Notes

Far-UV Photochemistry of 1,1-Dimethyl-1-silacyclopent-3-ene: Photoextrusion of Dimethylsilylene and Stereoselective 1,4-Addition of Methanol to an Intermediate Vinylsilirane

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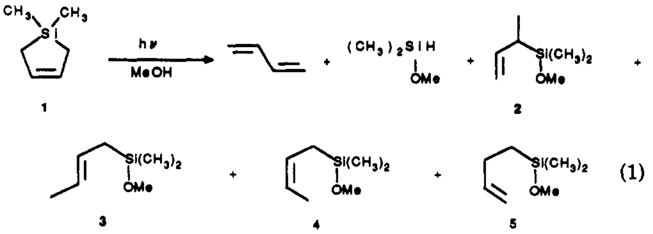
Summary: Photolyses of 1,1-dimethyl-1-silacyclopent-3-ene at 214 nm in methanol give 1,3-butadiene, methoxydimethylsilane, (*Z*)-2-butenylmethoxydimethylsilane, and 3-butenylmethoxydimethylsilane as primary products. According to quantum yields for product formation and viscosity effects, the predominant photoprocess is disengagement of dimethylsilylene, which is trapped by methanol in competition with 1,2-addition of the silylene to the initially formed 1,3-butadiene. Deuterium labeling studies indicate that the resultant vinylsilirane then undergoes stereoselective 1,4-addition of methanol.

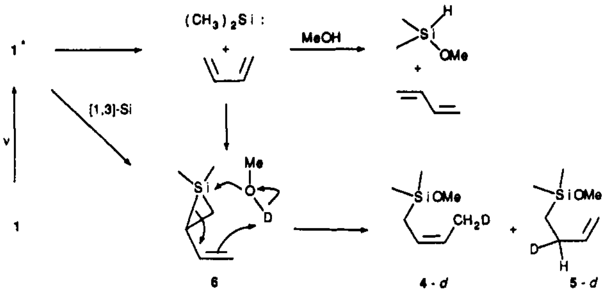
In previous studies we have shown that replacement of carbon by silicon at the allylic positions of cycloalkenes facilitates the formation of photoalcoholysis products. Most striking are 1,1-dimethyl-1-silacyclopent-2-ene and 1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene, which upon 214-nm photolysis in alcohols as weakly acidic as *tert*-butyl alcohol give rise to alcohol adducts via carbocation intermediates produced through proton transfer to the double bond.[1,2] We now report that when silicon is not directly attached to the double bond, as with 1,1-dimethyl-1-silacyclopent-3-ene (1), photoprotonation to give β-silyl-stabilized carbocations is not a significant process. Instead the photochemistry reflects a preference for excited-state disengagement of dimethylsilylene.

Results and Discussion

Preparative direct photolysis of 10^{-2} M solutions of silacyclopent-3-ene 1[3] in methanol, either with the unfiltered output of a 450-W Hanovia medium-pressure mercury lamp or at 214 nm with a Philips zinc lamp, gave 1,3-butadiene, methoxydimethylsilane, and methanol adducts 2–5 (eq 1). Products 2–5 were isolated by preparative GC and identified by comparison of capillary GC retention times, as well as ^1H,^{13}C NMR and IR spectral data, to independently synthesized samples. Photoproducts 2 and 4 were completely separated on a preparative scale, whereas 3 and 5, which were minor products, had to be characterized as a mixture.



Scheme I



Compound 5 was synthesized by a previously reported method.[2] Known[4] compounds 2–4 were prepared in ca. 80% combined yield, as a mixture, by reaction of chloromethoxydimethylsilane with the Grignard reagent prepared from a *Z,E* mixture of 1-chloro-2-butenes in THF. Each isomer was separated by preparative GC and characterized by ^1H,^{13}C NMR and IR spectroscopy. The stereochemistry of 3 and 4 was assigned on the basis of IR and ^{13}C NMR spectroscopy. As reported previously,[4] adduct 3 exhibited an out-of-plane bending mode at 964 cm^{-1}, whereas the corresponding band of 4 appeared at 723 cm^{-1}. Furthermore, the C═C stretch of 3 at 1662 cm^{-1} was quite weak, in contrast to the medium intensity of this band at 1649 cm^{-1} in the case of 4. As with *Z* versus *E* olefins in general,[5] the ^{13}C chemical shifts of the vinyl methyl and methylene groups of 4 were upfield by 5.5 and 4.4 ppm, respectively, from the corresponding peaks of 3.

The volatile products, 1,3-butadiene and methoxydimethylsilane, were identified by GC–MS analyses and by comparison of GC retention times to authentic samples on three columns. Methoxydimethylsilane was further characterized by ^1H NMR spectroscopy of a sample, which was collected in a dry ice–acetone trap by purging a hexane extract of the photolysate with nitrogen; the product also contained hexane.

Photochemical product yields determined at 214 nm (Table I) showed a strong preference for formation of methoxydimethylsilane and cis methanol adduct 4. Of the minor products, 2 and 3 appeared to be secondary photoproducts of 4. This was evident from the ratio of percent yield to percent total products (Table II), which for 2 deviated by 28% over a 0.87–4.7% range of conversions.

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Table I. Quantum Yields[a,b] and Chemical Yields[a]

product	MeOH yield, %	quantum yield, Φ		
		MeOH	MeOH–hexane[c]	MeOH–dodecane[c]
$Me_2SiH(OMe)$	13 (0.55)	0.051 ± 0.005	0.063 ± 0.003	0.034 ± 0.005
2	3.1 (0.0079)	*d*	*d*	*d*
3	2.2 (0.053)	*d*	*d*	*d*
4	9.0 (0.65)	0.058 ± 0.001	0.045 ± 0.003	0.088 ± 0.003
5	2.4 (0.099)	0.010 ± 0.001	*d*	0.0044 ± 0.0005
1	71 (*e*)	*e*	*e*	*e*
% conversn	29[f] (1.4)[g]	2.1	2.0	3.2

[a] Determined at 214 nm; all chemical yields are absolute, i.e., relative to starting millimoles of reactant 1 at time zero in photolyses. [b] Average of duplicate runs utilizing uranyl oxalate as actinometer with an Acton 214-B-ID interference filter; see refs 2, 17, and 18. [c] 0.5 M methanol plus cosolvent. [d] Yield too low to quantify. [e] Not determined. [f] Based on unreacted starting material. [g] Based on total products.

Table II. Ratio of Product Yield (% P_i) to Total Yield ($\sum$% P_i) for 214-nm Photolysis of Silacyclopent-3-ene in Methanol

	% P_i/$\sum$% P_i[a,b]					
time, min	Me_2SiH-(OMe)	2	3	4	5	$\sum$% P_i
10	0.44	*c*	*c*	0.49	0.069	0.87
15	0.41	0.006	0.039	0.48	0.073	1.4
20	0.41	0.015	0.038	0.46	0.072	1.9
25	0.41	0.014	0.041	0.47	0.071	2.2
30	0.41	0.019	0.043	0.46	0.070	2.6
35	0.41	0.020	0.045	0.45	0.072	3.2
40	0.41	0.023	0.050	0.45	0.070	3.6
50	0.42	0.026	0.040	0.44	0.070	4.7
av	0.42	0.018	0.042	0.46	0.071	
% av dev[d]	2.2	28	7.1	2.2	1.6	

[a] % P_i is a product yield, and $\sum$ % P_i is the sum of all product yields. [b] Product yields were determined by GC analyses and are relative to starting millimoles of reactant 1 at time zero in the photolysis. [c] Barely detectable. [d] Average of absolute deviation from the mean.

In addition, 214-nm photolysis of **4** in methanol gave 13% **2** and 7.1% **3** at 40% conversion.

The predominance of **4** among products **2**–**5** can be attributed to 1,4-addition of methanol to the syn conformer of silirane **6** (Scheme I). 1,2-Addition of methanol was only a minor process, as indicated by the ratio **4**:**5** of 7.1 (0.87% conversion). Additional support for **6** as an intermediate comes from deuterium labeling studies. Preparative photolysis of **1** in methanol-*O*-*d* gave **4** with one deuterium exclusively at the vinyl methyl, while adduct **5** was monodeuterated at the allylic methylene group (Scheme I). The position deuterated in each photoproduct was assigned on the basis of ^1H, ^2H, and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of **4** showed the methyl group at 12.27 ppm as a 1:1:1 triplet; this chemical shift corresponded to the vinyl methyl rather than the vinyl methylene group at 17.4 ppm, according to the ^{13}C APT spectrum of the undeuterated sample. From the integrated intensity of the 1.5–1.6 ppm multiplet corresponding to the overlapping methyl and methylene groups in the ^1H NMR, adduct **4** was found to be essentially monodeuterated. ^2H NMR showed that deuterium was not present elsewhere in the molecule. In the case of **5**, the assignment of the allylic methylene group as being monodeuterated was completely straightforward. Since no deuterium was detected at the vinyl group by ^2H NMR spectroscopy, this compound was not formed by a mechanism involving photoprotonation of the double bond, followed by Si–C bond cleavage of the β-silacyclopentyl cation.[2]

1,4-Addition of methanol to a vinylsilirane generated through trapping of a silylene by 2,3-dimethyl-1,3-butadiene has been reported previously.[6] The analogous addition of methanol to **6** proceeds with cis stereoselectivity suggestive of the concerted 1,4-addition of alcohol. Cis-stereoselective 1,2-addition of methanol to a nonconjugated silirane is known.[7]

The intermediacy of a vinylsilirane in the photochemistry of silacyclopent-3-ene **1** notwithstanding, the principal photoprocess of **1** is extrusion of dimethylsilylene, as evidenced by the formation of methoxydimethylsilane with a quantum yield as high as 0.06 out of a total quantum yield for product formation of 0.11 (Table I). The 1,3-butadiene formed was not quantified. In addition to affording methoxysilanes through insertion[8] into the OH bond of methanol, silylenes are known to undergo 1,2-addition to 1,3-dienes to form vinylsiliranes.[6,9] Trapping by alcohols is essentially diffusion controlled,[10] suggesting that the ratio of **4** plus **5** to methoxydimethylsilane could depend on the viscosity of the medium, given that the silylene would be formed in the solvent cage with the 1,3-diene. On going from hexane (η = 0.313 cP at 20 °C) to dodecane (η = 1.508 cP at 20 °C), while keeping the temperature constant, the ratio of **4** plus **5** to methoxydimethylsilane increased from 0.71 to 2.7, or by a factor of 4 (Table I). Since the total quantum yield for product formation in methanol of 0.11 remained unchanged in the mixed solvents, 0.5 M methanol in hexane or dodecane, the decrease in quantum yield for methoxydimethylsilane results in a corresponding increase in the quantum yield for formation of methanol adducts. Conversions were kept low (2–3%) to minimize secondary photolysis of **4**.

The effect of viscosity on quantum yields indicates that a significant fraction of vinylsilirane **6** is produced by cage addition of dimethylsilylene to the initially formed 1,3-butadiene (Scheme I). Nonetheless, formation of **6** by excited-state 1,3 Si migration in photoexcited **1** is not excluded. This raises the possibility that secondary photolysis of **6** could afford dimethylsilylene.[11] Unlike recent

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(6) Ishikawa, M.; Ohi, F.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C23.

(7) (a) Tortorelli, V. J.; Jones, M.; Wu, S.; Li, Z. *Organometallics* **1983**, *2*, 759. (b) Tortorelli, V. J.; Jones, M., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 1425.

(8) (a) The insertion of dimethylsilylene into methanol is presumably stepwise, proceeding via a Lewis acid–base complex. Complexes of hindered silylenes with isopropyl alcohol or *sec*-butyl alcohol have been observed spectroscopically. (b) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487.

(9) (a) Zhang, S.; Conlin, R. T. *J. Am. Chem. Soc.* **1991**, *113*, 4272, and references cited therein. (b) Lei, D.; Gaspar, P. P. *J. Chem. Soc., Chem. Commun.* **1985**, 1149. (c) Lei, D.; Hwang, R.-J.; Gaspar, P. P. *J. Organomet. Chem.* **1984**, *271*, 1. (d) Ishikawa, M.; Nakagawa, K.-I.; Enokida, R.; Kumada, M. *J. Organomet. Chem.* **1980**, *201*, 151. (e) Ishikawa, M.; Nakagawa, K.-I.; Kumada, M. *J. Organomet. Chem.* **1979**, *178*, 105.

(10) For a comprehensive review on rate constants for silylene reactions, see: Safarik, I.; Sandhu, V.; Lown, E. M.; Strausz, O. P.; Bell, T. N. *Res. Chem. Intermed.* **1990**, *14*, 105.

(11) To avoid the remote possibility of secondary photolysis of low concentrations of vinylsilirane **6** in dilute methanol, as well as secondary photolysis of products **4** and **5**, conversions of **1** during quantum yield runs were kept low (Table I), and a bandpass filter was used to isolate the 214-nm line of the zinc lamp to ensure that >99% of the light was absorbed by **1** (Experimental Section).

work[9a] on the generation of stable, sterically crowded vinylsiliranes under nonnucleophilic conditions, the unhindered vinylsilirane 6, generated in the presence of methanol, is unlikely to build up to sufficient concentration to compete for light with 1. Upon photolysis, vinylsiliranes undergo 1,3 Si migration to give silacyclopent-3-enes and photorearrange to silylallenes.[9a,d,e] In the case of 6, such a 1,3 Si shift to regenerate 1 would have led to decreased quantum yields for 4 plus 5 in going from pure methanol to dilute methanol in hydrocarbon solvents (Table I), since the steady-state concentration of 6 would have been higher under the latter conditions. An isomeric allenic photoproduct[9a,d] of 6 also was not observed. Given the above, dimethylsilylene is formed directly from photoexcited 1. In this respect the photochemical and pyrolytic mechanisms for generation of dimethylsilylene from 1[12] are different. The thermolysis mechanism[12] involves a 1,3 Si shift to give the vinylsilirane, which then undergoes disengagement of dimethylsilylene in competition with Si–C and C–C one-bond cleavages.

Experimental Section

Spectra were recorded with the following spectrometers: GE GN-300 (300 MHz, ^{1}H; 75 MHz, ^{13}C; 46 MHz, ^{2}H NMR), Mattson 4020 Galaxy Series (FTIR), Perkin-Elmer 320 (UV). A Hewlett-Packard 5890 GC and HP-5970 mass selective detector were used for GC–MS analyses, which were performed at 70 eV with a 0.25 mm × 30 m DB-1 capillary column programmed at 40 °C for 4 min and then 280 °C at 10 °C min^{-1}.

Preparative GC separations were performed on a GOW-MAC (Series 580) gas chromatograph with He as carrier gas at 30 mL min^{-1} flow rate on the following columns: column A, 15 ft × $^1/_4$ in. 15% OV-101 on 60/80 mesh Chromosorb W; column B, 17 ft × $^1/_4$ in. 15% didecyl phthalate on 60/80 mesh Chromosorb W.

A Varian 1400 gas chromatograph equipped with a flame ionization detector and a HP 3390 A electronic intergrating recorder were used for analytical separations. Nitrogen was the carrier gas. Detector response was calibrated against standard mixtures utilizing either column C, 23 ft × $^1/_8$ in. 10% OV-101 on 100/120 mesh Chromosorb W HP, or column D, 24 ft × $^1/_8$ in. 23% Alltech AT-1700 on 80/100 mesh Chromosorb P-AW.

Methanol (EM Omnisolv, distilled from magnesium), hexane (EM Omnisolv, 99+%), and purified dodecane were used as solvents in photolyses. To purify dodecane (Fluka), 150 mL was washed twice with 25 mL of 18–24% fuming sulfuric acid (Aldrich), three times with 30 mL of 10% sodium bicarbonate, and twice with 40 mL of saturated sodium chloride and then dried over anhydrous sodium sulfate. The dodecane was fractionated at reduced pressure, and the middle fraction of the distillate was collected. After this treatment, the UV absorbance of the dodecane at 214 nm was reduced from 3.3 to 0.07.

1,1-Dimethyl-1-silacyclopent-3-ene (1). *cis*-1,4-Dibromobut-2-ene was synthesized from the corresponding diol by following the procedure of Feigenbaum and Lehn[13] and used to prepare silacyclopent-3-ene 1 by following the method of Manuel and co-workers.[3] The silacyclopentene was purified by preparative GC on column A at 83 °C. The ^{1}H NMR and IR spectral data were as reported previously:[3] CG–MS (70 eV) *m/z* (relative intensity) 112 (26), 98 (10), 97 (100), 95 (30), 71 (14), 69 (11), 59 (18), 58 (37), 53 (20), 45 (10), 43 (75), 42 (15); UV λ_{max} (methanol) 200 nm (ϵ 1880).

Synthesis of (*E*)- and (*Z*)-2-Butenylmethoxydimethylsilanes (3) and (4) and (1-Methyl-2-propenyl)methoxydimethylsilane (2). To 5.0 g (0.21 mol) of magnesium, 11.0 g (0.088 mol) of chloromethoxydimethylsilane (Petrarch), and 300 mL of THF under nitrogen was added, dropwise with mechanical stirring, 11.5 g (0.076–0.088 mol) of a mixture of *cis*- and *trans*-1-chlorobut-2-enes (Fluka, 60–70%) in 100 mL of THF over a period of 3 h at room temperature. After the addition was complete, the mixture was stirred for 1 h in a hot water bath and cooled, and 300 mL of pentane was added. The mixture was washed 12 times with 200 mL of water and dried over sodium sulfate. The bulk of the pentane was removed by distillation, and the residue was fractionated to give 10.3 g (81–95% yield) of a mixture of isomeric methoxysilanes, bp 74–77 °C (185 mmHg). GC analysis of the mixture showed a ratio of (1-methyl-2-propenyl)methoxydimethylsilane (2) to *trans*-2-butenylmethoxydimethylsilane (3) to *cis*-2-butenylmethoxydimethylsilane (4) of 1.4:2.3:1. The isomers were separated by preparative GC on column B at 72 °C. The spectral data were as follows.

(1-Methyl-2-propenyl)methoxydimethylsilane (2): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.09 (s, 6 H, methyl), 1.10 (d, J = 7.2 Hz, 3 H, methyl), 1.78 (quintet, t, J = 7.3, 1.5 Hz, 1 H, methine), 3.46 (s, 3 H, methoxy), 4.88 (dt, J = 17.0, 1.7 Hz, 1 H, vinyl), 4.97 (dt, J = 10.6, 1.7 Hz, 1 H, vinyl), 5.91 (ddd, J = 17.0, 10.6, 7.2 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, CDCl$_3$) δ −4.88, −4.68, 12.38, 27.87, 50.73, 110.96, 140.59; IR (CDCl$_3$) 3.24, 3.38, 3.44, 3.49, 3.53, 6.25 (m), 6.83, 6.87, 7.07, 7.98, 9.26, 9.64 μm; GC–MS (70 eV) *m/z* (relative intensity) 144 (1), 129 (2), 91 (3), 90 (8), 89 (100), 75 (10), 61 (4), 60 (57), 59 (66), 58 (6), 55 (3), 53 (2), 45 (7), 43 (9).

trans-2-Butenylmethoxydimethylsilane (3): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.10 (s, 6 H, methyl), 1.51–1.53 (m, 2 H, methylene), 1.63–1.66 (m, 3 H, methyl), 3.44 (s, 3 H, methoxy), 5.25–5.46 (complex m, 2 H, vinyl); ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.97, 18.02, 21.83, 50.42, 124.27, 125.61; IR (neat) 3.32, 3.38, 3.41, 3.47, 3.53, 6.01 (w), 6.88, 7.26, 7.66, 7.85, 8.40, 8.61, 9.15, 9.58, 10.37, 11.01, 11.81, 15.34 μm; GC–MS (70 eV) *m/z* (relative intensity) 144 (4), 129 (2), 101 (2), 97 (2), 90 (8), 89 (100), 75 (11), 60 (5), 59 (62), 58 (6), 55 (3), 45 (7), 43 (8).

cis-2-Butenylmethoxydimethylsilane (4): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.11 (s, 6 H, methyl), 1.56–1.61 (m, 5 H, methyl plus methylene), 3.45 (s, 3 H, methoxy), 5.35–5.48 (m, 2 H, vinyl); ^{13}C APT NMR (75 MHz, CDCl$_3$) δ −2.79 (methyl), 12.54 (methyl), 17.42 (methylene), 50.42 (methoxy), 122.24 (vinyl), 124.92 (vinyl); IR (neat) 3.31, 3.38, 3.40, 3.53, 6.06 (m), 6.90, 7.16, 7.34, 7.49, 7.99, 8.65, 9.14, 9.82, 10.09, 11.05, 11.95, 13.82, 14.90 μm; GC–MS (70 eV) *m/z* (relative intensity) 144 (4), 129 (2), 101 (2), 97 (2), 91 (4), 90 (8), 89 (100), 75 (12), 59 (72), 58 (7), 55 (3), 45 (10), 43 (11).

3-Butenylmethoxydimethylsilane (5). This compound was prepared as reported previously.[2] The spectral data were as follows: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.11 (s, 6 H, methyl), 0.68–0.74 (m, 2 H, methylene), 2.06–2.15 (m, 2 H, methylene), 3.43 (s, 3 H, methoxy), 4.88–5.04 (m, 2 H, vinyl), 5.88 (ddt, J = 17.0, 10.3, 6.3 Hz, 1 H, vinyl); ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.61, 15.00, 27.16, 50.23, 112.88, 141.23; GC–MS (70 eV) *m/z* (relative intensity) no parent, 129 (11), 101 (4), 97 (15), 89 (100), 75 (23), 59 (56), 55 (3), 47 (12), 43 (13). Homonuclear decoupling, irradiating at 2.10 ppm, gave the following spectrum: δ 0.11 (s, 6 H, methyl), 0.71 (br s, 2 H, methylene), 3.43 (s, 3 H, methoxy), 4.91 (dd, J = 10.0, 1.9 Hz, 1 H, vinyl), 5.01 (dd, J = 17.1, 1.9 Hz, 1 H, vinyl), 5.89 (dd, J = 17.0, 10.0 Hz, 1 H, vinyl). Thus the methylene group at 2.06–2.15 ppm was found to be attached to the vinyl group.

Methoxydimethylsilane. To 5.45 g (0.170 mol) of methanol, 22.0 g (0.170 mol) of quinoline, and 60 mL of heptane (Aldrich) was added, dropwise with stirring under nitrogen, 15.0 g (0.154 mol) of chlorodimethylsilane (Petrarch) in 50 mL of heptane. The reaction mixture was refluxed for 3 h. The mixture was distilled, collecting the fraction at 53–62 °C. The distillate was fractionated through a 12-in. Vigreux column to give 8.80 g (63.4%) of methoxydimethylsilane[14] at 33–40 °C. The product was further purified by preparative GC on column B at room temperature. The spectral data were as follows: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.20 (d, J = 2.8 Hz, 6 H, methyl), 3.46 (s, 3 H, methoxy), 4.58 (septet, J = 2.8 Hz, 1 H, silane); ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.08, 51.54; GC–MS (70 eV) *m/z* (relative intensity) 90 (6), 89 (64), 77 (4), 76 (7), 75 (100), 61 (4), 60 (5), 59 (63), 58 (6), 54 (12), 53 (9), 45 (70), 44 (13), 43 (23).

Preparative Direct Photolysis of 1,1-Dimethyl-1-silacyclopent-3-ene (1) in Methanol. A solution of 535 mg (4.46

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(13) Feigenbaum, A.; Lehn, J. M. *Bull. Soc. Chim. Fr.* **1973**, 198.

(14) Viswanathan, N.; Van Dyke, C. J. *J. Chem. Soc. A* **1968**, 487.

mmol) of silacyclopentene 1 in 250 mL of methanol (distilled from magnesium) was purged with nitrogen for 1.5 h and then irradiated with the unfiltered output of a Hanovia 450-W medium-pressure mercury lamp. The lamp and photolysate were cooled by circulating 0 °C methanol and water through the jacketed quartz apparatus. Progress of the photolysis was monitored by GC–MS analyses of aliquots to which an equal volume of hexane was added, followed by washing with water. In addition to starting alkene, seven products were observed which had retention times and mass spectra corresponding to authentic samples of 2–5, 1,3-butadiene,[15] and methoxydimethylsilane. After irradiating for 4 h, 40 mL of hexane was added and the photolysate was washed twice with 200 mL of water and dried over anhydrous sodium sulfate. The presence of 1,3-butadiene and methoxydimethylsilane was established by GC–MS and by comparison of GC retention times on three columns: capillary DB-1, 0.25 mm × 30 m at 40 °C, 1,3-diene (1.35 min), silane (1.57 min); column C at 55 °C, flow rate, 6 mL min^{-1}, 1,3-diene (8.0 min), silane (10.0 min); column D, 23% AT-1700 at 60 °C, flow rate, 19 mL min^{-1}, 1,3-diene (16.2 min), silane (28.3 min). A sample of methoxydimethylsilane was also obtained by purging the warm hexane extract with nitrogen for 1.5 h, collecting the sample in a dry ice–acetone trap. The methoxydimethylsilane, which was contaminated with hexane, was then identified by ^{1}H NMR spectroscopy. The bulk hexane extract of the photolysate was concentrated to ca. 1.5 mL and subjected to preparative GC on column B at 76 °C. Products 3 and 5 were not separable, preparatively, and were thus characterized as a mixture. The identity of each product was established by comparison of ^{1}H and ^{13}C NMR spectra and in the case of 2 and 4 IR spectral data as well, to authentic samples.

Preparative Direct Photolysis of 1,1-Dimethyl-1-silacyclopent-3-ene (1) in Methanol-*O*-d_1. A solution of 1.0 g (8.91 mmol) of silacyclopentene 1 and 30 mL of methanol-*O*-d_1 (Aldrich, 99.5+ atom % D) in 220 mL of cyclohexane (Aldrich) was irradiated with a Hanovia 450-W medium-pressure mercury lamp for 4 h as described above. The photolysate was washed twice with 250 mL of water, dried over anhydrous sodium sulfate, and concentrated to ca. 1.5 mL by distillation of the solvent. The products were isolated by preparative GC on column B (76 °C). Products 3-*d* and 5-*d* could not be separated preparatively, and thus, the individual ^{1,2}H and ^{13}C NMR spectra (vide infra) are extracts from composite spectra.

[1-(Deuteriomethyl)-2-propenyl]methoxydimethylsilane (2-*d*): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.09 (s, 6 H, methyl), 1.08 (dt, *J* = 7.2, 2 Hz, 2 H, deuteriomethyl), 1.77 (br q, *J* = 7 Hz, 1 H, methine), 3.46 (s, 3 H, methoxy), 4.88 (dt, *J* = 17.0, 1.7 Hz, 1 H, vinyl), 4.97 (dt, *J* = 10.6, 1.7 Hz, 1 H, vinyl), 5.91 (ddd, *J* = 17.0, 10.6, 7.2 Hz, 1 H, vinyl); ^{2}H NMR (46 MHz, CDCl$_3$) δ 1.12; ^{13}C NMR (75 MHz, CDCl$_3$) δ −4.48, −4.65, 12.12 (t, *J* = 19 Hz), 27.81, 50.75, 110.98, 140.62; GC–MS (70 eV) *m*/*z* (relative intensity) 145 (1), 130 (2), 91 (4), 90 (10), 89 (100), 76 (4), 75 (7), 61 (4), 59 (66), 58 (6), 45 (7), 43 (10).

(*trans*-1-Deuterio-2-butenyl)methoxydimethylsilane (3-*d*): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.10 (s, 6 H, methyl), 1.52 (br d, *J* = 7 Hz, 2 H, methylene), 1.61–1.65 (complex m, 2 H, deuteriomethyl), 3.43 (s, 3 H, methoxy), 5.25–5.46 (complex m, 2 H, vinyl); ^{2}H NMR (46 MHz, CDCl$_3$) δ 1.61; ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.97, 16.72 (t, *J* = 19 Hz), 21.85, 50.42, 124.24, 125.61; GC–MS (70 eV) *m*/*z* (relative intensity) 145 (4), 130 (3), 91 (9), 89 (100), 76 (4), 75 (8), 61 (3), 60 (6), 59 (57), 58 (6), 45 (7), 43 (9).

(*cis*-1-Deuterio-2-butenyl)methoxydimethylsilane (4-*d*): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.11 (s, 6 H, methyl), 1.51–1.61 (m, 4 H, deuteriomethyl plus methylene), 3.45 (s, 3 H, methoxy), 5.35–5.48 (m, 2 H, vinyl); ^{2}H NMR (46 MHz, CDCl$_3$) δ 1.61; ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.81, 12.27 (t, *J* = 19 Hz), 17.40, 50.42, 122.18, 124.92; GC–MS (70 eV) *m*/*z* (relative intensity) 145 (4), 130 (2), 91 (3), 90 (9), 89 (100), 82 (8), 76 (4), 71 (3), 67 (6), 59 (63), 58 (10), 57 (25), 56 (6), 44 (10), 43 (15), 41 (8).

(2-Deuterio-3-butenyl)methoxydimethylsilane (5-*d*): ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.12 (s, 6 H, methyl), 0.69–0.72 (m, 2 H, methylene), 2.06–2.15 (m, 1 H, deuteriomethylene), 3.43 (s, 3 H, methoxy), 4.88–5.04 (m, 2 H, vinyl), 5.88 (ddd, *J* = 17.0, 10.3, 6.3 Hz, 1 H, vinyl); ^{2}H NMR (46 MHz, CDCl$_3$) δ 2.11; ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.60, 14.93, 26.84 (t, *J* = 19 Hz), 50.26, 112.93, 141.23; GC–MS (70 eV) *m*/*z* (relative intensity) no parent, 130 (10), 102 (2), 101 (3), 100 (3), 98 (12), 97 (3), 91 (4), 90 (9), 89 (100), 76 (6), 75 (26), 60 (5), 59 (52), 45 (11), 43 (11).

Determination of Photoproduct Yields and Concentration versus Time Profiles for 214-nm Photolyses of 1,1-Dimethyl-1-silacyclopent-3-ene (1) in Methanol. Photolyses at 214 nm were performed with an immersion well apparatus placed in a 0 °C constant-temperature bath. The light source was a Philips zinc lamp (Model 93106E, Ealing), which was cooled by a stream of air. All photolysates were purged with argon 1 h prior to and during photolyses. Photolyses were monitored at time intervals by GC and GC–MS analyses of aliquots. Each 0.5–0.75-mL aliquot was subjected to a standard workup involving addition of 0.5 mL of hexane followed by washing one to three times with 1 mL of water and drying over anhydrous sodium sulfate. A solution of 100 mg (0.894 mmol, 0.0223 M) of silacyclopentene 1 and 22.4 mg (0.125 mmol) of *n*-nonane (internal standard) in 40 mL of methanol (distilled from magnesium) was irradiated. Aliquots over a 3.6–30% range of conversions were worked up and analyzed by GC on column C at 55 °C (6 mL min^{-1} flow rate). In order of elution, 1,3-butadiene, methoxydimethylsilane, and methanol adducts 2, 5, 3, and 4 were observed at 8, 10, 72, 79, 84, and 95 min, respectively. Percentage yields at 30% conversion are collected in Table I. A run at lower conversions (0.87–4.7%) was conducted in an analogous manner with a solution of 306 mg (2.73 mmol, 0.0649 M) of silacyclopentene 1 and 13.2 mg (0.103 mmol) of *n*-nonane in 42 mL of methanol (distilled from magnesium). Ratios of percent product to total products are summarized in Table II.

Quantum Yield Determinations at 214 nm. The method for performing quantum yield determinations at 214 nm utilizing uranyl oxalate actinometry[16] was as reported previously.[2,17,18] The light from the Philips zinc lamp was passed through an Acton 214-1B interference filter (42.5% transmittance at 214 nm, 410-Å bandwidth). The internal temperature of the sample was maintained at 12 °C by circulating methanol–water from a constant-temperature bath through a jacketed aluminum cell holder. Solutions of 1,1-dimethyl-1-silacyclopent-3-ene (1) in 3.0 mL of methanol or 0.5 M methanol in hexane or dodecane were purged with nitrogen for 30 min prior to the photolyses. Actinometry was performed before and after each photolysis. The average deviation of light output for the entire set of quantum yield runs was 8.3%.

The photolysates of methanol runs were diluted with an equal volume of hexane and washed one to three times with 1 mL of water, dried over anhydrous sodium sulfate, and analyzed by GC on column C by following the procedure described for 214-nm photolyses. Runs employing hexane or dodecane as a cosolvent were washed with water and dried prior to product analysis. Data are reported for the initial concentration of reactant (M), light absorbed at 214 nm (mEinsteins), quantum yield of photoproducts, and percent conversion of each run.

Pure Methanol as Solvent. Run 1: 0.0247 M, 0.0130 mEinsteins, methoxydimethylsilane, 6.64 × 10^{-4} mmol, Φ = 0.0510; product 4, 7.62 × 10^{-4} mmol, Φ = 0.0585; product 5, 1.25 × 10^{-4} mmol, Φ = 0.0096, conversion, 2.09%. **Run 2:** 0.0247 M, 0.0130 mEinsteins, methoxydimethylsilane, 6.76 × 10^{-4} mmol, Φ = 0.0519; product 4, 7.46 × 10^{-4} mmol, Φ = 0.0573; product 5, 1.44 × 10^{-4} mmol, Φ = 0.0110, conversion, 2.11%.

0.508 M Methanol in Hexane as Solvent. Run 1: 0.0234 M, 0.0130 mEinsteins, methoxydimethylsilane, 8.16 × 10^{-4} mmol, Φ = 0.0626; product 4, 5.59 × 10^{-4} mmol, Φ = 0.0429, conversion, 1.96%. **Run 2:** 0.0234 M, 0.0130 mEinsteins, methoxydimethylsilane, 8.23 × 10^{-4} mmol, Φ = 0.0632; product 4, 6.24 × 10^{-4} mmol, Φ = 0.0479, conversion, 2.06%.

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[15] Authentic 1,3-butadiene was prepared by thermolysis of butadiene sulfone (Aldrich).

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[17] Steinmetz, M. G.; Seguin, K. J.; Udayakumar, B. S.; Behnke, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 6601.

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0.500 M Methanol in Dodecane as Solvent. Run 1: 0.0212 M, 0.0163 mEinsteins, methoxydimethylsilane, 4.72 × 10^{-4} mmol, $\Phi = 0.0290$; product 4, 1.48 × 10^{-3} mmol, $\Phi = 0.0907$; product 5, 7.75 × 10^{-5} mmol, $\Phi = 0.0048$, conversion, 3.19%. **Run 2:** 0.0212 M, 0.0163 mEinsteins, methoxydimethylsilane, 5.20 × 10^{-4} mmol, $\Phi = 0.0319$; product 4, 1.41 × 10^{-3} mmol, $\Phi = 0.0864$; product 5, 6.32 × 10^{-5} mmol, $\Phi = 0.0039$, conversion, 3.13%.

Photolysis of *cis*-2-Butenylmethoxydimethylsilane (4) in Methanol. A solution of 102 mg (0.708 mmol) of butenylsilane 4 and 17.9 mg (0.14 mmol) of *n*-nonane (internal standard) in 40 mL of methanol was irradiated at 214 nm for 4 h, following the general procedure for direct photolyses. GC–MS analyses of aliquots after workup showed only three peaks with retention times and mass spectra corresponding to authentic samples 2, 3, and 4. After a 1.8-h irradiation, GC analysis of an aliquot on column C gave 40% of reactant 1, 12.6% of product 2, and 9.94% of product 4. Upon completion of the photolysis, GC analysis showed 55% of 1 had reacted to give 21% of 2 and 11% of 4. The photolysis was diluted with 40 mL of pentane and washed twice with 40 mL of water, followed by drying over anhydrous sodium sulfate. The bulk of the pentane was distilled, and the reactant and photoproducts were isolated by preparative GC on column B at 72 °C. Each of the products was further identified by comparison of ^{1}H,^{13}C NMR, IR, and MS data to authentic samples.

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Registry No. 1, 16054-12-9; 2, 75732-19-3; 2-*d*, 141556-99-2; 3, 75732-22-8; 3-*d*, 141557-00-8; 4, 75732-23-9; 4-*d*, 141557-01-9; 5, 98582-83-3; 5-*d*, 141557-02-0; methoxydimethylsilane, 18033-75-5; *cis*-1,4-dibromobut-2-ene, 18866-73-4.

OM920058P

THF Ring-Opening and H/D Exchange Reactions of $(C_5H_4Me)_2Zr(H)(THF)^+$. Evidence for Hydrogenolysis of Zr–Cp Bonds

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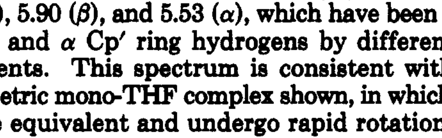
Summary: The cationic hydride $Cp'_2Zr(H)(THF)^+$ (**5**; Cp′ = C_5H_4Me) reacts slowly in THF solution via THF ring opening to yield $Cp'_2Zr(O^nBu)(THF)^+$ (**7**). Hydride **5** undergoes rapid H/D exchange with D_2 at the Zr–H site, and slow H/D exchange at the β Cp′–H sites. No H/D exchange at the α Cp′-H or Cp′-CH_3 sites is detected. It is proposed that H/D exchange at the Zr–H site proceeds by a conventional σ-bond metathesis process and that exchange at the β Cp′-H site involves an intermediate (Cp′)(methylcyclopentadiene)Zr species formed by D_2 addition across a Zr–Cp′ bond. Exchange of H^- and $^nBuO^-$ ligands between Cp'_2Zr centers also leads indirectly to H/D exchange at the β Cp′-H sites of **7**.

Cationic d^0 alkyl complexes of general form $Cp_2Zr(R)^+$ (1) and $Cp_2Zr(R)(L)^+$ (2; L = labile ligand) are believed to be the active species in Cp_2ZrX_2-based Ziegler–Natta olefin polymerization catalysts.[1] Cationic hydrides $Cp_2Zr(H)^+$ (3) and $Cp_2Zr(H)(L)^+$ (4) are of interest in this context as they are the expected products of β-H elimination or hydrogenolysis reactions of 1 and 2 and hence of chain-transfer reactions in Cp_2ZrX_2-based catalysts. Hydrides of this type are also intermediates in catalytic olefin/pyridine coupling reactions and likely intermediates in olefin hydrogenation reactions.[1] We recently reported the synthesis of $Cp'_2Zr(H)(THF)^+$ (5; Cp′ = C_5H_4Me) and its use in the synthesis of alkyls $Cp'_2Zr(CH_2CH_2R)(THF)^+$.[2] Complex 5 is one of the few cationic zirconium hydrides known, the others being the insoluble Cp analogue $Cp_2Zr(H)(THF)^+$, several phosphine hydrides $(C_5H_4R)_2Zr(H)(PR_3)_2^+$, and {ethylenebis(tetrahydroindenyl)}$Zr(H)(NMe_2Ph)^+$.[3,4] In this note we describe the THF ring opening and H/D exchange chemistry of 5.

Results and Discussion

Synthesis and Solution Structure of $Cp'_2Zr(H)(THF)^+$ (5). Hydride 5 is prepared in situ in THF by reaction of $Cp'_2Zr(CH_3)(THF)^+$ (6) with H_2 (23 °C, 7 d, 1.2 atm, eq 1).[2,5] The low-temperature ^{1}H NMR spectrum of 5 (−40 °C) in THF-d_8 solution features a resonance at δ 5.72 characteristic of a terminal Zr–H, a single Cp′-CH_3 resonance, and three broad singlets (4/2/2 ratio) at δ 6.08 (α and β), 5.90 (β), and 5.53 (α), which have been assigned to the β and α Cp′ ring hydrogens by difference NOE experiments. This spectrum is consistent with (i) the C_s-symmetric mono-THF complex shown, in which the Cp′ rings are equivalent and undergo rapid rotation but the sides of a given Cp′ ring are diastereotopic, or (ii) a C_s-symmetric bis(THF) complex.[6] At higher temperatures,



6 5 (1)

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[5] The counterion is BPh_4^- in all cases.

[6] (a) Exchange of THF and THF-d_8 is rapid on the chemical time scale so that resonances for coordinated THF are not observed. (b) Only the mono-THF complex is isolated. See ref 2.

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