Organometallics **2005,** *24,* 3731−3736

Highly Selective Synthesis and Structural Characterization of Bis(silyl)-[3]-ferrocenophane Derivatives

Mariusz Majchrzak, Bogdan Marciniec,* Maciej Kubicki, and Adam Pawełczyk

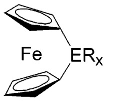
Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland

Received March 15, 2005

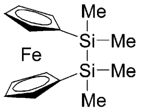
Bis(silyl)-[3]-ferrocenophanes have been easily prepared via ring-closing silylative coupling of 1,1′-bis(vinylsilyl)ferrocenes catalyzed by ruthenium hydride complexes. Dimethylvinylsilyl derivative **1** reacts under optimum conditions to give regioselectively and quantitatively disilacyclic product containing an *exo*-methylene (**3**) bond between two silicon atoms. The reaction with (diphenylvinylsilyl)ferrocene (**2**) permits stereoselective synthesis of the product with a *cis*-vinylene (**4**) bond between the silicon atoms. The structures of both products, which cannot be synthesized via a ring-closing metathesis procedure, have been confirmed using NMR and X-ray crystal structure methods.

Introduction

The discovery of ferrocene dates back to the 1950s, and since then it has been an interesting research material for scientists worldwide.[1] Ferrocene and its various derivatives have found application in many fields such as synthetic organic chemistry, materials science, and catalysis.[2] Ferrocene has been found to be easily functionalized. This feature is particularly evident in the preparation of bridged ferrocenes—the so-called "ring system"—ferrocenophanes.[3] The bridges of ferrocenophanes contain a few carbon atoms (for review see ref 4) or heteroatom combinations such as group 13 (**B**), group 14 (Si, the first example of **A**: $ER_x = SiPh_2$,[6] Ge, Sn), group 15 (P, As, N[7]), and group 16 (S, Se) (**A**) (ref 5 and references within). The compounds of this type are usually used for syntheses of inorganic polymers via ring-opening polymerization (ROP).



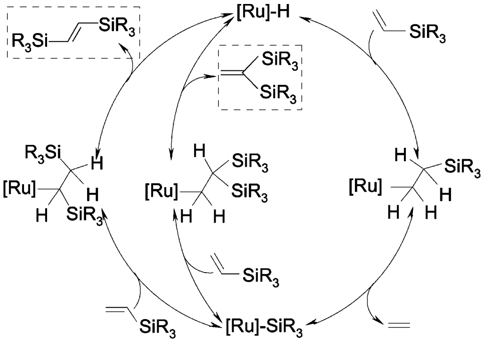
A



B

In contrast, the [2]-ferrocenophane (**B**) containing a disilane bridge which cannot be applied to ROP is used as a monomer in insertion reactions of acetylenes and 1,3-diene in the presence of palladium complex $[Pd(PPh_3)_4]$, giving cyclic unsaturated organometallic ring systems.[8]

Scheme 1. Mechanism of Silylative Coupling Reaction



where: R = Me, Et, Pr, OMe, OEt, OPr, $OSiMe_3$,

An alternative way to get this type of silicon compounds is the reaction of silylative coupling of vinylsilanes in the presence of transition metal complexes (e.g., ruthenium and rhodium) containing or generating [M]−H and [M]−Si bonds. The silylative homo-coupling reaction of monovinyl organosilicon compounds proceeds through cleavage of the ═C−Si bond of the vinyl-substituted silicon compounds and the activation of the ═C−H bond of the second vinylsilane molecules.[9] The mechanism of this reaction (see Scheme 1) involving β-silyl elimination and insertion of a C═C double bond into the resulting [M−Si] bond has been proved by insertion of ethylene and vinylsilane into [M−Si] (where M = Ru, Rh) bonds as well as by a series of elaborate

---

* Corresponding author. Tel: (+48)-61-8291-366. Fax: (+48)-61-8291-508. E-mail: marcinb@amu.edu.pl.

(1) Kealy, T. J.; Pouson, P. L. *Nature* **1951**, *168*, 1039.

(2) (a) *Ferrocene, Homogeneous Catalysis-Organic Synthesis-Materials Science*; Togni, A., Hayasi, T., Eds.; VCH: New York, 1995. (b) *Matallocenes*, Togni, A., Helterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998.

(3) (a) Plesske, K. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 312; *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 394. (b) Bublitz, D. E.; Reinehart, K. L., Jr. *Org. React.* **1967**, *2*, 231.

(4) Heo, R. W.; Lee, T. R. *J. Organomet. Chem.* **1999**, *578*, 31−42.

(5) Hudson, R. D. A. *J. Organomet. Chem.* **2001**, *637−639*, 47−69.

(6) Osborne, A. G.; Whiteley, R. H. *J. Organomet. Chem.* **1975**, *101*, C27.

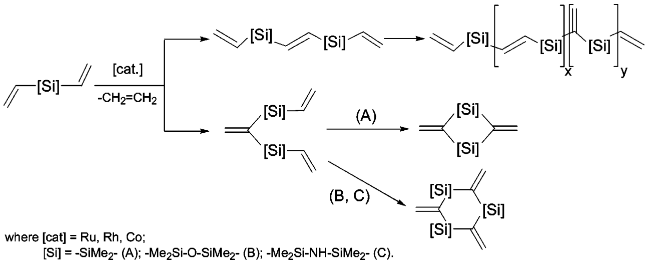
(7) Yamaguchi, I.; Sakano, T.; Ishii, H.; Osakada, K.; Yamamoto, T. *J. Organomet. Chem.* **1999**, *584*, 213.

(8) Finckh, W.; Tang, B.-Z.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904.

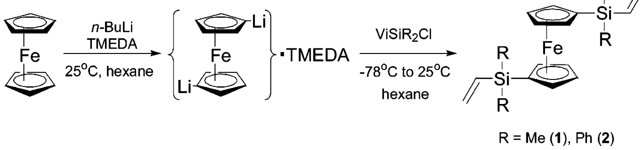
(9) (a) Marciniec, B.; Pietraszuk, C. *Curr. Org. Chem.* **2003**, *7*, 691−735. (b) Marciniec, B.; Pietraszuk, C. *Metathesis of Silicon-Containing Olefins*; Grubbs, R. H., Ed.; *Handbook of Metathesis*, Vol. 2; Wiley-VCH: New York, 2003. (c) Marciniec, B. *Appl. Organomet. Chem.* **2000**, *14*, 527−538; *Mol. Cryst. Liq. Cryst.* **2000**, *353*, 173−182.

10.1021/om050194x CCC: $30.25

Scheme 2



Scheme 3



mass spectroscopic studies with deuterated styrene and vinylsilanes.[10]

The evidence for the non-metallacarbene mechanism of monovinylsilane transformation has been reported,[10] but it can be generalized for dimerization of divinyl-substituted silanes, siloxanes, and silazanes, leading subsequently to competitive linear oligomerization and ring-closing silylative coupling (Scheme 2).

The unique feature of the silylative coupling reaction distinguishing it from *cross*-metathesis is the formation of a 1,1-bis(silyl)ethene fragment under given conditions.[10b,11] Recently, we have reported a new facile and efficient silylative coupling cyclization of 1,2-bis(dimethylvinylsiloxy)ethane[12a] and of *N*,*N*′-dimethyl-*N*,*N*′-bis(dimethylvinylsilyl)ethane,[12b] giving cyclic products, subsequently used for regioselective synthesis of 1,1-bis(silyl)ethenes.

Therefore, the aim of the paper is to extend this reaction to the synthesis of novel cyclo-ferrocene-silicon compounds with the silicon-(*exo*-methylene or *cis*-vinylene)-silicon bridged structure by the respective reaction of bis(vinylsilyl)ferrocenyl derivatives **1** and **2**.

Results and Discussion

The synthesis of substrates was performed in "one pot" (without intermediate isolation). The lithiation of ferrocene can be conducted selectively to give dilithio-ferrocene (using *n*-BuLi in hexane in the presence of TMEDA), according to Scheme 3:

Starting from dilithio-ferrocene, bis(vinylsilyl)ferrocenyl derivatives **1** and **2** were obtained with good yields from 60% to 75%. The products−substrates were characterized by standard NMR methods.

At the subsequent stage of our experiment, the reactivity of the above-mentioned compounds in the silylative coupling cyclization reaction catalyzed by ruthenium(II) complexes was analyzed. Several catalytic tests were performed in order to establish the most favorable conditions for effective cyclization in the presence of various catalysts: [RuH(Cl)(CO)(PPh$_3$)$_3$] (**I**), [RuH(Cl)(CO)(PCy$_3$)$_2$] (**II**), [Ru(SiMe$_3$)(Cl)(CO)(PPh$_3$)$_2$] (**III**). In this case catalytic screenings were performed using the model processes of **1** and **2** (Scheme 4) to measure substrate conversions, selectivity, and the yield of **3** and **4** by GC and GC-MS methods.

Scheme 4

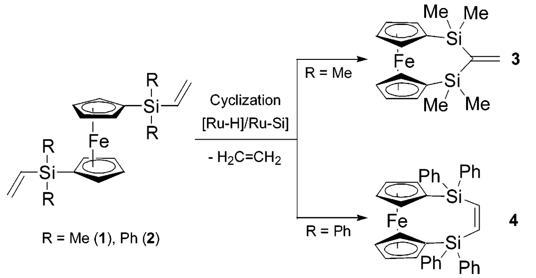


Table 1. Effect of Catalyst (I−III) on the Conversion of 1,1′-Bis(vinylsilyl)ferrocenes (1, 2) and Yield of Products 3 and 4[a]

monomer (group)	[Ru]	amount of catalyst (mol %)[b]	conversion of monomer (%)[c]	yield (%)[d]
1[e] (Me)	**I**	0.1	>99	99
	II	0.1	>99	99
	III	0.1	>99	99
2[f] (Ph)	**I**	1	87	87
	II	1	92	92
	III	1	89	89

[a] The selectivity of the reaction was over 99%. [b] Calculated to monomer. [c,d] Calculated by GC and NMR. [e] t = 5 h, toluene 1 M. [f] t = 18 h, toluene 0.25 M; T = 110 °C. (**1**) [(ViSiMe$_2$)$_2$Fc], (**2**) [(ViSiPh$_2$)$_2$Fc] where Fc = [Fe(C$_5$H$_4$)$_2$].

The results are collected in Table 1.

The preliminary study (see Table 1) allowed us to optimize highly stereoselective synthesis of cyclo-bis(silyl)ferrocenyl compounds. Depending on the groups substituted at the silicon atom, the conversions were 99% for substrate **1** and 87−92% for substrate **2**. In both cases, complex **II** was the most active and efficient as a catalyst in the intramolecular coupling reaction. This process successfully proceeded only in solvent. In particular, for the synthesis of product **4**, the correct concentration of substrate **2** in toluene was very important for conversion of **2** and the reaction progress.

Application of this catalytic system for silylative coupling cyclization of **1** and **2** gave exclusively disilacyclic products containing an *exo*-methylene or *cis*-vinylene bond between two silicon atoms. The structures of both cyclo-bis(silyl)ferrocenyl derivatives (**3** and **4**) were straightforwardly determined by ^{1}H, ^{13}C, and ^{29}Si NMR, DEPT spectra, and X-ray crystal structure analysis. Moreover, the analysis of mass products using FAB-MS, HR-MS, and elemental analysis additionally confirmed their cyclic structures.

For example, a comparison of the carbon spectrum with a fragment of DEPT spectrum (all protonated carbons) of product **3** revealed the existence of a quaternary carbon atom assigned to the signal at 156.29 ppm (C^b) and carbon atom (=CH$_2$, C^a, at 138.62 ppm) directly terminating the *exo*-bond (Figure 1).

---

[10] (a) Wakatsuki, Y.; Yamazaki, H.; Nakano, N.; Yamamoto, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 703. (b) Marciniec, B.; Pietraszuk, C. *J. Chem. Soc., Chem. Commun.* **1995**, 2003−2004. *Organometallics* **1997**, *16*, 4320.

[11] (a) Marciniec, B.; Lewandowski, M. *Tetrahedron Lett.* **1997**, *36*, 3777−3780. (b) Mise, T.; Takaguchi, Y.; Umem, T.; Shimizu, S.; Wakatsuki, Y. *Chem. Commun.* **1998**, 699. (c) Marciniec, B.; Lewandowski, M.; Bijpost, E.; Malecka, E.; Kubicki, M.; Walczuk-Guœciora, E. *Organometallics* **1999**, *20*, 3968.

[12] (a) Pawluć, P.; Marciniec, B.; Hreczycho, G.; Gaczewska, B.; Itami, Y. *J. Org. Chem.* **2005**, *70*, 370−372. (b) Pawluć, P.; Hreczycho, G.; Marciniec, B. *Synlett* **2005**, *7*, 1105−1108.

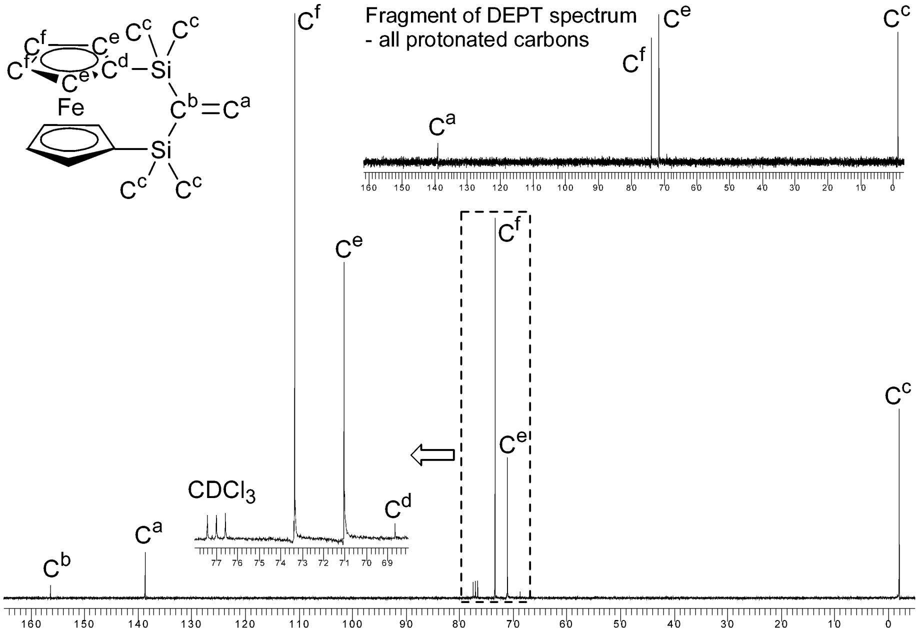


Figure 1. ^{13}C NMR and fragment of DEPT spectra of product **3**.

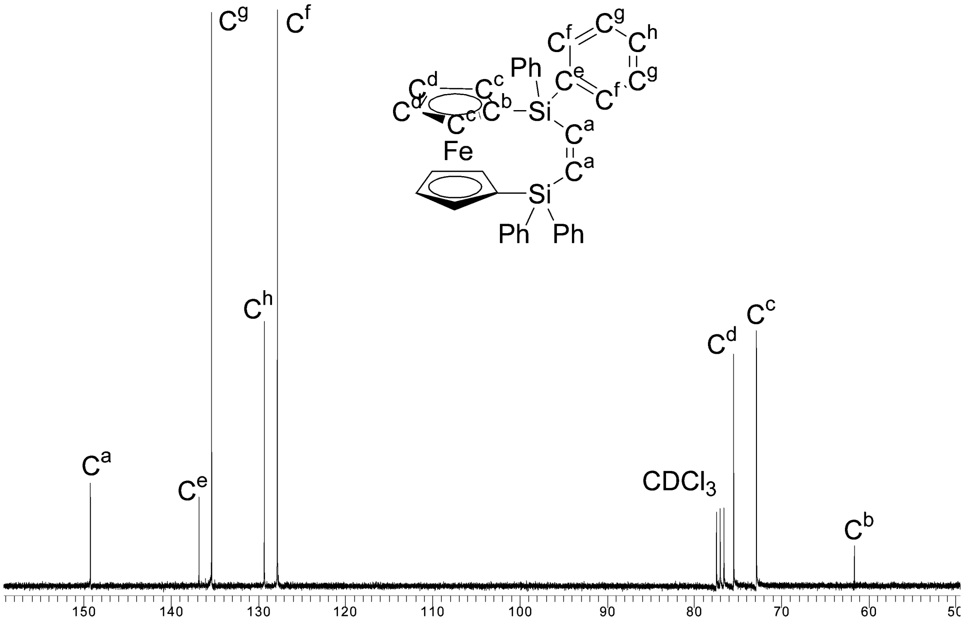


Figure 2. ^{13}C NMR spectra of product **4**.

Cyclic compound **3** was obtained according to the reaction mechanism presented in the Introduction. The structure of **4** was also confirmed (Figure 2). In this compound only a *cis*-fragment was observed.

The characteristic signal assigned to vinylene-carbon atoms was identified at 149.24 ppm (−H*C*=*C*H−, C^{a}). The steric effect of phenyl groups at silicon atoms led to such a product formation.

It is worth emphasizing that both processes give stereo- and/or regioselectively cyclo-bis(silyl)ferrocenophanes **3** and **4**, respectively, and with no linear products observed. Apparently, the intramolecular cyclization of monomers **1** and **2** under the conditions applied is much faster than the silylative coupling polycondensation.

The Structures of Both Bis(silyl)ferrocenophanes (3 and 4) Were Solved by the X-ray Method. Thermal ellipsoid representations of molecules **3a** and **4a** are shown in Figures 3 and 4, respectively. The overall conformations of both molecules differ significantly. In **3** both Cp rings and C−Si bonds are in almost ideal eclipsed disposition and the angle between two C(Cp)−Si vectors is 6.9° (Figure 3b), while in **4**, probably due to more bulky phenyl substituents and a more flexible C=C bridge, the conformation is closer to a staggered one with the angle between C−Si bonds of 46.3° (Figure 4b). A similar arrangement of the rings and C−Si bonds was observed in the related compounds: in siloxane-bridged ferrocenophanes the short Si−O−Si bridge enforced an almost eclipsed conformation and the angles between C−Si bonds were smaller for the tetramethyl derivative (0.6°, 5.2°, and 2.1° for three symmetry-independent molecules) than in the tetraphenyl one (13.6°).[13] Similarly, in (*Z*)-(1,1,4,4-tetramethyl-1,4-disila)ethane)-[3]-ferrocenophane, the

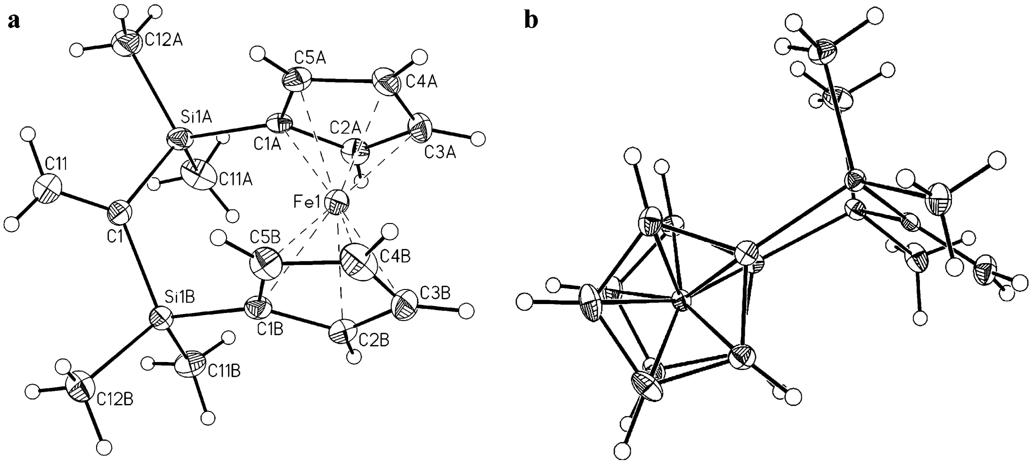


Figure 3. (a) Anisotropic ellipsoid representation of complex **3**. The ellipsoids are drawn at the 50% probability level; hydrogen atoms are depicted as spheres with arbitrary radii. (b) View perpendicular to the Cp plane.

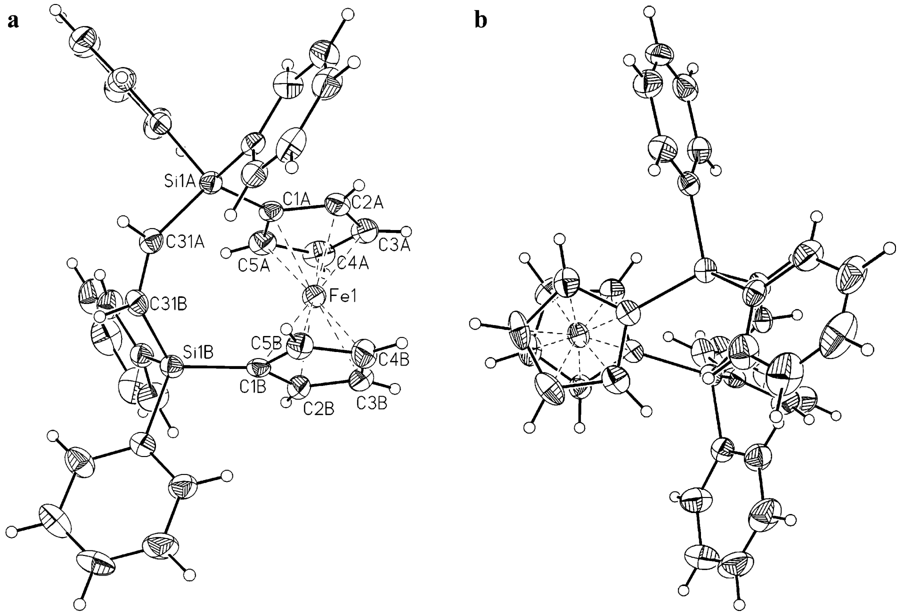


Figure 4. (a) Anisotropic ellipsoid representation of complex **4**. Ellipsoids are drawn at the 33% probability level; hydrogen atoms are depicted as spheres with arbitrary radii. (b) View perpendicular to the Cp plane.

tetramethyl analogue of **4**, the angle between C−Si bonds is 15.0°,[14] much smaller than in **4**.

Bond length and angle patterns in both compounds are typical: mean values of the Fe−C distance are 2.050(3) in **3** and 2.033(10) Å in **4**, as compared with the value of 2.04(2) Å found in the Cambridge Crystallographic Database;[15] mean values of the C−C bond lengths in cyclopentadienyl rings are 1.424(13) Å in **3** and 1.416(15) Å in **4** (CSD value is 1.42(2) Å). The Cp rings are planar (largest deviation from the least-squares plane is 0.011(2) Å and almost parallel; the dihedral angles between the least-squares planes are 2.75(15)° in **7** and 2.91(14)° in **4**. The crystallographic data of **3** and **4** are presented in Table 2.

Conclusions

Disilacyclic ferrocenophanes containing an *exo*-methylene or *cis*-vinylene fragment between two silicon atoms in the cyclic compound can be synthesized via highly selective and efficient ring-closing silylative coupling of bis(vinylsilyl)ferrocenyl derivatives, catalyzed by ruthenium hydride complexes. While the vinylmethyl-substituted silylferrocene undergoes intramolecular coupling, yielding regioselectively cyclo-ferrocenophane with *exo*-methylene, the vinylphenyl-substituted silylferrocene gives stereoselectively cyclo-ferrocenophane with a *cis*-vinylene group between two silicon atoms. ^{1}H, ^{13}C, and ^{29}Si DEPT spectra and X-ray crystal structure analysis confirm the cyclic structure of the products that cannot be synthesized via the ring-closing metathesis procedure.

Experimental Section

General Procedure: Monomer and Cyclic Product Characterization. ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz), and ^{29}Si NMR (60 MHz) and DEPT spectra were recorded on a Varian XL 300 MHz spectrometer in $CDCl_3$ solution. Chemical shifts are reported in δ (ppm) with reference to the residue portio solvent (CH_3Cl) peak for ^{1}H and ^{13}C and to TMS for ^{29}Si. Analytical gas chromatographic (GC) analyses were

---

(13) Angelakos, C.; Zamble, D. B.; Foucher, D. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1994**, *33*, 1709−1718.

(14) Finckh, W.; Tang, B.-Z.; Lough, A.; Manners, I. *Organometallics* **1992**, *11*, 2904−2911.

(15) Flack, H. D. *Acta Crystallogr. Part A* **1983**, *39*, 876.

Table 2. Crystal Data, Data Collection, and Structure Refinement

	3	4
formula	$C_{16}H_{22}FeSi_2$	$C_{36}H_{30}FeSi_2$
fw	326.37	574.63
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$
a (Å)	9.7611(8)	8.9732(9)
b (Å)	13.0367(10)	14.5210(11)
c (Å)	12.7297(10)	22.7141(16)
β (deg)	100.660(7)	90
V (Å^3)	1591.9(2)	2959.6(4)
Z	4	4
D_x (g cm^{-3})	1.362	1.2905
F(000)	688	1200
μ (mm^{-1})	1.082	0.614
T (K)	110(1)	295(1)
cryst size (mm)	0.2 × 0.2 × 0.07	0.55 × 0.1 × 0.1
θ range (deg)	3.26−28.00	3.03−27.00
hkl range	$-10 \le h \le 13$	$-11 \le h \le 11$
	$-17 \le k \le 17$	$-16 \le k \le 18$
	$-16 \le l \le 16$	$-28 \le l \le 28$
reflections		
collected	9932	20 011
unique (R_{int})	3821 (0.03)	6420 (0.048)
final $R(F)$ [$I > 2\sigma(I)$]	0.030	0.035
final $wR(F^2)$ [all data]	0.043	0.047
goodness of fit	0.92	0.76
max./min. $\Delta\rho$ (e Å^{-3})	0.30/−0.31	0.28/−0.25

performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m × 0.15 mm) and TCD. Mass spectra of the monomers and products were obtained by GC-MS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector). High-resolution mass spectroscopic (HRMS) analyses were made on a AMD-402 mass spectrometer and FAB mass spectra on an AMD-604 instrument (AMD Intectra GmbH). Thin-layer chromatography (TLC) was performed on plates coated with 250 μm thick silica gel (Aldrich), and column chromatography was performed with silica gel 60 (70−230 mesh; Fluka). Benzene and pentane were dried, having been distilled from sodium hydride; similarly toluene was from sodium and hexane from calcium hydride under argon. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the reactions were carried out under dry argon atmosphere.

Materials. The chemicals were obtained from the following sources: benzene, toluene, CH_2Cl_2, pentane, hexane, and *N,N,N′,N′*-tetramethylethylenediamine were purchased from Fluka, $CDCl_3$ from Dr Glaser A.G. Basel, chlorodimethylvinylsilane and chlorodiphenylvinylsilane from Gelest, and *n*-buthyllithium and ferrocene from Aldrich. CH_2Cl_2 was additionally passed through a column with aluminum oxide. The ruthenium complexes $[RuH(Cl)(CO)(PPh_3)_3]$ (**I**),[16a] $[RuH(Cl)(CO)(PCy_3)_2]$ (**II**),[16b] and $[Ru(SiMe_3)(Cl)(CO)(PPh_3)_2]$ (**III**)[10b] were prepared on the basis of the procedure described in the above literature.

Representative Procedure for Synthesis of 1,1′-Bis(vinylsilyl)ferrocene Derivatives. The title substrates were synthesized in a manner similar to that reported in ref 17a with modifications. For the first time, the method of synthesis of monomer **1** (Scheme 3) was described forty years ago, by means of hydrosilylation reaction.[17b] All solvents and chemicals were dried and distilled under argon prior to use. The main substrate—ferrocene was sublimed. The ferrocene (3.70 g, 19.89 mmol), hexane (80 mL), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA; 6.15 mL, 40.77 mmol) were placed into a 250 mL two-necked round-bottomed flask equipped with a magnetic stirring bar and condenser connected with a bubbler. After that, the *n*-butyllithium (25 mL, 40 mmol of 1.6 M solution in hexane) was added slowly dropwise to a suspension, the system was stirred for 20 h at room temperature, and a pale orange dilithium salt $[(Fe(\eta^5\text{-}C_5H_4Li)_2)\cdot TMEDA)]$ was formed. Then the system was cooled to −78 °C in order to instil 41.77 mmol of chlorodimethylvinylsilane (or chlorodiphenylvinylsilane). After 25 min the mixture was warmed to room temperature and stirred for additional 8 h. At the subsequent step, the final mixture was filtered off and excess solvent was removed under vacuum. The final products were isolated by the use of column chromatography with silica, using benzene/hexane as eluent. Each time two components were observed. The first, light yellow fraction corresponding to a small amount of ferrocene was discarded. The second fraction was collected and the solvent removed, obtaining pure compounds: $[Fe(\eta^5\text{-}C_5H_4SiMe_2CH{=}CH_2)_2]$ (**1**), rust-orange liquid, yield 5.29 g (75%), and $[Fe(\eta^5\text{-}C_5H_4SiPh_2CH{=}CH_2)_2]$ (**2**), reddish-yellow solid, yield 7.19 g (60%).

Analytical Data of $[Fe(\eta^5\text{-}C_5H_4SiMe_2CH{=}CH_2)_2]$, 1. ^1H NMR ($CDCl_3$; δ (ppm)): 0.27 (s, 12H, $-CH_3$); 4.04 (m, 4H, C_5H_4); 4.28 (m, 4H, C_5H_4); 5.69 (dd, 2H, $-CH{=}CH_2$); 5.97 (dd, 2H, $-CH{=}CH_2$); 6.27 (dd, 2H, $-CH{=}CH_2$). ^{13}C NMR ($CDCl_3$; δ (ppm)): −2.00 ($-CH_3$); 69.92 ($>C-Si$ in C_5H_4); 73.11, 71.42 (C_5H_4); 131.63 ($-CH{=}CH_2$); 139.05 ($-CH{=}CH_2$). ^{29}Si NMR ($CDCl_3$; δ (ppm)): −9.58. MS (FAB, *m/z* (%)): 354 (M^+, 100). HRMS calcd for $C_{18}H_{26}FeSi_2$: 354.09224. Found: 354.09252.

Analytical Data of $[Fe(\eta^5\text{-}C_5H_4SiPh_2CH{=}CH_2)_2]$, 2. ^1H NMR ($CDCl_3$; δ (ppm)): 4.06 (m, 4H, C_5H_4); 4.21 (m, 4H, C_5H_4); 5.78 (dd, 2H, $-CH{=}CH_2$); 6.29 (dd, 2H, $-CH{=}CH_2$); 6.62 (dd, 2H, $-CH{=}CH_2$); 7.37 (m, 16H, $m(p)\text{-}C_6H_5$); 7.28 (d, 8H, $o\text{-}C_6H_5$). ^{13}C NMR ($CDCl_3$; δ (ppm)): 66.28 ($>C-Si$ in C_5H_4); 72.39, 74.60 (C_5H_4); 127.57 ($m\text{-}C_6H_5$); 129.24 ($p\text{-}C_6H_5$); 134.26 ($Si-CH{=}CH_2$); 134.63 ($Si-C<$ in C_6H_5); 135.39 ($o\text{-}C_6H_5$); 136.15 ($Si-CH{=}CH_2$). ^{29}Si NMR ($CDCl_3$; δ (ppm)): −16.33. MS (FAB, *m/z* (%)): 602 (M^+, 100). HRMS calcd for $C_{38}H_{34}FeSi_2$: 602.15484. Found: 602.15523.

General Procedure of Catalytic Examinations. Catalytic tests of cyclization using silylative coupling reactions and catalytic screenings were essentially performed under argon using an earlier prepared toluene solution (1 and 0.25 M) with 1,1′-bis(vinylsilyl)ferrocenes derivatives, 1 (and 0.1) mol % of ruthenium catalysts, and decane as internal standard, at 110 °C for 5 h (and 18 h for 1,1′-bis(vinyldiphenylsilyl)ferrocene)). The composition of the reaction mixture was analyzed by GC and GC-MS. The substrate conversion, chemoselectivity of reaction, and yield were calculated by GC using the internal standard method.

Synthesis of (Bis(silyl)-[3]-ferrocenophane))ethene Derivatives. The syntheses were performed under argon using $[RuH(Cl)(CO)(PCy_3)_2]$ (**II**) as a catalyst. Reagents and solvents were dried and deoxygenated. The details are presented below.

$[(Fe(\eta^5\text{-}C_5H_4SiMe_2)_2)C{=}CH_2]$, {(1,1,3,3-Tetramethyl-2-*exo*-2-methylene-1,3-disila)-[3]-ferrocenophane}, 3. The monomer **1** (300 mg, 0.846 mmol), ruthenium complex **II** (1.2 mg, 1.65 × 10^{-3} mmol), and toluene (0.85 mL, 1 M) were placed in a 5 mL minireactor with a magnetic stirring bar and condenser connected with a bubbler. The reaction mixture was stirred and heated at 110 °C under an argon flow for 5 h. The excess solvent was removed under vacuum. The *gem*-cyclic product was isolated and purified by repeated reprecipitation with cold pentane from toluene to afford 254 mg of **3** (0.778 mmol) in 92% as a deep orange crystal.

Analytical Data. ^1H NMR ($CDCl_3$; δ (ppm)): 0.31 (s, 12H, $-CH_3$); 4.12 (m, 4H, C_5H_4); 4.32 (m, 4H, C_5H_4); 6.33 (s, 2H, $>C{=}CH_2$). ^{13}C NMR ($CDCl_3$; δ (ppm)): −2.09 ($-CH_3$); 68.65 ($>C-Si$ at C_5H_4); 71.04 (C_5H_4); 73.34 (C_5H_4); 138.62 ($>C{=}CH_2$); 156.29 ($>C{=}CH_2$, quaternary carbon atom). ^{29}Si NMR ($CDCl_3$; δ (ppm)): −8.71. MS (FAB, *m/z* (%)) 326 (M^+, 100). HRMS calcd for $C_{16}H_{23}FeSi_2$: 326.06094. Found: 326.05983. Anal. Calcd

---

(16) (a) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45. (b) Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043.

(17) (a) Garcia, B.; Casado, C. M.; Cuadrado, I.; Alonso, M. M.; Losada, J. *Organometallics* **1999**, *18*, 2349. (b) Greber, V.; Hallensleben, M. L. *Makromol. Chem.* **1965**, *83*, 148.

for $C_{16}H_{22}FeSi_2$: C, 58.88; H, 6.79, Found: C, 58.82; H, 6.74. Mp: 58.1−58.3 °C. Single crystals of **3** suitable for X-ray crystal structure analysis were obtained by recrystallization from benzene/hexane at room temperature.

[(Fe(η^5-$C_5H_4SiPh_2$)$_2$)CH=CH], {(*Z*)-(1,1,4,4-Tetraphenyl-1,4-disila)-2,3-ethene)-[3]-ferrocenophane}, 4. The monomer **2** (350 mg, 0.581 mmol), ruthenium complex **II** (4.2 mg, 5.78×10^{-3} mmol), and toluene (2.32 mL, 0.25 M), as a mixture, was heated in a 5 mL glass minireactor with a magnetic stirring bar and condenser connected with a bubbler at 110 °C under an argon flow for 18 h. Then excess solvent was removed under vacuum. The *Z*-cyclic product was isolated and purified by repeated reprecipitation with cold pentane from toluene to afford 277 mg of **4** (0.482 mmol) in 83% as a pale reddish powder.

Analytical Data. ^{1}H NMR ($CDCl_3$; δ (ppm)): 4.13 (m, 4H, C_5H_4); 4.17 (m, 4H, C_5H_4); 7.32−7.41 (m, 12H, *m(p)*-C_6H_5); 7.51 (s, 2H, Si−C*H*=C*H*−Si); 7.59 (d, 8H, *o*-C_6H_5). ^{13}C NMR ($CDCl_3$; δ (ppm)): 72.84 (C_5H_4); 75.47 (C_5H_4); 127.80 (*o*−C_6H_5); 129.29 (*p*−C_6H_5); 135.33 (*m*−C_6H_5); 136.78 (>*C*−Si at C_6H_5); 149.24 (Si−*C*H=*C*H−Si). ^{29}Si NMR ($CDCl_3$; δ (ppm)): −19.31. MS (FAB, *m/z* (%)): 574 (M^+, 100). HRMS calcd for $C_{36}H_{30}FeSi_2$: 574.12354. Found: 574.12316. Anal. Calcd for $C_{36}H_{30}FeSi_2$: C, 75.24; H, 5.26. Found: C, 75.16; H, 5.21. Mp: 189.8−190.2 °C. Single crystals of **4** suitable for X-ray crystal structure analysis were obtained by very slow recrystallization from benzene at room temperature.

X-ray Crystal Structure Analysis. For both compounds, the X-ray diffraction data were measured using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) by the ω-scan technique on a KUMA-KM4CCD diffractometer equipped with CCD camera[18] with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The temperature was controlled by an Oxford Instruments Cryosystem cooling device. The data were corrected for Lorentz−polarization effects[19] as well as for absorption.[20] Accurate unit-cell parameters were determined by a least-squares fit of 3369 (**3**) and 4103 (**4**). The structures were solved with SHELXS97[21] and refined with the full-matrix least-squares procedure on F^2 by SHELXL97.[22] Scattering factors incorporated in SHELXL93 were used. The function $\sum w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (AP)^2]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$, A = 0.01 for **7** and 0.001 for **4**. No empirical extinction corrections were applied. All non-hydrogen atoms were refined anisotropically. In **3** the positional parameters of hydrogen atoms were refined; in **4** they were put in idealized positions and refined as a "riding model". In both structures U_{iso} values of hydrogen atoms were set at 1.2 times U_{eq} of the appropriate carrier atom.

In the case of **4**, which crystallizes in the non-centrosymmetric space group, the absolute structure was determined on the basis of the Flack parameter, which converged at 0.003(11).[15]

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 250559 (**3**) and CCDC 250560 (**4**). Copies of the data may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. Fax: +44 (1223) 336-033, e-mail: deposit@ccdc.cam.ac.uk, or www: http://www.ccdc.cam.ac.uk.

Acknowledgment. This work was supported by the 3T09A 145 26.

Supporting Information Available: Tables giving X-ray crystallographic data for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050194X

---

[18] *CrysAlisCCD*, User Guide ver. 171; Oxford Diffraction Poland Sp.: Wrocław, Poland, 2003.

[19] *CrysAlisRed*, Program for Reduction of the Data from Kuma CCD Diffractometer, ver. 171; Oxford Diffraction Poland Sp: Wrocław, Poland, 2003.

[20] Blessing, R. H. *J. Appl. Crystallogr.* **1989**, *22*, 396−397.

[21] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473.

[22] Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.