Organometallics **1997,** *16,* 6017−6020

Novel Rearrangement Reactions. 3. Thermal Rearrangement of the Diruthenium Complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$

Yongqiang Zhang, Shansheng Xu, and Xiuzhong Zhou*

Department of Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received July 28, 1997[⊗]

Summary: The binuclear ruthenium complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ *(**3**) was obtained in poor yield by reaction of* $Ru_3(CO)_{12}$ *with* $C_5H_5Me_2SiSiMe_2C_5H_5$ *in boiling heptane. A thermal rearrangement reaction of **3** in heptane afforded the complex* $[(Me_2Si)(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ *(**4**), which was evidently formed via a metathesis between Si−Si and Ru−Ru bonds in **3**. Molecular structures of **3** and **4** have been determined by X-ray diffraction.*

Introduction

There is currently considerable interest in the synthesis and study of a variety of transition-metal complexes which either activate or contain a silicon−silicon bond.[1] We recently reported a novel rearrangement reaction involving an intramolecular metathesis between Si−Si and Fe−Fe bonds in the dinuclear iron complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**1**).[2] The reaction involves formally the rupture of one Si−Si and one Fe−Fe bond and the formation of two Si−Fe bonds. The rearrangement product $[(Me_2Si)(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ (**2**) has C_i symmetry, and the six-membered ring consisting of two silicon, two iron, and two bridgehead carbon atoms of the cyclopentadienyl ring adopts a stable chair conformation. Subsequently, an alternative mechanism was proposed on the basis of detailed investigations of the rearrangement stereospecificity, reaction intermediates, and crossover reaction.[3] In order to extend the applied range of the rearrangement, the similarity of electron configuration between ruthenium and iron prompted us to synthesize the related ruthenium analogue $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**3**) and to examine the metathetical reaction between Si−Si and Ru−Ru bonds.

Experimental Section

Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were distilled from appropriate drying agents under argon before use. Tetrahydrofuran, hexane, xylene, and heptane were distilled from sodium/benzophenone ketyl and purged with an argon atmosphere prior to use. $C_5H_5Me_2SiSiMe_2C_5H_5$[4] was prepared according to a literature methods. ^1H and ^{13}C NMR spectra were obtained on a Bruker AC-P200 spectrometer using $CHCl_3$ (δ 7.24 ppm (^1H), 77.0 ppm (^{13}C)) as an internal standard, while ^{29}Si NMR spectra were recorded on the same spectrometer using $SiMe_4$ as an internal standard. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Infrared spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer.

Preparation of Compounds 3 and 4. A solution of 1.80 g (7.2 mmol) of $C_5H_5Me_2SiSiMe_2C_5H_5$ and 1.0 g (1.93 mmol) of $Ru_3(CO)_{12}$ in 95 mL of heptane was refluxed for 4 h. Solvent was removed under vacuum to give a yellow-brown oily residue, which was introduced to an alumina column in a minimum amount of dichloromethane. Elution with hexane developed a yellow band, and after collection a crude product was obtained, which was further purified by preparative TLC to yield 60 mg (4%) of colorless crystals (**4**). Elution with hexane-dichloromethane (3:2) gave another yellow band, and after collection a crude oily product was obtained, which was further purified by preparative TLC to afford 50 mg (3%) of golden yellow crystals (**3**). Data for **3** are as follows: Mp: 171−172 °C. Anal. Calcd for $C_{18}H_{20}O_4Ru_2Si_2$: C, 38.70; H, 3.61. Found: C, 38.63; H, 3.48. ^1H NMR ($CDCl_3$): δ 0.27 (s, 12 H, $SiMe_2$), 5.22 (t, 4 H, Cp H), 5.73 (t, 4 H, Cp H). IR (ν_{CO}, cm^{-1}): 1976 (s), 1932 (m), 1807 (m), 1767 (s). Data for **4** are as follows: Mp: 209−210 °C. Anal. Calcd for $C_{18}H_{20}O_4Ru_2Si_2$: C, 38.70; H, 3.61. Found: C, 38.67; H, 3.56. ^1H NMR ($CDCl_3$): δ 0.47 (s, 12 H, SiMe), 5.37 (s, 8 H, Cp H). ^{13}C NMR ($CDCl_3$): δ 7.95 (SiMe), 87.1 (Cp), 98.1 (Cp), 99.8 (*ipso* Cp), 202.1 (Ru−CO). ^{29}Si NMR ($CDCl_3$): δ 20.8. IR (ν_{CO}, cm^{-1}): 1990 (s), 1933 (s), 1905 (sh, w).

Thermal Rearrangement of 3. A solution of complex **3** (90 mg) in 15 mL of heptane was refluxed for 11 h. The solvent was removed under vacuum. The residue was introduced to an alumina column in a minimum amount of dichloromethane. Elution with hexane yielded 30 mg (33%) of colorless crystals (**4**).

Crystallographic Studies. Crystals suitable for X-ray diffraction were obtained from hexane/dichloromethane solutions. All data sets were collected on Enraf-Nonius CAD-4 or Rigaku AFC 7R diffractometers with graphite-monochromated Mo Kα radiation. The corrections for empirical absorption were applied to intensity data. The structures of **3** and **4** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms for **4** were refined isotropically. Hydrogen atoms for **3** were included but not refined. All calculations for **4** were performed using the teXsan Crystallographic Software Package of Molecular Structure Corp., while for **3**, all calculations were performed on a PDP 11/14 computer

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

(1) (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351. (b) Braunstein, P.; Knorr, M. *J. Organomet. Chem.* **1995**, *500*, 21. (c) Elschenbroich, C.; Bretschneider-Hurley, A.; Hurley, J.; Massa, W.; Wocadlo, S.; Pebler, J.; Reijerse, E. *Inorg. Chem.* **1993**, *32*, 5421. (d) Amor, F.; de Jesus, E.; Royo, P.; Vazquez de Miguel, A. *Inorg. Chem.* **1996**, *35*, 3440. (e) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *Organometallics* **1996**, *15*, 2170. (f) Hojo, F.; Fujiki, K.; Ando, W. *Organometallics* **1996**, *15*, 3606. (g) Nelson, J. M.; Lough, A. J.; Manners, I. *Organometallics* **1994**, *13*, 3703. (h) Jutzi, P.; Krallmann, R.; Wolf, G.; Neumann, B.; Stammler, H. G. *Chem. Ber.* **1991**, *124*, 2391. (i) Gleiter, R.; Stahr, H.; Nuber, B. *Organometallics* **1997**, *16*, 646. (j) Pannell, K. H.; Sharma, H. K. *Organometallics* **1991**, *10*, 954. (k) Ueno, K.; Hamashima, N.; Ogino, H. *Organometallics* **1991**, *10*, 959. (l) Ueno, K.; Hamashima, N.; Ogino, H. *Organometallics* **1992**, *11*, 1435.

(2) Sun, H.; Xu, S.; Zhou, X.; Wang, R.; Wang, H. *J. Organomet. Chem.* **1993**, *444*, C41.

(3) Zhou, X.; Zhang, Y.; Xie, W.; Xu, S.; Sun, J. *Organometallics* **1997**, *16*, 3474.

(4) Kumada, K.; Kondo, T.; Mimura, K.; Ishikawa, M.; Yamamoto, K.; Ikeda, S.; Konda, M. *J. Organomet. Chem.* **1972**, *43*, 293.

(5) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

Table 1. Summary of X-ray Diffraction Data

	3	4
formula	$C_{18}H_{20}O_4Ru_2Si_2$	$C_{18}H_{20}O_4Ru_2Si_2$
fw	558.67	558.67
space group	$P\bar{1}$	$P2_1/n$
cryst syst	triclinic	monoclinic
Z	2	2
a (Å)	7.812(3)	9.043(6)
b (Å)	10.178(4)	10.681(4)
c (Å)	15.702(5)	10.866(5)
α, deg	76.11(3)	90
β, deg	78.16(3)	95.83(4)
γ, deg	70.87(3)	90
V (Å^3)	1042(1)	1044.1(9)
d_{calc} (g cm^{-1})	1.779	1.777
cryst size (mm)	0.10 × 0.15 × 0.40	0.20 × 0.20 × 0.30
radiation (Å^3)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, cm^{-1}	15.53	15.81
data collection method	$\omega-2\theta$	$\omega-2\theta$
max 2θ, deg	46	50
total no. of observns	2862	2069
no. of unique data, $I > 3\sigma(I)$	1562	1712
final no. of variables	235	159
R[a]	0.068	0.017
R_w[b]	0.068	0.028
goodness of fit	2.70	1.51

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 3

Bond Distances			
Ru(1)−Ru(2)	2.700(1)	Ru(2)−C(1)	1.86(2)
Si(1)−Si(2)	2.316(9)	Ru(2)−C(2)	2.05(1)
Ru(1)−C(1)	2.01(1)	Ru(2)−C(4)	1.83(1)
Ru(1)−C(2)	1.96(1)	Ru(1)−Cp(1)	1.906[a]
Ru(1)−C(3)	1.91(2)	Ru(2)−Cp(2)	1.901[a]
Bond Angles			
Ru(1)−Ru(2)−C(21)	108.9(4)	Ru(1)−C(11)−Si(1)	129.4(9)
Ru(2)−Ru(1)−C(11)	108.0(5)	Ru(2)−C(21)−Si(2)	124.6(6)
Ru(1)−C(1)−Ru(2)	88.4(7)	C(11)−Si(1)−Si(2)	120.6(5)
Ru(1)−C(2)−Ru(2)	84.6(6)	C(21)−Si(2)−Si(1)	116.0(4)

[a] The distance from the centroid of the Cp ring to the linked Ru atom.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 4

Bond Distances			
Ru−Si	2.4074(9)	Ru−Cp(1)	1.9155[a]
Ru−C(1)	1.859(3)	C(1)−O(1)	1.145(3)
Ru−C(2)	1.857(3)	C(2)−O(2)	1.147(3)
Bond Angles			
Ru*−Si−C(7)	111.30(8)	C(1)−Ru−C(2)	89.6(1)
Ru−C(7)−Si	130.5(1)	C(8)−Si−C(9)	106.3(2)
Si*−Ru−C(7)	100.76(6)		

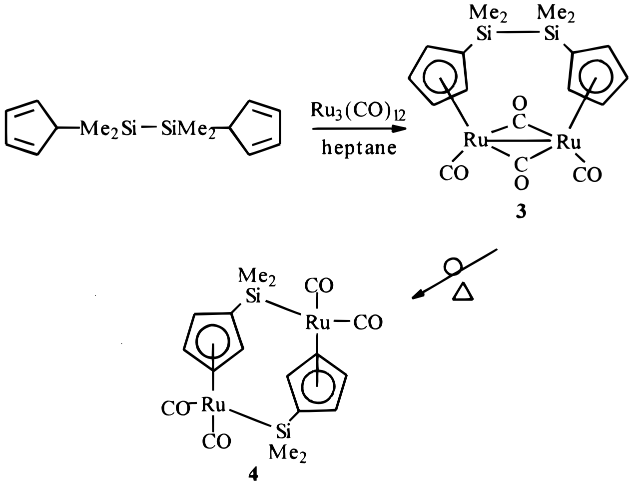
[a] The distance from the centroid of the Cp ring to the linked Ru atom.

using the SDP-PLUS program system. Neutral atom scattering factors were taken from the tabulations of Cromer and Waber.[5] For **3**, the maximum and minimum peaks on the final difference Fourier map corresponding to 1.3 and −1.16 e/Å^3 were associated with the Ru(1) atom. A summary of the crystallographic results is presented in Table 1. Selected bond distances and angles for **3** and **4** are given in Tables 2 and 3, respectively.

Results and Discussion

Synthesis of 3 and Its Thermal Rearrangement Reaction. We recently reported that the diruthenium complex $(Me_2Si)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ was prepared by heating a solution of $Ru_3(CO)_{12}$ and $C_5H_5Me_2SiC_5H_5$ in heptane.[6] The same method is successful for $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**3**). Thus, when $Ru_3(CO)_{12}$ and a 3-fold excess of the ligand $C_5H_5Me_2SiSiMe_2C_5H_5$ were heated under reflux in heptane for 4 h, **3** was obtained in 3% yield (Scheme 1). In addition, the rearrangement product **4** was simultaneously isolated in 4% yield. When the reaction time was prolonged to 7 h, only **4** was obtained in 6% yield. Changing the solvent did not produce a satisfactory result. Even **3** could not be formed in hexane, owing to the lower refluxing temperature. In xylene both **3** and **4** were not isolated since $Ru_3(CO)_{12}$ decomposed extensively over the course of the reaction. To illuminate the relationship between **3** and **4**, a heptane solution of pure **3** was refluxed for 11 h. It was found that **3**, despite the decomposition, was entirely converted into **4**. This indicates that **4** is the rearrangement product of **3**. The rearrangement result is totally consistent with the case previously reported for the iron analogue.[2]

Scheme 1



Complex **3** can undergo rearrangement in boiling heptane, and the rearrangement temperature is much lower than that of **1**, indicating that the rearrangement reaction of **3** proceeds more readily than that of **1**. According to the mechanism we proposed previously, the rearrangement involves initial thermal homolysis of metal-metal bonds and formation of an active intermediate containing two metal-centered radicals.[3] Since Ru−Ru bonds are usually weaker than Fe−Fe bonds, it is assumed that **3** is inclined to dissociate more readily than **1**. Thus, it is not difficult to understand that **3** with Ru−Ru bonds can undergo the rearrangement at lower temperature.

Complex **3** is an air-stable golden yellow solid, The IR spectrum of a KBr disk consists of two terminal carbonyl absorptions and two bridged carbonyl absorptions, which is consistent with the formulation. The ^{1}H NMR spectrum shows one singlet at 0.27 ppm ($Me_2SiSiMe_2$) and two groups of resonances at 5.22 and 5.73 ppm (AA′ and BB′ parts of the Cp AA′BB′ spin system). Complex **4** is obtained as air-stable colorless crystals. The ^{1}H NMR spectrum indicates one singlet at 0.47 ppm ($Me_2SiSiMe_2$) and only one group of resonances at 5.37 ppm (the Cp AA′BB′ spin system), possibly due to the difference of chemical shifts between α- and β-protons

---

[6] Zhou, X.; Zhang, Y.; Xu, S.; Tian, G.; Wang, B. *Inorg. Chim. Acta* **1997**, *262*, 109.

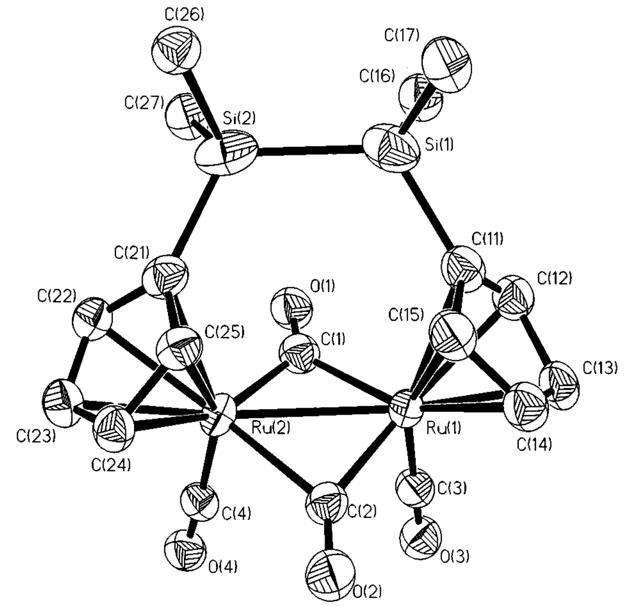


Figure 1. Molecular structure of $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)\text{-}Ru(CO)]_2(\mu\text{-}CO)_2$ (**3**). Hydrogen atoms are omitted for clarity.

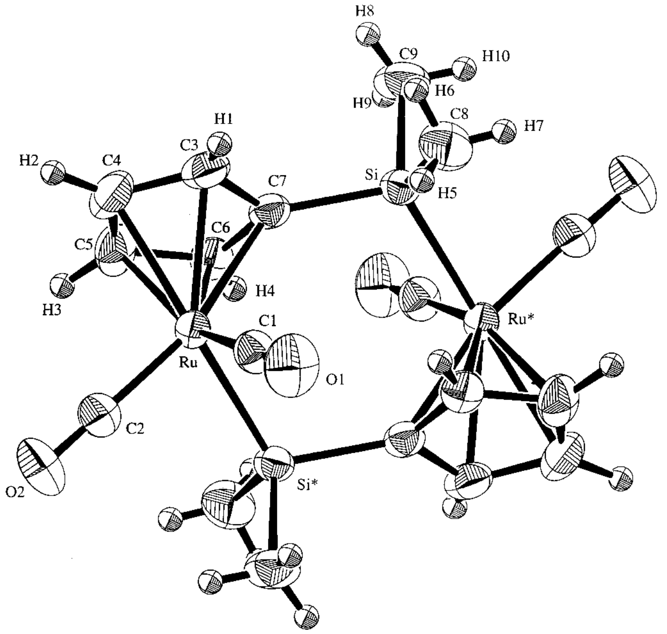


Figure 2. Molecular structure of $[(Me_2Si)(\eta^5\text{-}C_5H_4)Ru\text{-}(CO)_2]_2$ (**4**).

being too slight. The ^{13}C and ^{29}Si NMR spectra of **4** are rather analogous to those of its iron analogue **2**, except for the difference in chemical shifts.

The formation of **4** from **3** implies formally the rupture of one Si−Si and one Ru−Ru bond and the formation of two Si−Ru bonds. Under ordinary conditions, the reaction between Si−Si and Ru−Ru bonds is difficult; therefore, few examples of this type have been reported.[7] The driving force of this reaction presumably comes from the strain force of the cyclic structure of **3**, containing simultaneously one Si−Si and one Ru−Ru bond. This is based on the fact that no reaction was observed when a mixture of $Me_3SiSiMe_3$ and $[(\eta^5\text{-}t\text{-}BuC_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**5**) was heated at reflux.[8] In addition, this conclusion is further supported by studies on some reactions of iron analogues. We have found that no reaction was observed when a mixture of $PhMe_2SiSiMe_2Ph$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(\mu\text{-}CO)_2$ or solely $[(\eta^5\text{-}Me_5Si_2C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ in xylene was heated at reflux.[9] In the former case, Si−Si and Fe−Fe bonds exist in two different molecules, while in the latter, there is an absence of a six-membered cycle containing one Si−Si and one Fe−Fe bond. Similar treatment of the trisilane-bridged analogue $[(\eta^5{:}\eta^5\text{-}C_5H_4(SiMe_2)_3C_5H_4)\text{-}Fe(CO)]_2(\mu\text{-}CO)_2$ does not lead to the occurrence of the rearrangement reaction between Si−Si and Fe−Fe bonds.[10] All these things indicate that the six-membered ring consisting of two silicon, two iron (or ruthenium), and two bridgehead carbon atoms of the cyclopentadienyl ring is of significant importance to the rearrangement.

Crystal and Molecular Structures of Complexes 3 and 4. The molecular structure of **3** is shown in Figure 1. The molecule consists of two $[(\eta^5\text{-}C_5H_4)Ru\text{-}(CO)_2]$ moieties linked by one dislane bridge and one Ru−Ru bond, and its structure is very similar to that of the iron analogue.[2] **3** has mirror symmetry except for some twisting about the Si−Si bond, and the six-membered ring Ru(2)−Ru(1)−C(11)−Si(1)−Si(2)−C(21) constituting the molecular framework adopts a twist-boat conformation. It should be noted that the molecule of **3** prefers to take a carbonyl bridging configuration, similar to the case for the analogue $(Me_2Si)[(\eta^5\text{-}C_5H_4)\text{-}Ru(CO)]_2(\mu\text{-}CO)_2$,[6,11] rather than a nonbridging form appearing in the molecule of $[(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Ru_2\text{-}(CO)_4]$.[12] The Ru−Ru bond distance (2.700(1) Å) is close to that (2.706(1) Å) in $(Me_2Si)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ and slightly shorter than that in *trans*-$[(\eta^5\text{-}C_5H_5)Ru\text{-}(CO)]_2(\mu\text{-}CO)_2$ (2.735 Å),[13] presumably as a consequence of the existence of a disilyl bridge in **3**, and much shorter than those in the related compounds $[(\eta^5{:}\eta^5\text{-}C_5H_4\text{-}CH_2C_5H_4)Ru_2(CO)_4]$ (2.766(1) Å)[12] and $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)Ru_2\text{-}(CO)_4]$ (2.821(1) Å),[14] attributable to the existence of two bridging carbonyl groups. The Si−Si bond length (2.316(9) Å) is slightly shorter than that (2.346(4) Å) in the iron analogue.[2] The silicon methyl groups are almost eclipsed with one another (the smaller C−Si−Si−C torsion angles fall in the range of 1.07−7.11°, compared to 12.1−13.3° in **1**). The Cp ring planes in **3** are inclined toward one another at a shallower angle (91.9°) than is usually the case in related species: *e.g.* 103.53°, $(Me_2Si)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$;[6,11] 112.9°, $[(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Ru_2(CO)_4]$;[12] 151.5°, $[(\eta^5{:}\eta^5\text{-}C_{10}H_8)\text{-}$

---

[7] Brooks, A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3469.

[8] A solution of 70 mg (0.13 mmol) of **5** and 73 mg (0.50 mmol) of $Me_3SiSiMe_3$ in 15 mL of heptane was refluxed for 24 h. TLC monitoring of the reaction result indicated no formation of new products. After solvent was removed under vacuum, 40 mg of **5** was recovered. Data for **5** are as follows: Mp: 159−160 °C. Anal. Calcd for $C_{22}H_{26}O_4Ru_2$: C, 47.48; H, 4.71. Found: C, 47.30; H, 4.50. ^1H NMR ($CDCl_3$): δ 1.43 (s, 18 H, *t*-Bu), 5.20 (s, 4 H, Cp H), 5.48 (s, 4 H, Cp H). IR (ν_{CO}, cm^{-1}): 1960 (s), 1918 (w), 1767 (s), 1741 (m).

[9] Zhou, X.; Sun, H. unpublished results.

[10] Zhou, X.; Xie, W. To be submitted for publication.

[11] Bitterwolf, T. E.; Leonard, M. B.; Horine, P. A.; Shade, J. E.; Rheingold, A. L.; Staley, D. J.; Yap, G. P. A. *J. Organomet. Chem.* **1996**, *512*, 11.

[12] Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G.; Rendle, M. C. *J. Chem. Soc., Dalton Trans.* **1989**, 1807.

[13] Mills, O. S.; Nice, J. P. *J. Organomet. Chem.* **1967**, *9*, 339.

[14] Vollhardt, K. P. C.; Weidman, T. W. *J. Am. Chem. Soc.* **1983**, *105*, 1676.

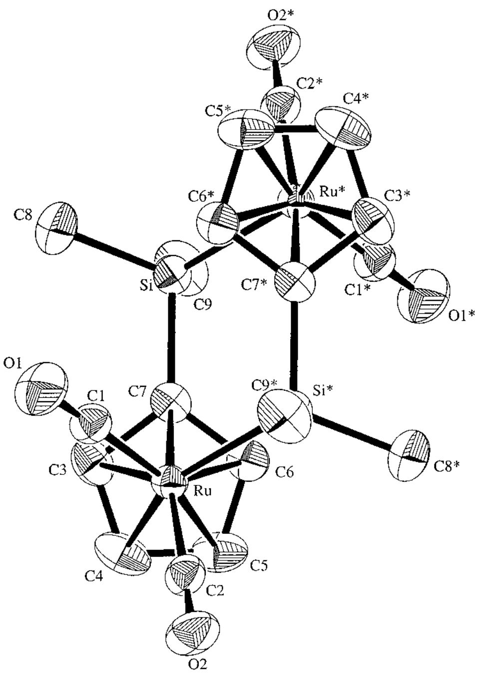


Figure 3. View of **4** along the straight line from the centroid of the Cp ring to the linked Ru atom.

$Ru_2(CO)_4$].[14] This indicates that the dihedral angle between the two Cp rings decreases with an increase in the bridge length. The two silicon atoms are bent out of the linked cyclopentadienyl rings by 0.318 and 0.075 Å, respectively.

The molecular structure of **4** is shown in Figure 2. The molecule consists of two [$(Me_2)Si(\eta^5\text{-}C_5H_4)Ru(CO)_2$] moieties linked by two Ru−Si bonds. Like many related analogues,[2,15] **4** has C_i symmetry, and the six-membered ring Ru−Si*−C(7*)−Ru*−Si−C(7) constituting the molecular framework adopts a stable chair conformation (Figure 3). The Ru−Si distance (2.4074(9) Å) is shorter than the estimated Ru−Si single-bond length (2.44 Å)[16] and also shorter than those (2.452(3)-2.507(8) Å)[17] in acyclic molecules, and a similar phenomenon was also observed in the iron analogue **2**.[2] This may be a factor in the smooth advancement of the rearrangement reaction.

Acknowledgment. We are grateful to the National Science Foundation of the People's Republic of China and the Doctoral Foundation of State Education Commission of the People's Republic of China for financial support of this work.

Supporting Information Available: Tables of final positional and thermal parameters of the non-hydrogen atoms, general temperature factors, and bond distances and angles for **3** and **4** (10 pages). Ordering information is given on any current masthead page.

OM9706424

---

(15) (a) Sharma, S.; Cervantes, J.; Mata-Mata, J. L.; Brun, M. C.; Cervantes-Lee, F.; Pannell, K. H. *Organometallics* **1995**, *14*, 4269. (b) Zhou, X.; Xie, W.; Xu, S. *Chin. Chem. Lett.* **1995**, 1183.

(16) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 221 ff.

(17) (a) Crozat, M. M.; Watkins, S. E. *J. Chem. Soc., Dalton Trans.* **1972**, 2512. (b) Howard, J. A. K.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 59.