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1-Metalla-3-silacyclobutanes. Synthesis and Characterization of $(\eta^5\text{-}C_5H_5)_2\overline{M(CH_2Si(CH_3)_2C}H_2)$, M = Ti, Zr, Nb, and Mo

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The metathetical reaction of $[Mg(CH_2)_2Si(CH_3)_2]_n$ with a variety of metallocene dihalides $(\eta^5\text{-}C_5H_5)_2MX_2$, where M = Ti, Zr, and Nb and X = Cl or M = Mo and X = I, proceeds with the formation of the corresponding 1-metalla-3-silacyclobutane complexes $(\eta^5\text{-}C_5H_5)_2\overline{M(CH_2Si(CH_3)_2C}H_2)$. These thermally stable metallacycles have been characterized by elemental analysis and solution ^1H NMR, ^{13}C NMR, or EPR measurements. A molecular weight determination of $(\eta^5\text{-}C_5H_5)_2\overline{Ti(CH_2Si(CH_3)_2C}H_2)$ has confirmed its mononuclear formulation, and an X-ray structural analysis has been performed to examine the conformational structure of the four-membered TiC_2Si ring. This compound crystallizes in a monoclinic unit cell of $P2_1/m$ symmetry with refined lattice parameters of $a = 7.864$ (2) Å, $b = 11.637$ (3) Å, $c = 15.279$ (3) Å, $\beta = 102.01$ (2)°, $V = 1367.6$ (5) $Å^3$, $Z = 4$, and $\rho_{calcd} = 1.283$ g/cm^3. The crystallographic asymmetric unit consists of two independent molecules that each lie on a crystallographic mirror plane. Full-matrix least-squares refinement (based on F_o^2) of 2074 diffractometry data ($F_o^2 \geq \sigma(F_o^2)$) converged with final discrepancy indices of $R(F_o) = 0.047$, $R(F_o^2) = 0.048$, and $R_w(F_o^2) = 0.073$ with $\sigma_1 = 1.27$.

Introduction

Metallacyclobutanes have been strongly implicated as reactive intermediates in a number of important organometal-assisted or -catalyzed reactions.[1] For the olefin metathesis reaction, available chemical evidence provided by Tebbe and Parshall,[2] Grubbs,[3] Schrock,[4] and their coworkers has shown that the interconversion between a metal carbene–olefin complex and a metallacyclobutane is involved in the propagation of the overall reaction. Recently, Rooney and Green[5] proposed that Ziegler–Natta polymerization of olefins may proceed via a 1,2-hydrogen shift from the α-carbon of the alkyl chain with subsequent formation of metal–carbene and metallacyclobutane intermediates.

During the past several years, a variety of synthetic routes have been reported which lead to the formation of metallacyclobutane compounds. These methods include oxidative addition of an olefin to a metal carbene[6] or a Lewis acid stabilized carbene[7] (i.e., Tebbe's reagent), distal hydrogen abstraction from an alkyl ligand,[8] protonation of a metal-coordinated allyl,[9] and oxidative addition of a cyclopropane.[10] However, the synthetic utility of any one of these methods to prepare a diverse range of metallacyclobutanes containing different metals is fairly limited. Consequently, systematic studies of the stereochemical influence of the metal's size and electronic configuration on the molecular structure, thermal stability, and chemical reactivity of an analogous series of metallacyclobutane compounds have been thwarted. To develop a more general synthetic route for this purpose, we have begun to explore the use of magnesacyclic reagents, $[Mg(CH_2)_2Z]_n$,

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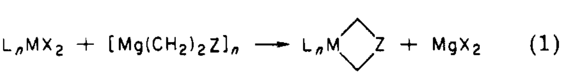
where Z = CH_2, $C(CH_3)_2$, or $Si(CH_3)_2$, for the preparation of metallacyclobutanes[11-13] from the corresponding organometal dihalide, L_nMX_2 (eq 1). The metathesis reaction of $[Mg(CH_2)_2Si(CH_3)_2]_n$ with several metallocene dihalides, $(\eta^5\text{-}C_5H_5)_2MX_2$, has led to the isolation of a series of thermally stable, mononuclear 1-metalla-3-silacyclobutane complexes, $(\eta^5\text{-}C_5H_5)_2\overline{M(CH_2Si(CH_3)_2CH_2)}$, where M = Ti, Zr, Nb, and Mo. Details concerning the synthesis and characterization of these compounds as well as the outcome of an X-ray structural analysis of $(\eta^5\text{-}C_5H_5)_2\overline{Ti(CH_2Si(CH_3)_2CH_2)}$ are described herein. These preliminary results suggest that magnesacyclic reagents, such as $[Mg(CH_2)_2Si(CH_3)_2]_n$, may offer an attractive alternative route for the preparation of metallacycles containing different metals.


(1)

Experimental Section

General Considerations. All operations, unless otherwise noted, were performed under vacuum or an atmosphere of prepurified nitrogen or argon on a double-manifold, high-vacuum line or in a Vacuum Atmosphere glovebox, respectively. Solvents were prepurified by using standard methods and vacuum distilled into storage flasks containing $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}Cl)_2]_2Zn$[14] prior to use. Sublimed magnesium chips (Alfa), bis(chloromethyl)dimethylsilane (Petrarch or Aldrich), titanocene dichloride (Strem), vanadocene dichloride (Strem), and zirconocene dichloride (Pfaltz and Bauer) were used as purchased without further purification. Niobocene dichloride[15] and molybdenocene diiodide[16] were prepared by using published procedures.

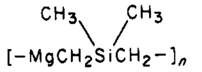
^1H and ^{13}C NMR spectra were recorded by a Varian CFT-20 NMR spectrometer operating in the FT mode. Spectra were measured in THF-d_8, C_6H_6-d_6, or $CHCl_3$-d_1 with Me_4Si as the internal standard. The EPR spectra were measured with an IBM/Bruker ER200D-SRC spectrometer under the control of an ASPECT computer system. The microwave frequency was monitored with a Hewlett-Packard 5340A frequency counter. The magnetic field of the spectrometer is calibrated by an internal NMR gaussmeter to within ±0.01 G. Molecular weights were determined cryoscopically by a locally constructed instrument, similar to the design provided by Shriver.[17] Elemental analyses were performed by Dornis and Kolbe Microanalytical Laboratories, Mulheim, West Germany.

Preparation of Compounds. $[Mg(CH_2)_2Si(CH_3)_2]_n$. The preparation of this magnesacyclic reagent can be accomplished by two different routes in reasonably good yield.

Method 1. This approach is patterned after the procedure described by Bickelhaupt and co-workers[12] for the preparation of $[Mg(CH_2)_3]_n$ from 1,3-dibromopropane. To a 1-L three-necked flask equipped with a reflux condenser, a pressure-equalizing funnel, and a N_2 inlet adapter were added 9.1 g (0.374 mol) of Mg chips and several crystals of I_2. The reaction vessel was evacuated and filled with N_2. Activation of the Mg was accomplished by heating the flask with a bunsen burner. Upon cooling, ca. 400 mL of freshly distilled ether was added. To the addition funnel containing ca. 25 mL of ether was added 20 mL (21.5 g, 0.137 mol) of bis(chloromethyl)dimethylsilane via syringe. The silane reagent was added dropwise over a 4-h period during which the reaction mixture was agitated by placing the reaction flask into the water bath of a Branson B242 sonic cleaner. After an additional 16 h of sonication, roughly half of the ether was removed under vacuum and ca. 50 mL of dry oxygen-free dioxane was added via syringe to precipitate the magnesium chloride. Another 100 mL of solvent was removed, and ca. 300 mL of THF was added to dissolve $[Mg(CH_2)_2Si(CH_3)_2]_n$. The insoluble $MgCl_2$(dioxane) was removed by filtration. Removal of the solvent from the filtered solution gave a white solid, which upon reprecipitation from a THF/toluene solution provided 7.0 g of $[Mg(CH_2)_2Si(CH_3)_2]_n$ (46% yield based on $Si(CH_3)_2(CH_2Cl)_2$).

Method 2. This alternative method is based on the method of massive entrainment described by Pearson et al.[18] and removes the need to sonicate the reaction mixture. To a 1-L flask fitted with a reflux condenser, a pressure-equalizing addition funnel, and a N_2 inlet adapter were added 12.8 g (0.527 mol) of Mg turnings and ca. 450 mL of freshly distilled THF. To the pressure-equalizing funnel containing ca. 180 mL of THF were added 23.0 mL (24.7 g, 0.157 mol) of bis(chloromethyl)dimethylsilane and 13.0 mL (0.151 mol) of 1,2-dibromoethane via syringe. After initial addition of ca. 5 mL of the THF solution of the alkyl dihalides, the remainder was added over a 30-h period at room temperature with rapid stirring. Upon completion of the addition, the reaction mixture was refluxed gently for 3 h. Dry, oxygen-free dioxane (50 mL) was added to the stirred reaction mixture, and the white precipitate of $MgCl_2$(dioxane) was allowed to settle overnight. The addition of 5 mL of dioxane gave no further precipitate. The reaction mixture was filtered, and the volume of the supernatant was reduced in vacuo to give a thick slurry. Freshly distilled pentane was added, and the white suspension was collected and washed three times with pentane and dried in vacuo at room temperature for 24 h to yield 8.3 g of the desired magnesacycle. The cooling of the supernatant to -30 °C for several days provided an additional 1.3 g of product or a combined yield of 9.6 g (55% overall yield based on $Si(CH_3)_2(CH_2Cl)_2$).

This pyrophoric compound is soluble in THF, slightly soluble in ether, and insoluble in aromatic and aliphatic hydrocarbons. Methanolysis of a benzene slurry of $[Mg(CH_2)_2Si(CH_3)_2]_n$ yields only Me_4Si as verified by ^1H NMR measurements: ^1H NMR spectrum (THF-d_8) δ -0.17 (CH_3, s), -1.78 (CH_2, s); ratio of peak areas, 3:2. Anal. Calcd for $C_4H_{10}MgSi$ (empirical formula): C, 43.39; H, 9.14. Found: C, 43.47; H, 9.12. The upfield shift of the methylene protons in $[Mg(CH_2)_2Si(CH_3)_2]_n$ is similar to that observed by Bickelhaupt and co-workers[12a] for the oligimeric magnesacycle, $[Mg(CH_2)_3]_n$. In their case, the α and β protons resonate at δ -0.38 and 2.19, respectively. Our analytical and spectroscopic data are consistent with the formulation depicted for $[Mg(CH_2)_2Si(CH_3)_2]_n$.


$$[-MgCH_2Si(CH_3)_2CH_2-]_n$$

$(\eta^5\text{-}C_5H_5)_2\overline{M(CH_2Si(CH_3)_2CH_2)}$, M = Ti, Zr, Nb, and Mo. The same general procedure was employed to prepare the titanium, zirconium, and niobium 1-metalla-3-silacyclobutane compounds. The reaction assembly consisting of a round-bottom flask charged with 500 mg of $[Mg(CH_2)_2Si(CH_3)_2]_n$ and equipped with an addition side arm containing an appropriate amount of the metallocene dichloride and a pressure-equalizing fritted filter assembly were attached via a horizontal pivotal adapter to a high vacuum line and evacuated. A 10% molar excess of $[Mg(CH_2)_2Si(CH_3)_2]_n$ was generally used. A 30–40-mL sample of THF was vacuum transferred onto the magnesacycle and the metallocene dichloride added slowly to the rapidly stirred solution at room temperature. After several hours, the THF was removed and pentane was vacuum transferred onto the residue. After filtration, slow removal of solvent from the pentane solution yielded crystals of the air- and moisture-sensitive 1-metalla-3-

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[11] Bickelhaupt and co-workers have reported the synthesis of $(\eta^5\text{-}C_5H_5)_2\overline{M(CH_2CR_2CH_2)}$ (M = Ti, Zr, Hf; R = H, Me) from the reaction of the appropriate 1,3-dimagnesioalkane[12] with the corresponding metallocene dichloride.[13]

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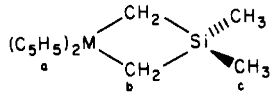
Table I. Analytical Data

compound	color	yield,[a] %	% C calcd	% C found	% H calcd	% H found
$(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$	red-orange	95	63.63	63.62	7.49	7.63
$(\eta^5\text{-}C_5H_5)_2Zr(CH_2Si(CH_3)_2CH_2)$	yellow	44	54.66	54.59	6.55	6.53
$(\eta^5\text{-}C_5H_5)_2Nb(CH_2Si(CH_3)_2CH_2)$	maroon	48	54.32	54.36	6.51	6.52
$(\eta^5\text{-}C_5H_5)_2Mo(CH_2Si(CH_3)_2CH_2)$	red-brown	55	53.83	53.79	6.46	6.50

[a] The isolated yields are based on metallocene dihalide.

Table II. NMR Spectral Data at Ambient Temperature for $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$



M	^{1}H NMR[a] H_a (C_5H_5)	H_b (CH_2)	H_c (CH_3)
Ti	5.54 (s)	2.50 (s)	0.11 (s)
Zr	5.67 (s)	1.55 (s)	0.23 (s)
Mo	4.22 (s)	−1.00 (s)	0.33 (s)

M	^{13}C NMR[b] C_a (C_5H_5)	C_b (CH_2)	C_c (CH_3)
Ti	110.11	70.55	0.92
Zr	109.07	45.99	1.94
Mo	88.40	−34.56	7.87

[a] Chemical shifts are given in parts per million downfield relative to Me_4Si. [b] Chemical shifts (ppm) were obtained from proton-decoupled spectra.

Table III. Data for the X-ray Diffraction Analysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$

A. Crystal Data

crystal system	monoclinic
space group	$P2_1/m$ (C_{2h}^2, No. 11)
a, Å	7.864 (2)
b, Å	11.637 (3)
c, Å	15.279 (3)
β, deg	102.01 (2)
V, Å^3	1367.6 (5)
fw, amu	264.30
d(calcd), g/cm^3	1.283
Z	4
μ, cm^{-1}	7.04

B. Data Collection and Analysis Summary

cryst dimens, mm	0.525 × 0.275 × 0.125
reflctns sampled	±*hkl* ($5° < 2\theta < 50°$)
2θ range for centered reflctns, deg	26–35
scan rate, deg/min	2
scan-width, deg	$1.1 + 0.9 \tan\theta$
no. of std reflctns	3 (3% variation)
% cryst decay	none
total no. of measd reflctns	3161
no. of unique data used	2074 ($F_o^2 > \sigma(F_o^2)$)
agreement between equivalent data	
$R_{av}(F_o)$	0.016
$R_{av}(F_o^2)$	0.015
transmissn coeff	0.827–0.917
P	0.03
$R(F_o)$	0.047
$R(F_o^2)$	0.048
$R_w(F_o^2)$	0.073
σ_1 error in observn of unit weight	1.27
no. of variables	244
data to parameter ratio	8.5:1

silacyclobutane product. These compounds are thermally stable and can be alternatively purified by sublimation at 10^{-4} mm and 60 °C.

Attempts to prepare $(\eta^5\text{-}C_5H_5)_2Mo(CH_2Si(CH_3)_2CH_2)$ from the reaction of $[Mg(CH_2)_2Si(CH_3)_2]_n$ with $(\eta^5\text{-}C_5H_5)_2MoCl_2$ gave only small amounts of the desired product. On the basis of the comments provided by Diversi et al.[20] in their paper describing the synthesis and characterization of $(\eta^5\text{-}C_5H_5)_2Mo(CH_2(CH_2)_2CH_2)$, the reaction was repeated with molybdenocene diiodide using the general procedure described previously. This alternative approach proceeds with a reasonable yield of $(\eta^5\text{-}C_5H_5)_2Mo(CH_2Si(CH_3)_2CH_2)$ which was purified by recrystallization.

These 1-metalla-3-silacyclobutanes have been characterized by C/H analysis (Table I) and by NMR (Table II) or EPR methods in solution at ambient temperatures. Although the microanalytical data are consistent with the chemical formulation of the Ti, Zr, Nb, and Mo derivatives as $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$, the molecular weight of the Ti analogue was determined to confirm its formulation as a mononuclear compound. The molecular weight was found to be 251 ± 20 as compared to the actual value of 264.3 for $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$. The solution EPR spectrum for $(\eta^5\text{-}C_5H_5)_2Nb(CH_2Si(CH_3)_2CH_2)$ exhibits the expected 10-line pattern due to the hyperfine coupling of the unpaired electron with the nuclear magnetic moment of the ^{93}Nb nucleus (100% abundance, $I = {}^9/_2$). No additional ligand coupling with the α protons of the 1-nioba-3-silacyclobutane ring was observed. From the measured magnetic field at each resonance line, the corresponding isotropic parameters for $(\eta^5\text{-}C_5H_5)_2Nb(CH_2Si(CH_3)_2CH_2)$ of $g_{iso} = 1.9991$ and $A_{iso}(^{93}Nb) = 90.6$ G were calculated from a modified form of the Breit–Rabi equation.[19].

Reaction of $[Mg(CH_2)_2Si(CH_3)_2]_n$ with $(\eta^5\text{-}C_5H_5)_2VCl_2$. The reaction of $[Mg(CH_2)_2Si(CH_3)_2]_n$ and $(\eta^5\text{-}C_5H_5)_2VCl_2$ was also performed but does not proceed with the formation of a stable vanadacyclic product. Sublimation or pentane extraction of the reaction product gave a blue compound, which is soluble in benzene and dichloromethane and only sparingly soluble in ether. Its solution ^{1}H NMR spectrum is featureless from −2 to 18 ppm, and its solution EPR spectrum contains a *weak* 8-line pattern with $A(^{51}V)$ identical with that of vanadocene dichloride. Its visible absorption spectrum in diethyl ether displays a band at 470 nm and a shoulder at 550 nm as is observed for $(\eta^5\text{-}C_5H_5)_2VCl$.[21] The results of a C/H microanalysis (Found: C, 55.23; H, 4.69) further support our formulation of this blue compound as $(\eta^5\text{-}C_5H_5)_2VCl$ (Calcd: C, 55.22; H, 4.65).

X-ray Data Collection and Structural Analysis for $(C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$. A crystalline sample was sealed

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Table IV. Positional Parameters for $(\eta^5\text{-}C_5H_5)_2\overline{Ti(CH_2Si(CH_3)_2CH_2}){}^a$

atom	*x*	*y*	*z*
	A. Molecule 1		
Ti	0.45918 (8)	0.2500	0.59374 (5)
Si	0.6307 (1)	0.2500	0.7717 (1)
C1	0.5680 (4)	0.1265 (3)	0.6942 (2)
MeC1	0.5094 (10)	0.2500	0.8649 (4)
MeC2	0.8697 (7)	0.2500	0.8189 (4)
C2	0.1718 (5)	0.2500	0.5055 (4)
C3	0.1871 (5)	0.1547 (3)	0.5601 (3)
C4	0.2051 (4)	0.1916 (3)	0.6469 (2)
C5	0.7372 (8)	0.2500	0.5567 (5)
C6	0.6510 (7)	0.1550 (6)	0.5156 (4)
C7	0.5152 (6)	0.1918 (4)	0.4533 (3)
H1	0.668 (4)	0.091 (2)	0.685 (2)
H2	0.502 (4)	0.081 (2)	0.709 (2)
H3	0.389 (7)	0.250	0.849 (3)
H4	0.550 (6)	0.190 (4)	0.905 (3)
H5	0.930 (6)	0.250	0.776 (3)
H6	0.897 (5)	0.188 (3)	0.851 (2)
H7	0.154 (5)	0.250	0.446 (3)
H8	0.183 (4)	0.084 (3)	0.542 (2)
H9	0.218 (4)	0.150 (2)	0.697 (2)
H10	0.810 (7)	0.250	0.592 (4)
H11	0.670 (5)	0.086 (3)	0.533 (3)
H12	0.441 (5)	0.146 (3)	0.419 (3)
	B. Molecule 2		
Ti	−0.08509 (8)	0.2500	0.21102 (5)
Si	0.1501 (2)	0.2500	0.0977 (1)
C1	0.1945 (5)	0.2500	0.2224 (3)
C2	−0.0910 (6)	0.2500	0.0696 (3)
MeC	0.2397 (9)	0.1200 (8)	0.0524 (4)
C3	−0.0172 (5)	0.0743 (3)	0.2911 (3)
C4	−0.1588 (5)	0.1205 (3)	0.3171 (3)
C5	−0.2943 (5)	0.1198 (3)	0.2448 (3)
C6	−0.2385 (6)	0.0735 (3)	0.1728 (3)
C7	−0.0653 (6)	0.0470 (3)	0.2016 (3)
H1	0.256 (3)	0.187 (2)	0.247 (2)
H2	−0.133 (4)	0.186 (2)	0.038 (2)
H3	0.209 (6)	0.125 (4)	−0.007 (3)
H4	0.358 (6)	0.116 (4)	0.068 (3)
H5	0.231 (7)	0.057 (4)	0.073 (4)
H6	0.095 (4)	0.067 (3)	0.330 (2)
H7	−0.165 (4)	0.148 (3)	0.372 (2)
H8	−0.388 (4)	0.143 (3)	0.240 (2)
H9	−0.299 (4)	0.072 (3)	0.119 (2)
H10	−0.001 (5)	0.021 (3)	0.175 (2)

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figures.

in a glass capillary tube under a prepurified N_2 atmosphere and optically aligned on a Picker goniostat which is controlled by a Krisel Control diffractometer automation system. Procedures analogous to those described previously[22] were employed to determine the lattice parameters of the monoclinic unit cell and to collect the intensity data for the structural analysis. Duplicate reflections, previously corrected for absorption[23] and Lorentz–polarization effects, were averaged to provide 2074 unique reflections with $F_o^2 \geq \sigma(F_o^2)$ for the structural analysis. Detailed information regarding the lattice parameters and the data collection procedure are summarized in Table III.

An initial attempt to estimate the coordinates of the Ti atom(s) with the heavy-atom method was unsuccessful due to substantial overlap of Harker and other interatomic vectors observed in the corresponding three-dimensional, unsharpened Patterson map. This difficulty is attributed to the fact that the ultimate structural analysis revealed the asymmetric unit consists of two independent 1-titana-3-silacyclobutane molecules both of which lie on a crystallographic mirror plane. Consequently, the two Ti, the two Si, and several C atoms possess general coordinates of $x\ ^1/_4\ z$ which lead to the appearance of a large number of interatomic vectors of the form $u\ ^1/_2\ w$ on the Patterson map.

Table V. Selected Interatomic Distances (Å) and Bond Angles (deg) for Non-Hydrogen Atoms in $(\eta^5\text{-}C_5H_5)_2\overline{Ti(CH_2Si(CH_3)_2CH_2}){}^{a-c}$

molecule 1		molecule 2	
	A. Interatomic Distances		
Ti-C1	2.146 (3)	Ti-C1	2.169 (4)
Ti-C2	2.379 (4)	Ti-C2	2.152 (5)
Ti-C3	2.370 (3)	Ti-C3	2.385 (4)
Ti-C4	2.406 (3)	Ti-C4	2.372 (4)
Ti-C5	2.370 (7)	Ti-C5	2.372 (4)
Ti-C6	2.382 (6)	Ti-C6	2.392 (4)
Ti-C7	2.377 (5)	Ti-C7	2.374 (3)
Ti-Cp(1)	2.088 (3)	Ti-Cp	2.072 (4)
Ti-Cp(2)	2.084 (6)	C1-Si	1.865 (5)
C1-Si	1.863 (3)	C2-Si	1.855 (5)
Si-MeC1	1.872 (8)	Si-MeC	1.862 (8)
Si-MeC2	1.868 (5)	C3-C4	1.368 (6)
C2-C3	1.378 (5)	C4-C5	1.366 (5)
C3-C4	1.373 (5)	C5-C6	1.376 (7)
C4-C4′	1.359 (6)	C6-C7	1.377 (6)
C5-C6	1.378 (7)	C7-C3	1.378 (6)
C6-C7	1.344 (7)		
C7-C7′	1.354 (10)		
	B. Bond Angles		
C1-Ti-C1′	84.1 (2)	C1-Ti-C2	83.7 (2)
Cp(1)-Ti-Cp(2)	132.9 (2)	Cp-Ti-Cp′	132.5 (3)
Ti-C1-Si	87.2 (1)	Ti-C1-Si	87.0 (2)
C1-Si-C1′	101.0 (2)	Ti-C2-Si	87.7 (2)
MeC1-Si-MeC2	109.7 (3)	C1-Si-C2	101.6 (2)
MeC1-Si-C1	112.0 (2)	MeC-Si-MeC′	108.7 (5)
MeC2-Si-C1	110.9 (2)	MeC-Si-C1	112.0 (2)
C3-C2-C3′	107.2 (5)	MeC-Si-C2	111.2 (2)
C2-C3-C4	108.2 (3)	C7-C3-C4	107.9 (4)
C3-C4-C4′	108.2 (2)	C3-C4-C5	107.9 (4)
C6-C5-C6′	106.7 (6)	C4-C5-C6	108.9 (4)
C5-C6-C7	108.0 (5)	C5-C6-C7	107.0 (4)
C6-C7-C7′	108.6 (3)	C6-C7-C3	108.3 (4)

[a] Cp or Cp(n) denotes cyclopentadienyl ring centroid. [b] Prime denotes the symmetry-related atom on opposite side of crystallographic mirror plane. [c] The esd's for the interatomic distances and bond angles were calculated from the standard errors of the fractional coordinates of the corresponding atomic positions.

The structural solution was accomplished by using the approximate positions for the two Ti and two Si atoms that were interpolated from the first *E* map calculated with MULTAN 78[24] and the phase assignments for the set with the highest figure of merit. Subsequent Fourier summations provided the approximate coordinates for the remaining non-hydrogen atoms. A difference Fourier synthesis utilizing only low-angle data with $(\sin\theta)/\lambda < 0.40$ Å^{-1} was employed to determine the approximate coordinates for the hydrogen atoms. Full-matrix least-squares refinement (based on F_o^2)[25–29] with anisotropic temperature factors for the

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(22) Jones, S. B.; Petersen, J. L. *Inorg. Chem.* **1981**, *20*, 2889.

(23) The absorption correction was performed with the use of the general polyhedral shape routine of the program DTALIB. The distance from the crystal center to each face and the corresponding orientation angles (ϕ and χ) needed to place each face in diffracting position were provided to define the crystal's shape, size, and orientation with respect to the diffractometer's coordinate system.

(24) Declerq, J. P.; Germain, D.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1973**, *A29*, 231.

(25) The least-squares refinement[26] of the X-ray diffraction data was based upon the minimization of $\sum w_i|F_o^2 - S^2F_c^2|$, where w_i is the individual weighting factor and S is the scale factor. The discrepancy indices were calculated from the expressions: $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$, $R(F_o^2) = \sum|F_o^2 - F_c^2|/\sum F_o^2$, and $R_w(F_o^2) = [\sum w_i|F_o^2 - F_c^2|/\sum w_iF_o^4]^{1/2}$. The standard deviation of an observation of unit weight, σ_1, equals $[\sum w_i|F_o^2 - F_c^2|/(n - p)]^{1/2}$, where n is the number of observations and p is the number of parameters varied (viz., 244) during the last refinement cycle.

21 non-hydrogen atoms and isotropic temperature factors for the 22 hydrogen atoms converged with final discrepancy indices with $R(F_o) = 0.047$, $R(F_o^2) = 0.048$, and $R_w(F_o^2) = 0.073$ with $\sigma_1 = 1.27$. A final difference Fourier summation was essentially featureless.

The values of the positional parameters from the last least-squares cycle are provided in Table IV for all of the atoms. Interatomic distances and angles of interest and their esd's, which were calculated from the estimated standard errors of the fractional atomic coordinates, are given in Table V. Tables of refined thermal parameters, the carbon–hydrogen distances and angles, specific least-squares planes, and the observed and calculated structure factors are available as supplementary material.[30]

Results and Discussion

The reaction of $[Mg(CH_2)_2Si(CH_3)_2]_n$ with $(\eta^5\text{-}C_5H_5)_2MX_2$ (M = Ti, Zr, and Nb and X = Cl; M = Mo and X = I) proceeds with formation of the corresponding 1-metalla-3-silacyclobutane derivatives. As expected the presence of a Si atom in the four-membered MC_2Si ring greatly enhances the thermal stability of these compounds in comparison to the corresponding metallacyclobutane derivatives. For example, Bickelhaupt and co-workers[13] have reported that $(\eta^5\text{-}C_5H_5)_2M(CH_2C(CH_3)_2CH_2)$, where M = Ti or Zr, readily decomposes in solution within several hours. In contrast, these 1-metalla-3-silacyclobutanes are sufficiently stable that they can be easily sublimed without noticeable decomposition at 60 °C and 10^{-4} mm pressure. The Si atom in the β position of the four-membered ring effectively blocks the participation of the metal carbene–olefin or β-hydride elimination pathways which are normally invoked to rationalize the organic products formed during the thermal decomposition of the corresponding d^0 titanacyclobutane[31] and related d^2 molybdenacyclopentane[20] compounds.

For the diamagnetic 1-metalla-3-silacyclobutane derivatives of Ti, Zr, and Mo, the ^1H and $^{13}C\{^1H\}$ NMR spectra each exhibit three characteristic resonances (Table II). The corresponding ^1H chemical shifts for the ring and for the methylene protons of $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$, M = Ti and Zr, are essentially identical with those reported by Bickelhaupt and co-workers[13] for $(\eta^5\text{-}C_5H_5)_2M(CH_2C(CH_3)_2CH_2)$, M = Ti and Zr. As expected the methyl protons in the former are shifted accordingly upfield. In contrast, the ^{13}C resonances appear to be more sensitive to the nature of the four-membered ring and the metal's electronic configuration. Although the ^{13}C chemical shifts for the cyclopentadienyl rings in $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$ and $(\eta^5\text{-}C_5H_5)_2M(CH_2C(CH_3)_2CH_2)$ are comparable for M = Ti and Zr, the corresponding resonances for the methylene carbons in the former compounds are shifted ca. 12.9 and 20.5 ppm upfield, respectively. For d^2 bis(cyclopentadienyl)molybdenacyclic compounds the available ^1H and ^{13}C NMR data are limited to those reported for the molybdenacyclopentane compound $(\eta^5\text{-}C_5H_5)_2Mo(CH_2(CH_2)_2CH_2)$.[20] Although the ^1H and ^{13}C NMR resonances for the cyclopentadienyl rings are comparable for $(\eta^5\text{-}C_5H_5)_2Mo(CH_2Si(CH_3)_2CH_2)$ and $(\eta^5\text{-}C_5H_5)_2Mo(CH_2(CH_2)_2CH_2)$, the methylene proton and carbon resonances of the former are shifted upfield from Me_4Si to δ −1.00 and −34.56, respectively, as compared to δ −1.8 and 14.5, respectively, for the latter. Presumably, the large upfield shift for the methylene ^{13}C resonance observed for $(\eta^5\text{-}C_5H_5)_2Mo(CH_2Si(CH_3)_2CH_2)$ arises in part due to the orientation of its lone electron pair which is expected to reside in an orbital oriented parallel to the MoC_2 plane.[33]

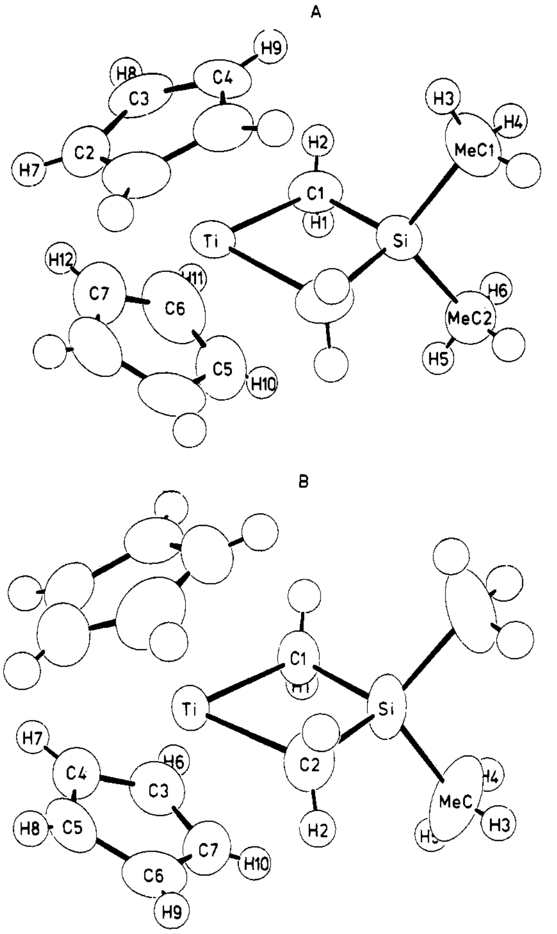

Figure 1. Perspective views of the molecular configurations of the two $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$ molecules with the appropriate numbering scheme corresponding to molecule 1 (A) and molecule 2 (B), respectively. The thermal ellipsoids are scaled to enclose 50% probability. The radii of the spheres for the hydrogen atoms were arbitrarily reduced for clarity.

The reaction of $[Mg(CH_2)_2Si(CH_3)_2]_n$ with vanadocene dichloride proceeds with the formation of a blue compound. Analytical and spectroscopic data indicate that this vanadium-containing product is $(\eta^5\text{-}C_5H_5)_2VCl$. Apparently, the smaller covalent radius of vanadium compared to those of the other metals examined here sterically inhibits the formation of the desired vanadacyclic product.

Description of the Molecular Structure of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$. The molecular structure of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$ was determined by X-ray diffraction methods. The monoclinic crystal lattice for this compound contains two independent molecules that each lie on a crystallographic mirror plane. For molecule 1,

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(26) The scattering factors employed in all of the structure factor calculations where those of Cromer and Mann[27] for the non-hydrogen atoms and those of Stewart et al.[28] for the hydrogen atoms with corrections included for anomalous dispersion.[29]

(27) Cromer, D. T.; Mann, J. *Acta Crystallogr., Sect. A* **1968**, *A24*, 231.

(28) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(29) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

(30) The computer programs that were used for the X-ray diffraction data analysis are described in: Petersen, J. L. *J. Organomet. Chem.* **1979**, *155*, 179.

(31) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

(32) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(33) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136.

depicted in Figure 1A with the appropriate labeling scheme, the mirror plane contains the Ti, Si, MeC1, and MeC2 atoms of the $Ti(CH_2)_2Si(CH_3)_2$ moiety and C2 and C5 of the cyclopentadienyl rings. In this case, a staggered arrangement of the cyclopentadienyl rings is observed. In contrast, for molecule 2, illustrated in Figure 1B with the corresponding atom-labeling scheme, the mirror plane contains the Ti, Si, C1, and C2 atoms of the titanasilacyclobutane ring. Under these circumstances (in the absence of a crystallographic disorder) the two cyclopentadienyl rings adopt an eclipsed orientation.

In general, the molecular configuration of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$ is analogous to that reported by Bruno and Marks[8a] for $(\eta^5\text{-}C_5Me_5)_2Th(CH_2Si(CH_3)_2CH_2)$ and by Grubbs and co-workers[7b] for $(\eta^5\text{-}C_5H_5)_2Ti(CH_2CRR'CH_2)$, were R = *tert*-butyl and R′ = H, R = C_6H_5 and R′ = H, and R = R′ = CH_3. The ligands provide a pseudotetrahedral environment about the metal. The structural parameters about the Ti atom exhibit normal values. The respective Ti–C distances of 2.146 (3), 2.169 (4), and 2.152 (5) Å, the Ti–Cp(*n*) distances of 2.088 (3), 2.084 (6), and 2.072 (4) Å, and the Cp(*n*)–Ti–Cp(*n*) angles of 132.9 (2) and 132.5 (3)° for the two independent molecules are comparable to those observed for related bis(cyclopentadienyl)titanacyclic compounds containing three-,[33] four-,[7b,34] and five-membered rings.[35] The four-membered titanacyclic ring in $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$ exhibits a (nearly) planar configuration. For molecule 1 the folding of the TiC_2Si ring along the C1⋯C1′ vector is 7.7° compared to 5.8° in $(\eta^5\text{-}C_5Me_5)_2Th(CH_2Si(CH_3)_2CH_2)$[8a] and to 3.25° in $(\eta^5\text{-}C_5H_5)_2Ti(CH_2CH(C_6H_5)CH_2)$.[7b] For molecule 2 the TiC_2Si ring is constrained to be planar within the limitations of the room temperature X-ray data.[36] Substantially larger dihedral angles of 24.4 and 22.4° between the C–Pt–C and C-C-C planes of the platinacyclobutane rings of $Pt(CH_2C(CH_3)_2CH_2)(P(C_2H_5)_3)_2$[8c] and $Pt(C(CN)_2CH_2C(CN)_2)(P(C_6H_5)_3)_2$,[37] respectively, have been observed, however.

The replacement of the β-carbon atom of the titanacyclobutane ring by a silicon atom produces a noticeable increase in the magnitude of the C–Ti–C bond angle. For the titanacyclobutane rings of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2CRR'CH_2)$ for which structural data is available,[7b] the C–Ti–C bond angle varies within a small range from 74.8 to 75.3°. By comparison the corresponding bond angle in $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$ is ca. 9° larger at 83.9° (av). This increase is accompanied by a comparable decrease in the average C–Si–C bond angle of 101.3° in the TiC_2Si ring as compared to the corresponding C–C–C bond angle of 110.9 (6)° in $(\eta^5\text{-}C_5H_5)_2Ti(CH_2C(CH_3)_2CH_2)$.[7b] These stereochemical adjustments, however, do not significantly modify the Ti–C–Si bond angle of ca. 87°, which is essentially equal to the Ti–C–C bond angle in the latter.

Solution molecular weight measurements and a structural analysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$ have confirmed the mononuclear structure of this 1-titana-3-silacyclobutane complex. Further structural studies are in progress for the remaining $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$ derivatives, where M = Zr, Nb, and Mo, to determine the extent to which the metal's size and electronic configuration influence the conformational structure of the 1-metalla-3-silacyclobutane ring. In addition, efforts are underway to examine the chemical reactivity and the electrochemistry of these thermally stable early transition-metal metallacyclic complexes.

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Registry No. $(\eta^5\text{-}C_5H_5)_2Ti(CH_2Si(CH_3)_2CH_2)$, 71515-00-9; $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Si(CH_3)_2CH_2)$, 89530-31-4; $(\eta^5\text{-}C_5H_5)_2Nb(CH_2Si(CH_3)_2CH_2)$, 89530-32-5; $(\eta^5\text{-}C_5H_5)_2Mo(CH_2Si(CH_3)_2CH_2)$, 89530-33-6; $Si(CH_3)_2(CH_2Cl)_2$, 2917-46-6; $(\eta^5\text{-}C_5H_5)_2VCl_2$, 12083-48-6; $(\eta^5\text{-}C_5H_5)_2VCl$, 12701-79-0; $(\eta^5\text{-}C_5H_5)_2TiCl_2$, 1271-19-8; $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, 1291-32-3; $(\eta^5\text{-}C_5H_5)_2NbCl_2$, 12793-14-5; $(\eta^5\text{-}C_5H_5)_2MoI_2$, 12184-29-1; 1,2-dibromoethane, 106-93-4.

Supplementary Material Available: Tables of refined thermal parameters, hydrogen bond distances, least-square planes, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(34) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149.

(35) Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454.

(36) For the Si atom the maximum root-mean-square thermal displacement ($\mu(3)$ = 0.313 (1) Å) is parallel to the *b* axis and thereby results in an elongation of the thermal ellipsoid perpendicular to the mirror plane (Figure 1B). Since the X-ray diffraction experiment provides a time-averaged representation of the crystal structure, the refined thermal parameters for the Si and MeC atoms may actually reflect a static disorder which involves the superposition of two symmetry-related puckered structures. This situation arises if the nucleus of the Si atom is displaced off the TiC_2 plane. An upper limit for this displacement can be estimated from an analysis of the relative magnitudes of the root-mean-square thermal displacements for Si. The mean value of 0.21 Å for the two in-plane root-mean-square thermal displacements ($\mu(1)$ = 0.179 (3) and $\mu(2)$ = 0.243 (2) Å) provides a reasonable estimate of the isotropic thermal displacement. For two half-weighted Si atoms with μ_{iso} = 0.21 Å, a displacement of 0.10 Å of the Si atom on either side of the mirror plane is sufficient to account for the observed elongation of its thermal ellipsoid. Under these circumstances the folding angle of the TiC_2Si ring in molecule 2 is ca. 4.5°.

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