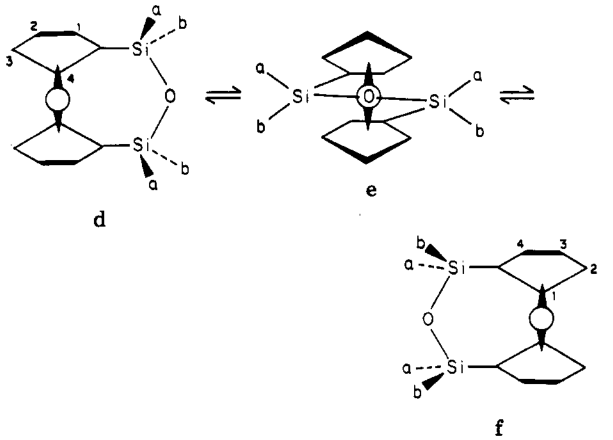
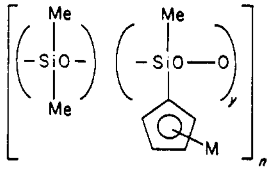
ene-, and trimethylene-bridged species respectively.[23]

During the process that interconverts mirror images (**d** → **f**) (eq 12), the Me$_2$SiOSiMe$_2$ bridge must transverse the "backside" of the molecule, at which point the bridgehead carbons should approach to within about 2.8 Å. In order to accommodate this small distance, we propose that the bridging siloxy group twists so as to give the C_2 symmetry intermediate (**e**) which allows the bridging group to slip through to the opposite side of the ring, interchanging Me- and Cp–H environments to give the averaged spectra observed. (In eq 12, the view is down the ClTiCl bisector; the Cl atoms are omitted for clarity.) Since the coalescence temperature depends on both the rate of interconversion and the chemical shift separation and since the latter is unknown, no lower bound for the rate can be estimated. Temperatures below −100 °C are required to freeze out bridge reversal processes of (3)ferrocenophanes, which have energy barriers of ca. 40 kJ/mol.[36]



The results presented here suggest that polysiloxanes may be useful as supports for anchoring metal complexes, but the degree of metal loading and the degree of crosslinking of the polymer will be crucial in determining whether or not the resulting polymers have useful physical properties. Fortunately, these factors are easily controlled with silicones, so that the synthesis of block copolymers, e.g., 14, is a reasonable synthetic goal.



14

Acknowledgment. We thank Dr. Louis Messerle for obtaining the low-temperature 360-MHz ^{1}H NMR spectra. We also thank the National Science Foundation (Grant No. CHE-7907748) for support of this research.

Registry No. 1/2, 31346-13-1; 3/4, 87337-95-9; 5, 87337-96-0; 6, 87337-97-1; 8, 87337-98-2; 10, 87338-00-9; 12, 87338-01-0; 13, 87337-99-3; TiCl$_4$·2Py, 17100-05-9; MeLi, 917-54-4; NaCp, 4984-82-1.

Supplementary Material Available: Tables of observed and calculated structure factors and temperature factors (Table V) (10 pages). Ordering information is given on any current masthead page.

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Photochemistry of 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene and α,ω-Bis(1-methyl-2,5-diphenyl-1-silacyclopentadienyl)alkanes[1]

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α,ω-Bis(1-methyl-2,5-diphenyl-1-silacyclopentadienyl)alkanes undergo intramolecular [2 + 2] cycloaddition with higher quantum yields than those of intermolecular cycloaddition of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene. These reactions occur through the singlet excited state. The cycloadducts also undergo photochemical and thermal cycloreversion reaction. The mechanism of these photochemical reactions is discussed.

It has been reported by Barton and Nelson[2] and by Nakadaira and Sakurai[3] that irradiation of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**1**) yields [2 + 2] photodimers in quantitative yield. A major isomer formed under irradiation with a high-pressure mercury arc lamp is the anti–trans dimer **2a**, while the other two dimers *anti–cis*-**2b** and *syn-trans*-**2c** are obtained as minor products along with **2a** under a variety of conditions.[3]

It has also been reported that the photodimers undergo a facile cycloreversion reaction to the monomer by irradiation with a low-pressure mercury lamp or by thermolysis.[3]

One of the important and interesting features of the reaction is that the photochemical dimerization proceeds with low-energy irradiation such as visible sunlight since **1** is yellow with its characteristic absorption at 371 nm (ϵ 20 400). In this paper, we report some details of the photochemical reaction of **1** as well as the synthesis and photochemical reactions of a new series of related compounds, α,ω-bis(1-methyl-2,5-diphenyl-1-silacyclopenta-

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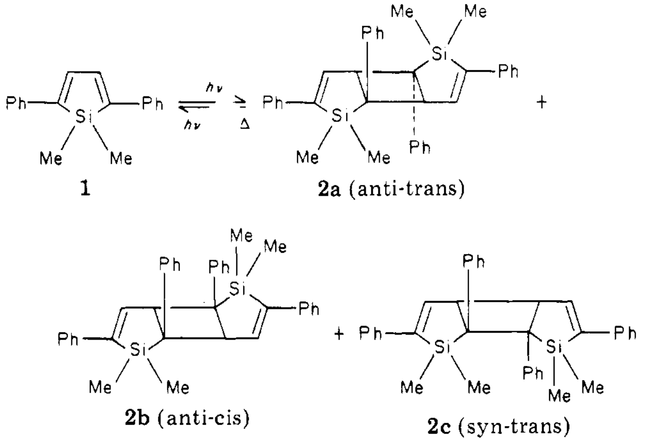
(1) Chemistry of Organosilicon Compounds 182.

(2) Barton, T. J.; Nelson, A. J. *Tetrahedron Lett.* **1969,** 5037.

(3) Nakadaira, Y.; Sakurai, H. *Tetrahedron Lett.* **1971,** 1183.

0276-7333/83/2302-1814$01.50/0 © 1983 American Chemical Society



1

2a (anti-trans)

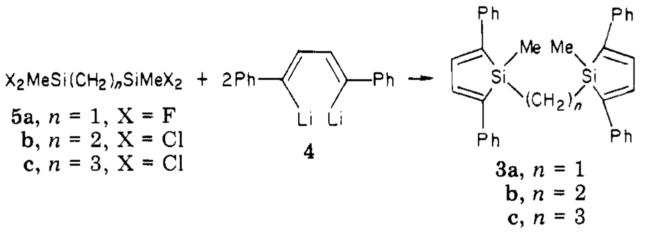
2b (anti-cis)

2c (syn-trans)

dienyl)alkanes (3), which have been designed for intramolecular photochemical reactions.

Results and Discussion

The reaction of 1,4-dilithio-1,4-diphenyl-1,3-butadiene with α,ω-bis(dihalomethylsilyl)alkane **5** gave **3a**, **3b**, and **3c** in 25, 54, and 58% yield, respectively.



$X_2MeSi(CH_2)_nSiMeX_2$ + 2Ph–C(Li)=CH–CH=C(Li)–Ph →

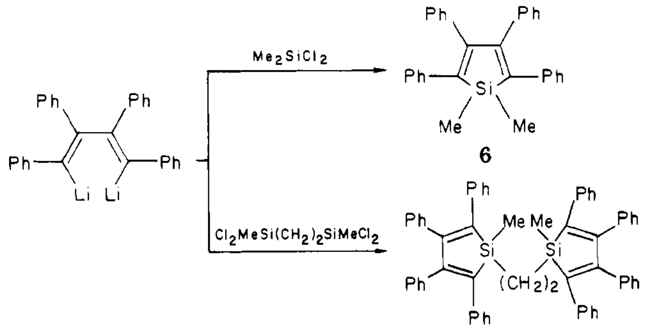
5a, n = 1, X = F
b, n = 2, X = Cl
c, n = 3, X = Cl

4

3a, n = 1
b, n = 2
c, n = 3

The preparation of **3b** and **3c** can be performed smoothly with the corresponding bis(dichloromethylsilyl)alkanes **5b** and **5c**, but the reaction of **4** with bis(dichloromethylsilyl)methane did not give **3a**. Bis(difluoromethylsilyl)methane (**5a**) afforded the desired **3a** only in low yield.

For the purpose of the comparison, tetraphenyl derivatives **6**[4] and **7** were prepared as shown below.



6

7

All the new compounds are yellow crystals similar to **1**. Elemental analyses and spectroscopic data satisfied the structures (see Experimental Section).

UV spectra of **1**, **3**, **6**, and **7** are listed in Table I. The absorption maxima of **3a–c** appeared almost at the same wavelengths as **1** reflecting the same chromophore. An interesting point to note is the fact that while the extinction coefficients of **3a–c** at 223–226 nm are reasonably twice as large as that of **1** at 225 nm, those of **3a–c** at 369–371 nm are only 1.1–1.5 times larger than that of **1** at 371 nm. This fact suggests that intramolecular interaction occurs in **3a–c**. Correspondingly, we have found that the molar extinction coefficient of **1** is concentration dependent as shown in Figure 1. The higher the concentration is, the lower the molecula extinction coefficient becomes. The order of the molecular extinction coefficients **3c** > **3b** > **3a** also seems to reflect the degree of separation of two chromophores in a molecule. Such hypochromism, in which the absorption intensity in electronic spectrum of a molecule is weaker than the sum of the intensities of individual chromophores, has been found for some molecules such as nucleic acids,[5] spirochromen,[6] diphenylsiloxanes,[7] and cyclic diacetylenes containing naphthalenes.[8] However, these molecules mostly have a fairly definite geometry holding the chromophoric groups in the fixed arrangement, and therefore the hypochromism observed for **1** and **3** with a soft structure is rather peculiar. This peculiar behavior in UV spectra of **1** may be related to the ready photochemical dimerization. In contrast, **6** obeys Lambert–Beer's law and does not undergo such a photoreaction.

Table I. UV Spectra of Siloles

compd	solv	λ_{max}, nm (ϵ_{max})
1	n-hexane	225 (13 400),[a] 371 (20 400)[a]
3a	n-hexane	223 (25 500), 371 (23 100)
3b	THF	226 (25 600), 371 (28 700)
3c	n-hexane	226 (26 600), 371 (30 400)
6	THF	247 (23 900), 359 (9 400)
7	THF	247 (47 200), 359 (15 200)

[a] Extrapolated to ϵ at zero concentration, see text.

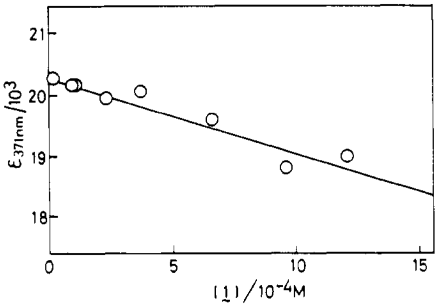
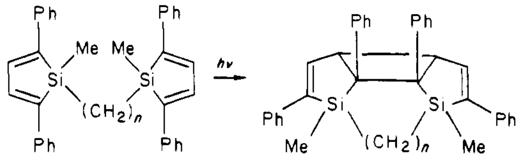


Figure 1. Relationship between ϵ_{371nm} and concentration of 1.

Irradiation of **3a–c** in THF with a 450-W high-pressure mercury lamp resulted in the formation of respective intramolecular [2 + 2] cycloadducts as colorless crystals in good yields. Mass, IR, and NMR spectra indicate the structure of these cycloadducts, and examination of molecular models shows that **8** can have only the syn–cis structure. The corresponding syn–cis dimer was not obtained in the photodimerization of **1**, but because of steric reasons, **3** gave **8** rather in high yields.



3a, n = 1
b, n = 2
c, n = 3

8a, n = 1 (84%)
b, n = 2 (86%)
c, n = 3 (85%)

Tetraphenylsilole (**6**) is known not to undergo the similar photodimerization.[2,3] The intramolecular photoaddition

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[5] Tinoco, I. *J. Am. Chem. Soc.* **1960**, *82*, 4785.

[6] Smoliński, *Tetrahedron Lett.* **1965**, 457.

[7] Brown, J. F., Jr.; Prescott, P. I. *J. Am. Chem. Soc.* **1964**, *86*, 1402.

[8] Ando, T.; Nakagawa, M. *Tetrahedron Lett.* **1966**, 4437.

Table II. Quantum Yields of Fluorescence (Φ_F) and Photochemical Cycloaddition (Φ_R) in THF[a]

compd	excitation wavelength, nm	λ_{max} in emission, nm	Φ_F[b]	Φ_R[c]
1	370	455	0.15	1.7×10^{-3}
3a	370	460	3.4×10^{-3}	0.17
3b	370	465	3.7×10^{-3}	0.14
3c	370	457	2.7×10^{-2}	0.15

[a] Concentrations: 1 5.00×10^{-5} M; **3a**, 3.60×10^{-5} M; **3b**, 2.24×10^{-5} M; **3c**, 2.27×10^{-5} M. [b] Φ_F values were determined by comparing integrated intensities of fluorescence spectra of the samples with that of 9,10-diphenylanthracene (Φ_F = 1). [c] Φ_R values were calculated from rates of disappearance of siloles determined by monitoring the decay rates at 370 nm with acridine as a standard.

Table III. Effects of Added Piperylene on Photocycloaddition of 1 in THF at 0 °C[a]

[1], mM	[piperylene], mM	conversn, %	yields of dimer, %		
			2a	2b	2c
2.69	0.00	70.7	67.5	19.6	12.9
2.81	3.91	83.5	73.3	17.4	9.3
2.64	6.63	66.0	65.9	19.6	14.5

[a] Both conversion and yield were determined by NMR.

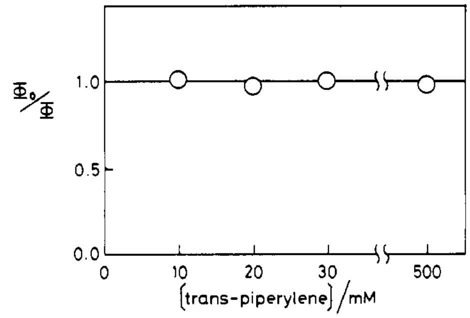


Figure 2. A Stern–Volmer plot of 1 ([1] = 2.37×10^{-4} M).

of the new compound 7 also did not occur, 7 being completely photochemically inert.

Table II shows quantum yields of both fluorescence (Φ_F) and photodimerization (Φ_R) measured in THF at room temperature. The quantum yields of photodimerization of **3a–c** are significantly larger than that of 1, indicating evidently higher efficiency of intramolecular cycloaddition than that of intermolecular cycloaddition. On the other hand, quantum yields of fluorescence of **3a–c** decreased considerably compared to that of 1, with decreasing distance between the two reacting moieties. The fact suggests that photocycloaddition of 1 and 3 occurs through the excited singlet state and competes with fluorescence.

The product distribution in the photodimerization of 1 is not qualitatively affected by addition of piperylene as shown in Table III. The quantum yield of the photodimerization of 1 also does not depend on added piperylene (Figure 2). These facts support qualitatively that photocycloaddition of 1 occurs through the excited singlet state.

Figures 3 and 4 show the effect of concentration on the quantum yields of both photodimerization and fluorescence of 1. The quantum yield of photodimerization increases with increasing concentration, whereas the reverse effect is observed for the quantum yield of fluorescence.

Dependence of emission intensity and quantum yields of both fluorescence and photocycloaddition of 1 on concentration seems to be self-consistent. These findings together with nondependence of the photoreaction on piperylene indicate strongly that the photocycloaddition reactions occur through the excited singlet state of 1 (S_1*). Interaction between an electronically excited species and a ground-state (S_0) molecule is important. Normally, such an interaction leads to the formation of an excimer that may give the dimer. The facile photochemical reaction of 3 can be regarded as an extreme case of 1.

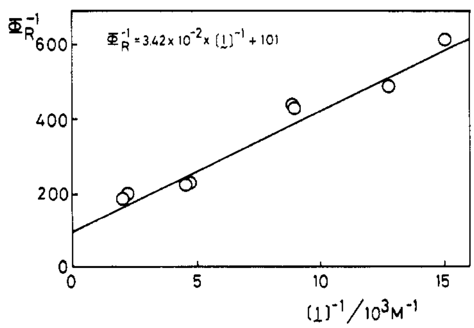


Figure 3. Relationship between Φ_R^{-1} and $[1]^{-1}$.

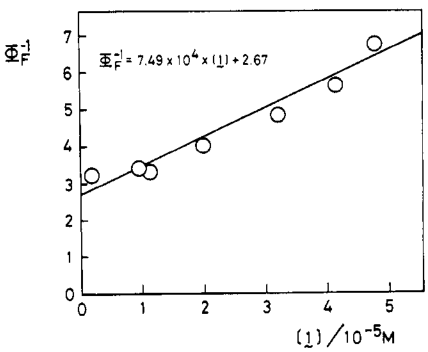
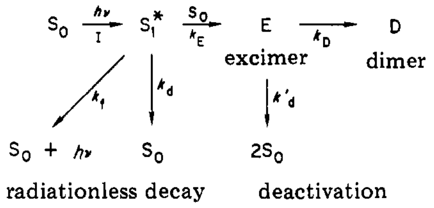


Figure 4. Relationship between Φ_F^{-1} and $[1]^{-1}$.

Scheme I



The photochemical reaction of 1 can be thus represented as shown in Scheme I.

Under the steady-state assumption for both S_1* and E, the following equations are obtained.

$$1/\Phi_R = \left[\frac{k'_d + k_D}{k_D}\left(1 + \frac{k_d + k_f}{k_E[S_0]}\right)\right]$$

$$1/\Phi_F = 1 + \frac{k_d}{k_f} + \frac{k_E}{k_f}[S_0]$$

Two linear relations shown in Figures 3 and 4 support the kinetic analysis and give relative rate constants for 1: $k_d/k_f = 1.7$, $k_E/k_f = 7.5 \times 10^4$ M^{-1}, and $k_d'/k_D = 100$.

Intramolecular photodimers **8a–c** undergo the cycloreversion reaction by either high-energy photolysis with

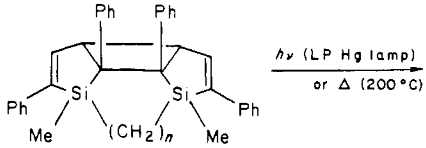
Table IV. Photocycloreversion Reaction (8 → 3)

compound	solvent THF	solvent PhH
8a (%)/3a (recovered %)	15/32	7/64
8b (%)/3b (recovered %)	25/27	11/38
8c (%)/3c (recovered %)	27/17	14/64

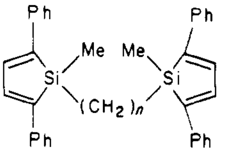
Table V. Thermal Cycloreversion Reaction (8 → 3)

compound	reaction time, h 0.5	2.0	3.5
8a (%)/3a (recovered %)	37/60	85/6	
8b (%)/3b (recovered %)	29/66	86/6	
8c (%)/3c (recovered %)	12/78	57/41	73/22

a low-pressure mercury lamp or thermolysis. Irradiation of a THF or benzene solution of 8 with a 10-W low-pressure Hg lamp in a quartz cell gave 3 as shown in Table IV. The reaction seems to reach to an equilibrium. The results of the thermal cycloreversion reaction are shown in Table V. At 200 °C 3a and 3b were obtained in high yield. It was found qualitatively that higher rates of the cycloreversion were observed for 3 with a shorter methylene bridge.



8a, *n* = 1
b, *n* = 2
c, *n* = 3



3a, *n* = 1
b, *n* = 2
c, *n* = 3

Experimental Section

General Remarks. NMR spectra were obtained by using Varian A-60 (60 MHz), Varian EM-390 (90 MHz), JEOL FX-90Q, and Varian XL-200 (200 MHz) instruments. Mass spectra were obtained by using a JEOL JMS D-300 GC-MS instrument. Infrared spectra were recorded on a Hitachi EPI-G2 grating spectrometer. UV and fluorescence spectra were obtained by using Hitachi 323 and MPF-4 spectrometers, respectively. Melting points were uncorrected. Microanalysis results were from the Instrumental Analysis Center for Chemistry, Tohoku University.

Preparation of Bis(difluoromethylsilyl)methane, 5a. Bis(dichloromethylsilyl)methane was prepared by a similar procedure to that reported earlier.[9] Thus dry hydrogen chloride was bubbled into a mixture of bis(trimethylsilyl)methane (80.2 g, 0.50 mol) and freshly sublimed aluminum chloride (3.33 g, 25.0 mmol) at 90 °C for 16 h. After addition of acetone (2 mL) to deactivate the catalyst, distillation gave the product in 69.3%: bp 24–25 °C (0.3 mmHg); ^{1}H NMR (CCl_4/CH_2Cl_2) δ 0.97 (s, 6 H), 1.28 (s, 2 H). The reaction of bis(dichloromethylsilyl)methane (12.9 g, 53.3 mmol) thus prepared and ethanol (10.0 g, 217 mmol) in ether (300 mL) with bubbling ammonia gave bis (diethoxymethylsilyl)methane (11.9 g, 42.3 mmol, 79.7%): bp 65–70 °C (0.8 mmHg); MS, m/e 265 ($M^+ - 15$); ^{1}H NMR (CCl_4/CH_2Cl_2) δ -0.13 (s, 2 H), 0.06 (s, 6 H), 1.15 (t, J = 7 Hz, 12 H), 3.72 (q, J = 7 Hz, 8 H). Anal. Calcd for $C_{11}H_{28}O_4Si_2$: C, 46.20; H, 10.16. Found: C, 46.44; H, 10.16.

Bis(diethoxymethylsilyl)methane (14.1 g, 50 mmol) was added slowly (30 min) to ice-cooled concentrated H_2SO_4 (100 g), and then ammonium hydrogen fluoride (14.3 g, 250 mmol) was added during a period of 3 h. After the mixture was stirred for 45 h at room temperature, **5a** was distilled from the mixture at room temperature (<1 mmHg) to a trap cooled with liquid nitrogen (7.5 g, 43 mmol, 86.0%): MS, *m/e* 161 ($M^+ - 15$); ^{1}H NMR ($CDCl_3/CH_2Cl_2$) δ 0.37 (m, 2 H), 0.43 (tt, J = 0.3 Hz, 7 Hz, 6 H). Anal. Calcd for $C_3H_8F_4Si_2$: C, 20.44; H, 4.57. Found: C, 20.23; H, 4.75.

Preparation of 1,3-Bis(dichloromethylsilyl)propane, 5c. First, 1-(dichloromethylsilyl)-3-(diphenylmethylsilyl)propane was prepared by hydrosilylation of allylmethyldiphenylsilane[10] (73.7 g 0.310 mol) with dichloromethylsilane (81.5 g, 0.709 mol) in the presence of a catalytic amount of chloroplatinic acid in isopropyl alcohol under nitrogen at 50 °C for 4 h. After evaporation of excess dichloromethylsilane, distillation gave the product in quantitative yield: bp 160 °C (0.3 mmHg); ^{1}H NMR (CCl_4/CH_2Cl_2) δ 1.89 (s, 3 H), 1.97 (s, 3 H), 2.3–3.2 (m, 6 H), 7.5–7.9 (m, 10 H). Dry hydrogen chloride was bubbled into a benzene (100 mL) solution of 1-(dichloromethylsilyl)-3-(diphenylmethylsilyl)propane (35.3 g, 0.10 mol) in the presence of freshly sublimed aluminum chloride (0.64 g, 4.8 mmol) at room temperature for 6.5 h. Acetone (1 mL) was added, and distillation gave pure **5c** in 80.4% yield: bp 80–82 °C (0.4 mmHg): ^{1}H NMR (CCl_4/CH_2Cl_2) δ 0.83 (s, 6 H), 1.13–2.03 (m, 6 H).

1,2-Bis(dichloromethylsilyl)ethane[11] was prepared according to the reference.

Preparation of a Solution of 1,4-Dilithio-1,4-diphenyl-1,3-butadiene. 1,4-Dibromo-1,4-diphenyl-1,3-butadiene[4] (10.9 g, 30.0 mmol) and ether (100 mL) were placed in a 500-mL three-necked flask. *n*-Butyllithium (60 mmol) was added to the solution at 0 °C for 20 min. After the mixture was stirred for 40 min, tetramethylethylenediamine (6.97 g, 60.0 mmol) in 50 mL of ether was added to the mixture. THF (100 mL) was then added to make a clear solution.

Preparation of Bis(1-methyl-2,5-diphenyl-1-silacyclopentadien-1-yl)methane, 3a. Bis(difluoromethylsilyl)methane (2.64 g, 15.0 mmol) in 50 mL of THF was added to a solution of 1,4-dilithio-1,4-diphenyl-1,3-butadiene at 0 °C. After usual workup, an orange-yellow viscous oil was obtained. Recrystallization from ether–benzene gave **3a** (1.90 g, 24.9%): mp 174–175 °C; MS, *m/e* 508 (M^+); ^{1}H NMR ($CDCl_3/CH_2Cl_2$) δ 1.41 (s, 6 H), 1.66 (s, 2 H), 6.97 (s, 4 H), 6.6–7.3 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ -3.4, -0.9, 126.3, 126.6, 128.4, 138.2, 138.6, 144.3; ^{29}Si NMR ($CDCl_3$) δ 2.03. Anal. Calcd for $C_{35}H_{32}Si_2$: C, 82.62; H, 6.34. Found: C, 82.50; H, 6.35.

Preparation of 1,2-Bis(1-methyl-2,5-diphenyl-1-silacyclopentadien-1-yl)ethane, 3b. A procedure similar to that used for the preparation of **3a** was employed: yield 54.2%; mp 241–242 °C; MS, *m/e* 522 (M^+); ^{1}H NMR ($CDCl_3/CH_2Cl_2$) δ 0.37 (s, 6 H), 1.02 (s, 4 H), 7.1–7.4 (m, 24 H); ^{13}C NMR ($CDCl_3$) δ -4.4, 6.4, 126.0, 126.7, 128.7, 138.9, 139.0, 143.4. Anal. Calcd for $C_{36}H_{32}Si_2$: C, 82.70; H, 6.55. Found: C, 82.90; H, 6.59.

Preparation of 1,3-Bis(1-methyl-2,5-diphenyl-1-silacyclopentadien-1-yl)propane, 3c. A procedure similar to that used for the preparation of **3a** was employed: 57.7% yield; mp 113–115 °C; MS, *m/e* 536 (M^+); ^{1}H NMR ($CDCl_3/CH_2Cl_2$) δ 0.40 (s, 6 H), 0.80–1.05 (m, 4 H), 1.15–1.47 (m, 2 H), 7.10 (s, 4 H), 7.1–7.4 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 4.2, 17.6, 18.4, 126.1, 126.6, 128.5, 138.5, 139.0, 144.1; ^{29}Si NMR ($CDCl_3$) δ 4.05. Anal. Calcd for $C_{37}H_{36}Si_2$: C, 82.78; H, 6.76. Found: C, 82.73; H, 6.82.

Preparation of 1,2-Bis(1-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadien-1-yl) ethane, 7. Diphenylacetylene (10.0 g, 56.2 mmol) and lithium wire (0.46 g, 66.0 mmol) were stirred in ether at room temperature for 27 h. THF (200 mL) and then 1,2-bis(dichoromethylsilyl)ethane (14.3 g, 56.0 mmol) were added to the mixture. After being stirred for 5.5 h, the mixture was hydrolyzed and worked up to give **7** in 2% yield: mp 261–264

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(10) Petrov, A. D.; Mironov, V. F. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1952**, 635; *Chem. Abstr.* **1953**, *47*, 10471.

(11) Petrashko, A. I. *Viskomol. Soed., Ser A* **1967**, *9*, 2034.

°C; MS, *m/e* 826 (M^+); ^1H NMR ($CDCl_3/CH_2Cl_2$) δ 0.36 (s, 6 H), 0.96 (s, 4 H), 6.6–7.3 (m, 40 H). Anal. Calcd for $C_{60}H_{50}Si_2$: C, 87.12; H, 6.09. Found: C, 86.82; H, 6.29.

Photochemical Reactions of 3. A THF (500-mL) solution of **3a** (531 mg, 1.04 mmol in a Pyrex photochemical reactor) was bubbled with argon and irradiated with a 450-W high-pressure Hg lamp for 3 h. The yellow color changed to colorless. After evaporation of the solvent, white crystals (444 mg, 83.7%) of **8a** were obtained: mp 166–168 °C; MS, *m/e* 508 (M^+); ^1H NMR ($CDCl_3/CH_2Cl_2$) δ 0.39 (s, 6 H), 0.39 (d, $J = 15$ Hz, 2 H), 4.60 (m, 2 H), 6.67 (m, 2 H), 6.9–7.4 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ –2.3, 0.3, 50.1 52.9, 124.0, 126.4, 127.4, 128.2, 140.1, 143.2, 145.7, 147.5; ^{29}Si NMR ($CDCl_3$) δ 32.7. Anal. Calcd for $C_{35}H_{32}Si_2$: C, 82.62; H, 6.34. Found: C, 82.36; H, 6.37.

Similarly, **8b** (522 mg, 86.4%) was obtained from **3b** (604 mg, 1.15 mmol): mp 172–173 °C; MS, *m/e* 522 (M^+); ^1H NMR ($CDCl_3$) δ –0.14 (s, 6 H), 1.32 (AA′BB′, 4 H), 4.39 (m, 2 H), 6.7–7.3 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ –2.7, 7.4, 43.8, 50.4, 122.0, 124.6, 125.3, 126.5, 127.3, 137.9, 141.5, 143.6, 144.1; ^{29}Si NMR ($CDCl_3$) δ 16.8. Anal. Calcd for $C_{36}H_{32}Si_2$: C, 82.70; H, 6.55. Found: C, 82.90; H, 6.59.

By a similar procedure to that of **3a**, **3c** (611 mg, 1.14 mmol) was irradiated to give **8c** (518 mg, 84.8%): mp 162–163 °C; MS, *m/e* 536 (M^+); ^1H NMR ($CDCl_3/CH_2Cl_2$) δ –0.18 (s, 6 H), 1.1–1.6 (m, 4 H), 1.9–2.3 (m, 2 H), 4.43 (m, 2 H), 6.7–7.1 (m, 2 H), 6.9–7.4 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 0.3, 16.5, 17.8, 48.5, 53.0 124.2, 126.7, 126.9, 127.4, 128.7, 129.4, 144.0, 140.3, 144.2, 146.2; ^{29}Si NMR ($CDCl_3$) δ 21.3. Anal. Calcd for $C_{37}H_{36}Si_2$: C, 82.78; H, 6.76. Found: C, 82.91; H, 6.82.

Registry No. **1**, 7688-03-1; **2a**, 33492-52-3; **2b**, 33375-55-2; **2c**, 33375-56-3; **3a**, 87433-06-5; **3b**, 87433-07-6; **3c**, 87433-08-7; **4**, 55373-67-6; **5a**, 87433-09-8; **5b**, 3353-69-3; **5c**, 16957-21-4; **6**, 7641-40-9; **7**, 87433-10-1; **8a**, 87450-36-0; **8b**, 87433-11-2; **8c**, 87433-12-3; Me_2SiCl_2, 75-78-5; (*Z*,*Z*)-1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene, 57956-30-6; bis(dichloromethylsilyl)methane, 4519-03-3; bis(trimethylsilyl)methane, 2117-28-4; bis(diethoxymethylsilyl)methane, 18048-25-4; 1-(dichloromethylsilyl)-3-(diphenylmethylsilyl)propane, 87433-13-4; allylmethyldiphenylsilane, 17922-43-9; dichloromethylsilane, 75-54-7; 1,4-dibromo-1,4-diphenyl-1,3-butadiene, 55373-68-7; diphenylacetylene, 501-65-5.

Activation of C–H and C–C Bonds in Alkanes by First-Row Group 8 Atomic Transition-Metal Ions in the Gas-Phase. Mechanistic Details from a Study of Deuterium and ^{13}C-Labeled Hydrocarbons[†]

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The first step in the interaction of saturated hydrocarbons with atomic group 8 metal ions involves oxidative addition of either a C–H or a C–C bond to the metal. At low energies this is followed by unimolecular rearrangement and elimination of smaller alkanes or molecular hydrogen. The present report is a continuation of our ion beam studies of these processes, in which we make extensive use of deuterium and ^{13}C-labeled normal, branched, and cyclic alkanes to elucidate mechanistic details. While overall patterns of reactivity are similar, the labeling results reveal subtle differences in comparing the behavior of Fe^+, Co^+, and Ni^+. For example, dehydrogenation of linear alkanes by Ni^+ proceeds exclusively via a 1,4-elimination process, while dehydrogenation by Fe^+ and Co^+ occurs via a mixture of 1,4 and 1,2 eliminations and seems to be accompanied by some scrambling. In several cases involving the reactions of Fe^+, product distributions are best explained by assuming that β-alkyl transfers occur as one step in the decomposition of reaction intermediates. The fragmentation of a hydrocarbon molecule by reaction with a group 8 metal ion is highly specific and occurs without the extensive rearrangements that often accompany electron-impact ionization. This suggests the use of gas-phase metal ion reactions as a novel chemical ionization technique to determine not only the structure but also the original label distribution in a molecule.

Introduction

Considerable interest in the subject of C–H bond activation at transition-metal centers has developed in the past several years, stimulated by the observation that even saturated hydrocarbons can react with little or no activation energy under appropriate conditions.[2] Interestingly, gas-phase studies of the reactions of saturated hydrocarbons at transition-metal centers were reported as early as 1973.[3] More recently, ion cyclotron resonance[4–7] and ion beam experiments[8–10] have provided many examples of activation of both C–H and C–C bonds of alkanes by transition-metal ions. Facile addition of C–H or C–C bonds to metal centers requires first that the process be energetically feasible, preferably exothermic (Scheme I). Metal–hydrogen bonds in the range of 60 kcal/mol would require metal–carbon bond energies greater than 35 kcal/mol for 1 to be more stable than the reactants.[11,12]

Scheme I

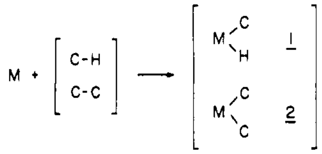

Table I. Thermochemical Data[a, b]

bond energies	Fe^+	Co^+	Ni^+
$D°(M^+–H)$	58 ± 5	52 ± 4	43 ± 2
$D°(M^+–CH_3)$	69 ± 5	61 ± 4	48 ± 5
$D°(M^+–CH_2)$	96 ± 5	85 ± 7	86 ± 6

[a] All values in kcal/mol. [b] See ref 8, 9, and 16.

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