Zirconium-Induced Lateral Insertion of a Formaldehyde Unit into a 1-Sila-3-zirconacyclobutane Ring. Structural Characterization of (η^5-C$_5$H$_5$)$_2$Zr(OCH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$)

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The reaction of paraformaldehyde with (η^5-C$_5$H$_5$)$_2$Zr(CH$_2$Si(CH$_3$)$_2$CH$_2$) proceeds stoichiometrically with the lateral insertion of a formaldehyde unit into a zirconium–carbon bond. The isolated product (η^5-C$_5$H$_5$)$_2$Zr(OCH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$) has been characterized by ^{1}H and ^{13}C NMR measurements and elemental analysis. The conformational structure of the 1-oxa-4-sila-6-zirconacyclohexane ring was confirmed by X-ray diffraction methods. The relatively short Zr–O bond distance of 1.941 (2) Å and the obtuse Zr–O–C1 bond angle of 143.1 (2)° are consistent with substantial π-donation from a filled O 2p orbital into the empty Zr d orbital. This zirconacyclic compound crystallizes in a monoclinic unit cell of $P2_1/c$ symmetry with refined lattice parameters of a = 12.422 (2) Å, b = 6.438 (1) Å, c = 19.593 (3) Å, β = 95.16 (1)°, V = 1560.6 (4) Å^3, and ρ_{calcd} = 1.437 g/cm^3. Full-matrix least-squares refinement (based on F_o^2) converged with final discrepancy indices of $R(F_0)$ = 0.029, $R(F_o^2)$ = 0.040, and $R_w(F_o^2)$ = 0.056 with σ_1 = 1.25 for 2468 diffractometry data with $F_o^2 > \sigma(F_o^2)$.

Introduction

Bis(cyclopentadienyl) early transition-metal complexes have become useful reagents for the investigation of many important reactions in organometallic chemistry, including olefin metathesis,[1] the homogeneous reduction of dinitrogen[2] and CO,[3,4] hydrozirconation-transmetalation,[5] and the activation of C–H bonds.[6] The diverse reactivity exhibited by these complexes in many instances relies on the availability of a vacant orbital at a d^0 metal center. The spatial orientation of this orbital in the coordinatively unsaturated (η^5-C$_5$H$_5$)$_2$ML$_2$-type complexes, as shown by various theoretical[7] and experimental[8] treatments, is directed primarily normal to the plane that bisects the L–M–L bond angle. This arrangement suggests that nucleophilic attack of the electron-deficient metal may involve lateral coordination of the incoming substrate.

We have recently reported that the metathetical reaction of [MgCH$_2$Si(CH$_3$)$_2$CH$_2$]$_x$ with a variety of metallocene dihalides provides a convenient method to prepare a series of 1-sila-3-metallacyclobutane complexes, (η^5-C$_5$H$_5$)$_2$M(CH$_2$Si(CH$_3$)$_2$CH$_2$), where M = Ti, Zr, Nb, and Mo.[9] The inherent stability introduced by placement of a Si atom in the β-position of the four-membered ring blocks the olefin[10] and β-hydrogen[11] elimination pathways normally

associated with the related metallacyclobutanes. With the elimination of these competitive decomposition side reactions for (η^5-C$_5$H$_5$)$_2$M(CH$_2$Si(CH$_3$)$_2$CH$_2$), one anticipates that the coordinatively unsaturated Ti and Zr derivatives may provide suitable model systems to investigate the insertion of small molecules into an early transition metal–carbon bond of a saturated four-membered metallacyclic ring. Consequently, a systematic study of the chemical reactivity of these compounds with a variety of appropriate nucleophilic reagents has been undertaken. In this paper we wish to report the outcome of the reaction of (η^5-C$_5$H$_5$)$_2$Zr(CH$_2$Si(CH$_3$)$_2$CH$_2$) with paraformaldehyde, which proceeds smoothly with the insertion of one OCH$_2$ unit into a Zr–C bond and leads to the formation of (η^5-C$_5$H$_5$)$_2$Zr(OCH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$). The results of an X-ray structure determination of this 1-oxa-4-sila-6-zirconacyclohexane compound are described and provide valuable stereochemical information about the nature of the insertion reaction.

Experimental Section

General Considerations. All manipulations were performed in a Vacuum atmosphere glovebox or on a double-manifold high vacuum line. Nitrogen was purified by passage through successive columns containing activated BTS catalyst and Linde 4A molecular sieves. Solvents were dried by using standard methods and vacuum transferred into storage flasks containing [(η^5-C$_5$H$_5$)$_2$Ti(μ-Cl)$_2$]$_2$Zn prior to use. (η^5-C$_5$H$_5$)$_2$Zr(CH$_2$Si(CH$_3$)$_2$CH$_2$) was prepared and recrystallized by previously published methods,[9] and paraformaldehyde was purchased from Aldrich and used without further purification.

^{1}H and ^{13}C NMR spectra were recorded on a Varian CFT-20 NMR spectrometer operating in the FT mode. Spectra were measured in C$_6$H$_6$-d_6 with the residual proton resonance as the internal standard. Elemental analyses were performed by Dornis and Kolbe Microanalytical Laboratories, Mulheim, West Germany.

Preparation of (η^5-C$_5$H$_5$)$_2$Zr(OCH$_2$CH$_2$Si(CH$_3$)$_2$CH$_2$). The

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Table I. Data for X-ray Diffraction Analysis of

$(\eta^5\text{-}C_5H_5)_2\overline{Zr(OCH_2CH_2Si(CH_3)_2CH_2)}$

A. Crystal Data

cryst system	monoclinic
space group	$P2_1/c$ (C_{2h}^5, No. 14)
a, Å	12.422 (2)
b, Å	6.438 (1)
c, Å	19.593 (3)
β, deg	95.16 (1)
V, Å^3	1560.6 (4)
fw, amu	337.65
d(calcd), g/cm^3	1.437
Z	4
μ, cm^{-1}	7.55

B. Data Collection and Analysis Summary

cryst dimens, mm	0.52 × 0.22 × 0.30
reflctns sampled	$\pm hkl$ (5° ≤ 2θ ≤ 50°)
2θ range for centered reflctns, deg	32-39
scan rate, deg/min	2
scan width, deg	1.1 + 0.9 tan θ
no. of std reflctns	3
% cryst decay	34
total no. of measd reflctns	2859
no. of unique data used in refinement	2767 ($F_o^2 \geqslant 0$)
agreement between equivalent data	
$R_{av}(F_o)$	0.017
$R_{av}(F_o^2)$	0.016
transmissn coeff	0.760-0.857
P	0.03
discrepancy indices for data with $F_o^2 > \sigma(F_o^2)$	
$R(F_o)$	0.029
$R(F_o^2)$	0.040
$R_w(F_o^2)$	0.056
σ_1	1.25
no. of variables	251
data to parameter ratio	11.0:1

reaction of 0.500 g of $(\eta^5\text{-}C_5H_5)_2\overline{Zr(CH_2Si(CH_3)_2CH_2)}$ with a twofold excess of paraformaldehyde was conducted in a sealed glass tube. The 15-mL pentane suspension was heated for 20 h at 70 °C in an oil bath and then after being cooled was transferred to a fritted-filter assembly for workup. After separation of the insoluble solids, the solvent was removed in vacuo to give an oily product. Heating of the product mixture at 70 °C under 10^{-4} torr pressure was sufficient to remove any volatile material and resulted in the sublimation of the colorless crystalline product onto the walls of the flask. A total of 450 mg (80% yield) of $(\eta^5\text{-}C_5H_5)_2\overline{Zr(OCH_2CH_2Si(CH_3)_2CH_2)}$ was isolated. A parallel reaction was run in a sealed NMR tube, and the reaction mixture exhibited a comparable ^1H NMR spectrum to that of the isolated insertion product. ^1H NMR spectrum (C_6H_6-d_6): δ 5.79 (C_5H_5, s), 4.10 (OCH_2, t, $^3J_{H-H}$ = 6.5 Hz), 0.80 (CH_2Si, t, $^3J_{H-H}$ = 6.5 Hz), 0.53 ($ZrCH_2Si$, s), 0.21 (CH_3, s); ratio of peak areas 5:1:1:1:3. Gated decoupled ^{13}C NMR spectrum (mult, $^1J_{^{13}C-H}$ in Hz): δ 111.2 (C_5H_5, d, 171), 70.1 (OCH_2, t, 142), 24.64 ($ZrCH_2Si$, t, 117), 21.6 (CH_2Si, t, 118), 1.14 (CH_3, q, 116). Anal. Calcd for $C_{15}H_{22}OSiZr$: C, 53.36; H, 6.57. Found: C, 53.30; H, 6.60.

X-ray Data Collection and Structural Analysis of $(\eta^5\text{-}C_5H_5)_2\overline{Zr(OCH_2CH_2Si(CH_3)_2CH_2)}$. A colorless crystal was sealed in a glass capillary tube under a prepurified N_2 atmosphere. The sample was transferred to and optically aligned on a Picker goniostat that is computer controlled by a Krisel Control diffractometer automation system. Analogous procedures to those described previously[12] were utilized to determine the lattice parameters for the monoclinic unit cell and to collect the X-ray diffraction data for the structural analysis. Duplicate reflections, which were previously corrected for crystal decomposition, absorption, and Lorentz–polarization effects, were averaged to

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Table II. Positional Parameters for

$(\eta^5\text{-}C_5H_5)_2\overline{Zr(OCH_2CH_2Si(CH_3)_2CH_2)}^a$

atom	x	y	z
Zr	0.24240 (2)	0.15616 (3)	0.14888 (1)
Si	0.25310 (6)	0.10023 (11)	-0.02297 (3)
O	0.3077 (1)	0.3723 (2)	0.0971 (1)
C1	0.3847 (3)	0.4077 (5)	0.0498 (2)
C2	0.3866 (2)	0.2320 (5)	-0.0014 (2)
C3	0.2065 (2)	-0.0393 (4)	0.0514 (1)
MeC1	0.1536 (4)	0.3012 (7)	-0.0553 (2)
MeC2	0.2749 (4)	-0.0841 (7)	-0.0944 (2)
C4	0.3419 (3)	-0.1729 (6)	0.1883 (2)
C5	0.3082 (3)	-0.0854 (6)	0.2457 (2)
C6	0.3622 (4)	0.1004 (7)	0.2566 (2)
C7	0.4322 (3)	0.1226 (6)	0.2068 (2)
C8	0.4181 (3)	-0.0451 (6)	0.1639 (2)
C9	0.0929 (3)	0.1861 (8)	0.2288 (2)
C10	0.0443 (2)	0.1098 (6)	0.1689 (2)
C11	0.0459 (2)	0.2614 (8)	0.1200 (2)
C12	0.0963 (3)	0.4311 (7)	0.1492 (3)
C13	0.1280 (3)	0.3840 (7)	0.2165 (2)
H1	0.364 (2)	0.533 (5)	0.026 (1)
H2	0.454 (3)	0.434 (5)	0.079 (2)
H3	0.414 (2)	0.268 (5)	-0.040 (2)
H4	0.443 (2)	0.129 (4)	0.014 (2)
H5	0.132 (2)	-0.068 (4)	0.040 (1)
H6	0.241 (2)	-0.158 (4)	0.055 (1)
H7	0.142 (3)	0.396 (6)	-0.027 (2)
H8	0.175 (3)	0.365 (6)	-0.090 (2)
H9	0.077 (3)	0.243 (7)	-0.069 (2)
H10	0.330 (3)	-0.176 (5)	-0.082 (2)
H11	0.216 (3)	-0.146 (5)	-0.107 (2)
H12	0.296 (3)	-0.009 (6)	-0.132 (2)
H13	0.322 (3)	-0.283 (6)	0.169 (2)
H14	0.256 (3)	-0.129 (5)	0.267 (2)
H15	0.358 (3)	0.179 (5)	0.284 (2)
H16	0.473 (3)	0.245 (6)	0.203 (2)
H17	0.450 (3)	-0.075 (5)	0.128 (2)
H18	0.102 (3)	0.117 (6)	0.263 (2)
H19	0.016 (3)	-0.012 (5)	0.161 (2)
H20	0.022 (2)	0.249 (5)	0.079 (2)
H21	0.107 (3)	0.540 (6)	0.134 (2)
H22	0.166 (3)	0.468 (6)	0.246 (2)

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

provide 2767 unique reflections ($F_o^2 \geq 0$) that were all used in the structural analysis. Specific details with regard to the lattice parameters and the data collection procedure are provided in Table I.

An initial position for the Zr atom was determined from an interpretation of an unsharpened three-dimensional Patterson map. Subsequent Fourier summations provided approximate coordinates for the remaining non-hydrogen atoms. Successive difference Fourier syntheses utilizing only low-angle data with $(\sin \theta)/\lambda < 0.40$ Å^{-1} were employed to determine approximate coordinates for all of the hydrogen atoms. Full-matrix least-squares refinement[13-17] (based on F_o^2) with anisotropic temperature factors for the 18 non-hydrogen atoms and isotropic temperature factors for the 22 hydrogen atoms converged with final discrepancy

(13) The least-squares refinement[14] of the X-ray diffraction data was based upon the minimization of $\sum \omega_i |F_o^2 - S^2 F_c^2|$, where ω_i is the individual weighting 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 $R_w(F_o^2) = [\sum \omega_i |F_o^2 - F_c^2|^2/\sum \omega_i F_o^4]^{1/2}$. The standard deviation of an observation of unit weight, σ_1, equals $[\sum \omega_i |F_o^2 - F_c^2|/(n - p)]^{1/2}$, where n is the number of observations and p is the number of parameters varied during the last refinement cycle.

(14) The X-ray scattering factor tables utilized in the structure factor calculations were those of Cromer and Mann[15] for the non-hydrogen atoms and those of Stewart et al.[16] for the hydrogens. Appropriate corrections for anomalous dispersion were included.[17]
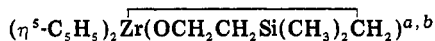
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Table III. Interatomic Distances (Å) and Bond Angles (deg) for Nonhydrogen Atoms in

$(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)^{a,b}$

A. Interatomic Distances

Zr–O	1.941 (2)	C4–C5	1.357 (5)
Zr–C3	2.297 (2)	C5–C6	1.379 (6)
O–C1	1.409 (4)	C6–C7	1.371 (6)
C1–C2	1.513 (5)	C7–C8	1.370 (6)
C2–Si	1.877 (3)	C8–C4	1.372 (5)
Si–MeC1	1.861 (4)	C9–C10	1.362 (5)
Si–MeC2	1.874 (4)	C10–C11	1.369 (6)
Si–C3	1.849 (3)	C11–C12	1.360 (6)
Zr–Cp(1)	2.242 (4)	C12–C13	1.376 (7)
Zr–Cp(2)	2.251 (4)	C13–C9	1.375 (7)

B. Bond Angles

O–Zr–C3	91.0 (1)	C8–C4–C5	108.3 (3)
Zr–O–C1	143.1 (2)	C4–C5–C6	107.8 (4)
O–C1–C2	111.5 (2)	C5–C6–C7	108.1 (4)
C1–C2–Si	114.9 (2)	C6–C7–C8	107.5 (3)
C2–Si–C3	112.0 (1)	C7–C8–C4	108.2 (3)
Si–C3–Zr	109.8 (1)	C13–C9–C10	107.8 (4)
C2–Si–MeC1	108.0 (2)	C9–C10–C11	108.2 (4)
C3–Si–MeC1	111.1 (2)	C10–C11–C12	108.3 (4)
C2–Si–MeC2	105.7 (2)	C11–C12–C13	107.9 (4)
C3–Si–MeC2	111.0 (2)	C12–C13–C9	107.7 (4)
MeC1–Si–MeC2	108.8 (2)	Cp(1)–Zr–Cp(2)	130.2 (2)

^{a} Cp(n) denotes cyclopentadienyl ring centroid. ^{b} 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.

indices with $R(F_o) = 0.029$, $R(F_o^2) = 0.040$, and $R_w(F_o^2) = 0.056$ with $\sigma_1 = 1.25$ for the 2468 data with $F_o^2 \geq \sigma(F_o^2)$. A final difference Fourier map verified the completeness of the structural refinement.

The positional parameters from the last least-squares refinement cycle are provided in Table II for all of the atoms. The interatomic distances and bond angles and their esd's, which were calculated from the estimated standard errors of the fractional atomic coordinates, are given in Table III for the non-hydrogen atoms. Tables of the refined thermal parameters, the carbon-hydrogen distances and angles, and the observed and calculated structure factors for $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$ are available as supplementary material.[18]

Results and Discussion

The reaction of $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Si(CH_3)_2CH_2)$ with paraformaldehyde proceeds smoothly with insertion of one OCH_2 fragment into a Zr–C bond and thereby leads to an expansion of the number of atoms in the zirconacyclic ring from four to six. The identification of the insertion product as $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$ has been accomplished by NMR and X-ray diffraction methods. The molecular configuration of this 1-oxa-4-sila-6-zirconacyclohexane compound is depicted in Figure 1 with the appropriate numbering scheme for all of the atoms. The pseudotetrahedral ligand arrangement about the Zr(IV) center is characterized by Cp(1)–Zr–Cp(2) and O–Zr–C3 bond angles of 130.2 (2) and 91.0 (1)°, respectively. These angles are comparable to those found in other tetravalent $(\eta^5\text{-}C_5H_5)_2ZrL_2$-type complexes.[19]

Figure 1. Perspective view of the molecular structure of $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$ with the atom numbering scheme. The thermal ellipsoids are scaled to enclose 50% probability. For purposes of clarity the radii of the spheres for the hydrogen atoms were arbitrarily reduced. Selected bond lengths (Å): Zr–O = 1.941 (2); Zr–C3 = 2.297 (2); C1–O = 1.409 (4). Bond angles (deg): C3–O–Zr = 91.0 (1); Zr–O–C1 = 143.1 (2).

The 1-oxa-4-sila-6-zirconacyclohexane ring of $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$ adopts a distorted boat conformation. Within the ring several significant stereochemical features are visible. The insertion of a OCH_2 fragment into one of the Zr–C bonds is accompanied by the formation of a relatively short Zr–O bond of 1.941 (2) Å and produces a rather obtuse Zr–O–C1 bond angle of 143.1 (2)°. This structural arrangement is comparable to that observed for the seven-membered zirconacyclic products obtained from the coupling reactions of (s-trans-butadiene)zirconocene with ketones.[20] The corresponding Zr–O bond distances and Zr–O–C bond angles in $(\eta^5\text{-}C_5H_5)_2Zr(OC(C_6H_5)_2CH_2C(H)=C(H)CH_2)$[21] and $(\eta^5\text{-}C_5H_5)_2Zr(OC(i\text{-}C_3H_7)_2CH_2C(H)=C(H)CH_2)$[22] are 1.946 (4) Å, 150.5 (4)° and 1.961 (7) Å, 155.2 (7)°, respectively. These Zr–O bonds are all ca. 0.2 Å shorter than a typical Zr–O single bond of 2.15–2.20 Å[23] and thereby reflect a substantial degree of multiple bond character, which arises from π-donation from the in-plane O 2p orbital into the empty Zr d_{z^2}-like orbital.[24] This π-donation further increases the metal's electron density and leads to a ca. 0.06-Å lengthening of the Zr–C bond from 2.240 (5) Å in the parent zirconacycle[25] to 2.297 (2) Å in $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$. An analogous antibonding influence is observed for the Zr–C bonds in $(\eta^5\text{-}C_5H_5)_2Zr(OCR_2CH_2C(H)=C(H)CH_2)$ (R = C_6H_5[21] and $i\text{-}C_3H_7$[22]) and is consistent with the results of our structural studies of $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$ (M = Zr, Nb, and Mo).[25] A comparison of the appropriate M–C bond distances for the latter 1-sila-3-metallacyclobutane compounds has revealed that occupation of the metal's d_{z^2}-like orbital produces a simultaneous lengthening of the M–C

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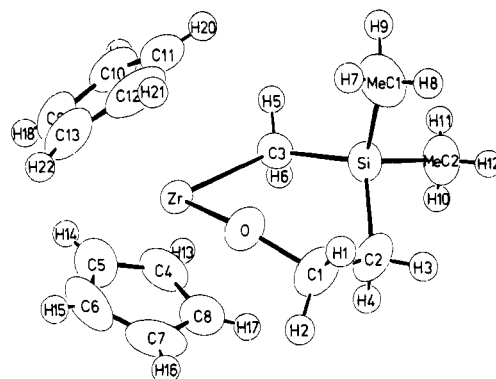
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bond and a reduction of the C–M–C bond angle. Although the observed elongation of the Zr–C bond is considerably smaller for each of the substituted carbonyl insertion products, their similarity collectively reflects the nature of the Zr–O multiple-bonding interaction in these 1-oxa-2-zirconacycloalkane rings.

The remaining structural parameters within the six-membered ring of $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$ exhibit normal single bond distances and essentially tetrahedral bond angles. The CO bond distance of the inserted oxymethylene group has been lengthened to 1.409 (4) Å, and the bond distance of the newly formed C1–C2 single bond is 1.513 (5) Å. In general, the corresponding ^1H and ^{13}C NMR parameters have typical values, except for those associated with the CH_2 group attached to the zirconium. The ^1H and ^{13}C chemical shifts for this methylene group are shifted by ca. 1 and 20 ppm, respectively, upfield from their corresponding values in $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Si(CH_3)_2CH_2)$. The basis for understanding these upfield shifts becomes more evident upon consideration of the relative positions of the corresponding NMR resonances for $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$ (M = Zr and Mo).[9] Occupation of the LUMO in the d^0 zirconacycle by an electron pair leads to substantial upfield shifts of 2.55 and 80.55 ppm for the methylene proton and carbon resonances, respectively, of the d^2 molybdenacycle. This trend thereby suggests that the upfield shifts observed for the corresponding methylene NMR resonances of $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$ probably reflect the partial occupation of the LUMO due to π-donation from the in-plane oxygen p-orbital of the 1-oxa-4-sila-6-zirconacyclohexane ring.

Nature of the Formaldehyde Insertion Reaction

Current efforts to develop a fundamental understanding of the mechanistic aspects of metal-promoted hydrogenation of CO have suggested that the OCH_2[26] moiety may play an intermediary role in Fischer–Tropsch chemistry. Although the formation of free formaldehyde in large amounts from synthesis gas is thermodynamically unfavorable, Fahey[27] has provided kinetic evidence that supports its participation as a reaction intermediate in the homogeneous hydrogenation of CO to alcohols, polyols, and formate esters. From desorption experiments and infrared data, Hattori and co-workers[28] have concluded that the reaction of CO with H_2 on MgO proceeds with formation of adsorbed formaldehyde. In addition, the close chemical interrelationships associated with oxymethylene, hydridoformyl, hydroxycarbene, and formaldehyde species have encouraged exploratory studies of the metal coordination modes and the chemical transformations associated with the OCH_2 unit.[29] Although the reaction of formaldehyde with various transition-metal complexes has provided valuable stereochemical information about the $M(CH_2O)$ interaction,[30] few examples of the insertion of a OCH_2 unit

Scheme I
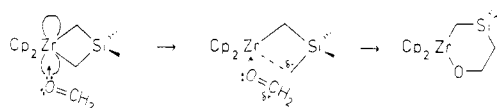
into a M–C bond have been reported.[31] In principal, this reaction represents a possible propagation step in Fischer–Tropsch chemistry since insertion of OCH_2 into a M–C bond of a surface bound methylene fragment leads simultaneously to the lengthening of the hydrocarbon backbone via C–C bond formation and the introduction of an oxygen functionality.

The coordinative unsaturation and the inherent oxophilicity of tetravalent zirconium provide ideal conditions to promote insertion of OCH_2 into a Zr–C bond of the saturated zirconacyclic ring of $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Si(CH_3)_2CH_2)$. Whereas CO insertion into an acyclic[32] or cyclic[33] metal–alkyl bond proceeds via alkyl migration to a precoordinated metal carbonyl, the fact that only the oxygen atom of formaldehyde can function as a σ electron-pair donor suggests that OCH_2 insertion probably involves an entirely different route. In this case, the orientation of the LUMO of electron-deficient canted zirconocene moiety[7] coupled with the steric bulk introduced by the dimethylsilyl group of the 1-sila-3-zirconacyclobutane ring restricts the OCH_2 unit to a lateral approach.[34] Therefore, the subsequent insertion reaction is most likely initiated by electron-pair donation of a lone pair from the O into the d_{z^2}-like LUMO of the d^0 Zr(IV) center. Since electron occupation of this orbital has been shown by structural studies of $(\eta^5\text{-}C_5H_5)_2M(CH_2Si(CH_3)_2CH_2)$ (M = Zr, Nb, and Mo)[25] to exhibit an antibonding influence on the M–C bond, precoordination of the OCH_2 moiety is expected to proceed with the lengthening of the Zr–C bonds. The Zr–C bond of the adjacent methylene is further weakened by the electron-pair repulsion and steric influences introduced by the incoming substrate. Collectively, these factors encourage lateral insertion of the OCH_2 unit leading to the formation of a new carbon–carbon single bond and the subsequent enlargement of the zirconacyclic ring (Scheme I).

Although this reaction was performed in a 2:1 excess of paraformaldehyde, no evidence for the formation of the corresponding diinsertion product was observed. Presumably, the reduced oxophilicity of the Zr atom in $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2Si(CH_3)_2CH_2)$ is a major factor that prohibits the insertion of a second OCH_2 unit into the remaining Zr–C bond. In addition, an intramolecular pathway leading to C–C bond formation such as observed by Bercaw and co-workers[35] during the carbonylation of $(\eta^5\text{-}C_5Me_5)_2Zr(CH_3)_2$ is not available to stabilize the hypothetical diinsertion product in this case.

The reaction of paraformaldehyde with $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Si(CH_3)_2CH_2)$ provides a fundamental example of the ability of an electron-deficient, early transition-metal center to direct insertion into a M–C σ bond of a metallacyclic ring. Further studies are underway to determine the extent that the Zr can be used to induce insertion of

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other nucleophiles including CO, NO, SO_2, CO_2, and CH_3CN, as well as other substituted carbonyls into a Zr–C bond of $(\eta^5\text{-}C_5H_5)_2Zr(CH_2Si(CH_3)_2CH_2)$.

Silafunctional Compounds in Organic Synthesis. 25.[1] The Aluminum Chloride Catalyzed Rearrangement of Alkenyl(chloromethyl)silanes to Allyl- and Cyclopropylsilanes
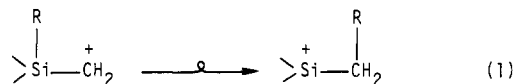
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Alkenyl(chloromethyl)dimethylsilanes undergo the aluminum chloride catalyzed rearrangement to form the corresponding allyl- and/or cyclopropylchlorosilanes, depending upon the structure of the alkenyl group. The reaction courses appear to be determined primarily by the stability of the α- or β-silyl carbocation species. The synthetic utility of the rearrangement products has been shown by their conversion to alcohols via the hydrogen peroxide oxidation of the carbon–silicon bond.

The Wagner–Meerwein type rearrangement involving migration of an organic group from silicon to the α-carbon atom has been recognized as one of the typical cationic rearrangements of organosilicon compounds (eq 1).[2] However, there has been no report dealing with the migration of an alkenyl group. We describe herein the aluminum chloride catalyzed rearrangement of alkenyl(chloromethyl)dimethylsilanes to allyl- and/or cyclopropylsilanes (eq 2). The present rearrangement may be re-

(1)

(2)
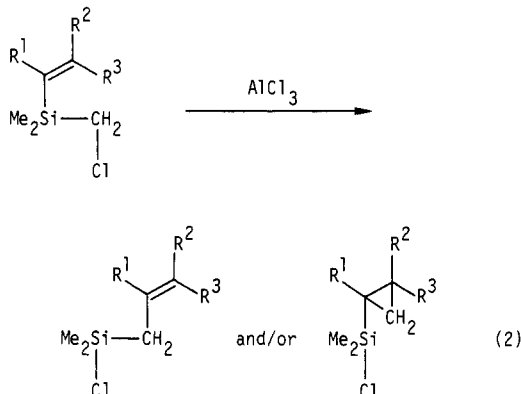
garded as a silicon version of the well-known rearrangement among homoallyl, cyclopropylcarbinyl, and cyclo-
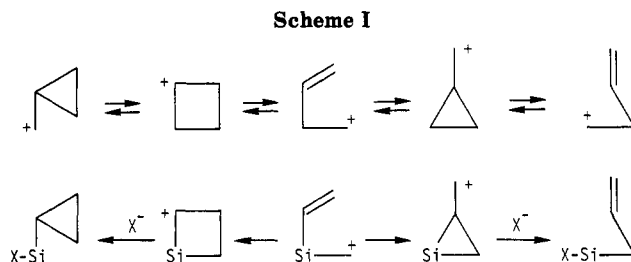
Scheme I

butyl carbocations,[3] as shown in Scheme I.

This paper reports electronic and steric factors that determine the reaction courses and synthetic utilities of the rearranged silafunctional compounds.

Results and Discussion

$AlCl_3$-Catalyzed Rearrangement. Six representative compounds 1–6, listed in Table I, were examined in this study. The rearrangement was carried out in dry dichloromethane (1 mL/1 mmol) at room temperature. Upon addition of freshly sublimed $AlCl_3$ (ca. 10 mol %), a slightly exothermic reaction occurred and was completed in 5–25 min. The rearrangement products allyl- and/or cyclopropylchlorosilanes were methylated with the methyl Grignard reagent and characterized.

The results are summarized in Table I, in which the starting materials are listed in the order of decreasing allyl/cyclopropyl ratios. The reaction courses are highly dependent upon the structure of the alkenyl group. The characteristic features are summarized as follows. (1) A (Z)-1-alkenylsilane gives an allylsilane exclusively. (2) An (E)-1-alkenylsilanes affords an allylsilane predominantly, together with a cyclopropylsilane as a minor product. (3) An α-substituted vinylsilane forms a cyclopropylsilane

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