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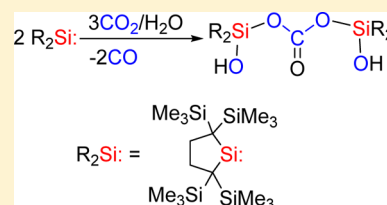
Reactions of an Isolable Dialkylsilylene with Carbon Dioxide and Related Heterocumulenes

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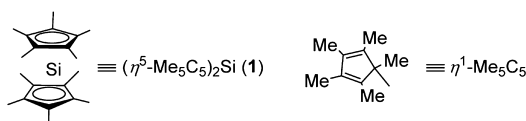
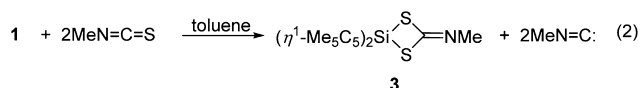
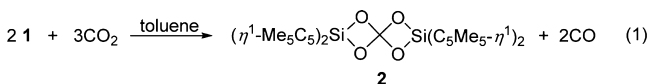
Supporting Information

ABSTRACT: An isolable dicoordinate dialkylsilylene, 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl (**6**), was found to react with CO₂ and ArN=C=X (X = O, S) smoothly to give the corresponding bis(silyl)carbonate, 4-imino-1,3-dioxasiletane and 4-imino-1,3-dithiasiletane derivatives in high yields, respectively. The molecular structures of these products were determined by X-ray crystallography. All these reactions are parallel to those of a hypercoordinate silylene with η^5 -pentamethylcyclopentadienyl ligands, decamethylsilicocene, reported by Jutzi et al. and are suggested to involve similarly the formation of the corresponding Si=X doubly bonded compounds (X = O, S) at the initial steps. Mechanistic details of the multistep reaction of a model dialkylsilylene with CO₂ were investigated using DFT calculations.



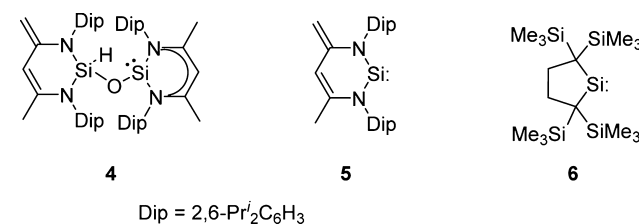
INTRODUCTION

Among the effective methods to reduce global carbon dioxide emission is its chemical reduction to carbon monoxide,¹ being achieved using CO dehydrogenase/acetyl-CoA synthase,² photoreduction,³ electrochemical reduction,⁴ metal-based oxygen abstraction,⁵ etc. While transition-metal catalysts usually play a dominant role in these reduction reactions,⁶ some low-valent group 14 element compounds, such as coordinated disilyne⁷ and digermene,⁸ have been found recently to show considerable reduction ability toward CO₂. A number of reactions of transient and isolable silylenes (silicon divalent compounds) with various carbon unsaturated compounds such as alkenes, alkynes, carbonyl compounds, imines, nitriles, and isonitriles have been investigated extensively to date.⁹ However, only a few studies of the reactions of silylenes with carbon dioxide and related heterocumulenes have been reported. Jutzi et al. have found that decamethylsilicocene, a stable, hypercoordinate and highly nucleophilic silylene, reacts with X=C=Y type compounds (X, Y = O, S, NR) to give rather unusual products, as typically shown in eqs 1 and 2.¹⁰



Recently, Driess et al. have reported that CO₂ is reduced by the intramolecular donor-stabilized siloxysilylene **4**,¹¹ while the related N-heterocyclic silylene **5**¹² does not react with CO₂ (Chart 1). As a natural extension of our recent studies on the

Chart 1. Structural Formulas of Silylenes 4–6



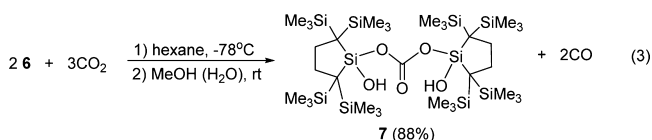
reactions of an isolable dialkylsilylene, 2,2,5,5-tetrakis(trimethylsilyl)silacyclopentane-1,1-diyl^{13,14} (**6**; Chart 1), with ketones,^{15a} imines,^{15b} and nitriles,^{15c} we have investigated herein the reactions of **6** with carbon dioxide, an isocyanate, and an isothiocyanate, in order to compare the reactivity of **6**, known as an ambiphilic silylene with low-lying LUMO and high-lying HOMO,^{14d} to that of the highly nucleophilic decamethylsilicocene **1**.¹⁰ The appearance of the reactions of dialkylsilylene **6** is quite similar to those of silicocene **1**, though the electronic and steric properties are significantly different between the two silylenes. The DFT calculations for the multistep reaction of a model dialkylsilylene with CO₂ revealed that it proceeds smoothly with the rate-limiting initial [1 + 2] addition of the silylene to CO₂.

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RESULTS AND DISCUSSION

Reactions of Silylene 6 with CO_2 , $\text{ArN}=\text{C}=\text{O}$, and $\text{ArN}=\text{C}=\text{S}$. When dry CO_2 is introduced into a hexane solution of dialkylsilylene 6 at -78°C , the color changes from orange to pale yellow within 15 min. Addition of methanol at room temperature and then removal of the volatiles from the mixture in vacuo gives bis(silyl) carbonate 7 in good yield. Though no experiment aimed at the detection of carbon monoxide was made, the overall reaction of 6 with CO_2 could be described as shown in eq 3. The NMR spectral data of 7 in



CDCl_3 are in good accord with its structural features. A singlet ^1H resonance at 0.21 ppm and a single ^{29}Si NMR resonance at a 3 ppm region are indicative of the eight trimethylsilyl groups in 7 being nearly equivalent; see the Experimental Section and the Supporting Information for the NMR spectral details.

The molecular structure of 7 determined by X-ray single-crystal analysis is shown in Figure 1 together with pertinent

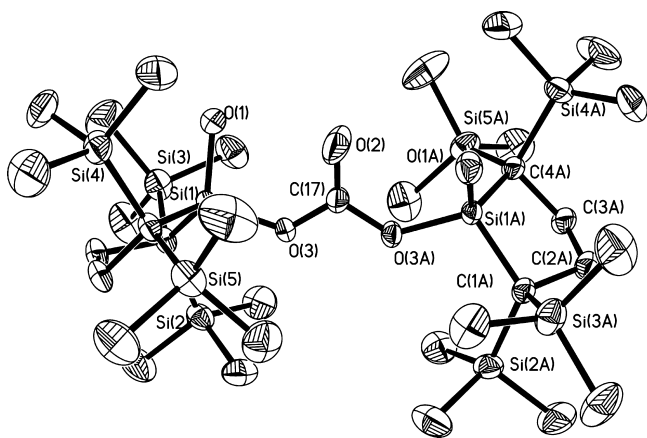
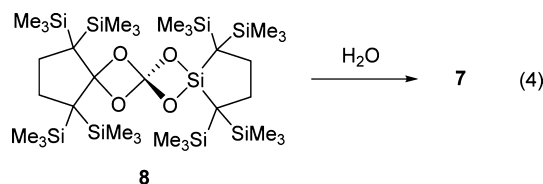


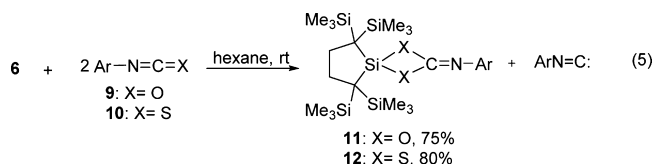
Figure 1. Molecular structure of 7. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si1–O1 = 1.668(2), Si1–O3 = 1.700(16), Si1–C1 = 1.865(2), Si1–C4 = 1.873(2), C17–O3 = 1.304(2), C17–O2 = 1.198(5); O1–Si1–O3 = 104.76(10), O1–Si1–C1 = 111.53(13), O3–Si1–C1 = 108.88(10), O1–Si1–C4 = 113.90(12), O3–Si1–C4 = 115.62(10), C1–Si1–C4 = 102.23(10), O2–C17–O3 = 123.61(15), O2–C17–O3A = 123.60(15), O3–C17–O3A = 112.80(3), C17–O3–Si1 = 127.24(17), C2–C1–Si1 = 98.98(15).

structural parameters. The O2–C17 (C=O) bond length (1.198(5) Å) of 7 and all other bond distances and angles around the carbonate moiety were similar to those of a related bicyclic disilaoxanyl carbonate reported recently,⁷ while the O–C(=O)–O bond angle of the former (112.8°) is slightly narrower than that of the latter (117.20°).

Product 7 is easily inferred to form via the hydrolysis of spiro compound 8 (eq 4) by the water contamination in methanol, and hence, the primary product of the reaction of CO_2 with 6 is regarded to be 8, being analogous to 2 obtained by the reaction of silicocene 1 with CO_2 (eq 1). The mechanisms of the multistep silylene– CO_2 reaction are discussed in a later section in combination with the DFT calculation results.



The reactions of dialkylsilylene 6 with isocyanate 9 and isothiocyanate 10 gave the corresponding dioxasiletane (11) and dithiasiletane derivatives (12) in high yields along with the formation of the corresponding aryl isocyanide, which was confirmed by GC-MS (eq 5). Products 11 and 12 were characterized by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy and finally X-ray crystallography.



Dialkylsilylene 6 reacted with carbon disulfide but gave only a mixture of unidentified products, while Jutzi et al. have reported the formation of rather unusual products during the reaction of 1 with CS_2 .¹⁰

The dioxasiletane ring system of 11 has not yet been reported in the literature. As shown in the molecular structure (Figure 2), 11 has a planar 1,3-dioxasiletane ring with an sp^2 -

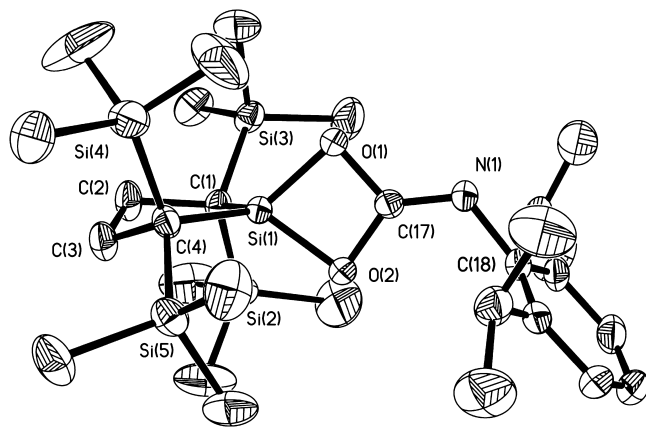


Figure 2. Molecular structure of 11. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected interatomic distances (Å) and angles (deg): Si1–O1 = 1.7069(18), Si1–O2 = 1.7204(18), Si1–C1 = 1.850(3), Si1–C4 = 1.855(3), Si1–C17 = 2.185(3), Si4–C4 = 1.920(3), O1–C17 = 1.362(3), O2–C17 = 1.367(3), N1–C17 = 1.248(3), N1–C18 = 1.425(3); O1–Si1–O(2) = 77.25(9), O1–Si1–C1 = 118.52(10), C17–O2–Si1 = 89.34(13), C17–O1–Si1 = 90.10(13), O1–C17–O2 = 103.24(18), C17–N1–C18 = 121.5(2), O2–Si1–C1 = 116.63(10), O1–Si1–C4 = 119.43(10), O2–Si1–C4 = 20.83(11), C1–Si1–C4 = 103.70(12), N1–C17–O1 = 125.5(2), N1–C17–O2 = 131.2(2).

hybridized carbon atom in a single crystal; inner angles of the ring are 77.25 (O–Si–O), 103.24 (O–C–O), 90.10 (Si–O–C) and 89.34° (Si–O–C). Interestingly, the Si(1)–C(17) distance of 2.185(3) Å in 11 is obviously shorter than the sum of the van der Waals radii of Si and C (3.70 Å), similarly to the short Si–Si distances in 1,3-dioxasiletanes.¹⁶ The latter bonding has been suggested to be an unsupported Si–Si π

bond in a dibridged π complex, on the basis of the very small J_{SiSi} value^{17a} and theoretical considerations.^{17b} The four-membered ring of **11** may also be characterized as a dibridged π complex with an unsupported Si–C π bond, though more elaborate analysis would be required for a definitive conclusion.¹⁸

As shown in Figure 3, the bond parameters around the four-membered ring of dithiasiletane **12** determined by the single-

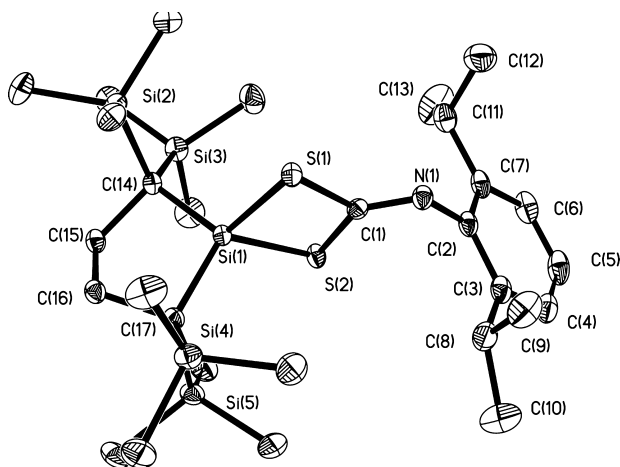
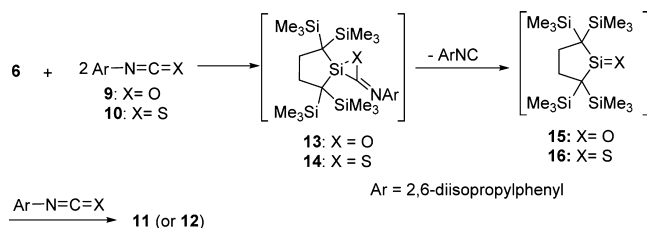


Figure 3. ORTEP drawing of **12**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si1–C1 = 1.775(3), Si1–Si1 = 2.1711(9), Si2–C1 = 1.786(2), Si2–Si1 = 2.1718(9), Si1–C17 = 1.869(3), Si1–C14 = 1.872(3), Si1–C1 = 2.636(3), N1–C1 = 1.253(3), N1–C2 = 1.412(3); C1–Si1–Si1 = 83.19(8), C1–Si2–Si1 = 82.93(9), C17–Si1–C14 = 101.96(11), C14–Si1–Si1 = 115.30(8), C17–Si1–Si2 = 113.69(9), Si1–Si1–Si2 = 84.12(3), N1–C1–Si2 = 127.9(2), Si1–C1–Si2 = 109.58(13), N1–C1–Si1 = 122.49(19), C1–N1–C2 = 120.6(2).

crystal X-ray crystal analysis are very similar to those of **3** reported by Jutzi et al.¹⁰

Because products **11** and **12** are analogous to those obtained by the reactions of silococene **1** with isothiocyanates (eq 2), these reactions would proceed via a pathway similar to that proposed for the latter reactions (eq 1).¹⁰ Thus, as shown in Scheme 1, dialkylsilylene **6** undergoes [1 + 2] cycloaddition

Scheme 1. Pathways of the Reactions of Dialkylsilylene **6** with Isocyanate **9** and Isothiocyanate **10**

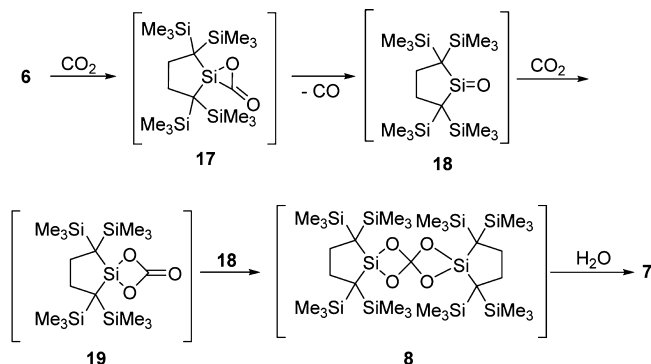


with isocyanate **9** and isothiocyanate **10** to initially produce the highly strained iminosiliranones **13** and **14**, respectively, which expel ArNC to give silanone **15** and silanethione **16**.¹⁹ Compounds **15** and **16** in turn react with **9** and **10** to give **11** and **12**, respectively. While the proposed pathways suggest that **15** and **16** may be rather long lived in the systems, the evidence for the existence of either **13/14** or **15/16** was not obtained. Silanethione **16** has been isolated via the reaction of **6**

with a phosphine sulfide,²⁰ and the reaction of a diarylsilanethione with an isothiocyanate to give the corresponding 4-imino-1,3-dithiasiletane has been reported by Okazaki, Tokitoh, et al.²¹ The possible reactions of **11** and **12** with **15** and **16** to give the corresponding tetraspiro compounds such as **8** may be prevented by the severe steric hindrance between the reagents.

The apparently complex reaction of silylene **6** with carbon dioxide would proceed as shown in Scheme 2, being in accord

Scheme 2. Pathway Proposed for the Reaction of Dialkylsilylene **6** with CO₂

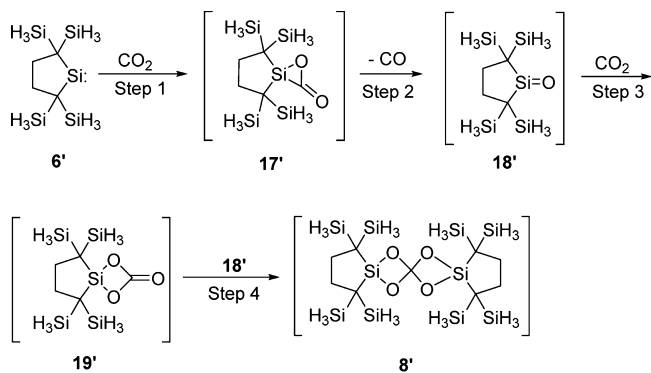


with a similar reaction of **1**.¹⁰ The intermediary formation of **17–19** is in line with the reactions of **6** with the related heterocumulenes **9** and **10**. The following two questions emerge for the mechanistic details for the proposed pathway. (1) While Jutzi et al. have proposed that the highly nucleophilic silylene **1** may initially attack the central carbon of CO₂ to give a zwitterionic intermediate, $(\eta^1\text{-Me}_3\text{C}_5)_2\text{Si}^+\text{-C}(=\text{O})\text{O}^-$ (**20**), during the reaction shown in eq 1, does the initial attack of **6**, which is ambiphilic and less nucleophilic than **1**, occur at an oxygen atom of CO₂? (2) Do all of the reaction steps occur smoothly with reasonably low activation barriers?

DFT Calculations of the Reaction of a Model Silylene with CO₂. In order to get further insight into the mechanism, hybrid density functional BMK calculations in conjunction with the 6-31G(d,p) basis set were performed for the reaction pathway shown in Scheme 3 of the model silylene **6'** with CO₂.

The potential energy profile and the activation and reaction parameters of the stationary points for steps 1–3 are given in Figure 4 and Table 1, as calculated relative to those of the silylene **6'** + 2CO₂ system. Molecular structures at the

Scheme 3. Stepwise Reaction Pathway Investigated by BMK Calculations



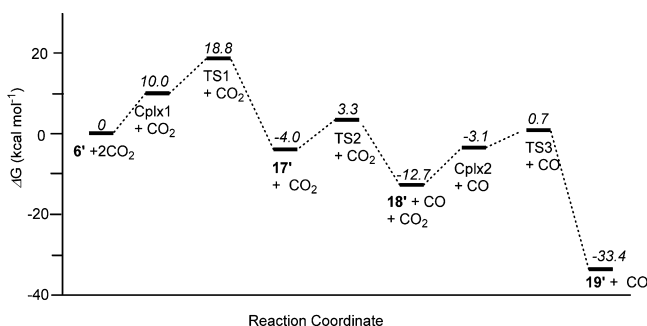


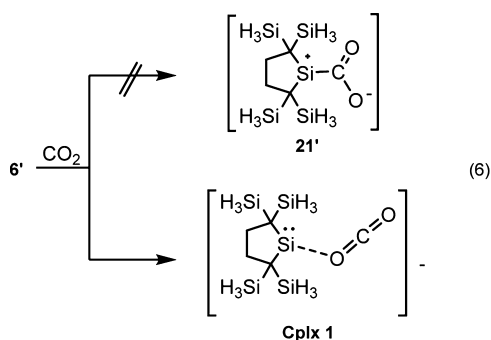
Figure 4. Reaction pathway of $6' + 2\text{CO}_2$ (steps 1–3). Reaction and activation free energies (ΔG in kcal mol^{-1}) are given in italics.

Table 1. Activation and Reaction Parameters for Steps 1–3 Calculated at the BMK/6-31G(d,p) +ZPE Level^{a,b}

system	ΔE (kcal mol ⁻¹)	ΔH (kcal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	ΔG (kcal mol ⁻¹)
Cplx1 ($6' \cdots \text{CO}_2$) + CO_2	1.0	0.8	-30.9	10.0
TS1 + CO_2 (step 1)	7.2	6.5	-41.3	18.8
$17' + \text{CO}_2$	-15.4	-16.1	-40.6	-4.0
TS2 + CO_2 (step 2)	-8.0	-8.7	-40.2	3.3
$18' + \text{CO} + \text{CO}_2$	-11.3	-10.5	7.4	-12.7
Cplx2 ($18' \cdots \text{CO}_2$) + CO	-13.8	-13.6	-35.2	-3.1
TS3 + CO (step 3)	-10.8	-11.0	-39.2	0.7
$19' + \text{CO}$	-45.2	-45.7	-41.2	-33.4

^aRelative activation and reaction parameters were calculated on the basis of those of free $6' + 2\text{CO}_2$. ^bParameters for TS1–TS3 should read as ΔE^\ddagger , ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger .

stationary points are shown in the Supporting Information. Step 1 was found to proceed without formation of a previously proposed zwitterionic intermediate such as $21'$ for the reaction of silylene $6'$ (eq 6). Complex $21'$ was not found as a minimum



for step 1; instead, a complex with a weak interaction between silylene Si and CO_2 oxygen (Cplx 1) was located as a minimum that was 10 kcal mol^{-1} higher in energy than the starting mixture (Figure 4).²²

Step 1 is basically the concerted [1 + 2] addition of silylenes $6'$ to a $\text{C}=\text{O}$ double bond of CO_2 through the complex. The activation free energy ΔG^\ddagger of 18.8 kcal mol^{-1} for the step is the largest among steps 1–4 but is low enough for the reaction to proceed at low temperatures. The three-membered-ring system $17'$ is 4.0 kcal mol^{-1} more stable than the starting system but is followed by a low-energy CO extrusion reaction to give $18'$ (step 2), whose ΔG^\ddagger value is only 7.3 kcal mol^{-1} from $17'$ (Table 1 and Figure 4). The concerted [2 + 2] cycloaddition of silanone $18'$ with another CO_2 molecule occurs readily, giving

the four-membered-ring compound $19'$ with a ΔG^\ddagger value of 13.4 kcal mol^{-1} from the silanone $18' + \text{CO}_2$ system. The ΔG^\ddagger value is even lower than that for the step 1 reaction (Scheme 3). The overall reaction from step 1 to step 3 is largely exergonic with a ΔG value of -33.4 kcal mol^{-1} .

Because step 4 involves two molecules of silylene $6'$, the reaction and activation parameters are calculated relative to a 1:1 mixture of $18'$ and $19'$ and shown in Table 2. The addition

Table 2. Reaction and Activation Parameters for the Stationary Points for Step 4 Calculated at the BMK/6-31G(d,p) +ZPE Level of Theory^{a,b}

system	ΔE (kcal mol ⁻¹)	ΔH (kcal mol ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	ΔG^c (kcal mol ⁻¹)
$19' + 18'$	0	0	0	0 (-46.0)
Cplx 3 ($19' \cdots 18'$)	-19.7	-20.3	-53.8	-4.2 (-50.2)
TS4 (step 4)	-17.1	-18.1	-60.1	-0.1 (-46.1)
$8'^c$	-41.1	-42.1	-58.4	-24.6 (-70.7)

^aParameters were calculated relative to those of $19' + 18'$.

^bParameters for TS4 should read ΔE^\ddagger , ΔH^\ddagger , ΔS^\ddagger , and ΔG^\ddagger . ^c ΔG values calculated relative to that of $26' + 3\text{CO}_2$ are shown in parentheses.

of silanone $18'$ to cyclic carbonate $19'$ giving the spiro compound $8'$ is very facile with almost no barrier. The present theoretical calculations show that all the elementary reactions involved proceed with rather low activation free energies, supporting the reaction pathway shown in Scheme 3. The total reaction, $26' + 3\text{CO}_2 \rightarrow 19' + 2\text{CO}$, is largely exergonic with a ΔG value of -70.7 kcal mol^{-1} , as shown in parentheses in Table 2.

In conclusion, the isolable dialkylsilylene **6** was found to react with isocyanate and isothiocyanate at low temperatures, giving the 4-iminodioxasiletane and 4-iminodithiasiletane derivatives in high yields via the intermediary formation of the corresponding $\text{Si}=\text{X}$ doubly bonded compounds ($\text{X} = \text{O}, \text{S}$). In the reaction of **6** with CO_2 , the corresponding 4-oxo-1,3-dioxasiletane formed similarly reacts with an additional CO_2 , affording the corresponding bis(silyl)carbonate via hydrolysis. All of these reactions are very similar to those of decamethylsilicocene (**1**), despite very different electronic features between the two silylenes. The DFT calculations have revealed that all the steps of the reaction of a model dialkylsilylene with CO_2 proceed with sufficiently low activation energies, supporting the proposed mechanism.

EXPERIMENTAL SECTION

All synthetic experiments were performed under argon or nitrogen in a standard vacuum system unless otherwise noted. ^1H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (80 MHz) spectra were recorded with tetramethylsilane as an external standard on a Bruker AV-400 MHz instrument. GC-MS spectra were measured with an Agilent 7890a gas chromatograph coupled to an Agilent 5975c mass spectrometer. High-resolution MS were measured on a Thermo Scientific LTQ Orbitrap XL spectrometer. Melting points are uncorrected. Silylene **6** was prepared according to the literature procedures.¹³ Silylene **6** and other air-sensitive materials were handled in an MBraun glovebox. All products were purified by flash chromatography or GPC (LC-9101, Japan Analytical Industry Co. Ltd.).

The full ^1H , ^{13}C , and ^{29}Si NMR spectra of all new compounds (**7**, **10**, and **11**) have been provided in the Supporting Information.

Reaction of Silylene 6 with CO_2 . Carbon dioxide gas was injected into a stirred hexane solution of silylene **6** (75 mg, 0.2 mmol)

at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 20 min at $-78\text{ }^{\circ}\text{C}$. Then methanol (0.1 mL) was added and the mixture was stirred for 10 min at that temperature. The solvent was removed under vacuum, and the product was isolated as the pure substance from the resulting residue by flash chromatography.

7: white solid (147 mg, 88%); mp $252\text{--}253\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 2.02 (s, 2H), 1.95 (s, 8H), 0.21 (s, 72H); ^{13}C NMR (100 MHz, CDCl_3) δ 121.8, 30.1, 10.1, 2.4; ^{29}Si NMR (80 MHz, CDCl_3) δ 42.26, 3.44; HRMS m/z $[\text{M} - \text{H}]^+$ calcd for $\text{C}_{33}\text{H}_{81}\text{O}_5\text{Si}_{10}$ 837.3782, found 837.3823.

Reactions of Silylene 6 with Isocyanate 9 and Isothiocyanate 10. A hexane solution of isocyanate **9** (0.41 mmol) was added to silylene **6** (75 mg, 0.2 mmol) in hexane (10 mL) at $-30\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 1/2 h at the same temperature. Then the solvent was removed under vacuum. The residue was dissolved in 1-pentane. Yellow crystals of **11** formed upon cooling the solution to $-40\text{ }^{\circ}\text{C}$ for 1 day.

11: yellow solid (89 mg, 75%); mp $204\text{--}205\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.11–7.03 (m, 3H), 3.17 (m, 2H), 2.08 (s, 4H), 1.20 (s, 12H), 0.24 (s, 36H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.7, 140.2, 139.7, 123.8, 122.3, 30.2, 28.4 (s), 23.1, 10.3, 2.4; ^{29}Si NMR (80 MHz, C_6D_6) δ 53.40, 4.07; HRMS m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{57}\text{NO}_2\text{Si}_5$ 592.3360, found 592.3308.

Compound **12** was obtained by a treatment of **6** with isothiocyanate **10** similar to that above.

12: yellow solid (99.6 mg 80%); mp $108\text{--}110\text{ }^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.13–7.15 (m, 3H), 2.98–3.05 (m, 2H), 2.11 (s, 4H), 1.28 (s, 12H), 0.25 (s, 36H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 144.1, 138.1, 124.6, 122.9, 36.1, 28.3, 22.6, 16.4, 3.4; ^{29}Si NMR (80 MHz, CDCl_3) δ 25.83, 4.43; ESI-HRMS $[\text{M} + \text{H}]^+$ m/z calcd for $\text{C}_{29}\text{H}_{57}\text{NS}_2\text{Si}_5$ 624.2857, found 624.2852.

X-ray Structure Determination. Single crystals of **7**, **11**, and **12** suitable for X-ray analysis were obtained by recrystallization from hexane. The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) using the ω – 2θ scan mode. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELX-2000.²³ Crystal and refinement data for **7**, **11**, and **12** are described in the Supporting Information. Supplementary crystallographic data for **7**, **11**, and **12** have been deposited with the CCDC; the file numbers are 943610, 981554, and 981555, respectively.

Calculation Details. All calculations were performed on an SGI Altix 450 server using the Gaussian 03 package.²⁴ Geometry optimizations of all stationary points were performed by using the DFT (BMK)²⁵ method in conjunction with the 6-31G(d,p) basis set. GaussView was used for visual inspection of the final geometries and vibrational frequencies as well as for drawing pictures of the optimized structures. All of the structures obtained herein were verified by examination of their Hessian matrix as minima (all frequencies real) or transition states (one imaginary frequency). Zero-point vibrational energies (ZPE) were incorporated into the total energies without a scale factor. At every transition state, the transition vector was animated with the GaussView program, and if necessary, the intrinsic reaction coordinate (IRC) was computed to connect the corresponding minima.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, tables, and xyz and CIF files giving X-ray crystallographic data and NMR spectra of **7**, **11** and **12**, theoretical details, and all computed molecule Cartesian coordinates in a format for convenient visualization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(18) In this relation, we have performed theoretical calculations for a model compound of **11** (**11'**, where all SiMe₃ substituents of **11** were replaced with SiH₃ groups) at the BMK/6-31G(d,p) level. The calculated structure of **11'** around the ring was similar to that of **11** with an Si...O distance of **11'** (2.170 Å). The Wiberg bond index between the ring Si and O of **11'** is very small (0.024), suggesting no direct bonding between the atoms.

(19) One-electron transfer from silylene **6** to **9** and **10** was suggested by a reviewer as a mechanism for the initial step of the [1 + 2] addition reactions. However, theoretical calculations at the BMK/6-31G(p,d) level for model compounds of **9** and **10** (**9'** and **10'**, where the SiMe₃ groups in **9** and **10** are all replaced by SiH₃ groups) have shown that the LUMOs of **9'** and **10'** (0.210 and -0.522 eV) are much higher than that of **6'** (-1.517 eV). The adiabatic reaction energy for **6' + 10'** forming **6* + 10*** is 174.1 kcal/mol endothermic. These theoretical results and the fact that the reactions were carried out in nonpolar hexane solvent suggest that the electron-transfer mechanism would be less probable. The unusual reaction of **6** with CS₂ (LUMO level, -1.304 eV) may involve the proposed mechanism. See also the Supporting Information.

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(22) At the same level of calculations, the zwitterionic intermediate ($\eta^1\text{-Me}_5\text{C}_5\text{Si}^+\text{-C(=O)O}^-$) (**20**) was located at $\Delta G = 10.7$ kcal mol⁻¹ during the reaction of silicocene **1** and CO₂. The cyclization product, the α -silaacetolactone derivative **22**, is 11.4 and 22.1 kcal/mol more stable than **1 + CO₂** and **20**, respectively. Because the energy difference between **20** and **22** is very large, **20** may not be a real intermediate during the reaction, while the present calculations failed to locate the transition states connecting **20** and **22** or **1 + CO₂** and **22**. See the Supporting Information for details.

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