Me_4 affords the bis-NHC adduct of formal arylsilyliumylidene cation, $[(\text{Im-Me}_4)_2\rightarrow\text{Si(Eind)}]^+[\text{Br}^-]$ (**3a**). The NHC adducts **2a′** and **3a** can also be prepared by the dehydrobromination of Eind-substituted dibromohydrosilane, (Eind)$SiHBr_2$ (**4a**), with NHCs. The NHC-coordinated silicon compounds have been characterized by spectroscopic methods. The molecular structures of bis-NHC adduct, $[(\text{Im-}^i\text{Pr}_2\text{Me}_2)_2\rightarrow\text{Si(Eind)}]^+[\text{Br}^-]$ (**3a′**), and **4a** have been determined by X-ray crystallography.

Keywords: silicon; *N*-heterocyclic carbenes; bromosilylenes; silyliumylidenes; dehydrobromination

1. Introduction

Over many years, a number of unsaturated silicon compounds have been successfully obtained by virtue of the complexation of metal ions and/or coordination of ligands (mainly Lewis bases) in addition to steric protection with bulky substituents [1–11]. Among them, the coordination chemistry of highly-reactive halosilylenes, i.e., halogen-substituted divalent Si(II) species, have attracted a lot of attention as potentially useful precursors for the construction of a wide range of silicon-containing compounds [12–17]. Figure 1 shows recent examples of coordination-stabilized arylhalosilylenes and their derivatives [18–24]. In 2010, Filippou's group reported the first *N*-heterocyclic carbene (NHC) adducts of arylchlorosilylenes bearing sterically large *m*-terphenyl groups, (Im-Me_4)$\rightarrow$SiCl(Ar) (**Ic** and **Id**) (Ar = 2,6-$(\text{Mes})_2\text{C}_6\text{H}_3$ (Mes = 2,4,6-$Me_3C_6H_2$) (**c**) and 2,6-$(Tip)_2C_6H_3$ (Tip = 2,4,6-$^{i}Pr_3C_6H_2$) (**d**)), which were prepared by the dehydrochlorination of the aryldichlorohydrosilanes, $(Ar)SiHCl_2$, with NHC ($Im\text{-}Me_4$ = 1,3,4,5-tetramethylimidazol-2-ylidene) along with the formation of imidazolium chloride, $[(Im\text{-}Me_4)H]^+[Cl^-]$ [18]. The NHC adduct **Id** reacted with $[Li^+][CpMo(CO)_3]^-$ to afford the silylidene complex, $Cp(CO)_2Mo{=}Si(Ar)(Im\text{-}Me_4)$ (**IId**), and the subsequent treatment with $B(C_6H_4\text{-}4\text{-}Me)_3$ produced the first silylidyne complex, $Cp(CO)_2Mo{\equiv}Si(Ar)$ (**IIId**), featuring a metal-silicon triple bond [19,25].

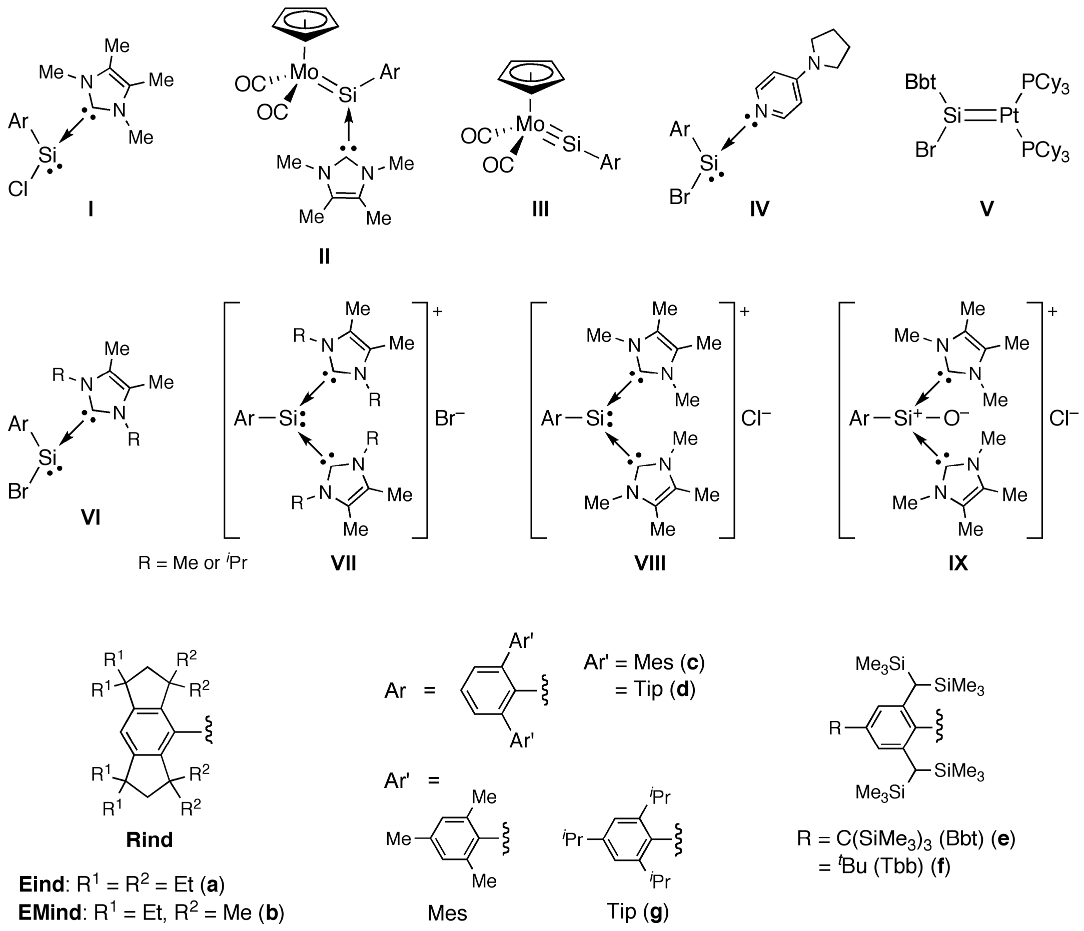


Figure 1. Examples of coordination-stabilized arylhalosilylenes and their derivatives. Each one of the possible canonical forms is depicted.

In 2011, we reported on the 4-pyrrolidinopyridine (PPy) adducts of arylbromosilylenes with fused-ring bulky Rind groups, PPy→SiBr(Rind) (**IVa** and **IVb**) (Rind = 1,1,3,3,5,5,7,7-octa-R-substituted *s*-hydrindacen-4-yl; Eind (**a**: $R^1 = R^2$ = Et) and EMind (**b**: R^1 = Et, R^2 = Me)) [26,27], which were formed by the addition of PPy to 1,2-dibromodisilenes, (Rind)BrSi=SiBr(Rind) (**1a** and **1b**) [20]. Also in 2011, Cui reported on the related NHC-coordinated aminochlorosilylene [28], and recently Driess's group reported on the aminochlorosilylene-nickel complex [29]. In 2012, a platinum complex of arylbromosilylene, $(Bbt)BrSi{=}Pt(PCy_3)_2$ (**Ve**), was synthesized by the treatment of 1,2-dibromodisilene, (Bbt)BrSi=SiBr(Bbt) (**1e**), bearing the bulky Bbt groups (Bbt = 2,6-$\{CH(SiMe_3)_2\}_2$-4-$C(SiMe_3)_3$-C_6H_2 (**e**)) [30] with $Pt(PCy_3)_2$ [21,31]. In this context, some arylbromosilylidene and arylsilylidyne complexes of nickel and platinum were reported [32–34]. In 2013, Filippou's group reported the unprecedented dicationic NHC complexes of silicon(II) and NHC adducts of iodesilyliumylidene cation SiI^+ [35]. Subsequently, we reported the reaction of 1,2-dibromodisilenes (**1b**, **1e**, and **1f**) having EMind, Bbt, and Tbb groups (Tbb = 2,6-$\{CH(SiMe_3)_2\}_2$-4-^{t}Bu-C_6H_2 (**f**)) with NHCs ($Im\text{-}Me_4$ and $Im\text{-}^{i}Pr_2Me_2$) ($Im\text{-}^{i}Pr_2Me_2$ =

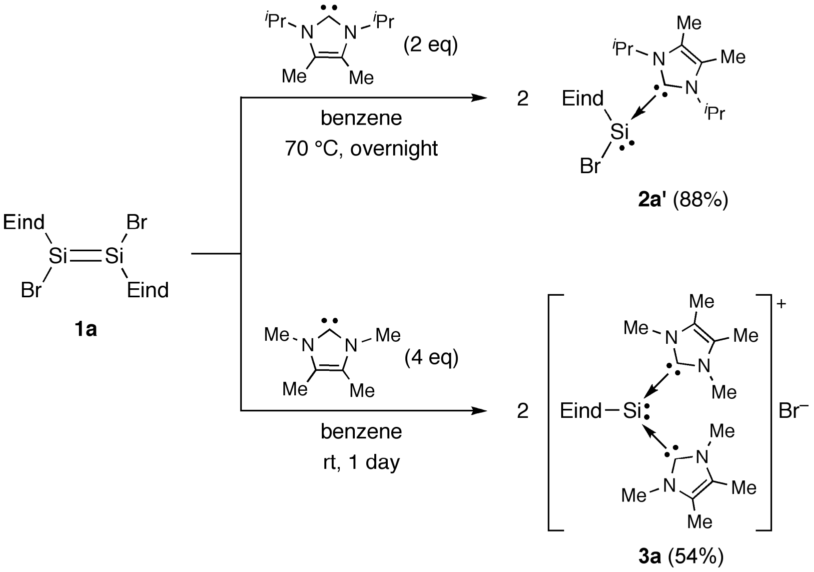
1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) leading to the formation of mono-NHC adducts of arylbromosilylenes, NHC→SiBr(Ar) (**VIb′** and **VIe**), and the bromide salts of the bis-NHC adducts of formal arylsilyliumylidene cations, $[(\mathrm{NHC})_2{\rightarrow}\mathrm{Si(Ar)}]^+[\mathrm{Br}^-]$ (**VIIb**, **VIIb′**, and **VIIf**) [22]. Inoue's group also reported the synthesis of chloride salts of bis-NHC adducts of formal arylsilyliumylidene cations, $[(\text{Im-Me}_4)_2{\rightarrow}\mathrm{Si(Ar)}]^+[\mathrm{Cl}^-]$ (**VIIIc** and **VIIIg**) (Ar = Tip (**g**)) [23] and their unique conversion to silicon analogues of acylium ions, $[(\text{Im-Me}_4)_2{\rightarrow}\mathrm{Si(O)(Ar)}]^+[\mathrm{Cl}^-]$ (**IXc** and **IXg**) [24]. Recently, Inoue's group reported on the chalcogen-atom transfer and exchange reactions of NHC-bound heavier silaacylium ions, $[(\text{Im-Me}_4)_2{\rightarrow}\mathrm{Si(E)(Ar)}]^+[\mathrm{Cl}^-]$ (E = S, Se, and Te) [36].

In this article, we describe the preparation and characterization of NHC-coordinated silicon compounds bearing the bulky Eind group, which have been obtained by two different synthetic procedures, i.e., the NHC-induced fragmentation of the Eind-based 1,2-dibromo-disilene and the dehydrobromination of the Eind-based dibromohydrosilane with NHCs.

2. Results and Discussions

2.1. Reactions of (Eind)BrSi=SiBr(Eind) (1a) with NHCs

We first performed an NMR tube scale reaction of Eind-based 1,2-dibromodisilene, (Eind)BrSi=SiBr(Eind) (**1a**) [20], in C_6D_6 with two equivalents of the sterically more bulky NHC, Im-^{i}Pr$_2$Me$_2$, relative to Im-Me$_4$. The progress of the reaction was monitored by ^{1}H NMR spectroscopy, indicating the selective formation of the mono-NHC adduct of the arylbromosilylene, (Im-^{i}Pr$_2$Me$_2$)→SiBr(Eind) (**2a′**), after overnight heating at 70 °C. In the ^{29}Si NMR spectrum, only one signal was observed at δ = 18.0 ppm, which is comparable to those of (Im-^{i}Pr$_2$Me$_2$)→SiBr(EMind) (**VIb′**) (δ = 13.1 ppm) and (Im-Me$_4$)→SiBr(Bbt) (**VIe**) (δ = 10.9 ppm) [22]. The ^{13}C signal at δ = 170.6 ppm for **2a′** is characteristic of a carbene carbon atom, similar to those for **VIb′** (δ = 169.7 ppm) and **VIe** (δ = 167.5 ppm) [22]. Based on the NMR tube experiment, the mono-NHC adduct **2a′** was synthesized as an orange solid in 88% crude yield (Scheme 1).



Scheme 1. Reactions of **1a** with *N*-heterocyclic carbenes (NHCs).

We also examined the reaction of **1a** with four equivalents of Im-^{i}Pr$_2$Me$_2$. After 1-day heating at 70 °C in C_6D_6, the ^{29}Si NMR spectrum indicated the formation of a mixture containing the mono-NHC adduct **2a′** (δ = 18.0 ppm) as the major product and the bis-NHC adduct of the arylsilyliumylidene cation, $[(\text{Im-}^i\text{Pr}_2\text{Me}_2)_2{\rightarrow}\mathrm{Si(Eind)}]^+[\mathrm{Br}^-]$ (**3a′**) (δ = −59.6 ppm), as the minor product. The latter ^{29}Si signal was shifted upfield compared to the former, and was similar to those of the formal arylsilyliumylidene cations, $[(NHC)_2{\to}Si(EMind)]^+[Br^-]$ (**VIIb** and **VIIb′**) (δ = −60.8 and −75.9 ppm) and $[(Im\text{-}Me_4)_2{\to}Si(Tbb)]^+[Br^-]$ (**VIIf**) (δ = −70.9 ppm) [22]. However, we found that the reaction was not completed even after prolonged heating (longer than 1 week), probably due to the severe steric repulsion between the Eind group and Im-^{i}Pr$_2$Me$_2$ molecules. Thus, we were unable to isolate **3a′**. Nevertheless, single red crystals of **3a′** could be obtained from the reaction mixture, whose structure was determined by X-ray crystallography (Figure 2).

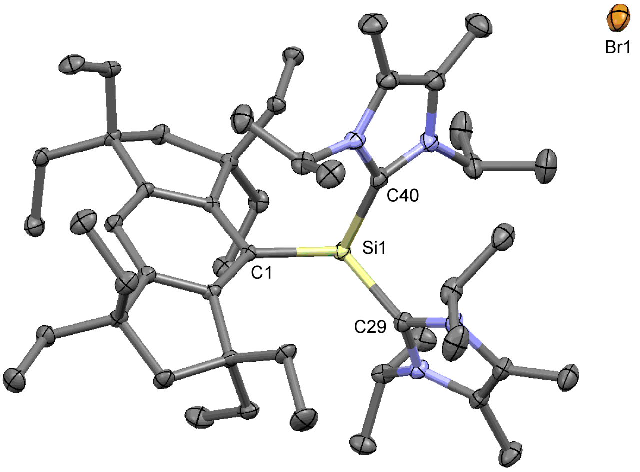


Figure 2. Molecular structure of **3a′**. The thermal ellipsoids are shown at the 50% probability level. All hydrogen atoms and benzene molecule are omitted for clarity.

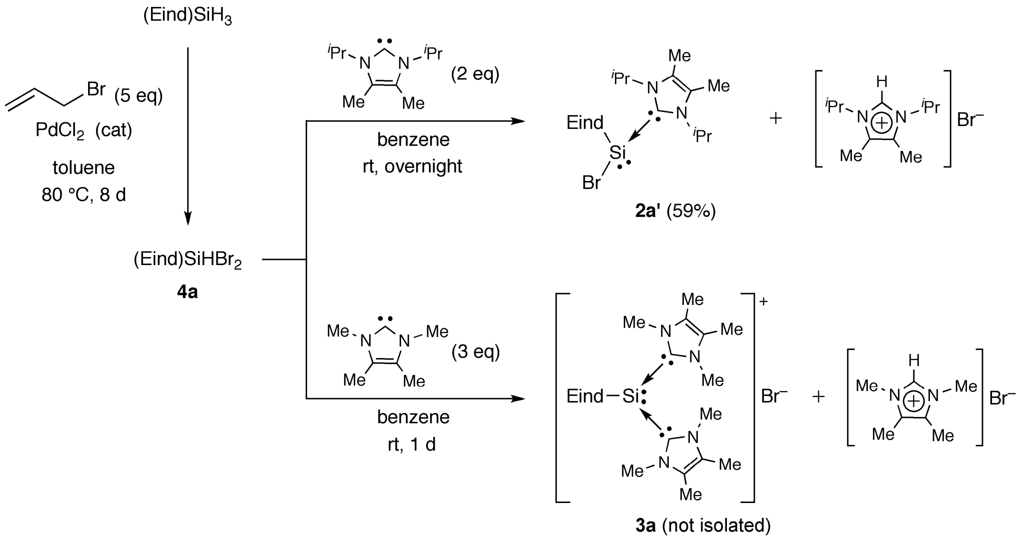
Figure 2 shows a separated ion pair of **3a′** in the crystal. The closest Si· · · Br distance (7.6669(6) Å) is analogous to that of **VIIb′** (7.732(3) Å) [22], thus being much longer than the sum of the van der Waals radii of Si and Br (3.95 Å). The Si atom is three-coordinate adopting a distorted pyramidal geometry, which can be explained by the presence of a lone pair of electrons. The sum of the surrounding angles around the Si atom (ΣSi = 327.3°) is almost the same as that of **VIIb′** (ΣSi = 327.0°) [22]. The Si–C(Rind) bond length in **3a′** (Si1–C1 = 1.9482(19) Å) is similar to that in **VIIb′** [1.927(8) Å] [22] and longer than typical Si–C bonds (ca. 1.88 Å), suggesting the high s-character of the lone pair of electrons on the Si atom and the high p-character of the Si–C(Rind) bond. The Si←C(NHC) coordination distances in **3a′** (Si1–C29 = 1.953(2) and Si1–C40 = 1.942(2) Å) are comparable to those observed in **VIIb′** (1.955(9) and 1.979(8) Å) [22].

We next investigated the reaction of **1a** with two equivalents of the less bulky NHC, Im-Me$_4$, and C_6D_6. After 1 day at room temperature, two signals mainly appeared at δ = 73.3 and −63.3 ppm in the ^{29}Si NMR spectrum, corresponding to the unreacted **1a** and the bis-NHC adduct of the arylsilyliumylidene cation, $[(Im\text{-}Me_4)_2{\to}Si(Eind)]^+[Br^-]$ (**3a**). This indicated that the NHC-arylbromosilylene adduct, (Im-Me$_4$)→SiBr(Eind) (**2a**), which serves as a potential intermediate, is more reactive toward Im-Me$_4$ compared to **1a**. When the dibromodisilene **1a** was treated with four equivalents of Im-Me$_4$ in benzene, the bis-NHC adduct **3a** was efficiently formed (Scheme 1). We obtained **3a** as an orange powder in 54% crude yield. The upfield-shifted ^{29}Si resonance for **3a** (δ = −63.3 ppm) suggests the contribution of the canonical form due to the bis(imidazolium) adduct of a silyl anion, whose electronic structure was previously supported by the theoretical calculations of **VIIb′** and **VIIf** [22]. In the ^{13}C NMR spectrum of **3a** in CD_3CN, one NHC carbene signal was observed at δ = 162.0 ppm, comparable to those for **VIIb** (δ = 160.5 ppm), **VIIb′** (δ = 162.4 ppm), and **VIIf** (δ = 160.4 ppm) [22].

*2.2. Reactions of (Eind)SiHBr$_2$ (**4a**) with NHCs*

We also examined another synthetic route for the NHC-coordinated silicon compounds, i.e., the dehydrobromination of the Eind-substituted dibromohydrosilane, (Eind)SiHBr$_2$ (**4a**), with NHCs

(Scheme 2). The precursor (**4a**) was prepared as pale brown crystals by the dibromination of the Eind-based trihydrosilane, (Eind)SiH_3 [37,38], with allyl bromide in the presence of a catalytic amount of $PdCl_2$ [39]. We found that this reaction exclusively afforded **4a** even using an excess amount of allyl bromide with prolonged heating (longer than 1 week), most likely due to the steric bulkiness of the Eind group. In this context, Kunai, Ohshita, and their co-workers previously reported the selective dibromination of trihydrosilanes with $CuBr_2$ in the presence of CuI [40]. The formation of **4a** was deduced on the basis of the spectroscopic data (Figures S1–S4). In the ^{1}H NMR spectrum, the Si–H signal was found at $\delta = 6.89$ ppm with satellite signals, due to the ^{29}Si nuclei [$^1J(^{29}\mathrm{Si}–^1\mathrm{H}) = 288$ Hz]. The ^{29}Si NMR signal appeared at $\delta = -28.7$ ppm, similar to that of (Bbt)$SiHBr_2$ ($\delta = -28.47$ ppm) [41]. The infrared spectrum exhibited a Si–H stretching band at 2317 cm^{-1} in the KBr-pellet (Figure S4) and at 2298 cm^{-1} in THF [42,43]. The molecular structure of **4a** was determined by single-crystal X-ray diffraction analysis (Figure 3). The hydrogen atom on the silicon atom was located on difference Fourier maps and isotropically refined. In the crystal, the $SiHBr_2$ group is fixed in one conformation with respect to the rotamer around the Si–C bond. A similar conformation was also observed in the crystal of (Eind)PCl_2 [44]. The Si–C bond length for **4a** (1.8746(18) Å) is comparable to those of typical Si–C bonds (ca. 1.88 Å).



Scheme 2. Reactions of **4a** with NHCs.

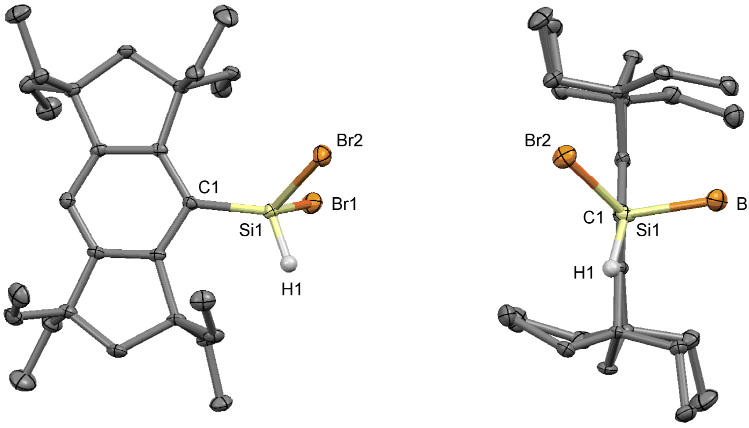


Figure 3. Molecular structure of **4a**: Side view (**left**), front view (**right**). The thermal ellipsoids are shown at the 50% probability level. The hydrogen atoms, except for the Si–H group, are omitted for clarity.

As shown in Scheme 2, the reaction of **4a** with two equivalents of Im-^{i}Pr$_2$Me$_2$ proceeded more smoothly at room temperature in comparison to the reaction of **1a** with Im-^{i}Pr$_2$Me$_2$ (Scheme 1), producing the mono-NHC adduct **2a′** in 59% crude yield. The reaction of **4a** with three equivalents of Im-Me$_4$ also afforded the bis-NHC adduct **3a** on the basis of the NMR data. In these reactions, it is essential to remove the byproducts, imidazolium bromides, $[(\text{NHC})\text{H}]^+[\text{Br}^-]$, for the isolation procedure of the silicon products, which may be considered as a disadvantage when compared to the no-byproduct strategy of using **1a** as a precursor (vide supra). Actually, the separation of **3a** and $[(\text{Im-Me}_4)\text{H}]^+[\text{Br}^-]$ was found to be difficult in our experiments. However, dibromodisilene **1a** can only be obtained by a two-step synthesis from the trihydrosilane, (Eind)SiH$_3$; thus the bromination of (Eind)SiH$_3$ with *N*-bromosuccinimide (NBS) first affords the tribromosilane, (Eind)SiBr$_3$, then the reduction of (Eind)SiBr$_3$ with two equivalents of lithium naphthalenide (LiNaph) produces **1a** [20]. Therefore, the dehydrobromination of **4a** with NHCs can be considered as a convenient short-step synthesis for NHC-coordinated silylene derivatives.

3. Materials and Methods

3.1. General Procedures

All manipulations of the air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a glove box under an inert atmosphere of argon. Anhydrous hexane, benzene, and toluene were dried by passage through columns of activated alumina and supported copper catalyst supplied by Nikko Hansen & Co., Ltd. (Osaka, Japan). Anhydrous pentane and acetonitrile were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan), and used without further purification. Deuterated benzene (C_6D_6, benzene-*d*$_6$) was dried and degassed over a potassium mirror in vacuo prior to use. Deuterated acetonitrile (CD_3CN, acetonitrile-*d*$_3$) was dried and distilled over calcium hydride (CaH_2) prior to use. (Eind)SiH$_3$ [37,38], (Eind)BrSi=SiBr(Eind) (**1a**) [20], 1,3,4,5-tetramethylimidazol-2-ylidene (Im-Me$_4$) [45] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene(Im-^{i}Pr$_2$Me$_2$) [45] were prepared by the literature procedures. All other chemicals and gases were used as received.

Nuclear magnetic resonance (NMR) measurements were carried out using a JEOL ECS-400 spectrometer (399.8 MHz for ^{1}H, 100.5 MHz for ^{13}C, and 79.4 MHz for ^{29}Si) or JEOL JNM AL-300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 59 MHz for ^{29}Si) (JEOL Ltd., Tokyo, Japan). Chemical shifts (δ) are given by definition as dimensionless numbers and relative to ^{1}H chemical shifts of the solvents for ^{1}H (residual C_6D_5H in C_6D_6, ^{1}H(δ) = 7.15, residual CD_2HCN in CD_3CN, ^{1}H(δ) = 1.94), and ^{13}C chemical shifts of the solvent for ^{13}C (C_6D_6: ^{13}C(δ) = 128.06 and CD_3CN: ^{13}C(δ) = 118.26). The signal of tetramethylsilane (^{29}Si(δ) = 0.0) was used as an external standard in the ^{29}Si NMR spectra. The absolute values of the coupling constants are given in Hertz (Hz) regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). The mass spectra were recorded by a JEOL JMS-T100LC AccuTOF LC-plus 4G mass spectrometer (ESI-MS) with a DART source. The elemental analyses were performed in the Microanalytical Laboratory at the Institute for Chemical Research (Kyoto University, Uji, Japan). Melting points (m.p.) were determined by a Stanford Research Systems OptiMelt instrument. We were unable to obtain a satisfactory elemental analysis for **2a′** and **3a**, probably due to their extremely high air- and moisture-sensitivity as well as a contamination of NHCs and unidentified compounds associated with some thermal decomposition (Figures S5–S10).

3.1.1. Synthesis of (Eind)SiHBr$_2$ (***4a***)

To a solution of (Eind)SiH$_3$ (4.09 g, 9.91 mmol) in toluene (30 mL) was added PdCl$_2$ (38.0 mg, 0.21 mmol) and allyl bromide (4.2 mL, 48.5 mmol). The reaction mixture was heated at 80 °C for 8 days. After the solvent was removed in vacuo, the residue was dissolved in hexane and the resulting mixture was centrifuged to remove the insoluble materials. The supernatant was concentrated to dryness and the resulting residue was recrystallized from pentane to afford **4a** as pale brown crystals in 81% yield (4.58 g, 8.02 mmol).

^{1}H NMR (399.8 MHz, C_6D_6, 30 °C): δ = 0.78 (t, *J* = 7.3 Hz, 12 H, CH_2CH_3), 0.80 (br. s, 12 H, CH_2CH_3), 1.48–1.65 (m, 8 H, CH_2CH_3), 1.76 (s, 4 H, CH_2), 2.11 (br. s, 8 H, CH_2CH_3), 6.89 (s, 1 H, satellite, $J_{\text{Si–H}}$ = 288 Hz, Si*H*), 7.01 (s, 1 H, Ar*H*). ^{13}C NMR (100.5 MHz, C_6D_6, 25 °C): δ = 9.3, 10.5 (br), 33.5, 34.2 (br), 42.6 (br ×1), 44.8 (br ×1), 47.9 (br ×2), 54.7 (×2), 123.6, 125.1, 150.8 (one aromatic peak is broadened at 155–158); ^{29}Si NMR (79.4 MHz, C_6D_6, 30 °C): δ = −28.7 (d, $J_{\text{Si–H}}$ = 288 Hz). IR (KBr, cm^{-1}): ν = 2317 (Si−H); IR (THF, cm^{-1}): ν = 2298 (Si−H). DART-HRMS (positive-mode) Calcd. for $C_{28}H_{46}Br_2Si$ + H: 569.1814. Found: 569.1820. Anal. Calcd. for $C_{28}H_{46}Br_2Si$: C, 58.94; H, 8.13. Found: C, 59.41; H, 8.19. Melting point (argon atmosphere in a sealed tube) 102–105 °C.

3.1.2. Synthesis of (Im-^{i}Pr$_2$Me$_2$)→SiBr(Eind) (**2a′**)

(Method A) Reaction of (Eind)BrSi=SiBr(Eind) (**1a**) with Im-^{i}Pr$_2$Me$_2$

A mixture of **1a** (158 mg, 0.16 mmol) and Im-^{i}Pr$_2$Me$_2$ (63.0 mg, 0.35 mmol) was dissolved in benzene (5 mL). The reaction mixture was heated overnight at 70 °C. After the solvent was removed in vacuo, the residue was washed with pentane to afford **2a′** as an orange solid in 88% crude yield (190 mg, 0.28 mmol). We were unable to isolate **2a′** in pure form, because **2a′** was not thermally stable in solution, gradually giving Im-^{i}Pr$_2$Me$_2$ and unidentified compounds (Figure S5).

^{1}H NMR (399.8 MHz, C_6D_6, 60 °C): δ = 0.81–1.00 (m, 24 H, CH_2CH_3), 1.12 (br. s, 6 H, $CH(CH_3)_2$–(Im-^{i}Pr$_2$Me$_2$)), 1.19 (d, *J* = 7.0 Hz, 6 H, $CH(CH_3)_2$–(Im-^{i}Pr$_2$Me$_2$)), 1.61 (s, 6 H, CH_3–(Im-^{i}Pr$_2$Me$_2$)), 1.62–1.95 (m, 20 H, CH_2 + CH_2CH_3), 5.00–5.27 (m, 2 H, $CH(CH_3)_2$–(Im-^{i}Pr$_2$Me$_2$)), 6.71 (s, 1 H, Ar*H*). ^{13}C NMR (100.5 MHz, C_6D_6, 70 °C): δ = 9.3, 9.4, 9.9, 10.0, 10.5, 20.7, 21.4, 24.6, 33.7 (br, overlapped, Im-^{i}Pr$_2$Me$_2$ and CH_2CH_3), 42.8, 48.4, 51.1 (Im-^{i}Pr$_2$Me$_2$), 54.5, 119.9, 125.9 (Im-^{i}Pr$_2$Me$_2$), 147.2, 148.5, 153.7, 170.6 (Im-^{i}Pr$_2$Me$_2$); ^{29}Si NMR (79.4 MHz, C_6D_6, 25 °C): δ = 18.0. HRMS (ESI, positive) Calcd. for $C_{39}H_{65}BrN_2Si$ + H: 669.4179. Found: 669.4211. Melting point (argon atmosphere in a sealed tube) 152–156 °C (dec.).

(Method B) Reaction of (Eind)SiHBr$_2$ (**4a**) with Im-^{i}Pr$_2$Me$_2$

A mixture of **4a** (476 mg, 0.97 mmol) and Im-^{i}Pr$_2$Me$_2$ (352 mg, 1.95 mmol) was dissolved in benzene (7 mL). After stirring overnight at room temperature, the resulting orange suspension was filtered through a polytetrafluoroethylene (PTFE) syringe filter to remove the insoluble materials. The filtrate was concentrated to dryness and the resulting residue was washed with pentane to afford **2a′** as an orange solid in 59% crude yield (197 mg, 0.29 mmol).

3.1.3. Synthesis of [(Im-Me$_4$)$_2$→Si(Eind)]$^+$[Br]$^-$ (**3a**)

(Method A) Reaction of (Eind)BrSi=SiBr(Eind) (**1a**) with Im-Me$_4$

A mixture of **1a** (102 mg, 0.11 mmol) and Im-Me$_4$ (54 mg, 0.43 mmol) was dissolved in benzene (6 mL). After stirring for 1 day at room temperature, the resulting orange solid was separated and washed with a mixture of hexane and benzene to afford **3a** as an orange powder in 54% crude yield (85.2 mg, 0.12 mmol). We were unable to isolate **3a** in pure form, because **3a** was not thermally stable in solution leading to the contamination of Im-Me$_4$ and unidentified compounds (Figure S8).

^{1}H NMR (399.8 MHz, CD_3CN, 20 °C): δ = 0.61 (br. t, *J* = 6.3 Hz, 12 H, CH_2CH_3), 0.80 (t, *J* = 7.3 Hz, 12 H, CH_2CH_3), 1.50–1.70 (m, 8 H, CH_2CH_3), 1.75 (br. s, 4 H, CH_2), 1.93−1.97 (m, overlapped, 8 H, CH_2CH_3), 2.15 (s, 12 H, CH_3–(Im-Me$_4$)), 3.25 (br. s, 12 H, CH_3–(Im-Me$_4$)), 6.75 (s, 1 H, Ar*H*). ^{13}C NMR (100.5 MHz, CD_3CN, 19 °C): δ = 9.2, 9.4, 10.0 (br, Im-Me$_4$), 34.1 (br, overlapped, Im-Me$_4$ and CH_2CH_3), 42.8, 48.1, 54.2, 121.8, 128.5 (Im-Me$_4$), 136.5, 150.7, 162.0 (Im-Me$_4$) (one aromatic peak is overlapped). ^{29}Si NMR

(79.4 MHz, CD_3CN, 25 °C): δ = −63.3. DART-HRMS (positive-mode) Calcd. for $C_{42}H_{69}BrN_4Si$ + H: 737.4553. Found: 737.4562. Melting point (argon atmosphere in a sealed tube) 169–174 °C (dec.).

(Method B) Reaction of (Eind)$SiHBr_2$ (**4a**) with Im-Me_4

A mixture of **4a** (70.3 mg, 0.12 mmol) and Im-Me_4 (50.6 mg, 0.41 mmol) was dissolved in benzene (6 mL). After stirring for 1 day at room temperature, an orange suspension was formed. An insoluble orange solid was collected by filtration, whose ^{1}H NMR spectrum indicated the formation of a mixture of **4a** and $[(\text{Im-Me}_4)\text{H}]^+[\text{Br}^-]$.

3.2. X-ray Crystallographic Studies of **3a′** *and* **4a**

Single crystals suitable for X-ray diffraction measurements were obtained from benzene for **3a′** and from hexane for **4a**. Intensity data were collected using a Rigaku XtaLAB P200 with a PILATUS 200K detector for **3a′** and a Rigaku AFC-8 with a Saturn 70 CCD detector for **4a** (Rigaku Corporation, Tokyo, Japan). All measurements were carried out using Mo $K\alpha$ radiation (λ = 0.71073 Å). The integration and scaling of the diffraction data were carried out using the programs CrysAlisPro [46] for **3a′** and CrystalClear [47] for **4a**. Lorentz, polarization, and absorption corrections were also performed. The structures were solved by an iterative method with the program of SHELXT [48], and refined by a full-matrix least-squares method on F^2 for all the reflections using the program SHELXL-2017/1 [49]. The non-hydrogen atoms were refined by applying anisotropic temperature factors. Positions of all the hydrogen atoms were geometrically calculated, and refined as riding models. The Si–H hydrogen atom was located on difference Fourier maps and isotropically refined. Full details of the crystallographic analysis and accompanying CIF files can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC numbers 1811699 and 1811700) via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

3.2.1. $[(\text{Im-}^i\text{Pr}_2\text{Me}_2)_2{\rightarrow}\text{Si(Eind)}]^+[\text{Br}^-]$ (**3a′**)

$C_{50}H_{85}BrN_4Si{\cdot}C_6H_6$, M = 928.32, crystal size 0.36 × 0.15 × 0.12 mm, triclinic, space group $P{-}1$ (#2), a = 10.6548(3) Å, b = 12.0149(2) Å, c = 21.7366(5) Å, α = 80.5199(18)°, β = 82.343(2)°, γ = 72.816(2)°, V = 2611.54(11) Å^3, Z = 2, D_x = 1.181 g cm^{-3}, μ(Mo $K\alpha$) = 0.849 mm^{-1}, 65594 reflections collected, 13761 unique reflections, and 579 refined parameters. The final $R(F)$ value was 0.0491 [$I > 2\sigma(I)$]. The final $R_w(F^2)$ value was 0.1364 (all data). The goodness-of-fit on F^2 was 1.031.

3.2.2. (Eind)$SiHBr_2$ (**4a**)

$C_{28}H_{46}Br_2Si$, M = 570.56, crystal size 0.16 × 0.17 × 0.41 mm, triclinic, space group $P{-}1$ (#2), a = 7.972(3) Å, b = 11.070(4) Å, c = 16.621(5) Å, α = 89.972(4)°, β = 80.770(3)°, γ = 73.314(5)°, V = 1385.1(8) Å^3, Z = 2, D_x = 1.368 g cm^{-3}, μ(Mo $K\alpha$) = 2.992 mm^{-1}, 22599 reflections collected, 6332 unique reflections, and 292 refined parameters. The final $R(F)$ value was 0.0298 [$I > 2\sigma(I)$]. The final $R_w(F^2)$ value was 0.0803 (all data). The goodness-of-fit on F^2 was 1.016.

4. Conclusions

We have synthesized some new NHC-coordinated silicon species having the fused-ring bulky Eind group by two methods; one is via the reactions of the stable diaryldibromodisilene, (Eind)BrSi=SiBr(Eind) (**1a**), with NHCs, and the other is the dehydrobromination of the aryldibromohydrosilane, (Eind)$SiHBr_2$ (**4a**), with NHCs. In both synthetic pathways, we have mainly obtained the mono-NHC adduct of the arylbromosilylene, $(\text{Im-}^i\text{Pr}_2\text{Me}_2){\rightarrow}\text{SiBr(Eind)}$ (**2a′**), and the bis-NHC adduct of the formal arylsilyliumylidenecation, $[(\text{Im-Me}_4)_2{\rightarrow}\text{Si(Eind)}]^+[\text{Br}^-]$ (**3a**), depending on the steric bulk of the NHCs ($\text{Im-}^i\text{Pr}_2\text{Me}_2$ vs. Im-Me_4). Further studies on the reactivities of the NHC-coordinated silicon compounds are now in progress.

Supplementary Materials: The following are available online at www.mdpi.com/2304-6740/6/1/30/s1, S1: NMR spectra of **4a**, **2a′**, and **3a** and IR spectrum of **4a** (PDF), S2: crystallographic details for **4a** and **3a′** (CIF) and S3: cif-checked files (PDF).

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