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Synthesis of Titanocene Derivatives of Tetramethyldisiloxane and Poly(methylsiloxane) and the Molecular Structure of the Disiloxane-Bridged Titanocene Dichloride (1,3-Bis(η^5-cyclopentadienyl)-1,1,3,3-tetramethyldisiloxane)titanium(IV) Dichloride

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Tetramethyldisiloxane and poly(methylsiloxane) react with chlorine to give 1,3-dichlorotetramethyldisiloxane and poly(methylchlorosiloxane). These chlorosiloxanes react with sodium cyclopentadienide to give 1,3-bis(cyclopentadienyl)tetramethyldisiloxane and poly(cyclopentadienylmethylsiloxane), respectively. The reactions of these compounds with sodium metal or *n*-butyllithium afford the anionic cyclopentadienide derivatives, which in turn react with $TiCl_4{\cdot}2py$ (py = pyridine) to yield 1,1′-η^5,η^5-$(Me_4Si_2O)(C_5H_4)_2TiCl_2$ (**10**) and $[1,1'\text{-}\eta^5,\eta^5\text{-}(Me_2Si_2O_2)(C_5H_4)_2TiCl_2]_n$. The crystal and molecular structure of **10** has been determined from a single-crystal X-ray diffraction analysis. The crystals are monoclinic of space group $P2_1/c$ with $a = 13.305$ (2) Å, b = 8.643 (2) Å, $c = 15.067$ (2) Å, $\beta = 96.350$ (5)°, and $Z = 4$. On the basis of 2118 reflections with $F_o^2 > 3\sigma(F_o^2)$, the structural data were refined by full-matrix least-squares methods to $R = 0.035$ and $R_w = 0.041$. The siloxy unit bridges the two cyclopentadienyl rings, the bridge lying completely to one side of the bisector of the Cl–Ti–Cl angle. The structure of **10** is compared with $(CH_2)_n(C_5H_4)_2TiCl_2$ (n = 1–3) which also contained a bridged framework as well as bis(cyclopentadienyl)titanium dichloride, the unbridged parent compound. The dichloride **10** reacts with MeLi to give the corresponding dimethyltitanocene derivative. Carbon monoxide reacts with **10** upon reduction with aluminum powder to form the titanocene(II) dicarbonyl complex.

Introduction

The anchoring of metal complexes that are homogeneous catalysts to polymeric supports, thus forming "hybrid" catalysts, is an area of continuing interest. Materials that have been used most commonly as supports include a variety of polymers, e.g., polystyrene, polybutadiene, polyamines, and polyacrylates, as well as inorganic supports, e.g., surface-modified silica, alumina, etc.[1-4] However, polysiloxanes have not been investigated extensively for their potential as a catalyst support.

Since SiH bonds readily undergo oxidative addition reactions with a variety of transition-metal complexes, it occurred to us that metals could be attached directly to a poly(methylsiloxane), $(\text{-OSi(H)Me-})_n$, in a simple, one-step reaction. Such was found to be the case, but the resulting compositions were unstable, expelling the metal and forming cross-linked polysiloxane gums,[5] possibly by metal-catalyzed redistribution reactions on silicon.[6-8] Since then, poly(phenylmethylsiloxanes), $(\text{-OSiPhMe-})_n$, have been used as substrates for metal atoms to form polymeric π-arene complexes attached to the silicone backbone.[9,10]

An alternate method of attaching metals indirectly to a silicone involves the use of silicones with pendant cyclopentadienyl (Cp) groups. Cp ligands are especially efficacious as anchoring groups since the metal is strongly bound by the η^5-coordination, thus minimizing catalyst "leaching" under reaction conditions,[11,12] and the polymer backbone is removed from direct contact with the metal so that undesired side reactions involving Si–O bond cleavage are also minimized. In this paper, we report our attempts to prepare such polymers, and the synthesis and structural characterization of a model, dimeric unit in which the Cp rings of titanocene dichloride are bridged with a 1,1,3,3-tetramethylsiloxy group, the smallest dimeric repeat unit of the polymer.

Experimental Section

All manipulations involving reactive organometals, e.g., RLi, NaCp, etc., were done under N_2 or Ar using standard Schlenk techniques. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN. IR spectra were recorded on a PE 457 spectrometer, and NMR spectra on a Varian T60A.

Preparation of 1,1,3,3-Tetramethyl-1,3-dichlorosiloxane (3). A 100-mL (76-g, 0.57-mol) sample of 1,1,3,3-tetramethyldisiloxane, obtained from the Dow Corning Corp. or from the hydrolysis of dimethylchlorosilane, and 250 mL of CCl_4 were placed in a 500-mL 3-neck flask equipped with a fritted glass gas inlet tube which dipped below the surface of the solution and a gas outlet tube connected to an oil bubbler. The mixture was cooled to 0 °C, and an approximate 1:1 mixture of Cl_2/N_2 was introduced through the fritted glass tube while the solution was stirred magnetically.

The chlorine gas mixture was passed through the solution until the 2100-cm^{-1} band of the Si–H stretch had disappeared. Typically, this occurred within 1 h after the initial appearance of a yellow color (unreacted Cl_2) in the solution. The CCl_4 was distilled at atmosphere pressure and the residue then distilled through a 20-cm packed column under vacuum: yield 60.6 g (52%); bp 31 °C (ca. 1 torr). The material has one sharp Me resonance at ca. δ 0.8. Anal. Calcd for $C_4H_{12}Cl_2Si_2O$: C, 23.65; H, 5.91. Found: C, 23.81; H, 6.02. Patnode and Wilcox first made compound **3**

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by the partial hydrolysis of Me_2SiCl_2.[13] The ready availability of Me_2SiHCl makes the route described here attractive for laboratory scale preparations.

Preparation of 1,1,3,3-Tetramethyl-1,3-bis(cyclopentadienyl)disiloxane (5). A 48-g (0.24-mol) sample of the 1,3-dichlorodisiloxane in ca. 100 mL of dry ether was added dropwise to a THF solution of 2 molar equiv of NaCp (previously prepared from Na foil and CpH) at −78 °C. After the addition was complete, the mixture was allowed to warm gradually to room temperature and then stirred for an additional hour. The mixture was poured into a large separatory funnel and washed with saturated NH_4Cl solution. The layers were separated, and the aqueous phase was washed twice with 100-mL portions of ether. The ether washings were combined with the organic layer and then dried over anhydrous $MgSO_4$. The mixture was filtered and the filtrate treated with activated charcoal. The THF was then removed under vacuum. The residue was used *immediately* to prepare the disodium salt (see below and discussion); yield 33 g (53%).

The crude product exhibited NMR peaks (δ(I)) at 6.6 (40), 3.5–3.2 (br d, 15), 0.43 (10), 0.22 (12), and 0.10 (59). Distillation of a portion of the crude product through a 10-cm packed column gave a fraction boiling at 74 °C (0.5 torr). This fraction had an NMR spectrum essentially the same as that of the crude product except that the δ 0.10 peak had a greatly diminished intensity and a new resonance at δ 0.17 is now the major SiMe peak. Although the boiling point of the product is in agreement with that reported,[14] satisfactory analyses were not obtained. The percent C and H were lower than calculated which suggests the presence of some siloxane oligomers formed by hydrolysis of SiCl bonds which had not reacted with the NaCp. Subsequent reactions using this material were quite satisfactory, however.

Preparation of Disodium 1,1,3,3-Tetramethyl-1,3-disiloxanediyl)bis(cyclopentadienide) (8). Typically, the crude 1,3-bis(cyclopentadienyl)disiloxane, prepared as above, was diluted with ether and added dropwise to an excess of sodium foil in ether. For example, 13.2 g (50.3 mmol) of compound **5** in 20 mL of ether was added to 5 g (217 mmol) of Na foil in 50 mL of ether. After addition was complete, the mixture was stirred for 6 h to give a pale pink solution which was filtered. The filtrate was used immediately or stored at 5 °C. An inert atmosphere is necessary for all manipulations involving the sodium cyclopentadienide salts.

Preparation of Poly(methylchlorosiloxane) (4). Dow Corning 1107 Fluid, a poly(methylhydridosiloxane) $(MeHSiO)_{\sim 55}$ (19.6 g, 20 mL, 0.36 mol, Si–H), was dissolved in 150 mL of CCl_4 and chlorinated as described above for $(Me_2HSi)_2O$. Care must be exercised to avoid excessive foaming. Chlorine addition was continued for 1 h after the first appearance of the yellow color in the solution, after which time all Si–H groups had been converted as evidenced by the lack of an Si–H stretch in the IR. The CCl_4 was distilled off under vacuum, and the residue was then dried under dynamic vacuum for several hours. The product is a milky, viscous liquid. Anal. Calcd for CH_3ClSiO: Si, 29.71; Cl, 37.49. Found: Si, 30.05; Cl, 37.95.

Preparation of Poly(cyclopentadienylmethylsiloxane) (6) and Poly(methyl(lithiocyclopentadienide)siloxane) (9). Sodium cyclopentadienide was prepared from 3.1 g (0.138 mol) Na foil and 12 mL (0.14 mol) of CpH in 150 mL of THF. To this NaCp solution, cooled to −78 °C, was added 13 g (0.15 mol, Si–Cl) of $(MeClSiO)_n$, prepared as above, diluted with ca. 50 mL of ether. Mechanical stirring is required since the mixture becomes viscous during the course of the reaction. After addition was complete, the mixture was stirred at −78 °C for 0.5 h, allowed to warm to room temperature, then transferred to a large separatory funnel, and hydrolyzed with saturated NH_4Cl solution. The aqueous phase was washed with two 50-mL portions of THF, and the combined washings and organic phase were dried over anhydrous Na_2SO_4. Removal of the solvent gave an extremely viscous, heat-sensitive oil which set to a gel on standing for several days. When freshly prepared, the NMR spectrum of the polymer exhibited a Cp peak at δ 6.6 and very broad SiMe resonances at δ 0.10 and −0.23 with intensity ratios of 2:1:1. There are also several broad, weak peaks at δ 3.3, 3.0, and 2.7. The NMR spectrum of a solution that had aged for several hours showed some changes. The relative intensity of the SiMe peak at δ −0.23 diminished while that of the δ 0.10 peak increased. The small peaks in the δ 3.3–2.7 region also increased in relative intensity. For best results, this polymer should be converted immediately into the anionic form as described below.

A solution of $(MeCpSiO)_n$ was prepared by adding 37 nmol of $(MeClSiO)_n$ in 50 mL of ether to 37 mmol of NaCp in 50 mL of THF. After reaction as above, the solution was filtered under N_2 to remove NaCl and 20 mL of 1.9 M *n*-BuLi (38 mmol) immediately added to the chilled, stirred filtrate to form a gelatinous precipitate and a brownish solution. As judged from its reaction with $TiCl_4 \cdot 2py$ (py = pyridine) (see below), this mixture contains poly(methyl(lithiocyclopentadienide)siloxane), $[Me(Li^+C_5H_4^-)SiO]_n$.

Preparation of $[(OSiMeCp)_2TiCl_2]_n$ (11). To a solution containing an estimated 28 mmol of $[Me(Li^+C_5H_4^-)SiO]_n$ was added 5.0 g (14 mmol) of $TiCl_4 \cdot 2py$, and the mixture was stirred mechanically overnight. A red precipitate and large red lumps formed in this time. The solids were broken up, filtered, and washed with water, ethanol, ether, and finally petroleum ether (30–60). The dried solid decomposed at 300 °C (turns black) and gave the following analysis: C, 33.45; H, 4.73; Si, 12.70; Ti, 10.91; Cl, 12.38. Calcd for $Me_2Si_2O_2(C_5H_4)_2TiCl_2(C_{12}H_{14}Cl_2O_2Si_2Ti)$: C, 30.46; H, 3.86; Si, 15.38; Ti, 13.12; Cl, 19.41. Overall yield: 4.9 g (71%).

Preparation of (1,3-Bis(η^5-cyclopentadienyl)-1,1,3,3-tetramethyldisiloxane)titanium(IV) Dichloride (10). An ether solution containing 6.0 mmol of $Na_2[Me_2Si(C_5H_4)]_2O$, prepared as above, was added to $TiCl_4 \cdot 2py$ (2.0 g, 5.7 mmol) suspended in benzene. After being stirred for 2 h, the red mixture was filtered. The ether was removed from the filtrate under vacuum and the benzene solution concentrated by heating under N_2. The benzene solution was then allowed to cool, first to room temperature and then to 5 °C, to yield red crystals: mp 188–190 °C; yield 80%. The NMR spectrum ($CDCl_3$) of the product showed only a symmetrical doublet of triplets centered at δ 6.37 and a sharp singlet at δ 0.12 with an intensity ratio of 4:6.06 (calculated 4:6). The center peaks of the triplets are separated by 13 Hz ($\Delta\delta_{AB}$), and the extreme splitting within the triplet is 5 Hz (J_{AB} = 2.5 Hz). Anal. Calcd for $C_{14}H_{20}Cl_2OSi_2Ti$: C, 44.33; H, 5.33. Found: C, 44.25; H, 5.51.

Preparation of Dimethyl-1,1′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)titanocene (12). The dichloride $[O(SiMe_2Cp)]_2TiCl_2$ (0.4 g, 1.0 mmol) was dissolved in 50 mL of dry ether and cooled to 0 °C. Methyllithium (1.17 mL, 1.8 M in ether) was diluted with 10 mL of ether and added dropwise to the dichloride solution over a period of 1 h. The mixture turned yellow-brown and was stirred at room temperature for 45 min. The ether was removed under vacuum and the residue taken up in hexane and filtered. After several recrystallizations from hexane, yellow crystals, mp 96–97 °C dec, were obtained. The mass spectrum showed peaks at P − 15 and P − 30, corresponding to loss of one and two methyl groups. The NMR spectrum of the product consisted of an A_2B_2 doublet of triplets centered at δ 6.20 and an overlapping pair of peaks at δ 0.15 and 0.13. The central peaks of the triplets are separated by 28 Hz ($\Delta\delta_{AB}$), and the extreme splitting within a triplet is 5 Hz (J_{AB} = 2.5 Hz). The area ratio of the Cp peaks to the combined Me peaks is 4:8.8 (calculated 4:9). Anal. Calcd for $C_{16}H_{26}OSi_2Ti$: C, 56.81; H, 7.69. Found: C, 56.88; H, 7.66.

Preparation of (1,3-Bis(η^5-cyclopentadienyl)-1,1,3,3-tetramethyldisiloxane)titanium Dicarbonyl. A mixture of 295 mg (0.778 mmol) of (1,3-(η^5-cyclopentadienyl)-1,1,3,3-tetramethyldisiloxane)titanium(IV) dichloride, 42 mg (1.54 mmol) of aluminum dust, a small pinch of mercuric chloride, and 40 mL of THF were placed in a 1-L flask equipped with a gas inlet. The large flask assures an adequate gas–liquid interface for the reaction. The reaction mixture was stirred under CO (1 atm) for 2 days at room temperature. The color of the solution gradually changed from red to green and finally to red-brown. The dark solution was filtered through a column (10 cm by 4 cm) of neutral alumina to remove $AlCl_3$ and the excess of Al dust. Elution with 25 mL of toluene eluted the product. After removal of the solvent, the red material was sublimed at 55 °C (0.1 torr). Recrystallization

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Table I. Summary of Crystallographic Statistics

a, Å	13.305 (2)
b, Å	8.643 (2)
c, Å	15.067 (2)
β, deg	96.35 (1)
V, Å^3	1721.9 (5)
Z	4
ρ_{obsd}, g cm^{-3}	1.42
ρ_{calcd}, g cm^{-3}	1.46
space group	$P2_1/c$
cryst dimens, mm	0.22 × 0.22 × 0.11
radiation	Mo Kα (monochromatized from graphite)
takeoff angle, deg	4
μ, cm^{-1}	9.34
scan speed, deg/min	2.5–12 (variable)
scan range	Mo Kα_1 – 0.8° to Mo Kα_2 – 0.8
bkgd/scan time	0.8
2θ limit, deg	50
reflections	2118 ($I > 3\sigma(I)$)
R_1	0.035
R_2	0.041
$[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\text{NO} - \text{NV})]^{1/2}$	1.27

from hexane at −25 °C gave red crystals (150 mg, 80%), mp 136 °C dec. The air-sensitive material was identified as $O[Si(CH_3)_2C_5H_4]_2Ti(CO)_2$ by its spectral properties. The 360-MHz ^1H NMR (C_6D_6) shows a doublet of triplets (six lines) centered at δ 4.88 (J_{AB} = 2.5 Hz, $\Delta\delta$ = 27 Hz) for the cyclopentadienyl protons (8 H) and a singlet at δ 0.21 (12 H) for the silicon methyl protons.

IR (*n*-hexane): δ(CO) 1960 and 1885 cm^{-1}, 3160 (m, br), 1450 (s), 1369 (s), 1350 (m), 1295 (w), 1281 (m), 1243 (m), 1240 (m, sh), 1211 (2, br), 1145 (w), 1130 (m), 1055 (m), 1048 (m), 1035 (m), 965 (2), 899 (m), 875 (m), 860 (w), 815 (m), 785 (w), 750 (m), 720 (s), 670 (w) cm^{-1}.

Mass spectrum: m/e (relative intensity) 364 (M, <1), 336 (M − CO, <1), 308 (M − 2CO, 100), 234 (20), 307 (16), 73 (11). Anal. Calcd for $C_{16}H_{20}O_3Si_2Ti$: C, 52.74; H, 5.49. Found: C, 52.41; H, 5.70.

Structure Determination of 10. Red, air-stable crystals of **10** suitable for data collection were grown from methylene chloride/ethanol solution. A crystal was affixed to a glass fiber and mounted on a Syntex P2$_1$ diffractometer (see Table I for relevant statistics). Initial rotation photographs and counter data indicated the crystal to be monoclinic of space group $P2_1/c$, and the measured density gave Z = 4.

The structure was solved by using the direct methods program MULTAN78 which revealed 11 of the 20 non-hydrogen atoms in chemically reasonable positions. Their positions and scale factors were refined once (R = 0.32) and a difference map revealed the positions of all other non-hydrogen atoms. Refinement of all positional and anisotropic thermal parameters of the heavy atoms lead to convergence at R = 0.052.

The positions of the 20 hydrogens were calculated by using the program HFINDR with C–H distances of 0.95 Å and isotropic temperature factors of 1 plus the isotropic temperature factor of the carbon to which the hydrogen was bonded. With the hydrogen atoms input to the least-squares refinement and their positional parameters only refined, final discrepancy factors of R = 0.035 and R_w = 0.041 were obtained. A listing of observed and calculated structure factors is available.

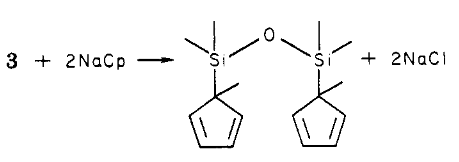
Results and Discussion

Both $(Me_2HSi)_2O$ (**1**) and Dow Corning 1107 Fluid, $(MeHSiO)_n$ (**2**), are cleanly chlorinated by a mixture of Cl_2 and N_2 to form the corresponding chlorides $(Me_2ClSi)_2O$ (**3**) and $(MeClSiO)_n$ (**4**) in good yield (eq 1, 2). The N_2 gas sweeps the product HCl gas out of the reaction mixture and minimizes reaction of the SiOSi groups with the HCl. These chlorosiloxanes are extremely moisture sensitive and are best handled under dry N_2.

$$\underset{\mathbf{1}}{(Me_2HSi)_2O} + 2Cl_2 \rightarrow \underset{\mathbf{3}}{(Me_2ClSi)_2O} + 2HCl \quad (1)$$

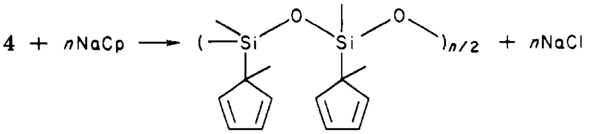
$$\underset{\mathbf{2}}{(MeHSiO)_n} + nCl_2 \rightarrow \underset{\mathbf{4}}{(MeClSiO)_n} + nHCl \quad (2)$$

Both **3** and **4** react readily with sodium cyclopentadienide, NaCp (Cp = C_5H_5), to give the alkylated siloxanes **5** and **6**. The NMR spectra of **5** and **6** show changes as the samples age (see Experimental Section). These changes are attributed to the gradual formation of isomers by the 1,5-hydrogen migration shown in eq 5.[15] The isomerization shown in eq 5 does not affect the conversion of the Cp groups to the anions since all isomers, **a**–**c**, give the same anion upon removal of the proton.



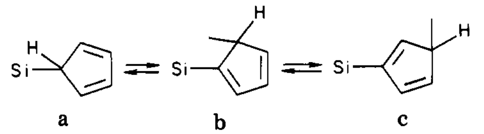
(3)

5



(4)

6

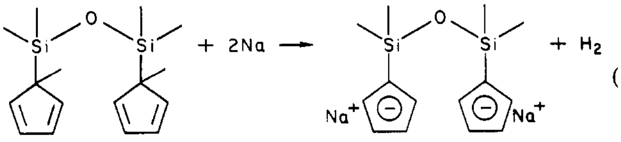


(5)

a **b** **c**

Prepared in the manner described here, compounds **5** and **6** set to gels after standing for several days (**6**) or weeks (**5**). Compound **5** has been prepared previously by the hydrolysis of $CpMe_2SiOEt$, and no particular instability was noted.[14] In the present preparation, the presence of silanol impurities, formed by the hydrolysis of some SiCl groups remaining after the alkylation step, may initiate the gradual polymerization of the compounds.

The Cp derivatives **5** and **6** are easily converted into their metalated derivatives by reaction with sodium metal or *n*-butyllithium (eq 6 and 7). These metalated Cp compounds react with $TiCl_4$·2py (py = pyridine) to give the titanocene complexes **10** and **11** in high yield. For these preparations, the use of $TiCl_4$·2py over $TiCl_4$ is



(6)

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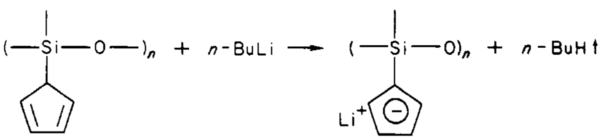

(7)

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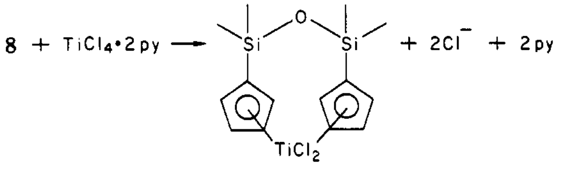

(8)

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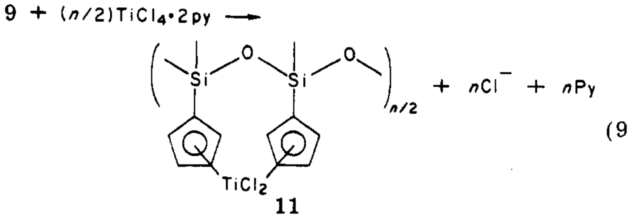


(9)

11

greatly preferred. The pyridine adduct is easily prepared by adding 2 equivalents of pyridine to a benzene solution of $TiCl_4$. The adduct precipitates as a yellow solid which is stable in air and is easily handled, and the reduced Lewis acidity of the adduct leads to fewer side reactions and easier workup of products.

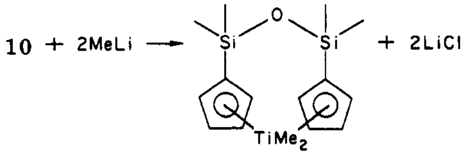
For the metalated polymer **11** the experimental elemental analyses are all lower than those calculated from the theoretical empirical formula. However, the experimentally determined atomic *ratios*, with the expection of H and Cl, agree well with theory. Found: $C_{12.1}H_{20.6}Si_{2.00}Ti_{1.00}Cl_{1.52}$. Theory: $C_{12}H_{14}Si_2TiCl_2$. During workup, the metalated polymer was washed with water and an IR spectrum of the polymer showed a strong, broad O–H stretch around 3500 cm^{-1}. The low values for the analysis and the high H ratio probably reflect the presence of entrapped water, and the low ratio for chlorine is possibly due to some hydrolysis of the Ti–Cl bonds and/or some reduction to Ti(III).

The polymer is seen to be essentially 100% metalated from the Si/Ti = 2.00 ratio. Due to the extremely high metal loading, the structure shown for **11** (eq 9) is undoubtedly an ideal since cross-linking is likely to occur via the bonding of two Cp groups from different chains to the same Ti center. Also, chain folding could cause two remote Cp groups to bind to the same Ti.

The metalated polymer **11** is a dull red solid, insoluble in all common solvents, and stable to 300 °C at which point it blackens. The insoluble nature of the polymer renders further reactions, e.g., with RLi, difficult. With BuLi, the surface darkens but the interior of clumps and aggregates remain unreacted.

The NMR spectrum of the model compound **10** exhibits a six-line spectrum for the cyclopentadienyl protons characteristic of an A_2B_2 pattern in which $J_{AB}/\Delta\delta \approx 0.10$ ($\Delta\delta$ is the separation between δ_A and δ_B in Hz).[16] From the observed frequencies, one obtains J_{AB} = 2.5 Hz and $\Delta\delta_{AB}$ = 13 Hz. The center of the A_2B_2 pattern lies at δ 6.37, considerably downfield from the Cp resonance of Cp_2TiCl_2 which occurs at δ 5.82. The SiMe groups give rise to a single resonance at δ 0.12. The simplicity of the NMR spectrum suggests that the molecule is fluxional (see below).

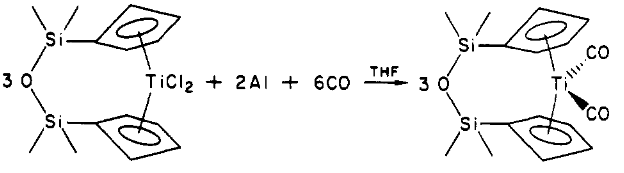
Complex **10** reacts with MeLi to give the dimethyl derivative **12** (eq 10). Complex **12** also exhibits an A_2B_2 pattern for the Cp protons (J_{AB} = 2.5 Hz, $\Delta\delta$ = 28 Hz) centered at δ 6.20 and single peaks for the SiMe and TiMe protons (δ 0.15 and 0.13). As with the dichloride **10**, the simplicity of the NMR spectrum of **12** indicates that the molecule is fluxional. The dimethyl derivative appears to have greater thermal stability than the parent dimethyltitanocene but like the latter decomposes to dark, ill-characterized material at its melting point.[17]



(10)

12

The procedure of Demerseman et al.[18] was used to prepare the bridged dicarbonyl complex **13** (eq 11) in good yield. Compound **13** was isolated in the form of red crystals, mp 136 °C dec. The compound is air sensitive, especially in solution. Complex **13** may be sublimed at 55 °C (10^{-2} torr) and is soluble in hexane, in which the IR spectrum shows two strong δ(CO) bands at 1960 and 1885 cm^{-1}. These values may be compared to 1975 and 1897 cm^{-1} of the parent $Cp_2Ti(CO)_2$.[19] The shift of ca. 15 cm^{-1} to lower frequency reflects the electron-releasing effect of the Si-substituted rings.



10 **13**

(11)

The mass spectrum of **13** contains the molecular ion (m/e 364) and two peaks corresponding to stepwise loss of the carbonyls. The 360-MHz ^1H NMR spectrum of **13** consists of a second-order A_2B_2 doublet of triplets centered at δ 4.88 with J_{AB} = 2.5 Hz and $\Delta\delta$ = 27 Hz and a singlet for the SiMe protons at δ 0.21.

Structure of 10. Any reasonable set of bond distances and angles for the bridging $Me_2SiOSiMe_2$ group of **10** and **12** shows that the "bite" of this group is much too large to give a structure with C_{2v} symmetry which is necessary for all four SiMe groups of **10** or **12** to be equivalent. Since these groups remain equivalent even to −80 °C in the 360-MHz spectra[20] of **10** and **12**, an x-ray structure of **10** was undertaken.[21] Table I lists the crystallographic statistics and relevant structural data (atomic coordinates, temperature factors, and bond lengths and angles) are collected in Tables II and III. Figure 1 shows a general view of the structure and also contains the numbering scheme used throughout the following discussion.

The coordination geometry about the titanium is the familiar distorted tetrahedron (the four ligands being the ring centroids and the halogens) found for titanocene derivatives of this type.[23-28] The Ti–Cl bond lengths are

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[16] Emsley, J. W.; Feeney, J.; Suttcliffe, Z. H. "High Resolution Nuclear Magnetic Resonance Spectroscopy"; Pergamon Press: New York, 1965; Vol. 1.

[17] Alt, H. G.; DiSanzo, F. P.; Rausch, M. D.; Velen, P. C. *J. Organomet. Chem.* **1976**, *106*, 257. The dark solid obtained by thermal decomposition of Cp_2TiMe_2 forms only trace quantities of $Cp_2Ti(CO)_2$ upon reaction with CO and, hence, does not contain appreciable amounts of $[Cp_2Ti]_n$ as claimed by Alt et al.: Curtis, M. D.; Fotinos, N. F., unpublished result, 1978.

[18] Demerseman, B.; Bouquet, G.; Bigorgne, M. *J. Organomet. Chem.* **1975**, *101*, C24.

[19] Calderazzo, F.; Salzmann, J. J.; Mosimann, P. *Inorg. Chim. Acta* **1967**, *1*, 65.

[20] 360-MHz ^1H NMR: **10** (C_7D_8, −50 °C), SiMe, δ 0.225, doublet of triplets at δ 6.316, 6.429 (J_{AB} = 2.52 Hz); **12** (C_7D_8, −60 °C), TiMe, δ 0.118, SiMe, δ 0.147, 5.822, 6.350 (br s, Cp protons).

[21] Computations were carried out on an Amdahl 470 V/7 computer. Programs used during the structural analysis were SYNCOR (data reduction by W. Shmonsees), MULTAN78 (direct methods solution program by P. Main), ORFLS (full-matrix least-squares refinement by Busing, Martin, and Levy), FORDAP (Fourier synthesis by A. Zalkin), ORFEE (distances, angles and their esd's by Busing, Martin, and Levy), ORTEP (thermal ellipsoid drawings by C. K. Johnson), PLANES (least-squares by D. M. Blow), and HFINDR (calculates hydrogen atom positions by A. Zalkin). Details of the weighting scheme etc. are given in ref 22.

[22] Curtis, M. D.; Green, J.; Butler, W. M. *J. Organomet. Chem.* **1979**, *164*, 371.

[23] Smith, J. A.; Von Seyerl, J.; Huttner, G.; Brintzinger, H. *J. Organomet. Chem.* **1979**, *173*, 175.

Table II. Final Position Parameters for $[(Me_2Si)_2O(C_5H_4)_2]TiCl_2$

atom	x^a	y	z
Ti	0.8046 (0)	0.3971 (1)	0.3183 (0)
Cl1	0.8692 (1)	0.3532 (1)	0.4692 (1)
Cl2	0.6748 (1)	0.5650 (1)	0.3487 (1)
Si1	0.6167 (1)	0.3469 (1)	0.1143 (1)
Si2	0.7677 (1)	0.6136 (1)	0.0992 (1)
O	0.6890 (2)	0.4729 (3)	0.0710 (2)
C1	0.5026 (4)	0.4388 (6)	0.1479 (4)
C2	0.5830 (4)	0.1920 (5)	0.0319 (3)
C3	0.6983 (5)	0.7817 (6)	0.1205 (5)
C4	0.8494 (5)	0.6478 (8)	0.0089 (3)
C5	0.6918 (2)	0.2588 (4)	0.2136 (2)
C6	0.6589 (3)	0.2325 (4)	0.2994 (2)
C7	0.7324 (3)	0.1521 (5)	0.3522 (3)
C8	0.8139 (3)	0.1247 (4)	0.3017 (3)
C9	0.7867 (3)	0.1851 (4)	0.2166 (2)
C10	0.8519 (3)	0.5598 (4)	0.2021 (2)
C11	0.8685 (3)	0.6474 (5)	0.2829 (2)
C12	0.9432 (3)	0.5768 (6)	0.3399 (3)
C13	0.9762 (3)	0.4457 (6)	0.2977 (3)
C14	0.9231 (3)	0.4379 (5)	0.2126 (3)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses.

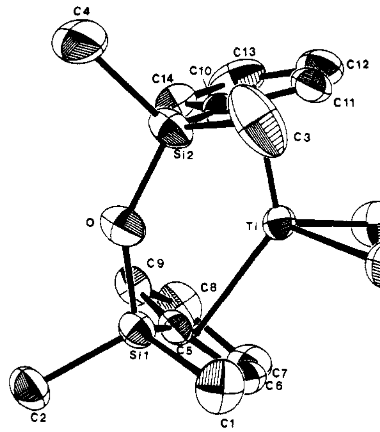

Figure 1. An ORTEP drawing of $[(Me_2Si)_2O(C_5H_4)_2]TiCl_2$.

significantly different, the difference being 0.032 Å which is 16 times the estimated standard deviation in this difference. The longer bond (Ti–Cl1) is the one which is trans to the siloxy unit which bridges the two cyclopentadienyl rings (see Figure 2). The Cl–Ti–Cl angle of 96.22 (5)° is within the range of angles observed for titanocene dichlorides[23-26,28] (see Table IV). The Ti–Cl bond lengths also fall within the range observed previously.

The Ti–Cp (centroid) distance, 2.07 Å, is not significantly different from those observed in similar structures (see Table IV). The Ti–C(Cp) distances show considerable variation as a consequence of the ring tilt, the nature of the ring bridges, and as a consequence of a "trans influence" of the asymmetry around the metal center.[29] Seen from the side, the Cp carbons may be divided into three sets, no matter what the orientation of the rings. The sets are the carbons "trans" to the second Cp ring (a), those "trans" to the chloride ligands (c), and those in between (b). The a set tends to exhibit longer Ti–C distances than the c set except in those cases where the ring bridge forces the c set apart, in which case the b set has the shortest Ti–C distances. Apparently, the π-donor characteristics of the chlorides gives stronger Ti–Cp binding with the c

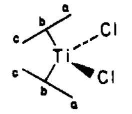

Table III. Interatomic Distances (A) and Bond Angles (deg) for $O(Me_2SiC_5H_4)_2TiCl_2$ (10)

	A. Bond Distances		
Ti-Cl1	2.381 (1)	Ti-Ct1[a]	2.065
-Cl2	2.339 (1)	-Ct2[a]	2.072
-C5	2.383 (4)	-C10	2.383 (3)
-C6	2.396 (4)	-C11	2.405 (4)
-C7	2.404 (4)	-C12	2.405 (4)
-C8	2.372 (4)	-C13	2.375 (4)
-C9	2.383 (4)	-C14	2.387 (4)
C5-C6	1.427 (5)	C10-C11	1.429 (5)
C6-C7	1.379 (5)	C11-C12	1.382 (6)
C7-C8	1.411 (5)	C12-C13	1.393 (6)
C8-C9	1.394 (5)	C13-C14	1.396 (6)
C9-C5	1.411 (5)	C14-C10	1.414 (5)
Si1-O	1.634 (3)	Si2-O	1.630 (3)
-C5	1.867 (3)	-C10	1.869 (4)
-C1	1.834 (5)	-C3	1.842 (6)
-C2	1.847 (4)	-C4	1.844 (5)
	B. Nonbonded Distances		
Si1-Ti	3.766 (1)	Si2-Ti	3.778 (1)
Ti-O	3.925 (2)		
	C. Bond Angles		
Cl1-Ti-Cl2	96.22 (5)	Si1-O-Si2	141.5 (2)
Ct1-Ti-Ct2[a]	130.8		
O-Si1-C1	111.3 (2)	O-Si2-C3	110.4 (2)
-C2	109.0 (2)	-C4	107.9 (2)
-C5	107.8 (1)	-C10	109.8 (1)
C1-Si1-C2	110.6 (2)	C3-Si2-C4	112.4 (3)
C5-C6-C7	109.5 (3)	C10-C11-C12	109.2 (4)
C6-C7-C8	108.1 (3)	C11-C12-C13	108.5 (4)
C7-C8-C9	107.3 (4)	C12-C13-C14	107.8 (4)
C8-C9-C5	109.8 (3)	C13-C14-C10	109.3 (4)
C9-C5-C6	105.2 (3)	C14-C10-C11	105.1 (3)

[a] Ct = ring centroid.

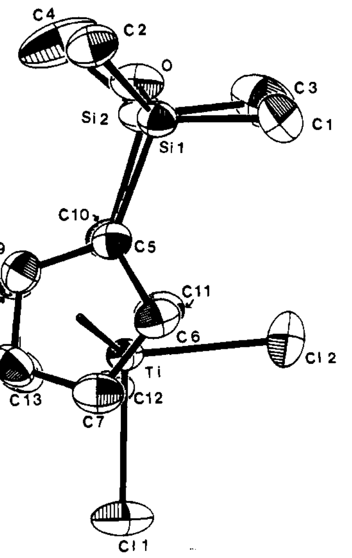

Figure 2. An alternative view of $[(Me_3Si)_2O(C_5H_4)_2]TiCl_2$.

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(24) Davis, B. R.; Bernal, I. *J. Organomet. Chem.* **1971**, *30*, 75.

(25) Epstein, E. F.; Bernal, I. *Inorg. Chim. Acta* **1973**, *7*, 211.

(26) Clearfield, A.; Warner, D. K.; Saldarriaga-Molina, C. H.; Ropal, R.; Bernal, I. *Can. J. Chem.* **1975**, *53*, 1622.

(27) Epstein, E. F.; Bernal, I.; Köpf, H. *J. Organomet. Chem.* **1971**, *26*, 229.

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(29) Curtis, M. D.; Fotinos, N. F.; Han, K. R.; Butler, W. M. *J. Am. Chem. Soc.* **1983**, *105*, 2686.

Table IV. Structural Data for Cp_2TiX_2 Complexes

	bond length (av), Å				bond angle, deg		
compound	Ti-X	Ti-Cp(⊥)	Ti-C(Cp)	C-C(Cp)	X-Ti-X	Cp-Ti-Cp	ref
Cp_2TiCl_2	2.36	2.06	2.37	1.38	94.4	131	26
$CpCp^*TiCl_2$[a]	2.33	2.06 2.09	2.40	1.42	94.8	130	28
$(CH_2)(C_5H_4)_2TiCl_2$	2.34	2.055	2.37-2.48		97.2	121	23
$(CH_2)_2(C_5H_4)_2TiCl_2$	2.35	2.05	2.35-2.39		94.8	128	23
$(CH_2)_3(C_5H_4)_2TiCl_2$	2.37	2.06	2.38-2.40	1.40	93.69	132.64	25
Cp_2TiS_5[b]	2.43	2.07	2.34-2.39	1.30-1.40	94.59	133.7	27
$(Me_4Si_2O)(C_5H_4)_2TiCl_2$	2.34 2.37	2.07	2.37-2.40	1.40	96.22	132.52	this work

[a] Cp* = pentamethylcyclopentadienyl. [b] Cp_2TiS_5 is included as an additional structural comparison.

set, whereas the a set compete with each other for the bonding electrons. A similar effect has been noted in *cis*-$CpMo(CO)_2L_2$ complexes where the Mo–C distances trans to the CO ligands are invariably longer than those trans to the L ligands when L is a π-donor.[29]

The carbon–carbon distances within the two cyclopentadienyl rings range from 1.379 (5) to 1.429 (5) Å with the two C–C bonds to the bridgehead carbons[30] (C5, C10) being apparently (but not significantly) longer than the other three bonds. This trend has also been noted for $(CH_2)_n(C_5H_4)_2TiCl_2$ (n = 1–3)[23–28] compounds. The maximum deviation of the Cp carbons from their least-squares planes is ±0.02 Å. The bond angles within the cyclopentadienyl rings range from 105° at the bridgehead carbon to 109° for the proximal carbons. Within the estimated standard deviations the two cyclopentadienyl rings are identical.

The Si–C bond lengths fall into two classes, the Si–C(Cp) and the Si–C(Me). The Si–C(Cp) distance averages 1.868 (4) Å while the Si–C(Me) bonds are in the range 1.834 (5) to 1.847 (4) Å. These distances are all shorter than the normal Si–C bond[31–33] which is 1.88–1.93 Å in polysiloxanes. We have no explanation, other than possible steric repulsion, why the $C(sp^2)$–Si distances are longer than the $C(sp^3)$–Si distances. The opposite trend would be expected. The angles around the silicons are in the range 107–112°. The average Si–O bond length of 1.632 (3) Å and the Si–O–Si bond angle of 141.47 (16)° are very similar to those expected for unstrained siloxanes.[34]

While many of the structural features of (**10**) are very similar to those exhibited by like structures (see Table IV), there are several features of the structure that are noteworthy. In **10** the bridge is asymmetrically disposed with respect to the bisector of the Cl–Ti–Cl angle (Figure 2). The bridgehead carbons (C5, C10) are adjacent to the C–C bonds between which the titanium lies. In the alkyl-bridged species the bridgehead carbons lie across the ring from the titanium or, in the trimethylene-bridged case, two bonds away from the titanium which is between two distal carbons (see Figure 3). In $Me_2Si(C_5H_4)_2TiCl_2$, the Me_2Si-bridged rings adopt a configuration like the methylene-bridged compounds.[35]

As a consequence of the large bite of the siloxy bridge, the bridgehead carbons are not the ring carbons of closest approach. The two bridgehead carbons are 3.38 Å apart while the two carbons of closest approach (C9, C14) are 2.84 Å apart. In the methylene-bridged compound the bridgehead carbons are the closest inter-ring carbons, being 2.30 Å apart, while in the ethylene-bridged analogue the closest inter-ring distance is 2.68 Å. In the trimethylene-bridged complex the closest inter-ring carbons are not the bridgehead carbons, the respective distances being 2.99 and 3.03 Å.

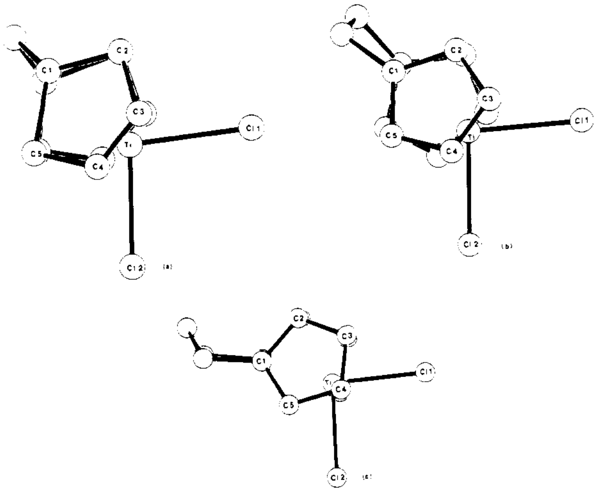

Figure 3. ORTEP drawings of (a) $CH_2(C_5H_4)_2TiCl_2$, (b) $(CH_2)_2(C_5H_4)_2TiCl_2$, and (c) $(CH_2)_3(C_5H_4)_2TiCl_2$ (atomic coordinates taken from ref 23 and 25).

Thus, it appears that the position of the bridge with respect to the bisector of the Cl–Ti–Cl angle is a consequence of the bit (or length) of the bridge. The size of the bridge is also reflected by the angle at which the two mean ring planes intersect. The angle in Cp_2TiCl_2 is 49.5°,[26] which compares with 65° for the methylene-bridged derivative[23] and 46.4° for the trimethylene-bridged species.[24,25] Thus, the angle of 48.84° for **10** suggests that the position adopted by the bridge causes no (or very little) tilting of the rings away from the position adopted in Cp_2TiCl_2.

The proton ^1H NMR of **10** shows, as seen for the other bridged species,[23,35] a symmetrical A_2B_2 pattern centered at δ 6.37 for the cyclopentadienyl protons of both rings. This indicates that the ligand framework must interconvert with its mirror image fast enough (on the NMR time scale) to make all the proximal hydrogens equivalent and all the distal hydrogens equivalent. The structure of **10** (Figure 2) shows that the methyl groups on the silicons are also inequivalent. However, even at −80 °C only one methyl signal was observed.[20] For the interconversion of the two mirror images to occur a mutual ring torsion of about 145° is required. This compares with minimal, 12°, and 72° torsions for the interconversion of the methylene-, ethyl-

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[30] The nomenclature adopted by Brintzinger et al.[23] for the cyclopentadienyl ring carbons as bridgehead, proximal, and distal is also used here.

[31] Higuchi, T.; Shimada, A. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1316.

[32] Turley, J. W.; Boer, F. P. *J. Am. Chem. Soc.* **1968**, *90*, 4026.

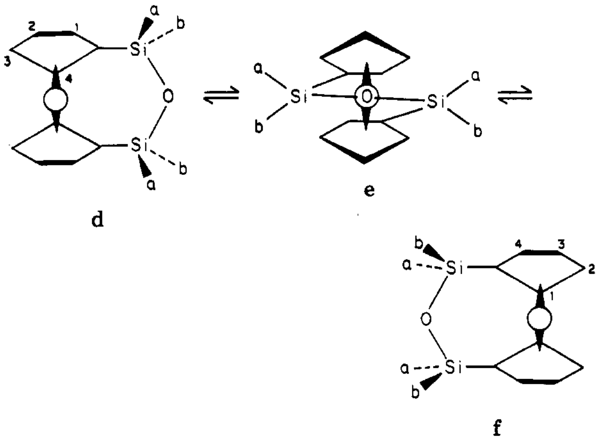
[33] Boer, F. P.; Flyn, J. J.; Turley, J. W. *J. Am. Chem. Soc.* **1968**, *80*, 6973.

[34] Wells, A. F. "Structural Inorganic Chemistry", 3rd ed.; Clarendon Press: Oxford, 1962.

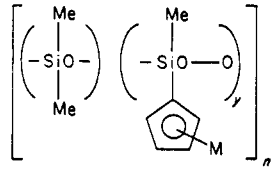
[35] Köpf, H.; Kahl, W. *J. Organomet. Chem.* **1974**, *64*, C37.

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

During the process that interconverts mirror images (**d** → **f**) (eq 12), the $Me_2SiOSiMe_2$ 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 cross-linking 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.



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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; $TiCl_4{\cdot}2Py$, 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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(36) Abel, E. W.; Booth, M.; Brown, C. A.; Orrel, K. G.; Woodford, R. L. *J. Organomet. Chem.* **1981**, *214*, 93.

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.