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Thermal rearrangement reaction of disilyl-bridged bis(tetramethylcyclopentadienyl) tetracarbonyl diruthenium The molecular structures of $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Ru\text{-}(CO)]_2(\mu\text{-}CO)_2$ and $[(Me_2Si(\eta^5\text{-}C_5Me_4)Ru(CO)_2]_2$

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Abstract

The binuclear ruthenium complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**2**) was obtained in poor yield by reaction of $Ru_3(CO)_{12}$ with $C_5Me_4HMe_2SiSiMe_2C_5Me_4H$ in boiling decalin. A thermal rearrangement reaction of **2** in decalin afforded the complex $[Me_2Si(\eta^5\text{-}C_5Me_4)Ru(CO)_2]_2$ (**3**), which was evidently formed via a metathesis between Si–Si and Ru–Ru bonds in **2**. This result is consistent with that of its parent complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**1**). The molecular structures of **2** and **3** have been determined by X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Thermal rearrangement reaction; Metal carbonyl; Bridged complexes

1. Introduction

Within the last few years transition metal silicon complexes that either activate or contain a silicon–silicon bond have been the focus of much attention [1–5]. We recently reported a novel rearrangement reaction involving an intramolecular metathesis between Si–Si and Fe–Fe bonds in the dinuclear iron complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Fe(CO)]_2(\mu\text{-}CO)_2$ [6]. Subsequent to the report of this rearrangement, a series of detailed investigations of the rearrangement stereospecificity, reaction intermediates and crossover reaction was conducted to propose an alternative mechanism [7–9]. The introduction of tetramethyl groups on the cyclopentadienyl rings indicated that the rearrangement became much more difficult [10]. The related ruthenium analog $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**1**) could occur the similar rearrangement reaction, but the yields of synthesis and rearrangement were poor [11]. We here report the synthesis of tetramethyl-substituted cyclopentadienyl diruthenium complex $(Me_2SiSiMe_2)$-$[(\eta^5\text{-}C_5Me_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**2**) and its thermal rearrangement reaction.

2. Experimental

Schlenk and vacuum line technique were employed for all manipulations of air- and moisture-sensitive compounds. Reaction solvents were distilled from appropriate drying agents under argon before use. Hep-

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tane and decalin were distilled from sodium/benzophenone ketyl and purged with argon atmosphere prior to use, $C_5Me_4HMe_2SiSiMe_2C_5Me_4H$ was prepared according to literature method [10]. Proton (^1H-NMR) spectra were obtained on a Bruker AC-P200 spectrometer using $CHCl_3$ (δ 7.24 ppm) as an internal standard. Elemental analyses were performed on a Perkin–Elmer 240C instrument. Infrared spectra were obtained as KBr disks and recorded on a Nicolet 5DX FT-IR spectrometer.

Table 1
Crystallographic data for complexes **2** and **3**

	2	**3**
Formula	$C_{26}H_{36}O_4Ru_2Si_2$	$C_{26}H_{36}O_4Ru_2Si_2$
Formula weight	670.88	670.88
Space group	$P2_12_12_1$	$P\bar{1}$
Crystal system	Orthorhombic	Triclinic
Z	4	1
a (Å)	14.447(3)	10.197(4)
b (Å)	16.303(4)	10.230(3)
c (Å)	11.936(3)	8.329(2)
α (°)	90	103.01(3)
β (°)	90	102.85(3)
γ (°)	90	118.38(2)
V (Å^3)	2811(1)	687.7(5)
D_{calc} (g cm^{-3})	1.585	1.620
Crystal size (mm)	$0.20\times0.20\times0.30$	$0.20\times0.20\times0.30$
Radiation (Å)	Mo–K_α (0.71069)	Mo–K_α (0.71069)
μ (cm^{-1})	11.89	12.15
Scan type	ω–2θ	ω–2θ
$2\theta_{max}$ (°)	50.0	50.0
Total number of reflections	2815	2410
Number of observations ($I>3.00\sigma(I)$)	2563	2123
Number of variables	308	227
R	0.024	0.020
R_w	0.028	0.025
Goodness-of-fit	1.46	1.07

Table 2
Selected bond distances (Å) and angles (°) for **2**

Bond distances			
Ru(1)–Ru(2)	2.7613(6)	Si(1)–Si(2)	2.360(2)
Ru(1)–C(1)	1.860(5)	Ru(1)–C(3)	2.049(6)
Ru(1)–C(4)	2.051(5)	Ru(2)–C(2)	1.852(6)
Ru(2)–C(3)	2.053(5)	Ru(2)–C(4)	2.046(6)
Si(1)–C(5)	1.884(6)	Si(2)–C(16)	1.884(5)
O(1)–C(1)	1.140(6)	O(2)–C(2)	1.158(7)
O(3)–C(3)	1.169(6)	O(4)–C(4)	1.178(6)
Bond angles			
Ru(1)–C(5)–Si(1)	131.4(2)	Ru(2)–C(16)–Si(2)	127.4(3)
Si(2)–Si(1)–C(5)	115.2(2)	Si(1)–Si(2)–C(16)	117.5(2)
Ru(1)–Ru(2)–C(16)	107.8(1)	Ru(2)–Ru(1)–C(5)	108.0(1)
Ru(1)–Ru(2)–C(2)	97.4(2)	Ru(2)–Ru(1)–C(1)	97.1(2)
Ru(1)–C(4)–Ru(2)	84.7(2)	Ru(1)–C(3)–Ru(2)	84.6(2)

Table 3
Selected bond distances (Å) and angles (°) for **3**

Bond distances			
Ru(1)–Si(1)	2.424(1)	Ru(1)–C(1)	1.867(3)
Ru(1)–C(2)	1.860(3)	Ru(1)–C(3)	2.261(3)
Ru(1)–C(4)	2.269(3)	Ru(1)–C(5)	2.291(3)
Ru(1)–C(6)	2.255(3)	Ru(1)–C(7)	2.266(3)
Si(1)–C(7*)	1.907(3)	O(1)–C(1)	1.147(4)
O(2)–C(2)	1.145(4)		
Bond angles			
Si(1)–Ru(1)–C(1)	87.97(9)	Si(1)–Ru(1)–C(2)	82.18(10)
Si(1)–Ru(1)–C(7)	98.68(7)	Ru(1)–C(7)–Si(1*)	136.4(1)
C(1)–Ru(1)–C(2)	90.4(1)	C(12)–Si(1)–C(13)	103.6(2)

2.1. Preparation of complexes 2 and 3

A solution of 0.84 g (1.18 mmol) of $C_5Me_4HMe_2SiSiMe_2C_5Me_4H$ and 1.00g (1.56 mmol) of $Ru_3(CO)_{12}$ in 30 ml of decalin was refluxed for 5 h. TLC monitoring the reaction indicated the disappearance of the starting material $Ru_3(CO)_{12}$. The solvent was removed under vacuum giving dark brown residue, which was dissolved in a minimum of CH_2Cl_2 and subjected on an alumina column. Elution of petroleum ether developed a yellow band, the crude product obtained from which was further purified by preparative TLC to yield 10 mg (1%) of colorless crystals of **3**. Elution with CH_2Cl_2 gave another yellow band, the crude oily product obtained from which was further purified by preparative TLC affording 70 mg (5%) golden yellow crystals of **2**.

Complex **2**, m.p.: 260°C (dec.). Anal. Calc. for $C_{26}H_{36}O_4Ru_2Si_2$: C, 46.55; H, 5.41. Found: C, 46.54; H, 5.42. ^1H-NMR ($CDCl_3$) δ 0.24 (s, 12H, SiMe), 1.89 (s, 12H, CpMe), 2.12 (s, 12H, CpMe). IR (ν_{CO}, cm^{-1}): 1975(s), 1926(m), 1754(s).

Complex **3**, m.p.: 264–6°C. Anal. Calc. for $C_{26}H_{36}O_4Ru_2Si_2$: C, 46.55; H, 5.41. Found: C, 46.73; H, 5.49. ^1H-NMR (CDCl3) δ 0.47 (s, 12H, SiMe), 2.07 (s, 12H, CpMe), 2.12 (s, 12H, CpMe). IR (ν_{CO}, cm^{-1}): 1987(s), 1976(sh, m), 1946(s), 1896(w).

2.2. Thermal rearrangement of 2

A solution of complex **2** (50 mg) in 10 ml of decalin was refluxed for 24 h. The solvent was removed under vacuum. TLC monitoring the reaction result indicated the formation of **3**.

2.3. Crystallographic studies

Crystals suitable for X-ray diffraction were obtained from hexane/dichloromethane solution. All data were collected on a Rigaku AFC 7R diffractometer with graphite monochromated Mo–K_α radiation. The corrections for empirical absorption were applied to intensity data. The structures of **2** and **3** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All calculations for **2** and **3** were performed using the TEXSAN Crystallographic Software Package of Molecular Structure Corp. Neutral atom scattering factors were taken from the tabulations of Cromer and Waber [12]. A summary of the crystallographic results is presented in Table 1. Selected bond distances and angles for **2** and **3** are given in Tables 2 and 3.

3. Results and discussion

*3.1. Synthesis of complex **2** and its thermal rearrangement reaction*

We recently reported that the diruthenium complex $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5H_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**1**) was prepared by heating a solution of $Ru_3(CO)_{12}$ and $C_5H_5Me_2SiSiMe_2C_5H_5$ in heptane [11]. The same treatment was not successful for tetramethyl-substituted analog **2**. Even if $Ru_3(CO)_{12}$ and the ligand $C_5Me_4HMe_2SiSiMe_2C_5Me_4H$ were heated at reflux in heptane for 30 h, no obvious reaction phenomenon was observed except for a slight decomposition of $Ru_3(CO)_{12}$. When the refluxing solvent was changed to decalin, thermal treatment of them only for 5 h afforded the expected product **2**. In addition, the rearranged product **3** was simultaneously isolated in 1% yield. In order to illuminate the relationship between **2** and **3**, complex **2** was heated in decalin for 24 h. TLC monitoring the reaction result indicated the formation of **3**, but we didn't isolate it owing to a very small amount, This indicated that the rearrangement of complex **2** is difficult, which is consistent with the case in diiron analog $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Fe(CO)]_2(\mu\text{-}CO)_2$ (**4**) [10]. Thermal treatment of **4** in xylene for 24 h afforded the related rearranged product only in 3% yield. It is obvious that the steric tetramethyl cyclopen-

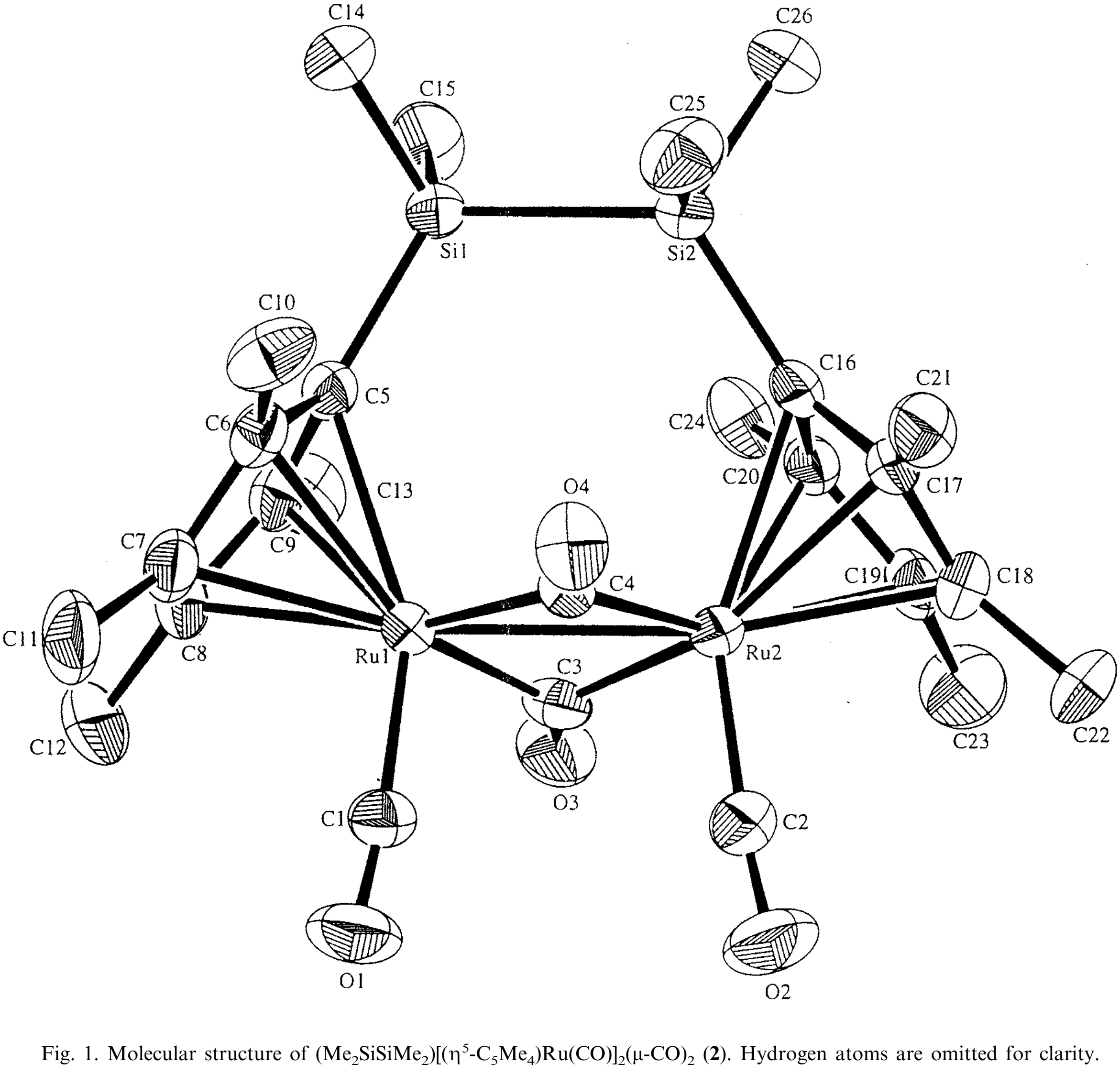


Fig. 1. Molecular structure of $(Me_2SiSiMe_2)[(\eta^5\text{-}C_5Me_4)Ru(CO)]_2(\mu\text{-}CO)_2$ (**2**). Hydrogen atoms are omitted for clarity.

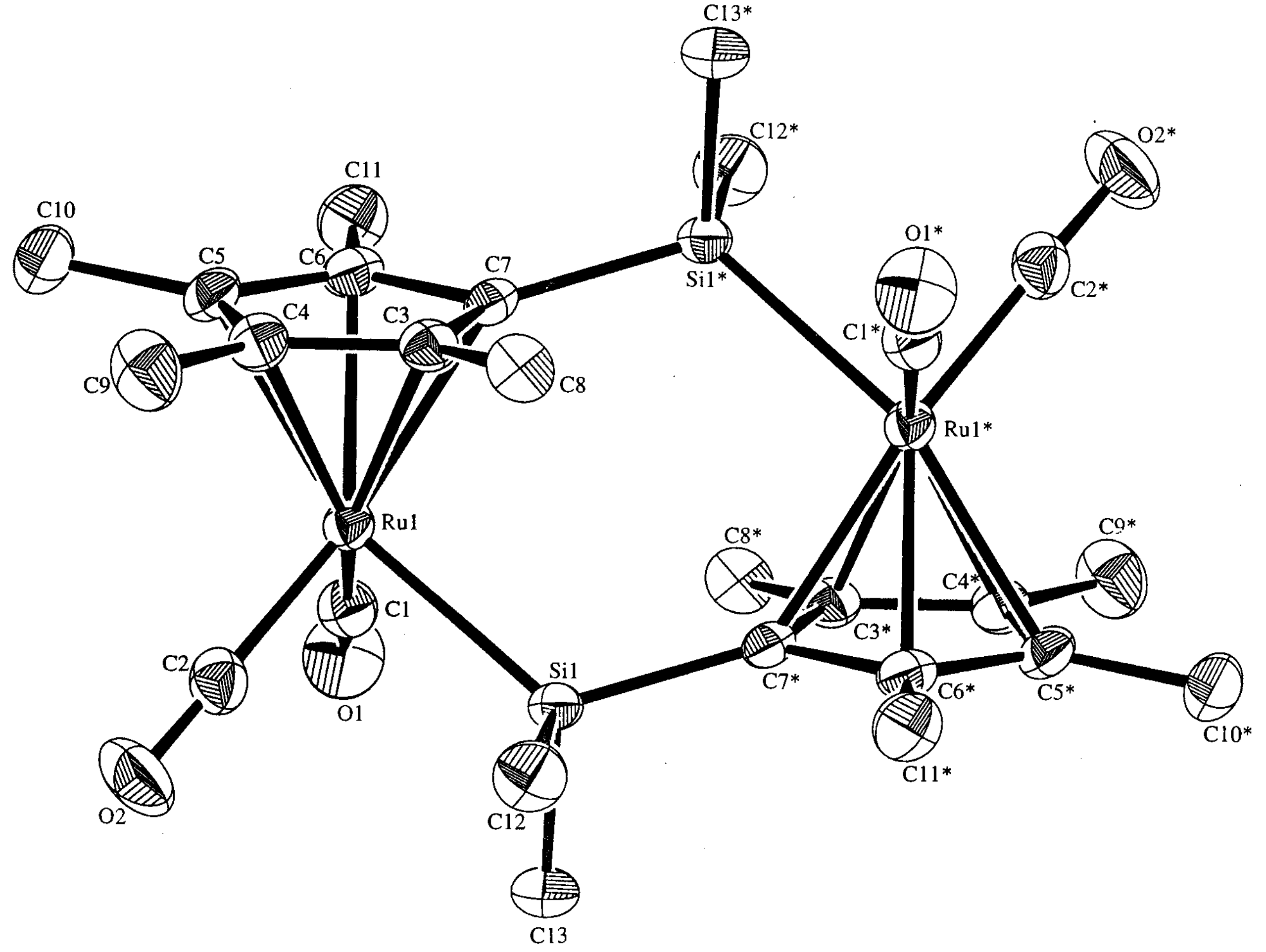
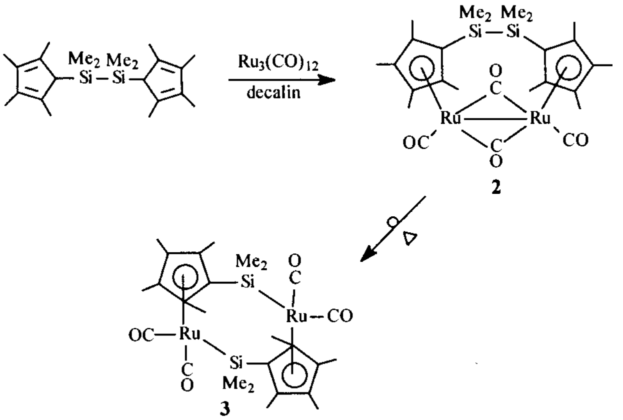


Fig. 2. Molecular structure of $[(Me_2Si)(\eta^5\text{-}C_5Me_4)Ru(CO)_2]_2$ (**3**). Hydrogen atoms are omitted for clarity.

tadienyl ligands hindered the progression of the rearrangement.



Complex **2** is air-stable golden yellow crystals. The ^{1}H-NMR spectrum shows one singlet at 0.24 ppm ($Me_2SiSiMe_2$) and two singlets at 1.89 and 2.12 ppm (α and β methyl groups of the Cp ring, respectively). Complex **3** is obtained as air-stable colorless crystals. The ^{1}H-NMR spectrum also indicates one singlet at 0.47 ppm (Me_2Si) and two singlets at 2.07 and 2.12 ppm (α and β methyl groups of the Cp ring, respectively). However, the difference (0.05 ppm) of its chemical shifts between α and β methyl group is much smaller than that (0.23 ppm) of **2**.

3.2. Crystal and molecular structures of complexes 2 and 3

The molecular structure of **2** is shown in Fig. 1. The molecule consists of two $[(\eta^5\text{-}C_5Me_4)Ru(CO)_2]$ moieties linked by one disilane bridge and one Ru–Ru bond. **2** has mirror symmetry except for some twisting about the Si–Si bond, and the six-membered ring Ru2–Ru1–C5–Si1–Si2–C16 constituting the molecular framework adopts a twist-boat conformation. This is different from the iron analog **4**, which has a precise C_2 symmetry and the corresponding six-membered ring of which adopts a hexagonal conformation [10]. The Ru–Ru (2.7613(6) Å) and Si–Si (2.360(2) Å) bonds are longer than those of the corresponding parent complexes (2.700(1) and 2.316(9) Å) [11], possibly owing to the steric repulsion between tetramethyl groups and bridged carbonyl groups. The Ru–Ru bond is also longer than those (2.706(1) and 2.735 Å) in the related analogs $(Me_2Si)[(\eta^5\text{-}C_5H_4)Ru(CO)_2](\mu\text{-}CO)_2$ [13,14] and *trans*-$[(\eta^5\text{-}C_5H_5)Ru(CO)_2](\mu\text{-}CO)_2$ [15], but close to that (2.766(1) Å) in $[(\eta^5{:}\eta^5\text{-}C_5H_4CH_2C_5H_4)Ru_2(CO)_4$ [16]. The dihedral angle (101.2°) between the two Cp ring planes is larger than that (91.9°) in the parent complex **1** [11], which should also be attributed to the consequence of tetramethyl substitution. The Si(1) and Si(2) atoms are bent out of the corresponding Cp ring planes by 0.220 and 0.134(, respectively. The dihedral angle between two $Ru_2(\mu\text{-}CO)$ planes is 167.5°. The silicon methyl groups are staggered with one another (the smaller C–Si–Si–C torsion angles fall in the range of 29.5(3)–32.7(3) Å).

The molecular structure of **3** is shown in Fig. 2. The molecule consists of two $[(\eta^5\text{-}C_5Me_4)Ru(CO)_2]$ moieties linked by two Ru–Si. **3** has C_i symmetry, and the six-membered ring Ru1–Si1–C7*–Ru1*–Si1*–C7 constituting the molecular framework adopts a stable chair conformation. The Ru–Si (2.424(1) Å) bond is longer than that of the parent complex $[Me_2Si(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ (2.4074(9) Å), but shorter than those (2.452(3)–2.507(8) Å) in acyclic analogs [17,18]. This indicated that the repulsion caused by tetramethyl substitution don't greatly influence the stability of the six-membered ring.

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