1,4-Dehydrogenation with a Two-Coordinate Cyclic (Alkyl)(amino)silylene

doi: 10.1002/chem.201901407

1,4-Dehydrogenation with a Two-Coordinate Cyclic (Alkyl)(amino)silylene

Taichi Koike, Tomoyuki Kosai, and Takeaki Iwamoto*[a]

Abstract: Cyclic (alkyl)(amino)silylene (CAASi) **1** successfully dehydrogenated 1,4-dihydroaromatic compounds with various substituents affording the corresponding aromatic compounds. The high substrate generality proved **1** to be a potential 1,4-dehydrogenation reagent for organic compounds. For the reaction with 9,10-dimethyl-9,10-dihydroanthracene, **1** activated not only benzylic C–H bonds but also aromatic C–H bonds to yield a silaacenaphthene derivative, which is an unprecedented reaction of silylenes. Experimental and computational results for the reaction with 9,10-dihydroanthracene and 1,4-cyclohexadiene are consistent with the notion that 1,4-dehydrogenation with CAASi **1** proceeds mainly via a stepwise hydrogen abstraction.

Introduction

Chemistry of silylenes (R_2Si), heavier element analogues of carbenes have shown tremendous development in the last few decades.[1a-c] Although silylenes are generally known as low-coordinate reactive intermediates in silicon chemistry, taming their high reactivity through bulky substituents and/or electron-donor groups bonded to the divalent silicon atom has enabled the isolation of various stable silylenes. Recently, isolable silylenes have emerged as effective ligands for transition metal complexes or as starting materials of novel silicon compounds ($R_2Si=X$; X = SiR_2, CNR, NR, O, S, Se, Te, etc.).[2]

Furthermore, owing to the intrinsic Lewis basicity (lone pair electrons) and Lewis acidity (vacant 3p orbital) on the divalent silicon atom, a number of small-molecule activation with either transient or isolable silylenes have been reported up to date. Such discoveries have brought attention to the application of silylenes as potential reagents for transformation of organic molecules in organic chemistry.[1d-f] For example, Woerpel et al. took advantage of the nature of silylenes to undergo reversible [1+2] cycloaddition with alkenes in the transfer reaction of di-*tert*-butylsilylene generated from its cyclohexene adduct **A** to various alkenes affording the corresponding silacyclopropanes **B**.[3] Okazaki and Tokitoh reported that two molecules of transient silylene Tbt(Mes)Si (**C**, Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Mes = 2,4,6-trimethylphenyl) cleave the C=C bond in benzene to yield a bis(silylene) adduct **D**.[4a] Our group also reported similar C=C bond cleavage of benzene derivatives using a isolable dialkylsilylene upon irradiation.[4b] Driess et al. found that cyclic diaminosilylene **E** activates the N–H bond of ammonia to yield triaminosilane **F**.[5] Recently, Aldridge et al. have reported the activation of dihydrogen with acyclic (amino)(boryl)silylene **G** to yield dihydridosilane **H**.[6] These results clearly indicate that judicious design of the substituents on the divalent silicon atom enables the activation of numerous organic molecules. However, application of silylenes as reagents for molecular transformation reactions other than silylation is scarce, due to the high tendency of silylenes to undergo cycloaddition or insertion reactions.[1]

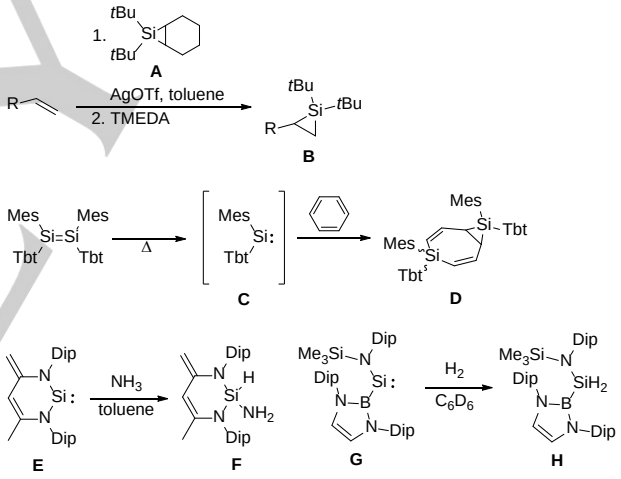


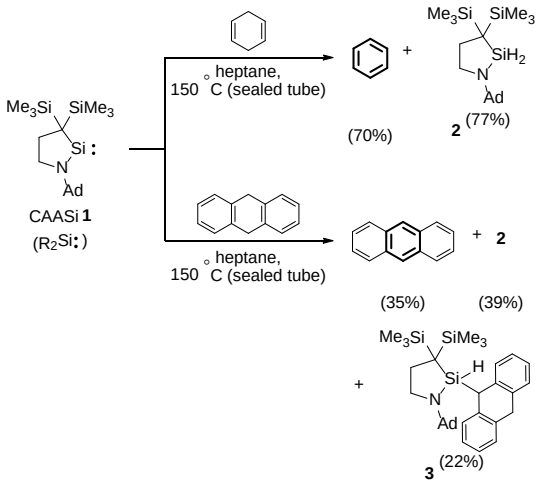
Chart 1. Examples of transformation reactions of organic molecules as well as small molecule activation reactions with silylenes (Mes: 2,4,6-trimethylphenyl, Dip: 2,6-diisopropylphenyl, Tbt: 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl).

Recently, we successfully synthesized the thermally stable cyclic (alkyl)(amino)silylene (CAASi) **1**, which is stable at temperatures up to 150 °C, and found that **1** underwent dehydrogenation of 1,4-cyclohexadiene (CHD) and 9,10-dihydroanthracene (DHA) to yield the corresponding aromatic compounds along with dihydrogenated CAASi (**2**) (Scheme 1).[7] This was the first intermolecular benzylic and allylic C–H bond activation with an isolable silylene.[8] Similar benzylic and allylic C–H bond activation with *N*,*N*'-diamidocarbenes have been reported for CHD and 9,10-dihydrophenanthrene by Bielawski's group.[9] By far, main group element compounds applicable as dehydrogenation reagents are limited, and such reagents with wide substrate generality should be crucial for improving cost-

[a] T. Koike, Dr. T. Kosai, Prof. Dr. T. Iwamoto
Department of Chemistry, Graduate School of Science,
Tohoku University, Aoba-ku, Sendai 980-8578 (Japan)
E-mail: takeaki.iwamoto@tohoku.ac.jp
Homepage: http://www.ssoc.chem.tohoku.ac.jp/en_index.html

Supporting information for this article and the ORCID identification number(s) for the author(s) of this article can be found under:

efficiency and to broaden the option of reagents accessible for synthesizing olefinic/aromatic molecules.



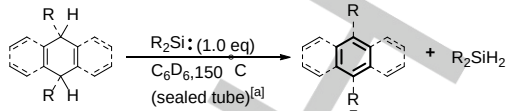
Scheme 1. Dehydrogenation of CHD and DHA with CAASi **1** (Ad = 1-adamantyl). The yields were determined by ^{1}H NMR spectroscopy.

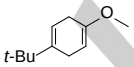
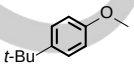
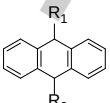
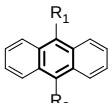
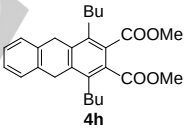
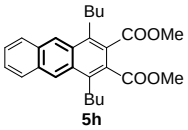
Herein, we report the successful dehydrogenation of a series of 1,4-dihydroaromatic compounds with CAASi **1**. We also examined the mechanistic details of the reaction by experimental and computational studies. These results indicate that **1** could be a 1,4-dehydrogenation reagent complementary to commonly used reagents represented by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and chloranils[10f,11] that have contributed to the synthesis of numerous polycyclic aromatic hydrocarbons (PAHs).[11h-j]

Results and Discussion

All 1,4-dehydrogenation reactions with CAASi **1** were conducted at 150 °C in [D_6]benzene placed in a sealed tube because reactions at lower temperature just elongate the completion of reaction (e.g. DHA: 240 h at 60 °C; 15 h at 150°C). CAASi **1** successfully dehydrogenated numerous CHD derivatives **4a**-**4h** (Table 1). Similar to the reaction with parent CHD, reaction with 1-heptadecyl substituted CHD (**4a**) provided heptadecylbenzene (**5a**) and dihydrogenated CAASi (**2**) with no sign of formation of C–H insertion product such as **3**. The reaction with **4b**, which has an electron-donating methoxy group and a *t*-butyl moiety also gave the corresponding anisole **5b** in good yield without formation of any conspicuous byproducts. The reaction with a CHD that has a fused five-membered ring (**4c**) gave **5c** with no sign of indene according to ^{1}H NMR spectroscopy. Reaction with 1,4-dihydronaphthalene (**4d**) afforded naphthalene (**5d**) and **2** in high yields. Compared to the reaction with DHA, C–H inserted product was not observed by ^{1}H NMR or mass spectroscopy. This is in good agreement with the previous result that allyl C–H inserted product of CHD is not observed as well.

Table 1. Dehydrogenation of CHD and DHA derivatives with CAASi **1**.

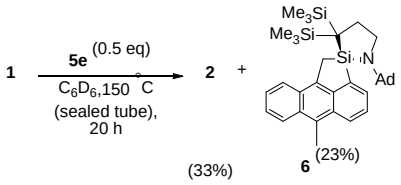


Substrate	Product	time	Product Yield[b] 5	2
 **4a**	 **5a**	16 h	81%	82%
 **4b**	 **5b**	37 h	72%	71%
 **4c**	 **5c**	42 h	53%	54%
 **4d**	 **5d**	16 h	83%	87%
 R_1 = R_2 = Me **4e**	 R_1 = R_2 = Me **5e**	20 h	30%[c]	63%[c]
R_1 = Et, R_2 = Me **4f**	R_1 = Et, R_2 = Me **5f**	72 h	22%	49%
R_1 = *i*-Pr, R_2 = Me **4g**	R_1 = *i*-Pr, R_2 = Me **5g**	100 days	0%[d]	24%[d]
 **4h**	 **5h**	16 h	21%[e]	21%[e]

[a] All reactions were conducted in a sealed tube heated at 150 °C. [b] Yields were calculated from ^{1}H NMR spectroscopy. [c] Silaacenapthene **6** (Scheme 2) was observed as the major byproduct in 13% yield. [d] CAASi **1** remained with unidentified byproducts. [e] Signs of unidentified byproducts were observed.

The reaction with 9,10-dialkylanthracenes **4e** and **4f** successfully yielded the corresponding anthracenes **5e**, **5f**, and dihydridosilane **2**, however, with large discrepancies in yields between the resulting anthracene derivatives and **2**.[12-13] While the yields of **2** for **4e** and **4f** were 63% and 49% respectively, anthracenes were only half of those numbers: 30% and 22%, respectively. Actually, in the reaction with **4e**, silaacenaphthene **6**[14] (Scheme 2) was generated in 13% yield as a major byproduct. As reaction with **1** and 9,10-dimethylanthracene (**5e**) yielded **6** as a major product together with formation of **2** (Scheme 2), **1** should dehydrogenate **4e** to provide **5e** and undergo further dehydrogenation of **5e** to yield **6**. This reaction is an unprecedented simultaneous activation of benzylic and aryl C–H bond with an isolable silylene. The reaction with isopropyl-substituted DHA **4g** proceeded very slowly to yield **2**, however, with no sign of formation of the corresponding anthracene **5g**.[15]

CAASi **1** remained even after 100 days of heating, implying that the benzyl hydrogen adjacent to the secondary carbon atom might be too sterically crowded for **1** to approach. Reaction with DHA with a carbonyl moiety (**4h**) afforded the corresponding anthracene **5h** and **2** in relatively low yields (21% and 21%) probably due to the numerous reaction sites such as ester groups available in **4h**.[16]



Scheme 2. Reaction of CAASi **1** with 9,10-dimethylanthracene (**5e**) (Ad = 1-adamantyl). The yields were determined by ^{1}H NMR spectroscopy.

To clarify the generality of the dehydrogenation reaction, reactions of 1,2-dihydroaromatic compounds with **1** were conducted. Although we carried out the reaction of 1,2-dihydronaphthalene (**7**) and tetralin (**8**) under the same conditions as **4d** (150 °C, [D_6]benzene, sealed tube), no reaction proceeded.

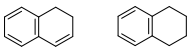
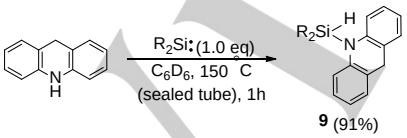


Chart 2. Substrates for attempted dehydrogenation with **1**.

Despite the success of dehydrogenation for 1,4-dihydroaromatic hydrocarbons with CAASi **1**, the reaction with 9,10-dihydroacridine, a heterocyclic hydroaromatic compound provided N–H insertion product **9** as the sole product in 91% yield rather than the corresponding aromatic compound, acridine (Scheme 3). Product **9** was characterized by multinuclear NMR spectroscopy and X-ray crystallographic analysis. Silylenes are known to insert into N–H bonds in ambient temperatures[1,5] and **1** likely to have followed the precedented reactivity of silylenes in prior to dehydrogenation.

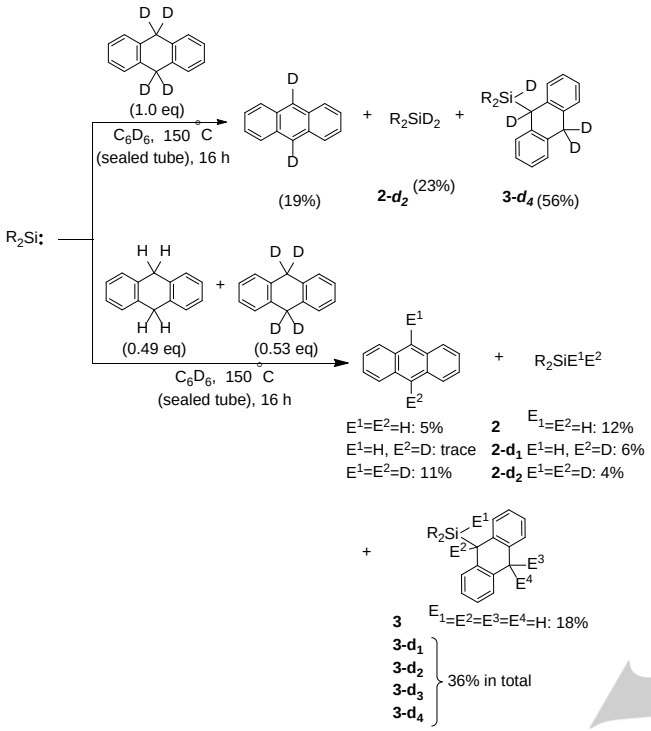


Scheme 3. Reaction of 9,10-dihydroacridine with CAASi **1**. The yield of **9** was determined by ^{1}H NMR spectroscopy.

Mechanism for the 1,4-dehydrogenation of **1** was investigated. Initially, we assumed that a C–H inserted product such as **3** is the intermediate of the reaction, because formation of **3** is concomitant to 1,4-dehydrogenation in the reaction with DHA.[7] Previously, Oestreich et al. reported the reaction of 1,4-cyclohexadienyl-substituted hydridosilane in the presence of a catalytic amount of $B(C_6F_5)_3$ to afford SiH_4 and benzene.[17] In this reaction, the borane abstracts the hydride at the 4-position in the cyclohexa-1,4-dienyl moiety and generates the benzene-coordinated silylium ion as an intermediate. Subsequently, the silylium ion is converted into hydridosilane by abstracting the hydride of $^-HB(C_6F_5)_3$. As **1** has a vacant 3p orbital that can work as a Lewis acid, **1** might as well behave the same manner as $B(C_6F_5)_3$ towards **3**. However, the reaction of **3** in the presence of **1** for 16 h (150 °C, [D_6]benzene, sealed tube) did not yield anthracene or **2**, indicating that **3** is not an intermediate in 1,4-dehydrogenation of DHA.

Consequently, 1,4-dehydrogenation was assumed to proceed via direct dehydrogenation of DHA by CAASi **1**. Initially, whether hydrogens other than the benzyl site are abstracted was clarified. Reaction with 9,9,10,10-tetradeuterated-9,10-dihydroanthracene (DHA-d_4) and **1** yielded anthracene-d_2 (19%), **2-*d*$_2$** (23%), and **3-*d*$_4$** (56%) as the major products with only trace sign of **2** and **2-*d*$_1$**, as well as no sign of anthracene or anthracene-d_1 judging from high-resolution mass and NMR spectroscopy (Figures S21-S22, S42-S44).[18] Therefore, 1,4-dehydrogenation should proceed simply via abstraction of benzyl hydrogens (Scheme 4). Then, crossover experiment was conducted to identify whether dehydrogenation proceeds via concerted or stepwise pathway. Reaction of **1** with an almost equimolar amount of DHA (0.49 eq) and DHA-d_4 (0.53 eq) afforded a mixture of anthracene (5%), anthracene-d_1 (trace), anthracene-d_2 (11%), dihydridosilanes **2** (12%), **2-*d*$_1$** (6%), **2-*d*$_2$** (4%), **3** (18%), **3-*d*$_1$**, **3-*d*$_2$** **3-*d*$_3$**, and **3-*d*$_4$** (**3-*d*$_{1\text{-}4}$** : 36% in total),[18] which were identified as follows. Anthracene and anthracene-d_2, which were also obtained by the reaction of **1** with 1.0 eq of DHA[7] or DHA-d_4 (Figures S21-S22), were identified by ^{1}H NMR spectroscopy (Figure S29). In addition to the ^{1}H NMR signals due to anthracene and anthracene-d_2, a quartet-like multiplet signal at around δ = 7.84-7.87 ppm (coupling constant = 3.2 Hz, 4H) which is assignable to the protons at the 1,4,5,8-position and a singlet signal at 8.21 ppm (1H) which is assignable to the proton at the 9-position, were observed (Figure S29) suggesting the formation of anthracene-d_1. Dihydridosilane **2** and its deuterated counterparts were identified by multinuclear NMR spectroscopy (Figures S29-S30) and high-resolution mass spectrometry (Figures S45-S50) as well as comparison of ^{1}H NMR spectrum with those observed during the reaction of **1** with 1.0 eq of DHA[7] or DHA-d_4 (Figures S21-S22) and with those of authentic sample of **2-*d*$_1$** prepared alternatively (Figures S23, S28). Moreover, the formation of C–H inserted products **3-*d*$_{1\text{-}4}$** was suggested by ^{1}H NMR integrals of the benzyl protons (Figure S29) and high-resolution mass spectroscopy (Figures S45-S50). Formation of silanes **3-*d*$_{1\text{-}3}$** implies that hydrogen and deuterium atoms at the benzyl positions are scrambling in the course of reaction. Thus, the C–H inserted products are more likely to be formed by a recombination of the hydridosilyl radical and 9,10-dihydro-9-anthryl radical intermediates after H–D scrambling rather than by a concerted pathway. This is in good agreement with the formation of the H–D scrambled monodeuteriosilane **2-*d*$_1$**. Overall results indicate that dehydrogenation of DHA by **1**

mainly proceeds via a stepwise pathway and more likely through a radical intermediate.



Scheme 4. Reactions of **1** with deuterated DHA (E = H or D). The yields were determined by ^{1}H NMR spectroscopy.

Entrapment of intermediates was attempted to identify whether the reaction proceeds via radical or ionic intermediate. However, we were not able to obtain distinct evidence of the intermediate by using radical scavengers due to the high reactivity of **1** itself. For example, reaction of **1** with TEMPO gave a complex mixture and reaction with di-*tert*-butyl peroxide and phenol gave O–O inserted product **10** and O–H inserted product **11**, respectively (Chart 3). Furthermore, we have measured EPR spectrum during the reaction of **1** with DHA in heptadecane at 150 °C, however, no significant EPR signals were observed. This implies that no paramagnetic species with a long lifespan exists in situ. These experimental results alone could not confirm whether the stepwise 1,4-dehydrogenation proceeds via ionic or radical pathway.

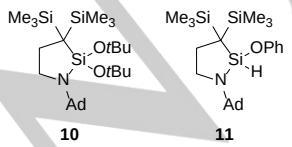
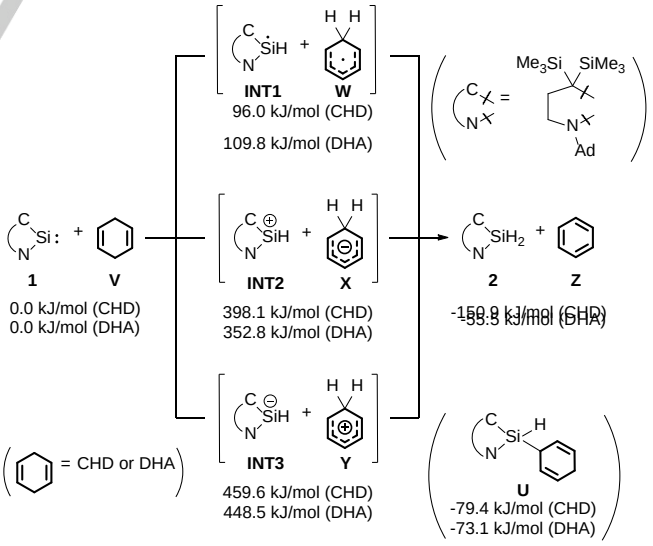


Chart 3. Products for the reaction of **1** with radical scavengers (Ad = 1-adamantyl).

We further examined the reaction routes theoretically using density functional theory (DFT) calculations on the (U)B3PW91-D3/6-31+G(d) level of theory for the reactions with CHD or DHA (Scheme 5) to discuss thoroughly with the experimental results. The results of the calculations were consistent with the experimental investigations. The reaction of **1** and cyclohexa-1,4-diene [**V**(CHD)] to form dihydridosilane **2** and benzene [**Z**(CHD)] is predicted to be considerably exergonic (Δ*G* (298.15 K) = −150.9 kJ/mol) at 298.15 K. The hydrogen abstraction of CAASi **1** from **V**(CHD) to form the corresponding silyl radical **INT1** and cyclohexadienyl radical [**W**(CHD)] is calculated to be moderately endergonic (Δ*G* = 96.0 kJ/mol). Conversely, the ionic pathway could be ruled out as the formation of the corresponding silyl cation **INT2** and cyclohexadienyl anion [**X**(CHD)] after the proton abstraction was found to be largely endergonic (Δ*G* = +398.1 kJ/mol), as well as the formation of silyl anion **INT3** and cyclohexadienyl cation [**Y**(CHD)] which is much more endergonic (Δ*G* = +459.6 kJ/mol).[19] The reaction of **1** with 9,10-dihydroanthracene [**V**(DHA)] providing **2** and anthracene [**Z**(DHA)] is also predicted to be moderately exergonic (Δ*G* = -55.5 kJ/mol) and similar radical pathway through the formation of **INT1** and 10-hydro-9-anthryl radical [**W**(DHA)] was calculated to be more favorable compared to the corresponding ionic pathways (Scheme 5). It should be noted that formation of the C–H insertion product **U**(DHA) (= **3**) (Δ*G* = -73.1 kJ/mol) is slightly more exergonic compared to formation of **2** and anthracene [**Z**(DHA)] (Δ*G* = −55.5 kJ/mol),[20] while formation of **2** and benzene [**Z**(CHD)] (Δ*G* = -150.9 kJ/mol) is substantially more exergonic compared to the formation of C–H insertion product **U**(CHD) (Δ*G* = −79.4 kJ/mol). The larger exergonicity for the formation of **2** and benzene [**Z**(CHD)] should be due to the formation of the aromatic ring and may be responsible for the selective formation of **2** and benzene.



Scheme 5. Free energy change (298.15 K) during hydrogen abstraction from CHD or DHA by **1** calculated at the (U)B3PW91-D3/6-31+G(d) level of theory (Solvent = heptane).

Although the competition of a concerted hydrogen abstraction or more complicated route could not be ruled out,[21] the experimental and calculation results are consistent with the notion that 1,4-dehydrogenation is likely to proceed via a stepwise hydrogen abstraction rather than a proton/hydride abstraction.

Conclusion

In conclusion, the scope and limitation of 1,4-dehydrogenation of CHD and DHA derivatives were explored and the observed vast generality of the reaction proved that CAASi **1** possesses the potential of regioselective hydrogen abstraction in the (double) allyl or benzyl site to form the corresponding aromatic hydrocarbons. Unexpected simultaneous activation of benzyl C–H bond and aromatic C–H bond was observed for the reaction with 9,10-dimethylanthracene to yield silaacenaphthene **6**. Moreover, careful investigation of the mechanism is consistent with the notion that dehydrogenation with **1** proceeds mainly via a stepwise hydrogen abstraction. However, the competition of a concerted hydrogen abstraction is not ruled out. The investigations in this study should pave new avenue for CAASis as a synthetic tool for aromatic compounds. Investigation of reaction conditions for activating more inert C–H bonds are further explored and should be reported in the near future.

Experimental Section

General Procedures

All reactions treating air-sensitive compounds were carried out under argon or nitrogen atmosphere using a high-vacuum line, standard Schlenk techniques, or a glovebox, as well as dry and oxygen-free solvents. The ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra were recorded on a Bruker Avance III 500 FT NMR spectrometer. The ^{1}H and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C of the solvents; [D$_6$]benzene (^{1}H δ 7.16 and ^{13}C δ 128.0).[22] The ^{29}Si NMR chemical shifts were relative to Me_4Si in ppm. Sampling of air-sensitive compounds was carried out using a VAC NEXUS 100027 type glovebox. Mass spectra were recorded on a JEOL JMS-Q1050 spectrometer or a Bruker Daltonics SolariX 9.4T spectrometer. X-ray analysis was carried out using a Bruker AXS APEXII CCD diffractometer. Recycling preparative HPLC using dry toluene as an eluent was performed at 5.0 mL/min rate using a Japan Analytical Industry Co., LC-9201 equipped with an JAIGEL-H column (Japan Analytical Industry Co., φ 20 mm × 600 mm).

Materials

Dry and degassed benzene, hexane, and THF were prepared using a VAC 103991 solvent purifier. Acetone, acetonitrile, and [D$_6$]benzene were degassed and dried by molecular sieves MS 4A. Heptane was distilled over lithium aluminium hydride and degassed prior to use. Boron tribromide in hexane solution, 1,4-cyclohexadiene, 9,10-dihydroacridine, 9,10-dihydroanthracene, 1,4-dihydronaphthalene, 9,10-dimethylanthracene, di-*tert*-butyl peroxide, ethanol, ferrocene, 10% Pd/C, phenol, sodium borodeuteride, and 1,3,5-tri-*tert*-butylbenzene were commercially available and used without further purification. N-(1-Adamantyl)-3,3-bis(trimethylsilyl)-1-aza-2-silacyclopentane-2,2-diyl [cyclic (alkyl)(amino)silylene (CAASi), **1**],[7] 1-heptadecylcyclohexa-1,4-diene,[23] 1-(*tert*-butyl)-4-methoxycyclohexa-1,4-diene,[23] 2,3,4,7-tetrahydro-1*H*-indene,[23] 9,10-dimethyl-9,10-dihydroanthracene,[24] 9-ethyl-10-methyl-9,10-dihydroanthracene,[24] 9-isopropyl-10-methyl-9,10-dihydroanthracene,[24] and 1,4-dibutyl-2,3-bis(methoxycarbonyl)-9,10-dihydroanthracene[25] were prepared according to the published procedures. H_2 gas was prepared by a YMC hydrogen generator YH-500 and preserved in a YMC MH canister YMH-60LP prior to use.

General Procedure for Dehydrogenation of CHD and DHA Derivatives with 1.

All dehydrogenation reactions were carried out in a flame-sealed tube unless otherwise noted. In a sealed tube, a mixture of **1** and CHD or DHA derivative (1.0 eq) in [D$_6$]benzene (0.45 mL) was placed. Heating the sealed tube at 150 ºC gave the corresponding aromatic compound and dihydridosilane **2**. The yields of the products were determined using ferrocene or 1,3,5-tri-*tert*-butylbenzene as an internal standard. Formation of the aromatic compound and **2** was confirmed by the comparison of the NMR spectra with those of the authentic samples. For details of the reaction with each substrate, see Supporting Information.

Reaction of 1 with 9,10-dimethylanthracene (5e)

In a sealed tube, a mixture of **1** (23 mg, 0.063 mmol) and 9,10-dimethylanthracene (6.7 mg, 0.0324 mmol) in [D$_6$]benzene (0.45 mL) was placed. Heating the mixture at 150 ºC for 20 h gave dihydridosilane **2** and silaacenaphthene **6** in 33% and 23% yields, respectively. Yields were determined by ^{1}H NMR spectrum using ferrocene as an internal standard. Formation of **2** and **6** were confirmed by the comparison of the NMR spectra with those of the authentic samples. Isolation of **6**: In a sealed tube, a mixture of **1** (99 mg, 0.27 mmol) and 9,10-dimethylanthracene (29 mg, 0.14 mmol) in heptane (1.0 mL) was placed. The mixture was heated at 150 ºC for 18 hours. After the mixture was cooled to room temperature, the mixture was concentrated and dissolved in toluene (2.0 mL). After separation with HPLC (eluent: toluene), the resulting yellow oil was recrystallized from hexane at –30 ºC to afford yellow crystals. Washing the crystals with hexane (0.2 mL) three times afforded analytically pure **6** (7.6 mg, 0.013 mmol) in 5% yield. **6**: yellow powder; m.p. 162°C (decomposition); ^{1}H NMR (500 MHz, [D$_6$]benzene, 24 °C, TMS) δ = –0.16 (s, 9H, Si*Me*$_3$), 0.42 (s, 9H, Si*Me*$_3$), 1.23 (brs, 6H, Ad), 1.66 (brs, 3H, Ad), 1.72-1.81 (m, 6H, Ad), 2.22-2.27 (dd, ^{2}J(H,H) = 13 Hz, ^{3}J(H,H) = 4.0 Hz, 1H, C*H*H), 2.44-2.48 (m, 1H, CH*H*), 2.73 (s, 3H, C*H*$_3$), 2.99-3.04 (m, 1H, C*H*H), 3.10 (d, ^{2}J(H,H) = 28 Hz, 1H, CH*H*), 3.14 (d, ^{2}J(H,H) = 28 Hz, 1H, C*H*H), 3.22-3.26 (m, 1H, CH*H*), 7.36-7.41 (m, 2H, Ar*H*), 7.49 (dd, ^{3}J(H,H) = 8.8 Hz, ^{3}J(H,H) = 6.3Hz, 1H, Ar*H*), 7.92 (d, ^{3}J(H,H) = 6.2 Hz,1H, Ar*H*), 8.11 (d, ^{3}J(H,H) = 8.8 Hz, 1H, Ar*H*), 8.15 (d, ^{3}J(H,H) = 8.2 Hz, 1H, Ar*H*), 8.41 (d, ^{3}J(H,H) = 8.4 Hz, 1H, Ar*H*); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]benzene, 25 °C, TMS) δ = 1.2 (*C*H$_3$), 2.9 (*C*H$_3$), 9.0 (*C*), 13.6 (*C*H$_3$), 19.1 (*C*H$_2$), 30.1 (*C*H), 30.8 (*C*H$_2$), 36.9 (*C*H$_2$), 43.6 (*C*H$_2$), 44.4 (*C*H$_2$), 53.2 (*C*), 125.0 (*C*H), 125.3 (*C*H), 125.8 (*C*H), 126.0 (*C*H), 126.1 (*C*H), 126.5 (*C*H), 128.7 (*C*), 129.5 (*C*), 130.9 (*C*), 131.3 (*C*), 132.3 (*C*H), 135.8 (*C*), 140.1 (*C*), 144.1 (C); ^{29}Si{^{1}H} NMR (99 MHz, [D$_6$]benzene, 24 °C, TMS) δ = 1.7 (*Si*Me$_3$), 3.0 (*Si*Me$_3$), 10.9 (alkyl)(amino)*Si*); HRMS (APCI): *m/z*: calcd for $C_{35}H_{49}NSi_3$, 567.3167 [M$^+$]; found, 567.3167; elemental analysis calcd (%) for $C_{35}H_{49}NSi_3$: C, 74.01; H, 8.70; N, 2.47%. found: C, 74.28; H, 8.77; N, 2.49%.

Reaction of 1 with 9,10-Dihydroacridine

In a sealed tube, a mixture of **1** (12 mg, 0.033 mmol) and 9,10-dihydroacridine (6.0 mg, 0.033 mmol) in [D$_6$]benzene (0.45 mL) was placed. Heating the mixture at 150 ºC for 1 hour gave diaminosilane **9** in

91% yield as a sole product. Yield of **9** was determined by ^{1}H NMR spectrum using ferrocene as an internal standard. Formation of **9** was confirmed by the comparison of the NMR spectra with that of the authentic sample. Isolation of **9**: In a sealed tube, a mixture of **1** (50 mg, 0.14 mmol) and 9,10-dihydroacridine (25 mg, 0.14 mmol) in heptane (0.40 mL) was placed. The mixture was heated at 150 ºC for 1 hour. After the volatile was removed in vacuo, recrystallization from hexane/toluene (10/1) solution at –30 ºC gave colorless crystals of **9** (45 mg, 0.083 mmol) in 60 % yield. **9**: colorless crystals; m.p. 164-166 °C; ^{1}H NMR (500 MHz, [D$_6$]benzene, 24 ºC, TMS) δ = 0.21 (s, 9H, Si*Me$_3$*), 0.34 (s, 9H, Si*Me$_3$*), 1.35 (d, ^2J(H,H) = 12 Hz, 3H, Ad), 1.43 (d, ^2J(H,H) = 12 Hz, 3H, Ad), 1.52 (d, ^2J(H,H) = 12 Hz, 3H, Ad), 1.69 (d, ^2J(H,H) = 12 Hz, 3H, Ad), 1.79 (brs, 3H, Ad), 2.12-2.16 (m, 1H, C*H*H), 2.43-2.44 (m, 1H, CH*H*), 2.88-2.91 (m,1H, C*H*H), 3.10 (t, ^3J (H,H) = 8.7 Hz, 1H, CH*H*), 3.64 (d, ^2J(H,H) = 17 Hz, 1H, C*H*H), 3.86 (d, ^2J(H,H) = 17 Hz, 1H, CH*H*), 5.58 (s with satellites (^{29}Si), ^1J(H,Si) = 232 Hz, 1H, Si*H*), 6.92-6.96 (m, 2H, Ar*H*), 7.02-7.05 (m, 2H, Ar*H*), 7.09-7.12 (m, 1H, Ar*H*), 7.13-7.16 (m, 1H, Ar*H*), 7.19-7.21 (m, 1H, Ar*H*), 7.23-7.25 (m, 1H, Ar*H*); ^{13}C{^{1}H} NMR (126 MHz, [D$_6$]benzene, 24 ºC, TMS) δ = 1.7 (*C*H$_3$), 2.1 (*C*H$_3$), 7.7 (*C*), 29.5 (*C*H$_2$), 30.2 (*C*H), 33.8 (*C*H$_2$), 37.0 (*C*H$_2$), 42.3 (*C*H$_2$), 42.6 (*C*H$_2$), 52.9 (*C*), 120.4 (*C*H), 122.3 (*C*H), 122.5 (*C*H), 122.9 (*C*H), 125.6 (*C*H), 126.3 (*C*H), 128.3 (*C*H), 128.4 (*C*H), 128.6 (*C*), 128.7 (*C*), 143.1 (*C*), 144.1 (*C*); ^{29}Si{^{1}H} NMR (99 MHz, [D$_6$]benzene, 24 ºC, TMS) δ = –13.6 ((alkyl)(amino)*Si*), 2.4 (*Si*Me$_3$), 4.5 (*Si*Me$_3$); MS (EI, 70 eV): *m*/*z* (%): 544 (100) [M$^+$], 529 (18) [M$^+$–Me]; elemental analysis calcd (%) for $C_{32}H_{48}N_2Si_3$: C, 70.52; H, 8.88; N, 5.14%. found: C, 70.63; H, 8.90; N, 5.42%.

Preparation of DHA-*d$_4$*

DHA-*d$_4$* was synthesized by an optimized procedure of the method reported earlier.[26] 9,10-Dihydroanthracene (180 mg, 1.00 mmol) and 10% Pd/C (10 wt% of 9,10-Dihydroanthracene) in D$_2$O/THF=1:2 (1.5 mL) were stirred at room temperature in a sealed Schlenk tube (10 mL) filled with H_2 gas. After 4 days, the mixture was diluted with THF (4.0 mL) and filtered using a disposable PTFE filter (pore size: 0.45 μm) to remove the catalyst. After removing the volatile in vacuo, the procedure mentioned above was repeated two more times. Resulting colorless crystals were recrystallized from ethanol at –30 ºC followed by Kugel-rohr distillation (60-90 ºC, 2.0 Pa), to give colorless crystals in 61% yield (9,10-Dihydroanthracene-*d$_4$*: 98% D content). The D content was calculated using the integral ratio of ^{1}H NMR spectrum. Formation of DHA-*d$_4$* was confirmed by the comparison of the NMR spectra with those reported in the literature.[27]

Synthesis of Dihydridosilane 2-*d$_1$*

In a Schlenk flask (50 mL), BBr_3 (1.0 M hexane solution, 0.14 mL, 0.15 mmol) was added to a mixture of dihydridosilane **2** (160 mg, 0.43 mmol) in hexane (10 mL). The resulting mixture was stirred for 24 h at room temperature. After the volatile was removed in vacuo, the resulting oil was recrystallized from hexane at –30 ºC for 2 weeks to give bromohydridosilane as colorless crystals. Without further purification, the obtained bromohydridosilane (23 mg, 0.052 mmol) was added into a mixture of $NaBD_4$ (D content >95%) (8.0 mg, 0.19 mmol) and CH_3CN (0.40 ml) placed in a screw top vial equipped with a magnetic stir bar and stirred for 17 h. After removing the volatile in vacuo, the crude mixture was diluted with hexane (3.0 mL) and filtered to remove insoluble materials. Recrystallization from acetone at –30 ºC gave **2-*d$_1$*** (13 mg, 0.034 mmol) in 8% yield. **2-*d$_1$***: colorless crystals; m.p. 69-71 °C; ^{1}H NMR (500 MHz, [D$_6$]benzene, 22 °C, TMS) δ = 0.20 (s, 18H, Si*Me$_3$*), 1.51-1.59 (m, 6H, Ad), 1.79-1.84 (m, 6H, Ad), 1.95 (brs, 3H, Ad), 2.00 (t, ^3J(H,H) = 6.5 Hz, 2H, C*H$_2$*), 2.83 (t, ^3J(H,H) = 6.5 Hz, 2H, C*H$_2$*), 4.94 (t, ^2J(H,D) = 3.2 Hz, 1H, Si*H*D); ^{2}H NMR (76.7 MHz, [D$_6$]benzene, 22 ºC) δ = 4.95 (d, ^2J(D,H) =3.3 Hz 1D, SiH*D*); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]benzene, 23 °C, TMS) δ = 0.8 (*C*H$_3$), 2.9 (*C*), 29.5 (*C*H$_2$), 30.3 (*C*H), 37.1 (*C*H$_2$), 43.2 (*C*H$_2$), 44.2 (*C*H$_2$), 51.7 (*C*); ^{29}Si{^{1}H} NMR (99 MHz, [D$_6$] benzene, 23 °C, TMS) δ = –26.3 (t, ^1J(Si,D) = 31.5 Hz, *Si*HD), 3.8 (*Si*Me$_3$); HRMS (APCI): *m/z*: calcd for $C_{19}H_{38}DNSi_3$, 366.2448 [M$^+$]; found, 366.2447; elemental analysis calcd (%) for $C_{19}H_{38}DNSi_3$: C, 62.22; H, 10.99; N, 3.82%. found: C, 61.84; H, 10.80; N, 3.72%.

Reaction of 1 with DHA-*d$_4$*

In a sealed tube, a mixture of **1** (65 mg, 0.18 mmol) and DHA-*d$_4$* (33 mg, 0.18 mmol) in [D$_6$]benzene (0.45 mL) was placed. The mixture was heated at 150 ºC for 16 hours. Anthracene-*d$_2$*, dihydridosilane **2-*d$_2$***, and benzylsilane **3-*d$_4$*** were obtained in 19%, 23%, and 56% yields respectively (Figure S21). Yields were determined by ^{1}H NMR spectrum using ferrocene as an internal standard. Formation of **2-*d$_2$***, anthracene-*d$_2$*, and **3-*d$_4$*** were confirmed by the comparison of the NMR spectra with those observed in the reaction of **1** with DHA and HRMS (APCI) spectra of the reaction mixture. HRMS (APCI): *m/z*: calcd for $C_{19}H_{37}D_2NSi_3$, 367.2510 [M$^+$]; found, 367.2510. calcd for $C_{33}H_{45}D_4NSi_3$ 548.3497 [M$^+$+H]; found, 548.3498. **2-*d$_2$***: ^{29}Si{^{1}H} NMR (99 MHz, [D$_6$]benzene, 25 ºC, TMS) δ = 3.8 (*Si*Me$_3$), –26.5 (q, ^1J(Si,D) = 30.7 Hz, *Si*D$_2$). **3-*d$_4$***: ^{29}Si{^{1}H} NMR (99 MHz, [D$_6$]benzene, 25 ºC, TMS) δ = 4.3 (*Si*Me$_3$), 2.2 (*Si*Me$_3$), 1.8 (t, ^1J(Si,D) = 32.7 Hz, (alkyl)(amino)D*Si*).

Crossover Experiment for the Reaction of Silylene 1 with DHA

In a sealed tube, a mixture of **1** (100 mg, 0.27 mmol), DHA (24 mg, 0.13 mmol), and DHA-*d$_4$* (28 mg, 0.15 mmol) in [D$_6$]benzene (0.45 mL) was placed. Heating the mixture at 150 ºC for 16 hours gave a mixture of anthracene (5%), anthracene-*d$_1$* (trace), anthracene-*d$_2$* (11%), dihydridosilanes **2** (12%), **2-*d$_1$*** (6%), **2-*d$_2$*** (4%), benzylsilanes **3** (18%), and **3-*d$_{1\text{-}4}$*** (36% in total) (Figure S29). Formation of the products was confirmed by the comparison with the NMR spectra of the reaction of **1** with DHA, reaction of **1** with DHA-*d$_4$*, pure **2-*d$_1$***, and HRMS (APCI) spectroscopy of the reaction mixture. HRMS (APCI): *m/z*: calcd for $C_{19}H_{39}NSi_3$ (**2**), 365.2385 [M$^+$]; found, 365.2385; calcd for $C_{19}H_{38}DNSi_3$ (**2-*d$_1$***), 366.2448 [M$^+$]; found, 366.2447; calcd for $C_{19}H_{37}D_2NSi_3$(**2-*d$_2$***), 367.2510 [M$^+$]; found, 367.2510; calcd for $C_{33}H_{49}NSi_3$ (**3**), 544.3246 [M$^+$+H]; found, 544.3251; calcd for $C_{33}H_{48}D_1NSi_3$ (**3-*d$_1$***), 545.3308 [M$^+$+H]; found, 545.3310; calcd for $C_{33}H_{47}D_2NSi_3$ (**3-*d$_2$***), 546.3371 [M$^+$+H]; found, 546.3373; calcd for $C_{33}H_{46}D_3NSi_3$ (**3-*d$_3$***), 547.3434 [M$^+$+H]; found, 547.3435; calcd for $C_{33}H_{45}D_4NSi_3$ (**3-*d$_4$***), 548.3497 [M$^+$+H]; found, 548.3498.

Reaction of 1 with di-*tert*-butyl peroxide

In a Schlenk flask (50 mL), a mixture of **1** (49 mg, 0.14 mmol) and di-*tert*-butyl peroxide (22 mg, 0.15 mmol), in benzene (0.3 mL) was placed and stirred for 10 min. at room temperature. After the volatile was removed in vacuo, the resulting white solid was recrystallized from hexane at –30 ºC to give di-*tert*-butoxysilane **10** (47 mg, 0.092 mmol) as colorless crystals in 67% yield. **10**: colorless crystals; m.p. 161 °C; ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C, TMS) δ = 0.37 (s, 18H, Si*Me$_3$*), 1.46 (s, 18H, *t*Bu), 1.60-1.68 (m, 6H, Ad), 2.00-2.08 (m, 9H + 2H, Ad + C*H$_2$*), 2.84 (t, ^3J(H,H) = 6.5 Hz, 2H, C*H$_2$*); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]benzene, 25 °C, TMS) δ = 3.3 (*C*H$_3$), 6.8 (*C*), 27.4 (*C*H$_2$), 30.5 (*C*H), 32.7 (*C*H$_3$), 37.4 (*C*H$_2$), 42.1 (*C*H$_2$), 43.3 (*C*H$_2$), 53.2 (*C*), 74.2 (*C*); ^{29}Si{^{1}H} NMR (99 MHz, [D$_6$] benzene, 25 °C, TMS) δ = –50.5 ((alkyl)(amino)*Si*), 2.2 (*Si*Me$_3$); MS (EI, 70 eV): *m*/*z* (%): 509 (100) [M$^+$], 452 (62) [M$^+$–*t*Bu]; elemental analysis calcd (%) for $C_{27}H_{55}NO_2Si_3$: C, 63.59; H, 10.87; N, 2.75%. found: C, 63.72; H, 10.94; N, 2.99%.

Reaction of 1 with phenol

In a Schlenk flask (50 mL), a mixture of **1** (52 mg, 0.14 mmol) and phenol (14 mg, 0.14 mmol) in benzene (0.3 mL) was placed and stirred for 10 min. at room temperature. After the volatile was removed in vacuo, the resulting white solid was recrystallized from hexane at –30 ºC to give phenoxysilane **11** (39 mg, 0.086 mmol) in 60% yield. **11**: a white powder; m.p. 72 °C; ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C, TMS) δ = 0.25 (s, 9H, Si*Me*$_3$), 0.28 (s, 9H, Si*Me*$_3$), 1.44-1.51 (m, 6H, Ad), 1.73-1.81 (m, 6H, Ad), 1.88 (brs, 3H, Ad), 2.00-2.06 (m, 1H, C*H*H), 2.14-2.19 (m, 1H, CH*H*), 2.85-2.90 (m, 1H, C*H*H), 3.04-3.09 (m, 1H, CH*H*), 5.57 (s with satellites (^{29}Si), ^{1}J(H,Si) = 236 Hz, 1H, Si*H*), 6.83 (tt, ^{3}J(H,H) = 7.2 Hz, ^{4}J(H,H) = 1.2 Hz, 1H, Ar*H*), 7.06-7.09 (m, 2H, Ar*H*), 7.10-7.15 (m, 2H, Ar*H*); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]benzene, 25 °C, TMS) δ = 1.2 (*C*H$_3$), 1.7 (*C*H$_3$), 6.9 (*C*), 28.6 (*C*H$_2$), 30.2 (*C*H), 37.0 (*C*H$_2$), 43.1 (*C*H$_2$), 43.7 (*C*H$_2$), 51.9 (*C*), 120.1 (*C*H), 121.9 (*C*H), 130.0 (*C*H), 155.7 (*C*); ^{29}Si{^{1}H} NMR (99 MHz, [D$_6$] benzene, 25 °C, TMS) δ = –14.5 ((alkyl)(amino)*Si*), 3.0 (*Si*Me$_3$), 3.1 (*Si*Me$_3$); MS (EI, 70 eV): *m*/*z* (%): 457 (100) [M$^+$], 442 (17) [M$^+$–Me]; elemental analysis calcd (%) for $C_{25}H_{43}NOSi_3$: C, 65.58; H, 9.47; N, 3.06%. found: C, 65.43; H, 9.43; N, 3.03%.

X-ray Analysis

Single crystals suitable for X-ray diffraction study were obtained by recrystallization in an inert atmosphere from toluene/hexane (1:10) for **9** at −30 °C. The single crystals for data collection coated by Apiezon® grease mounted on the glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer. X-ray diffraction data were collected on a Bruker AXS APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS[28] and the structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data (SHELXL-2014).[29] Molecular structure was analyzed by Yadokari-XG software.[30]

Crystal data of 9 (100 K) (CCCDC-1903066): $C_{32}H_{48}N_2Si_3$; Fw 545.01; triclinic; space group *P*-1 (#2), *a* = 10.7123(3) Å, *b* = 18.7257(5) Å, *c* = 20.1677(5) Å, α = 63.2270(10)°, β = 87.3810(10)°, γ = 89.6140(10)°, *V* = 3607.65(17) Å^3, *Z* = 4, *R*1 = 0.0369 ($I > 2\sigma(I)$), w*R*2 = 0.0987 (all data), GOF = 1.018.

Computational Study

All theoretical calculations were performed using Gaussian 09[31] and GRRM14[32] programs. Geometry optimization and frequency analysis for all compounds shown in Scheme 5 were performed at the (U)B3PW91-D3/6-31+G(d) level of theory. The concerted reaction routes calculated at the B3PW91-D3/6-31G(d) level of theory were summarized in the Supporting Information. The atomic coordinates for the optimized structure were summarized in the Supporting Information. Imaginary frequencies were not found in any of the optimized structures.

Acknowledgements

This work was supported by MEXT KAKENHI grant JP24109004 (T.I.) (Grant-in-Aid for Scientific Research on Innovative Areas “Stimuli-responsive Chemical Species”) and the JSPS KAKENHI grant JP15K13634 (T.I.). The authors thank Prof. Yujiro Hayashi (Tohoku University) for helpful advices for the synthesis of the deuterated substrate and Prof. Martin Oestreich (Technische Universität Berlin) for helpful discussion on the reaction mechanism.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: aromatic compound • C–H activation • dehydrogenation • main-group element • silylene

[1] For comprehensive reviews on silylenes, see: a) P. P. Gaspar, R. West, *The Chemistry of Organic Silicon Compounds*, Vol. 2, (Eds.: Z. Rappoport, Y. Apeloig,), Wiley, Chichester, **1998**, 2463-2568; b) Y. Mizuhata, T. Sasamori, N. Tokitoh, *Chem. Rev.* **2009**, *109*, 3479-3511; c) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111*, 354-396. For seminal studies on reaction of silylenes with small molecules, see also: d) B. Blom, M. Driess, *Struct. Bonding* **2014**, *156*, 85-123; e) B. Blom, D. Gallego, M. Driess, *Inorg. Chem. Front.* **2014**, *1*, 134-148; f) S. Inoue, *Discovering the Future of Molecular Sciences* (Ed.: B. Pignataro), Wiley-VCH, Weinheim, 2014, 243-273.

[2] For studies on disilene ($R_2Si=SiR_2$) synthesis from silylenes, see: a) S. Ishida, T. Iwamoto, C. Kabuto, M. Kira, *Nature* **2003**, *421*, 725-727; b) T. Kosai, S. Ishida, T. Iwamoto, *J. Am. Chem. Soc.* **2017**, *139*, 99-102; c) T. Kosai, S. Ishida, T. Iwamoto, *Dalton Trans.* **2017**, *46*, 11271-11281; d) T. Kosai, T. Iwamoto, *J. Am. Chem. Soc.* **2017,** *139*, 18146-18149; e) T. Kosai, T. Iwamoto, *Chem. Eur. J.* **2018**, *24*, 7774-7780. For studies on silanone ($R_2Si=O$) synthesis from silylenes, see: f) Y. Xiong, S. Yao, M. Driess, *J. Am. Chem. Soc.* **2009**, *131*, 7562-7563; g) Y. Xiong, S. Yao, R. Müller ,M. Kaupp, M. Driess, *Nat. Chem.* **2010**, *2*, 577-580; h) D. Wendel, D. Reiter, A. Porzelt, P. J. Altmann, S. Inoue, B. Rieger, *J. Am. Chem. Soc.* **2017**, *139*, 17193-17198; i) D. C. H. Do, A. V. Protchenko, M. Á. Fuentes, J. Hicks, E. L. Kolychev, P. Vasko, S. Aldridge, *Angew. Chem. Int. Ed.* **2018**, *57*, 13907-13911; *Angew. Chem.* **2018**, *130*, 14103-14107. For studies on silaimine ($R_2Si=NR$) synthesis from silylenes, see: j) M. Denk, R. Hayashi, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 10813-10814; k) S. Inoue, K. Leszczyńska, *Angew. Chem. Int. Ed.* **2012**, *51,* 8589-8593; *Angew. Chem.* **2012**, *124*, 8717-8721; l) P. Samuel, R. Azhakar, R. Ghadwal, S. Sen, H. Roesky, M. Granitzka, J. Matussek, R. Herbst-Irmer, D. Stalke, *Inorg. Chem.* **2012**, *51*, 11049-11054; m) H. Cui, C. Cu, *Dalton Trans.* **2015**, *44*, 20326-20329. For studies on silaketenimine ($R_2Si=C=NR$) synthesis from a silylene, see: n) T. Abe, T. Iwamoto, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2006**, *128*, 4228-4229. For studies on $R_2Si=X$ compounds (X = S, Se, Te) synthesis from silylenes, see: o) H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, M. Goto, *J. Am. Chem. Soc.* **1998**, 120, 11096-11105; p) N. Tokitoh, T. Sadahiro, K. Hatano, T. Sasaki, N. Takeada, R. Okazaki, *Chem. Lett.* **2002**, 31, 34-35; q) T. Iwamoto, K. Sato, S. Ishida, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **2006**, *128*, 16914-16920; r) S. Kostina, W. Leigh, *J. Am. Chem. Soc.* **2011**, 133, 4377-4388.

[3] For some studies on silylene transfer reactions, see: a) T. G. Driver, A. K. Franz, K. A. Woerpel, *J. Am. Chem. Soc.* **2002**, *124*, 6524-6525; b) J. Ćiraković, T. G. Driver, K. A. Woerpel, *J. Am. Chem. Soc.* **2002**, *124*, 9370-9371; c) T. G. Driver, K. A. Woerpel, *J. Am. Chem. Soc.* **2003**, *125*, 10659-10663.

[4] a) H. Suzuki, N. Tokitoh, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11572-11573; b) M. Kira, S. Ishida, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **2002**, *124*, 3830-3831.

[5] A. Jana, C. Schulzke, H. W. Roesky, *J. Am. Chem. Soc.* **2009**, *131*, 4600-4601.

[6] A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford, S. Aldridge, *J. Am. Chem. Soc.* **2012**, *134*, 6500-6503.

[7] T. Kosai, S. Ishida, T. Iwamoto, *Angew. Chem. Int. Ed.* **2016**, *55*, 15554-15558; *Angew. Chem.* **2016**, *128*, 15783-15787.

[8] Power and Jones reported the C–H activation of several heavy alkenes such as 1,3-/1,4-cyclohexadiene by dimetallynes (M= Ge, Sn) and transformed them into benzene in low yield: for most of the substrates, cycloaddition proceeded as the major reaction. For details, see: a) O. T. Summerscales, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2011**,

133, 11960-11963; b) O. T. Summerscales, C. A. Caputo, C. E. Knapp, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2012**, *134*, 14595-14603; c) T. J. Hadlington, J. Li, M. Hermann, A. Davey, G. Frenking, C. Jones, *Organometallics* **2015**, *34*, 3175-3185.

[9] J. P. Moerdyk, C. W. Bielawski, *Chem. Eur. J.* **2013**, *19*, 14773-14776.

[10] For studies on dehydrogenation, see: a) R. D. Haworth, *J. Chem. Soc.* **1932**, 1125-1133; b) R. P. Linstead, A. F. Millidge, S. L. Thomas, A. L. Walpole, *J. Chem. Soc.* **1937**, 1146-1157; c) L. F. Fieser, W. S. Johnson, *J. Am. Chem. Soc.* **1939**, *61*, 1647-1654; d) R. G. Harvey, L. Arzadon, J. Grant, K. Urberg, *J. Am. Chem. Soc.* **1969**, *91*, 4535-4541; e) R. G. Harvey, H. Cho, *J. Am. Chem. Soc.* **1974**, *96*, 2434-2441; f) P. P. Fu, R. G. Harvey, *Chem. Rev.* **1978**, *78*, 317-361.

[11] For general studies on DDQ and chloranils, see: a) *The Chemistry of Quinonoid Compounds,* Vol. 1, (Eds.: S. Patai, Z. Rappoport), A. Skancke, P. N. Skancke; b) E A. Braude, A. G. Brook, R. P. Linstead, *J. Chem. Soc.* **1954**, 3569-3574; c) E. A. Braude, L. M. Jackman, R. P. Linstead, G. Lowe *J. Chem. Soc.* **1960**, 3123-3132. For mechanistic studies on C–H bond activation with DDQ, see: d) B. M. Trost *J. Am. Chem. Soc.* **1967**, *89*, 1847-1851; e) O. R. Shehab, A. M. Mansour, *J. Mol. Struct.* **2013**, *1047*, 121-135; f) A. K. Turek, D. J. Hardee, A. M. Ullman, D. G. Nocera, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **2016**, *55*, 539-544; *Angew. Chem.* **2016**, *128*, 549-554; g) C. A. Morales-Rivera, P. E. Floreancig, P. Liu *J. Am. Chem. Soc.* **2017**, *139*, 17935-17944; For examples of DDQ applied for PAH synthesis, see: h) L. Zhai, R. Shukla, R. Rathore *Org. Lett.* **2009**, *11*, 3474–3477; i) S. R. Bheemireddy, P. C. Ubaldo, P. W. Rose, A. D. Finke, J. Zhuang, L. Wang, K. N. Plunkett, *Angew. Chem. Int. Ed.* **2015**, *54*, 15762-15766; *Angew. Chem.* **2015**, *127*, 15988-15992; j) Q. Wang, T. Y. Gopalakrishna, H. Phan, T. S. Herng, S. Dong, J. Ding, C. Chi, *Angew. Chem. Int. Ed.* **2017**, *56*, 11415-11419; *Angew. Chem.* **2017**, *129*, 11573-11577.

[12] a) P. P. Fu, R. G. Harvey, J. W. Paschal, P. W. Rabideau, *J. Am. Chem. Soc.* **1975**, *97*, 1145–1153; b) J. L. Mooney, Z. Marcinow, P. W. Rabideau, *J. Org. Chem.* **1986**, *51*, 527-532.

[13] 9,10-Dimethyl-DHA **4e** (9-methyl-MDHA, *cis*: *trans*= 95:5), 9-ethyl-MDHA **4f** (*cis*: *trans*= 5:1), 9-isopropyl-MDHA **4g** (*cis*: *trans*= 1:2) were synthesized in accordance with the reported procedures by Rabideau`s group. Molar ratio of *cis* and *trans* isomers was identified by ^{1}H NMR spectrum integrals and was consistent with the values stated in the literature. For ref. see (12b).

[14] For spectral data of **6**, see Experimental Section and Supporting Information.

[15] A complex mixture was obtained, which prohibited identification of products other than **1** and **2**.

[16] Reaction of CAASi **1** with ethyl formate (150 °C, [D$_6$]benzene, sealed tube) gave a complex mixture. This suggests that the low yield of **5h** might be due to the complex reaction with the ester moiety.

[17] A. Simonneau, M. Oestreich, *Nat. Chem.* **2005**, *7*, 816-822.

[18] For the multinuclear NMR and high-resolution MS spectra, see Supporting Information.

[19] The first transition states connected to **INT1**-**INT3** could not be identified in our hands, however, the remarkably lower energy levels of **INT1** + **W** should be enough to postulate that the reaction proceeds through **INT1** and **W**.

[20] Heating of dihydridosilane **2** and anthracene (150 °C, [D$_6$]benzene, sealed tube) for 16 h resulted in no reaction, which rules out the possibility of **3** generating from **2** and anthracene.

[21] Competition of a concerted hydrogen abstraction or a C–H insertion might not be ruled out judging from the results of the DFT calculations at the B3PW91-D3/6-31G(d) level of theory. For details, see Supporting Information.

[22] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.

[23] P. Lei, Y. Ding, X. Zhang, A. Adijiang, H. Li, Y. Ling, J. An, *Org. Lett.* **2018**, *20*, 3439-3442.

[24] J. L. Mooney, Z. Marcinow, P. W. Rabideau, *J. Org. Chem.* **1986**, *51*, 527-532.

[25] T. Takahashi, S. Li, W. Huang, F. Kong, K. Nakajima, B. Shen, T. Ohe, K. Kanno *J. Org. Chem.* **2006**, *71*, 7967-7977.

[26] H. Sajiki, T. Kurita, H. Esaki, F. Aoki, T. Maegawa, K. Hirota, *Org. Lett.* **2004**, *6*, 3521-3523.

[27] C. R. Goldsmith, R. T. Jonas, T. D. P. Stack, *J. Am. Chem. Soc.* **2002**, *124*, 83-96.

[28] SADABS, Empirical Absorption Correction Program; G. M. Sheldrick, Göttingen, Germany, 1996.

[29] G. M. Sheldrick, *Acta Crystallogr., Sect. A*, **2008**, *64*, 112-122

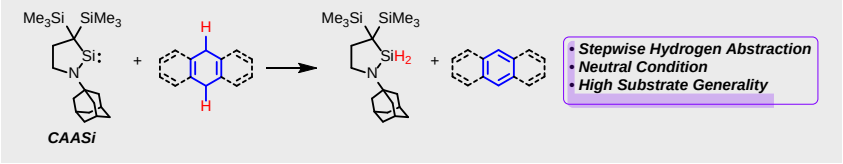
[30] Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita, (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *J. Cryst. Soc. Jpn.* **2009**, *51*, 218-224.

[31] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.Scuseria, M.A.Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Men-nucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian ,A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Strat-mann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dan-nenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[32] GRRM14, S. Maeda, Y. Harabuchi, Y. Osada, T. Taketsugu, K. Morokuma, K. Ohno, see http://grrm.chem.tohoku.ac.jp/GRRM/; S. Maeda, K. Ohno, K. Morokuma, *Phys. Chem. Chem. Phys.* **2013**, *15*, 3683-3701.

Entry for the Table of Contents

FULL PAPER



*Taichi Koike, Tomoyuki Kosai, Takeaki Iwamoto**

Page No. – Page No.

1,4-Dehydrogenation with a Two-Coordinate Cyclic (Alkyl)(amino)silylene

A two-coordinate cyclic (alky)(amino)silylene (CAASi) undergoes regioselective 1,4-dehydrogenation for numerous 1,4-cyclohexadiene and 9,10-dihydroanthracene derivatives. Experimental and computational studies indicated that the reaction proceeds mainly via a stepwise hydrogen abstraction.