Reactions of CpArCHCHArCp with $Ru_3(CO)_{12}$: An Unexpected Cleavage of a Bridging C−C Bond and Coupling of the Two Cyclopentadienyl Rings to Fulvalene Diruthenium Complexes

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Reactions of CpArCHCHArCp [Ar = Ph (**1**), *p*-$MeOC_6H_4$ (**2**)] with $Ru_3(CO)_{12}$ in refluxing xylene afforded the unexpected bridging C−C cleavage and cyclopentadienyl coupling products: the 2,2′-bisubstituted fulvalene diruthenium complexes (η^5:η^5-2,2′-$ArCH_2C_5H_3C_5H_3CH_2Ar)Ru_2(CO)_4$ [Ar = Ph (**5**), *p*-$MeOC_6H_4$ (**9**)] and the partially hydrogenated products (η^5:η^3-$ArCH_2C_5H_3C_5H_6CHAr)Ru_2(CO)_4$ [Ar = Ph (**4**), *p*-$MeOC_6H_4$ (**8**)], in addition to the normal bridged bis(cyclopentadienyl) tetracarbonyl diruthenium complexes (ArCHCHAr)[(η^5-C_5H_4)Ru(CO)]$_2$(μ-CO)$_2$ [Ar = Ph (**7**), *p*-$MeOC_6H_4$ (**10**)]. When ligand (^{t}BuC_5H_4)PhCHCHPh(^{t}BuC_5H_4) (**3**) reacted with $Ru_3(CO)_{12}$, the tetrasubstituted fulvalene diruthenium complex (η^5:η^5-$PhCH_2{}^t$Bu$C_5H_2C_5H_2{}^t$BuCH_2Ph)$Ru_2(CO)_4$ (**11**) and three normal bridged bis(cyclopentadienyl) diruthenium complexes (PhCHCHPh)[(η^5-^{t}BuC_5H_3)Ru(CO)]$_2$(μ-CO)$_2$ (**12**−**14**) were obtained. The molecular structures of **4**, **5**, **7**-*meso*, **7**-*rac*, **8**, **10**-*meso*, **11**, **12**, **13**, and **14** were determined by X-ray diffraction. The stereochemistry of the reaction was also studied, and the possible mechanism was discussed.

Introduction

Dinuclear metal complexes are often postulated as simple models with which to study the interactions of organic molecules with metal surfaces.[1] Cyclopentadienyl metal carbonyl dimers were reported to catalyze the allylic amination of olefins[2a,b] and indolization of alkynes.[2c,d] The bridged bis(cyclopentadienyl) ligands, including singly bridged ligand (η^5-C_5H_4)$_2$(Bridge) [S], doubly bridged ligand (η^5-C_5H_3)$_2$(Bridge)$_2$ [D], and fulvalene ligand η^5:η^5-$C_5H_4C_5H_4$ [Fv] (Scheme 1), have been extensively studied as frameworks for dinuclear metal complexes that are resistant to fragmentation and maintain two metal centers in close proximity even after the metal−metal bond cleavage.[3]

Among the group 6 and 8 metal carbonyl dimers with bridged bis(cyclopentadienyl) ligands, diruthenium complexes received attention for their special reactivity. The nature of the bridge has a remarkable effect on the metal−metal bond and its reactivity. Vollhardt and co-workers reported that in the $FvRu_2(CO)_4$ system reversible C−C, Ru−Ru, and Ru−C bond-cleavage steps lead to a photochemical process that can be thermally reversed.[4] For the Me_2Si-bridged bis(tetramethylcyclopentadienyl) tetracarbonyl diruthenium complex (Me_2Si)[C_5Me_4Ru(CO)]$_2$(μ-CO)$_2$, a photochemical albeit thermally irreversible rearrangement by Si−C bond cleavage was also observed.[5] The Me_2C-bridged bis(cyclopentadienyl) diruthenium complex (Me_2C)[(C_5H_4)Ru(CO)$_2$]$_2$ can be a fully reversible organometallic thermooptical switch through reversible C−H, Ru−H, Ru−C, and Ru−Ru bond-cleavage steps.[6] The tetramethyldisilylene- or digermylene-bridged bis(cyclopentadienyl) tetracarbonyl diruthenium complexes (Me_2EEMe_2)[Cp′Ru(CO)]$_2$(μ-CO)$_2$ (E = Si, Ge; Cp′ = C_5H_4, C_5Me_4) can thermally rearrange with metathesis between the E−E and Ru−Ru bonds.[7] Although many bridged bis(cyclopentadienyl) diruthenium complexes were synthesized in the past few decades, to the best of our knowledge, only two examples of complexes (CH_2CH_2)[Cp′Ru(CO)]$_2$(μ-CO)$_2$ (Cp′ = C_5H_4, C_9H_7)[8] are known for the CR_2−CR_2 (R = H, alkyl, aryl) bridge. In this paper, we will

Scheme 1

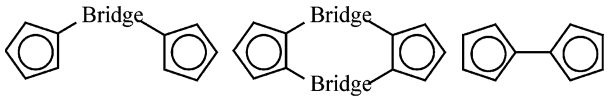

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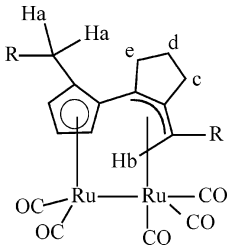
Chart 1



report the reactions of (ArCHCHAr)-bridged bis(cyclopentadiene) Cp′ArCHCHArCp′ (Cp′ = C_5H_5, $^tBuC_5H_4$, Ar = Ph, *p*-$MeOC_6H_4$) with $Ru_3(CO)_{12}$. The unexpected bridging C−C bond cleavage and cyclopentadienyl coupling products were obtained simultaneously.

Experimental Section

General Procedures. Schlenk and vacuum line techniques were employed for all manipulations. All solvents were distilled from appropriate drying agents under argon prior to use. ^{1}H NMR spectra were recorded on a Bruker AV300 or Bruker AC-P200 instrument. 2-D NMR experiments were carried out on a Varian Mercury VX300 instrument. IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. ESI mass spectra were obtained using a Thermo Finnigan LCQ Advantage instrument. CpPhCHCHPhCp[9] (**1**), 6-(*p*-methoxylphenyl)fulvene,[10] and 2-*tert*-butylphenylfulvene[10] were prepared by literature procedures.

Reaction of CpPhCHCHPhCp (1) with $Ru_3(CO)_{12}$. The solution of 350 mg (0.547 mmol) of $Ru_3(CO)_{12}$ and 280 mg (0.900 mmol) of CpPhCHCHPhCp (**1**) (as a mixture of *racemic* and *meso* isomers with a ratio of about 1:0.9, see Supporting Information) in 40 mL of xylene was refluxed for 8 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2 as eluent. Elution with petroleum ether/CH_2Cl_2 gave two yellow bands and an orange band, which afforded 10 mg (2%) of **4**, 20 mg (4%) of **5**, and 136 mg (27%) of **7**-*meso* as yellow or orange crystals, respectively. Finally elution with CH_2Cl_2 developed a yellow band, which gave 19 mg (4%) of **7**-*rac* as orange crystals.

4: mp 174 °C (dec). Anal. Calcd for $C_{29}H_{22}O_5Ru_2$: C, 53.37; H, 3.40. Found: C, 53.23; H, 3.39. ^{1}H NMR ($CDCl_3$, 300 MHz, see Chart 1 for key to assignments): δ 7.35−7.14 (m, 10H, C_6H_5), 5.58 (t, 1H, C_5H_3), 5.20 (m, 1H, C_5H_3), 3.55 (s, 1H, *H*b), 3.52 (d, J = 16.2 Hz, 1H, *H*a), 3.38 (t, 1H, C_5H_3), 3.24 (d, J = 16.2 Hz, 1H, *H*a), 3.00−2.59 (m, 4H, *H*c + *H*e), 2.23−2.00 (m, 2H, *H*d). IR (ν_{CO}, cm^{-1}): 2050 (s), 1985 (s), 1962 (s), 1910 (s), 1870 (w).

5: mp 230 °C (dec). Anal. Calcd for $C_{28}H_{20}O_4Ru_2$: C, 54.02; H, 3.24. Found: C, 53.97; H, 3.27. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35−7.24 (m, 6H, C_6H_5), 7.14−7.11 (m, 4H, C_6H_5), 5.66 (t, 2H, C_5H_3), 5.45 (t, 2H, C_5H_3), 4.28 (m, 2H, C_5H_3), 3.04 (s, 2H, PhCH_2), 3.02 (s, 2H, PhCH_2). IR (ν_{CO}, cm^{-1}): 1997 (s), 1958 (s), 1934 (s), 1918 (s).

7-*meso*: mp 206 °C (dec). Anal. Calcd for $C_{28}H_{20}O_4Ru_2$: C, 54.02; H, 3.24. Found: C, 53.89; H, 3.24. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.16−7.10 (m, 6H, C_6H_5), 6.82−6.78 (m, 4H, C_6H_5), 5.59 (br s, 2H, C_5H_4), 5.49 (m, 4H, C_5H_4), 5.36 (br s, 2H, C_5H_4), 4.14 (s, 2H, PhC*H*). IR (ν_{CO}, cm^{-1}): 1997 (s), 1962 (s), 1787 (sh, w), 1759 (s).

7-*rac*: mp 208 °C (dec). Anal. Calcd for $C_{28}H_{20}O_4Ru_2$: C, 54.02; H, 3.24. Found: C, 54.02; H, 3.13. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.13−6.89 (m, 10H, C_6H_5), 5.58 (m, 4H, C_5H_4), 5.51 (m, 2H, C_5H_4), 5.28 (m, 2H, C_5H_4), 3.86 (s, 2H, PhC*H*). IR (ν_{CO}, cm^{-1}): 2002 (s), 1962 (s), 1791 (m), 1744 (s).

Reaction of *rac*-CpPhCHCHPhCp (1-*rac*) with $Ru_3(CO)_{12}$. The pure *racemic* isomer **1**-*rac* was obtained by hydrolysis of the corresponding *racemic* calcium salt of ligand **1**.[9b] Using a procedure similar to that described above, reaction of **1**-*rac* with $Ru_3(CO)_{12}$ gave **4** (2%), **5** (4%), **7**-*meso* (7%), and **7**-*rac* (7%). ^{1}H NMR ($CDCl_3$, 300 MHz) of **1**-***rac***: δ 7.10−6.90 (m, 10H, C_6H_5), 6.45 (m, 1H, C_5H_5), 6.40−6.29 (m, 3H, C_5H_5), 6.20 (m, 1H, C_5H_5), 6.11 (br s, 1H, C_5H_5), 4.44 (d, J = 9.85 Hz, 1H, PhC*H*), 4.36 (d, J = 9.85 Hz, 1H, PhC*H*), 2.90 (br s, 2H, C_5H_5), 2.84 (br s, 2H, C_5H_5) (see Supporting Information).

Synthesis of Cp(*p*-$MeOC_6H_4$)CHCH(*p*-$MeOC_6H_4$)Cp (2). The synthesis of ligand **2** was carried out by a method similar to that for ligand **1**.[9] $HgCl_2$ (210 mg, 75 mmol) was added to 2.0 g (50 mmol) of granulated calcium metal in 25 mL of THF. After the mixture was stirred fiercely overnight, a grayish suspension was obtained that contained small pieces of suspended calcium. THF (80 mL) was added, and the mixture was cooled to 0 °C, then 6-(*p*-methoxylphenyl)fulvene (7.0 g, 38 mmol) was added. During the 36 h of stirring, an exothermic reaction ensued and the red color of the fulvene disappeared. After the mixture was poured into saturated aqueous ammonium chloride solution, phases were separated. The aqueous phase was extracted with ether (2 × 20 mL). The combined organic phase was washed with several small portions of water and then dried over anhydrous magnesium sulfate. After removal of the solvents, the crude product was recrystallized from pentane/CH_2Cl_2 at −30 °C to afford 3.15 g (45%) of pure **2** as a white solid. Mp: 150−151 °C. Anal. Calcd for $C_{26}H_{26}O_2$: C, 84.29; H, 7.07. Found: C, 84.56; H, 7.27. ^{1}H NMR ($CDCl_3$, 200 MHz, as a mixture of *meso* and *rac* isomers): δ 7.15−6.70 (m, 8H, C_6H_5), 6.62−5.78 (m, 6H, C_5H_5), 4.29 (s, 1H, PhC*H*), 4.26 (s, 1H, PhC*H*), 3.73 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 2.87−2.56 (m, 4H, C_5H_5).

Reaction of 2 with $Ru_3(CO)_{12}$. Using a procedure similar to that described above, reaction of **2** with $Ru_3(CO)_{12}$ gave **8** (2%), **9** (4%), **10**-*meso* (30%), and **10**-*rac* (3%) as yellow or orange crystals.

8: mp 157 °C (dec). Anal. Calcd for $C_{31}H_{26}O_7Ru_2$: C, 52.14; H, 3.67. Found: C, 51.98; H, 3.81. ^{1}H NMR ($CDCl_3$, 300 MHz, see Chart 1 for key to assignments): δ 7.15 (d, J = 8.70 Hz, 2H, C_6H_4), 7.06 (d, J = 8.70 Hz, 2H, C_6H_4), 6.84 (d, J = 8.70 Hz, 2H, C_6H_4), 6.79 (d, J = 8.70 Hz, 2H, C_6H_4), 5.55 (t, 1H, C_5H_3), 5.16 (t, 1H, C_5H_3), 3.80 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.52 (s, 1H, *H*b), 3.46 (d, J = 16.20 Hz, 1H, *H*a), 3.35 (t, 1H, C_5H_3), 3.17 (d, J = 16.20 Hz, 1H, *H*a), 2.98−2.62 (m, 4H, *H*c + *H*e), 2.24−2.01 (m, 2H, *H*d). IR (ν_{CO}, cm^{-1}): 2038 (s), 1980 (s), 1965 (s), 1922 (s), 1887 (w).

9: mp 199 °C (dec). Anal. Calcd for $C_{30}H_{24}O_6Ru_2$: C, 52.79; H, 3.54. Found: C, 52.65; H, 3.59. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.01 (d, J = 8.47 Hz, 4H, C_6H_4), 6.83 (d, J = 8.47 Hz, 4H, C_6H_4), 5.63 (t, 2H, C_5H_3), 5.40 (t, 2H, C_5H_3), 4.26, (t, 2H, C_5H_3), 3.78 (s, 6H, OCH_3), 2.96 (s, 2H, PhCH_2), 2.92 (s, 2H, PhCH_2). IR (ν_{CO}, cm^{-1}): 2010 (s), 1973 (s), 1958 (s), 1918 (s).

10-*meso*: mp 189 °C (dec). Anal. Calcd for $C_{30}H_{24}O_6Ru_2$: C, 52.79; H, 3.54. Found: C, 52.66; H, 3.50. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.82−6.67 (m, 8H, C_6H_4), 5.61 (br s, 2H, C_5H_4), 5.51 (t, 4H, C_5H_4), 5.39 (br s, 2H, C_5H_4), 4.09 (s, 2H, PhC*H*), 3.75 (s, 6H, OCH_3). IR (ν_{CO}, cm^{-1}): 1993 (s), 1966 (s), 1795 (m), 1759 (s).

10-*rac*: mp 222 °C (dec). Anal. Calcd for $C_{30}H_{24}O_6Ru_2$: C, 52.79; H, 3.54. Found: C, 52.48; H, 3.49. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.79 (d, J = 8.55 Hz, 4H, C_6H_4) 6.51 (d, J = 8.55 Hz, 4H, C_6H_4), 5.53−5.47 (m, 6H, C_5H_4), 5.22 (br s, 2H, C_5H_4), 3.76 (s, 2H, PhC*H*), 3.61 (s, 6H, OCH_3). IR (ν_{CO}, cm^{-1}): 1997 (s), 1954 (s), 1799 (sh, w), 1752 (s).

Synthesis of (^{t}BuC$_5$H$_4$)PhCHCHPh(^{t}BuC$_5$H$_4$) (3). Ligand **3** was prepared similarly as described above for **2** from 7.0 g (33 mmol)

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Table 1. Crystal Data and Summary of X-ray Data Collection for 4, 5, 7-*meso*, 7-*rac*, and 8

	4	**5**	**7-*meso***	**7-*rac***	**8**
formula	$C_{29}H_{22}O_5Ru_2$	$C_{28}H_{20}O_4Ru_2$	$C_{29}H_{22}Cl_2O_4Ru_2$	$C_{28.25}H_{20.50}Cl_{0.50}O_4Ru_2$	$C_{31}H_{26}O_7Ru_2$
fw	652.61	622.58	707.51	643.81	712.66
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$	$C2/c$	$P2(1)/n$
a (Å)	8.928(3)	24.070(7)	22.024(6)	28.419(9)	8.687(9)
b (Å)	10.143(4)	7.290(2)	14.171(5)	12.792(4)	11.673(12)
c (Å)	14.022(5)	16.239(5)	16.957(6)	16.503(5)	27.86(3)
α (deg)	98.909(6)	90	90	90	90
β (deg)	95.115(6)	124.083(4)	90.719(8)	118.054(4)	97.826(16)
γ (deg)	93.640(6)	90	90	90	90
V (Å^3)	1245.6(7)	2359.7(12)	5292(3)	5294(3)	2799(5)
Z	2	4	8	8	4
D_{calcd} (g cm^{-3})	1.740	1.752	1.776	1.615	1.691
μ (mm^{-1})	1.251	1.313	1.378	1.222	1.126
F(000)	648	1232	2800	2548	1424
cryst size (mm)	0.18 × 0.16 × 0.12	0.22 × 0.16 × 0.06	0.12 × 0.08 × 0.06	0.22 × 0.20 × 0.18	0.20 × 0.18 × 0.12
max. 2θ (deg)	52.96	52.78	52.80	52.76	52.72
no. of reflns collected	7213	6688	15 035	14 877	15 583
no. of indep reflns/R_{int}	5071/0.0340	2402/0.0342	5414/0.0835	5401/0.0305	5595/0.0340
no. of params	326	154	335	349	363
goodness-of-fit on F^2	1.012	1.056	0.956	1.150	1.075
R1, wR2 ($I > 2\sigma$(I))	0.0439, 0.0783	0.0276, 0.0522	0.0453, 0.0667	0.0334, 0.0887	0.0549, 0.1707
R1, wR2 (all data)	0.0934, 0.0958	0.0453, 0.0568	0.0992, 0.0794	0.0557, 0.1051	0.0770, 0.1890

of 2-*tert*-butylphenylfulvene in 31% yield as white solids. Mp: 123−124 °C. Anal. Calcd for $C_{32}H_{38}$: C, 90.94; H, 9.06. Found: C, 90.90; H, 8.96. MS (ESI): *m*/*z* 423 (M + 1). ^{1}H NMR ($CDCl_3$, 200 MHz, as a mixture of *meso* and *rac* isomers): δ 7.23−7.11 (m, 10H, C_6H_5), 6.00−5.75 (m, 4H, C_5H_4), 4.27 (s, 1H, PhC*H*), 4.25 (s, 1H, PhC*H*), 2.68−2.35 (m, 4H, C_5H_4), 1.12−0.92 (m, 18H, ^{t}Bu-*H*).

Reaction of 3 with $Ru_3(CO)_{12}$. Using a procedure similar to that described above, reaction of **3** with $Ru_3(CO)_{12}$ gave **11** (4%), **12** (5%), **13** (4%), and **14** (3%) as yellow or orange crystals.

11: mp 246 °C (dec). Anal. Calcd for $C_{36}H_{36}O_4Ru_2$: C, 58.84; H, 4.94. Found: C, 59.09; H, 4.88. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30−7.24 (m, 6H, C_6H_5), 7.06 (m, 4H, C_6H_5), 5.34 (s, 2H, C_5H_2), 4.17 (s, 2H, C_5H_2), 2.90 (s, 4H, PhCH_2), 1.22 (s, 18H, ^{t}Bu-*H*). IR (ν_{CO}, cm^{-1}): 1993 (s), 1950 (s), 1934 (s), 1910 (m).

12: mp 135 °C (dec). Anal. Calcd for $C_{36}H_{36}O_4Ru_2$: C, 58.84; H, 4.94. Found: C, 59.00; H, 4.82. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.20−7.14 (m, 6H, C_6H_5), 6.86 (m, 4H, C_6H_5), 5.62−5.15 (m, 6H, C_5H_3), 4.11 (br s, 2H, PhC*H*), 1.29 (s, 9H, ^{t}Bu-*H*), 1.27 (s, 9H, ^{t}Bu-*H*). IR (ν_{CO}, cm^{-1}): 1989 (s), 1962 (m), 1765 (s).

13: mp 235 °C (dec). Anal. Calcd for $C_{36}H_{36}O_4Ru_2$: C, 58.84; H, 4.94. Found: C, 59.00; H, 4.87. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.20−7.14, (m, 6H, C_6H_5), 6.81 (m, 4H, C_6H_5), 5.56 (br s, 2H, C_5H_3), 5.50 (br s, 2H, C_5H_3), 5.24 (m, 2H, C_5H_3), 4.12 (s, 2H, PhC*H*), 1.26 (s, 18H, ^{t}Bu-*H*). IR (ν_{CO}, cm^{-1}): 1989 (s), 1954 (s), 1799 (m), 1759 (s).

14: mp: 229 °C (dec). Anal. Calcd for $C_{36}H_{36}O_4Ru_2$: C, 58.84; H, 4.94. Found: C, 58.88; H, 4.72. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 6.94−6.78 (m, 10H, C_6H_5), 5.51−5.47 (m, 3H, C_5H_3), 5.40 (br s, 1H, C_5H_3), 5.12 (s, 1H, C_5H_3), 5.08 (s, 1H, C_5H_3), 3.70 (s, 1H, PhC*H*), 3.67 (s, 1H, PhC*H*), 1.31 (s, 9H, ^{t}Bu-*H*), 1.21 (s, 9H, ^{t}Bu-*H*). IR (ν_{CO}, cm^{-1}): 1997 (s), 1942 (s), 1771 (s).

Crystallographic Studies. Single crystals of complexes **4**, **5**, **7**-*meso*, **7**-*rac*, **8**, **10**-*meso*, **11**, **12**, **13**, and **14** suitable for X-ray diffraction were obtained from hexane/CH_2Cl_2 solution. Data collection was performed on a Bruker SMART 1000, using graphite-monochromated Mo Kα radiation ($\omega-2\theta$ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were using the SHELXTL-97 program system. The crystal data and summary of X-ray data collection are presented in Tables 1 and 2.

Results and Discussion

Reactions of CpArCHCHArCp [Ar = Ph (1), *p*-MeOC$_6$H$_4$ (2)] with $Ru_3(CO)_{12}$. The reaction of $Ru_3(CO)_{12}$ with the PhCH−CHPh-bridged bis(cyclopentadiene) ligand **1** (as a mixtures of *racemic* and *meso* isomers with a ratio of about 1:0.9) in refluxing xylene afforded not only the normal bridged bis(cyclopentadienyl) diruthenium complexes **7** (27% for **7**-*meso* and 4% for **7**-*rac*), but also the 2,2′-bisubstituted[11] fulvalene diruthenium complexes **5** (4%) and complexes **4** (2%), in which one of the cyclopentadienyl rings was partially hydrogenated (Scheme 2). The reactions can also be conducted in heptane, benzene, and toluene, which demand longer reaction time, but the amount of the C−C cleavage products seems to decrease. To further examine the stereochemistry of the reaction, the pure *racemic* isomer (**1**-*rac*) of ligand **1** was obtained by hydrolysis of the corresponding *racemic* calcium salt[9b] and used to react with $Ru_3(CO)_{12}$ instead of the mixture of *racemic* and *meso* isomers. However, similar products, **7**-*meso* (7%), **7**-*rac* (7%), **5** (4%), and complexes **4** (2%), were obtained. This opens up a possibility that the reaction itself has led to some sort of equilibration between the two stereochemistries and would suggest some equilibrium processes within the mechanism. To further confirm the relationship between the products, a xylene solution of **7**-*meso* or **7**-*rac* was heated alone or with $Ru_3(CO)_{12}$ under reflux for 8 h; no **4**, **5**, or any other product was observed by TLC monitoring. This suggests that the *racemic* and *meso* isomers of **7** cannot interconvert to each other; complexes **4** and **5** are formed during the reaction of $Ru_3(CO)_{12}$ with ligand **1** and not from complex **7**.

The reaction of $Ru_3(CO)_{12}$ with ligand **2** (as a mixture of *racemic* and *meso* isomers) gave similar products, **10**-*meso* (30%), **10**-*rac* (3%), **9** (4%), and **8** (2%).

All the compounds are yellow to orange air-stable crystals but slightly air-sensitive in solution. The IR spectrum of **4** shows five terminal carbonyl absorption peaks at 2050, 1985, 1962, 1910, and 1870 cm^{-1}. The ^{1}H NMR spectrum of **4** displays

(11) The sequence of the carbons in the parent fulvalene was labeled as shown.

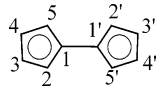
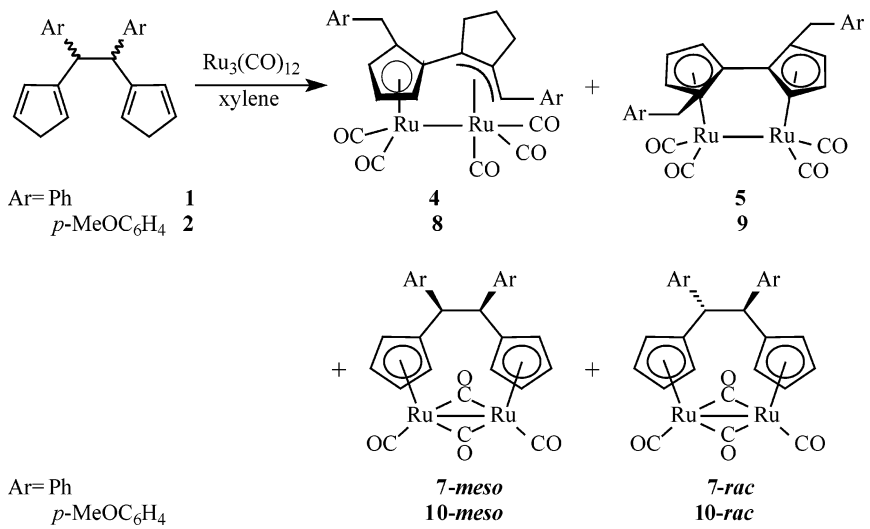


Table 2. Crystal Data and Summary of X-ray Data Collection for 10-*meso*, 11, 12, 13, and 14

	10-*meso*	**11**	**12**	**13**	**14**
formula	$C_{30}H_{24}O_6Ru_2$	$C_{36}H_{36}O_4Ru_2$	$C_{36}H_{36}O_4Ru_2$	$C_{37}H_{38}Cl_2O_4Ru_2$	$C_{36}H_{36}O_4Ru_2$
fw	682.63	734.79	734.79	819.71	734.79
cryst syst	triclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	9.869(5)	22.262(5)	10.579(4)	18.902(6)	11.022(4)
b (Å)	10.941(6)	7.069(2)	11.980(4)	17.305(5)	11.305(4)
c (Å)	13.370(7)	22.290(5)	14.910(5)	21.960(7)	15.355(5)
α (deg)	84.886(8)	90	76.461(5)	90	98.781(6)
β (deg)	70.146(8)	112.186(19)	73.896(5)	95.924(7)	106.070(5)
γ (deg)	64.953(8)	90	66.281(4)	90	112.801(5)
V (Å^3)	1227.6(12)	3248.1(14)	1645.9(10)	7145(4)	1620.2(10)
Z	2	4	2	8	2
D_{calcd} (g cm^{-3})	1.847	1.503	1.483	1.524	1.506
μ (mm^{-1})	1.276	0.966	0.953	1.032	0.969
F(000)	680	1488	744	3312	744
cryst size (mm)	0.20 × 0.18 × 0.16	0.24 × 0.20 × 0.16	0.32 × 0.22 × 0.20	0.18 × 0.16 × 0.14	0.32 × 0.28 × 0.22
max. 2θ (deg)	52.76	53.00	52.86	52.84	56.58
no. of reflns collected	7053	8467	10 049	20 453	10 408
no. of indep reflns/R_{int}	4918/0.0210	3313/0.0491	6676/0.0222	7304/0.1148	7584/0.0201
no. of params	345	193	385	440	385
goodness-of-fit on F^2	1.104	1.020	1.034	0.973	1.045
R1, wR2 ($I > 2\sigma(I)$)	0.0292, 0.0712	0.0433, 0.0849	0.0318, 0.0662	0.0578, 0.1025	0.0330, 0.0798
R1, wR2 (all data)	0.0484, 0.0906	0.0801, 0.0961	0.0572, 0.0757	0.1599, 0.1522	0.0613, 0.0902

Scheme 2



three multiplets for cyclopentadienyl protons at 5.58, 5.20, and 3.38 ppm,[12] one singlet and two doublets for benzyl protons at 3.55, 3.52, and 3.24 ppm, and two multiplets for the allyl and alkyl protons at 3.00−2.59 and 2.23−2.00 ppm, indicating the unusual structure. Single-crystal X-ray diffraction analysis shows that in complex **4** the two cyclopentadienyl rings were linked together, with one of them being partially hydrogenated. It contains a Ru−Ru bond, and one ruthenium atom is coordinated with a cyclopentadienyl ligand in an η^5 manner and the other ruthenium atom is coordinated in an η^3 manner with the allyl group consisting of the benzyl carbon and the two linked or substituted carbons of the partially hydrogenated cyclopentadienyl ring. Combining the ^{1}H NMR spectrum and the crystal structure with the aid of the ^{1}H−^{1}H COSY analysis (Figure 1), the signals at 2.23−2.00 (m, 2H), 3.00−2.59 (m, 4H), 3.55 (s, 1H), 3.52 (d, J = 16.20 Hz, 1H), and 3.24 (d, J = 16.20 Hz, 1H) ppm were assigned to Hd, Hc + He, Hb, and Ha (see Chart 1), respectively. Complex **8** has IR and ^{1}H NMR spectra similar to **4** except that in **8** the signal of Hb does not overlap with that of Ha (see Experimental Section), indicating a similar structure. It was reported that reaction of the CH_2 and Me_2Si or Me_2Ge doubly bridged bis(cyclopentadiene) with $Fe(CO)_5$ could also give complexes with η^5 and η^3 coordination mode similar to that of **4**.[13]

Complexes **7** and **10** are the normal intramolecular diruthenium complexes. All their IR spectra show two terminal and two bridging carbonyl absorptions at around 1997, 1960 cm^{-1}, and 1793, 1753 cm^{-1}. Their IR and ^{1}H NMR spectra are very similar to that for PhCHCHPh-bridged iron analogues.[9] An interesting feature of this reaction is the relative yield of the isomers of **7** and **10**, which is much more in favor of the *meso* form. Similarly, $(CH_2CH_2)[(C_9H_6)Ru(CO)(\mu\text{-}CO)]_2$[8b] and $(MeHC)[(C_9H_6)Ru(CO)_2]_2$[14] were obtained as 2:1 and 4:1 mixtures of the isomers, respectively, with the *meso* form predominating.

The ^{1}H NMR spectrum of **5** exhibits three triplets or multiplets for cyclopentadienyl protons at 5.66, 5.45, and 4.28 ppm[12] and two singlets for benzyl protons at 3.04 and 3.02 ppm.

(12) The chemical shift difference between the Cp-H protons of fulvalene ligands in the ^{1}H NMR spectra appears to correlate with the presence of metal−metal bonding, as observed earlier: (a) Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788. (b) See also ref 4.

(13) Wang, B.; Zhu, B.; Zhang, J.; Xu, S.; Zhou, X.; Weng, L. *Organometallics* **2003**, *22*, 5543.

(14) Schiavo, S. L.; Renouard, C.; Simpson, M. C.; Adams, H.; Bailey, N. A.; White, C. *J. Chem. Soc., Dalton Trans.* **1994**, 1731.

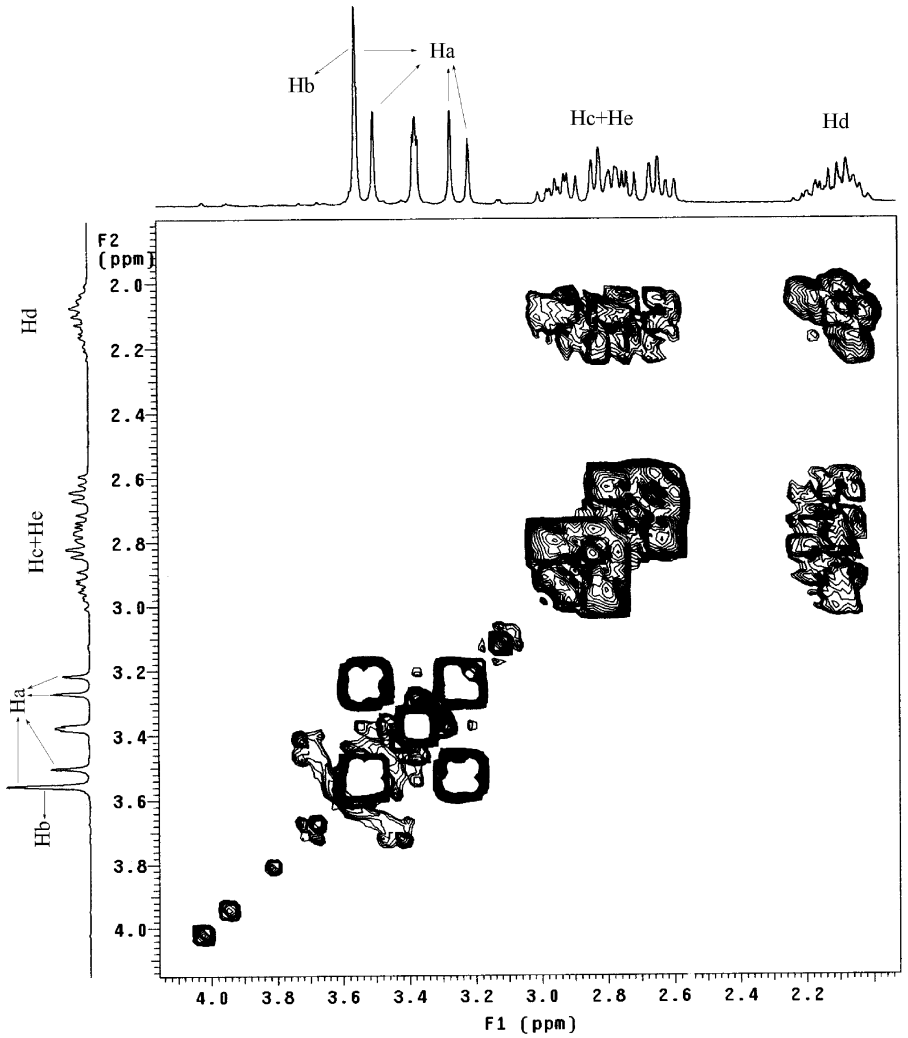


Figure 1. Partial $^1H-^1H$ COSY spectrum of complex **4** in $CDCl_3$.

Its IR spectrum shows only four terminal carbonyl absorptions at 1997, 1958, 1934, and 1918 cm^{-1}. The elemental analysis indicates that complexes **5** and **7** are isomers. Single-crystal X-ray diffraction analysis shows that the complex **5** is a 2,2′-bisubstituted fulvalene diruthenium complex, an analogue of the known complex $FvRu_2(CO)_4$ (**6**).[15] So the formation of **5** must be accompanied by the cleavage of the bridging C−C bond of the ligand and the coupling of the two cyclopentadienyl rings. Complex **9** has IR and ^1H NMR spectra and structure similar to those of **5**.

Reaction of ^{t}BuC$_5$H$_4$PhCHCHPhC$_5$H$_4^t$Bu (3) with Ru$_3$(CO)$_{12}$. To further examine the effect of the structure of the ligand on the C−C cleavage reaction, a *tert*-butyl group was introduced to the cyclopentadienyl rings. Reaction of ligand **3** (as a mixture of *racemic* and *meso* isomers) with $Ru_3(CO)_{12}$ in refluxing xylene afforded the fulvalene diruthenium analogue **11** (4%) and three isomers of the normal bridged bis(cyclopentadienyl) diruthenium complexes **12** (5%), **13** (4%), and **14** (3%) in low yield (Scheme 3). The partially hydrogenated η^5:η^3-analogue mentioned above was not obtained, possibly because the bulky *tert*-butyl may be resistant to the hydrogenation.

The ^1H NMR spectrum of **11** displays two singlets for the cyclopentadienyl protons at 5.34 and 4.17 ppm and a singlet for the benzyl and *tert*-butyl protons at 2.90 and 1.22 ppm, respectively. Its IR spectrum shows only four terminal carbonyl absorptions at 1993, 1950, 1934, and 1910 cm^{-1}, which is similar to that for **5** and **9**. The single-crystal X-ray diffraction analysis further proves it to be a 2,2′,4,4′-tetrasubstituted fulvalene diruthenium complex. Complexes **12**, **13**, and **14** have ^1H NMR and IR spectra similar to complexes **7** and **10**, indicating the similar structures. There are 10 normal intramolecular diruthenium complex isomers in theory for ligand **3** (Chart 2). When two phenyl groups lie in *meso* form, there are four isomers, and among them ③ and ④ are enantiomers. When two phenyl groups lie in *racemic* form, there are six isomers, and among them ⑤ and ⑥, ⑦ and ⑧, and ⑨ and ⓪ are enantiomers, respectively. In our case only three isomers (①, ②, and ⑤) of them were obtained, possibly due to the relative amount of the isomers in ligand **3**.

Molecular Structures. The molecular structures of **4** and **8** are shown in Figure 2 and the Supporting Information, respectively. The selected bond lengths and angles are listed in Table 3. Complexes **4** and **8** have similar structures. One ruthenium atom is coordinated with a cyclopentadienyl ligand in an η^5 manner, and the other ruthenium atom is coordinated in an η^3 manner with the allyl group consisting of the benzyl carbon and the two linked or substituted carbons of the partially hydrogenated cyclopentadienyl ring. The two benzyl groups result from the cleavage of the bridging C−C bond of the ligand and lie in *ortho*-positions of the new building C(17)−C(18) bond on the opposite side and point away from each other. The five carbonyls, three bound on η^3-Ru(1) and the other two bound

(15) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

Scheme 3

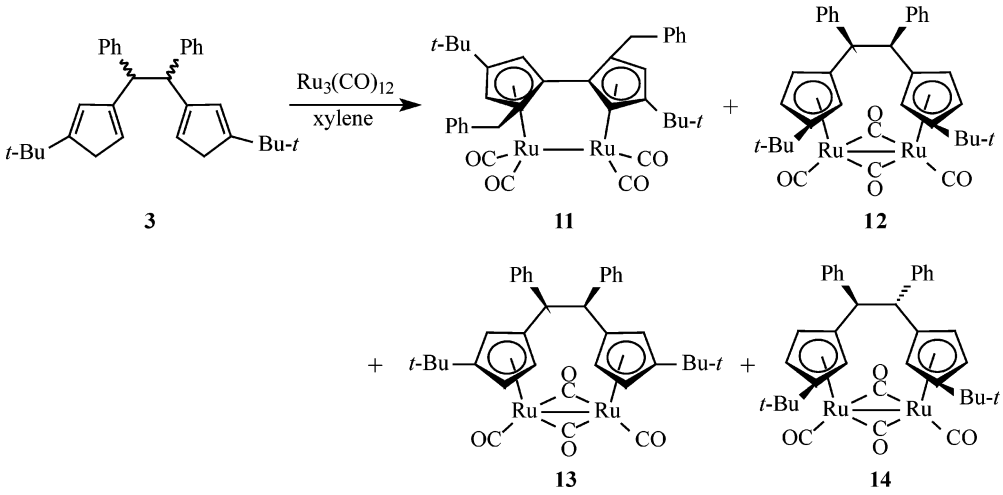
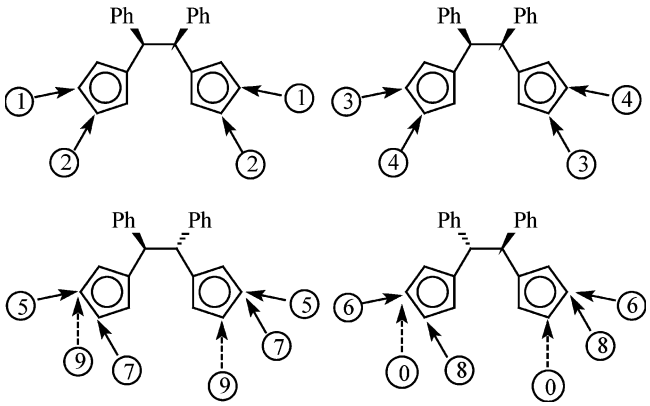


Chart 2



on η^5-Ru(2), are all terminal, which is consistent with their IR spectra. It is interesting that C(1)−O(1), one of the carbonyls bound on η^3-Ru(1), almost lies in the same line with Ru(2)−Ru(1) (∠Ru(2)−Ru(1)−C(13): 174.8(2)° for **4** and 173.7(2) for **8**). In both complexes, Ru(1), Ru(2), C(17), and the centroid of the cyclopentadienyl ring (CEN) are almost coplanar: the torsion angle of Ru(2)−Ru(1)−C(17)−CEN is 3.1° for **4** and 2.7° for **8**. The Ru(1)−C(η^3-allyl) bond length (average for **4**: 2.267 Å; **8**: 2.285 Å) is very close to Ru(2)−C(Cp) (average for **4**: 2.246 Å; **8**: 2.2482 Å). Similarly, the C−C(η^3-allyl) bond distances C(12)−C(13) and C(13)−C(17) [1.425(8), 1.414(7) Å for **4**, 1.419(10), 1.427(10) Å for **8**] are also close to those of C−C(Cp) (1.4236 Å for **4** and 1.4252 Å for **8**), which are much shorter than that of C(13)−C(14), C(14)−C(15), C(15)−C(16), and C(16)−C(17), the latter belonging to C−C single bonds. The five-membered ring C(13)−C(14)−C(15)−C(16)−C(17), resulting from a partially hydrogenated cyclopentadienyl ring, adopts a standard envelope conformation [C(13), C(14), C(16), and C(17) atoms are completely coplanar, with C(15) deviating from the plane by 0.4554 Å for **4** and 0.4571 Å for **8**]. The Ru−Ru bond lengths of 2.8583(9) Å for **4** and 2.867-(2) Å for **8** are quite comparable to the value of 2.845(1) Å for the similar complex (η^5-C_5H_4-η^3-$(CC_6H_5)C_6H_5$)$Ru(CO)_2Ru(CO)_3$[16] and much longer than the normal bis(cyclopentadienyl) diruthenium complexes due to the fact that the very strong (η^3-allyl)−Ru linkage stretches the relatively weak Ru−Ru bond in order to maintain its own optimal geometry.[17]

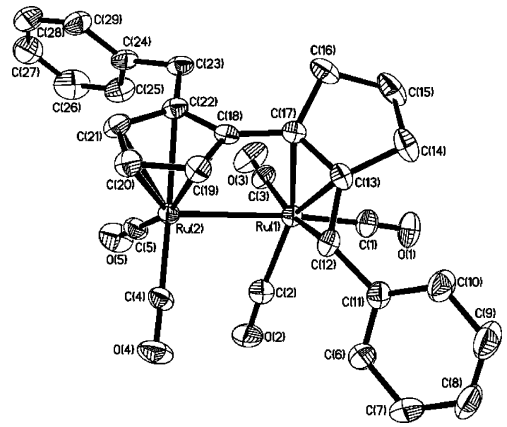


Figure 2. ORTEP diagram of **4**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengthes (Å) and Angles (deg) for 4 and 8

	4	**8**
Ru(1)−Ru(2)	2.8583(9)	2.867(2)
Ru(1)−C(12)	2.256(5)	2.289(7)
Ru(1)−C(13)	2.242(5)	2.261(7)
Ru(1)−C(17)	2.302(5)	2.304(7)
Ru(2)−C(Cp)(av)	2.246	2.2482
C(12)−C(13)	1.425(8)	1.419(10)
C(13)−C(14)	1.515(8)	1.526(9)
C(14)−C(15)	1.530(9)	1.536(11)
C(15)−C(16)	1.519(9)	1.522(11)
C(16)−C(17)	1.524(8)	1.514(10)
C(13)−C(17)	1.414(7)	1.427(10)
C(17)−C(18)	1.465(8)	1.475(10)
C(11)−C(12)−C(13)	126.0(5)	123.3(6)
C(12)−C(13)−C(17)	123.7(5)	125.2(6)
C(13)−C(17)−C(18)	125.0(5)	124.6(6)
C(23)−C(22)−C(18)	127.7(5)	128.3(7)
C(22)−C(23)−C(24)	114.8(5)	115.9(6)
Ru(2)−Ru(1)−C(17)	76.24(14)	76.41(18)
Ru(2)−Ru(1)−C(13)	96.58(15)	96.73(18)
Ru(2)−Ru(1)−C(12)	88.43(15)	89.61(19)

As shown in Figures 3 and 4, complexes **5** and **11** contain a pair of ruthenium atoms linked by a metal−metal bond and a substituted fulvalene ligand, with four terminal carbonyls. The selected bond lengths and angles for them and $FvRu_2(CO)_4$[4] (**6**) are listed in Table 4. Complex **5** has two benzyl groups at the 2,2′-positions and complex **11** has two more *tert*-butyl groups at the 4,4′-positions of the fulvalene ligand. Both the molecules possess crystallographically C_2 symmetry. Thus,

(16) Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1975**, *96*, 435.
(17) Cotton, F. A.; DeBoer, B. G.; Marks, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 5069.

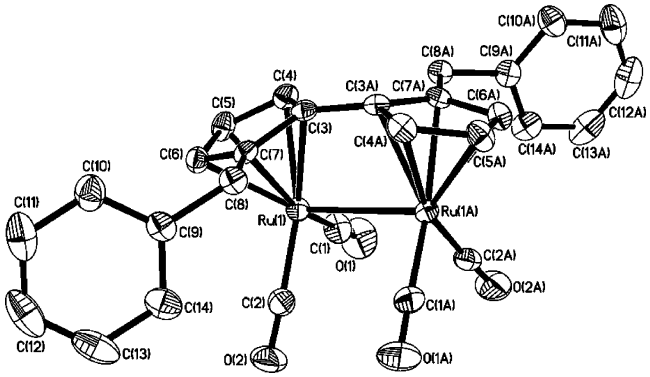


Figure 3. ORTEP diagram of **5**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

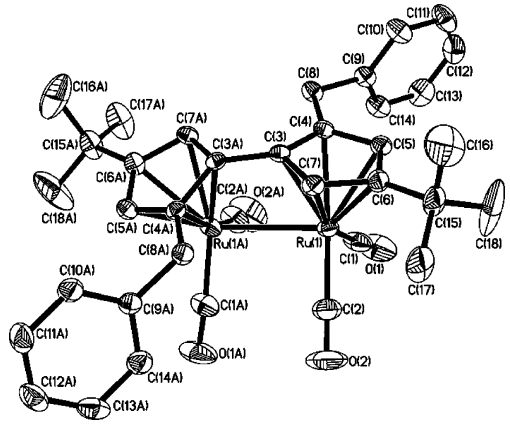


Figure 4. ORTEP diagram of **11**. Thermal ellipsoids are shown at the 30% level. Hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Lengthes (Å) and Angles (deg) for 5, 11, and $FvRu_2(CO)_4$ (6)[a]

	5	11	6
Ru(1)−Ru(1A)	2.8309(8)	2.8650(11)	2.821(1)
Ru(1)−C(1)	1.862(4)	1.852(5)	1.860(3)
Ru(1)−C(2)	1.861(4)	1.865(5)	1.866(3)
Ru(1)−CEN[b]	1.905	1.902	1.894
C(3)−C(3A)	1.458(5)	1.459(8)	1.457(3)
C−C(Cp)(av)	1.425	1.428	1.416
Ru(1A)−Ru(1)−C(1)	93.66(11)	95.87(18)	94.40(8)
Ru(1A)−Ru(1)−C(2)	93.73(11)	93.03(19)	93.32(7)
Ru(1A)−Ru(1)−CEN	104.6	104.3	105.4
C(1)−Ru(1)−C(2)	88.93(16)	90.2(2)	91.49(11)

[a] See ref 4a; **6** deviates from C_{2v} slightly, so half of its data was chosen for comparison. [b] CEN, centroid of the cyclopentadienyl ring.

although substituents were introduced to the fulvalene ligand in complexes **5** and **11**, their bond lengths and angles vary little compared with the mother complex **6** (Table 4). The dihedral angles between the two cyclopentadienyl planes are still relatively large (148.1° for **5** and 149.7° for **11**), comparable to that of **6** (151.5°). The normally planar fulvalene moiety is strained and leads to the expectation of a longer than normal Ru−Ru single-bond distance. Thus, the Ru−Ru bond distances of 2.8309(8) Å for **5** and 2.8650(11) Å for **11** are longer than those of **6** [2.821(1) Å] and the nonbridged[18] and singly or doubly bridged[4−8,19] bis(cyclopentadienyl) tetracarbonyl di-

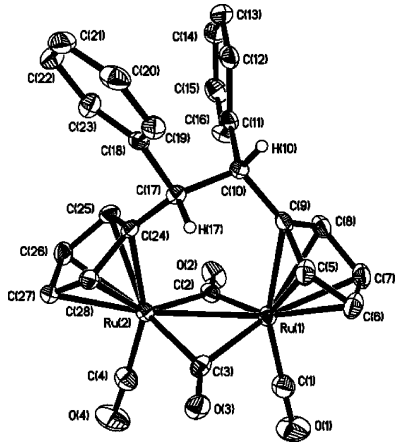


Figure 5. ORTEP diagram of **7**-*meso*. Thermal ellipsoids are shown at the 30% level. All hydrogen atoms except for the bridging-carbon protons have been omitted for clarity.

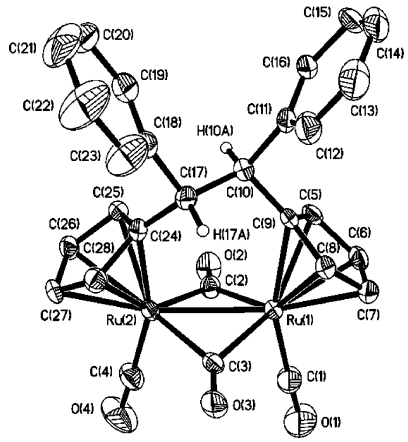


Figure 6. ORTEP diagram of **7**-*rac*. Thermal ellipsoids are shown at the 30% level. All hydrogen atoms except for the bridging-carbon protons have been omitted for clarity.

ruthenium complexes (Table 5). The Ru−Ru bond [2.8650(11) Å] in **11** is the longest up to now for the bis(cyclopentadienyl) diruthenium complexes. It is also worth noting that the torsion angles CEN−Ru(1)−Ru(1A)−CEN in **5** (17.3°) and **11** (17.5°) are much larger than that of **6** (4.3°), possibly attributed to the effects of the benzyl and *tert*-butyl substituents.

Complexes **7**-*meso*, **7**-*rac*, **10**-*meso*, **12**, **13**, and **14** are normal intramolecular diruthenium complexes (Figures 5−9 and Supporting Information). Complexes **12**, **13**, and **14** are three of 10 intramolecular diruthenium complex isomers of the reaction of ligand **3** with $Ru_3(CO)_{12}$. It is difficult to differentiate them from their ^{1}H NMR and IR spectra. Fortunately all their crystals are suitable for X-ray analysis. The orientation of the bridging-carbon protons can easily differentiate the isomers. The Ru−Ru bond distances in these complexes of around 2.70 Å are quite comparable to those in related linked compounds, e.g., $(CH_2CH_2)[(\eta^5\text{-}C_5H_4)Ru(CO)(\mu\text{-}CO)]_2$ [2.7037(10) Å][8a] and *trans*-$(CH_2CH_2)[(C_9H_6)Ru(CO)(\mu\text{-}CO)]_2$ [2.7185(7) Å].[8b] Their torsion angles CEN−Ru(1)−Ru(2)−CEN vary from 1.7° to 8.3°, while the corresponding angle in $(CH_2CH_2)[(\eta^5\text{-}C_5H_4)Ru(CO)(\mu\text{-}CO)]_2$ is only 0.9°. The difference may also be attributed to the introduction of substituents to the bridging carbons and the cyclopentadienyl rings.

Plausible Mechanism. The formation of the substituted fulvalene diruthenium complexes **5**, **9**, and **11**, and the partially hydrogenated complexes **4** and **8**, must be accompanied with the cleavage of the bridging C−C bond of the ligand and the

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Table 5. Structural Parameter Comparison for Bis(cyclopentadienyl) Diruthenium Complexes

complex	M−M (Å)	PL−PL[a] (deg)	CEN−M−M−CEN torsion angle (deg)	ref
trans-[(η^5-C_5H_5)Ru(CO)(μ-CO)]$_2$	2.735(2)			18
(CH_2)[C_5H_4Ru(CO)$_2$]$_2$	2.766(1)	112.9	39.9	19c
			49	
(CMe_2)[C_5H_4Ru(CO)$_2$]$_2$	2.7879(4)	119.3	32.9	6a
($SiMe_2$)[(η^5-C_5H_4)Ru(CO)(μ-CO)]$_2$	2.706(1)	103.53		6b, 19a
	2.7042(4)			
($GeMe_2$)[(η^5-C_5H_4)Ru(CO)(μ-CO)]$_2$	2.7036(6)	101.98		19b
(CH_2CH_2)[(η^5-C_5H_4)Ru(CO)(μ-CO)]$_2$	2.7037(10)		0.9	8a
($Me_2SiSiMe_2$)[(η^5-C_5H_4)Ru(CO)(μ-CO)]$_2$	2.700(1)	91.9		7
$FvRu_2(CO)_4$	2.821(1)	151.5	4.3	4
4	2.8583(9)			tw[b]
8	2.867(2)			tw
5	2.8309(8)	148.1	17.3	tw
11	2.8650(11)	149.7	17.5	tw
7-*meso*	2.7031(10)	99.1	1.7	tw
7-*rac*	2.6988(8)	100.4	4.7	tw
10-*meso*	2.6548(14)	82.1	4.0	tw
12	2.7102(10)	80.2	6.2	tw
13	2.7105(9)	98.3	8.3	tw
14	2.7052(6)	101.3	2.9	tw
(Me_2Si)$_2$[(η^5-C_5H_3)Ru(CO_2)]$_2$	2.8180(3)	122.86	24.2	19d
rac-(CH_2CH_2)[(C_9H_6)Ru(CO)(μ-CO)]$_2$	2.7185(7)		4.7	8b

[a] PL, plane of the cyclopentadienyl ring. [b] tw, this work.

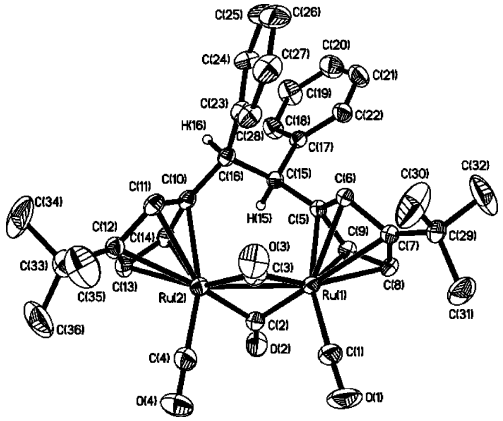

Figure 7. ORTEP diagram of **12**. Thermal ellipsoids are shown at the 30% level. All hydrogen atoms except for the bridging-carbon protons have been omitted for clarity.

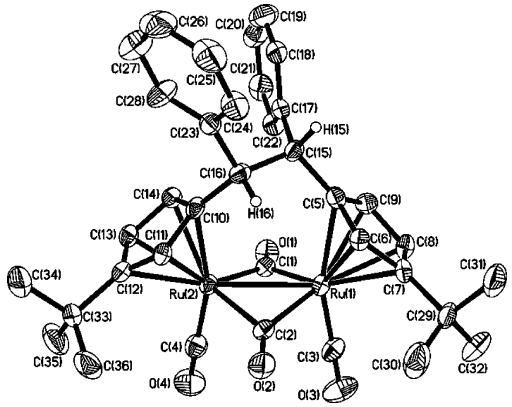

Figure 8. ORTEP diagram of **13**. Thermal ellipsoids are shown at the 30% level. All hydrogen atoms except for the bridging-carbon protons have been omitted for clarity.

coupling of the two cyclopentadienyl rings. Introduction of a methoxyl to the 4-position of the phenyl or a *tert*-butyl to the cyclopentadienyl ring does not seem to affect the bridging C−C cleavage and cyclopentadienyl coupling. The coupling positions are at the *ortho* positions of the bridgehead carbons. It easily led us to consider that a [3, 3] sigmatropic shift (Cope

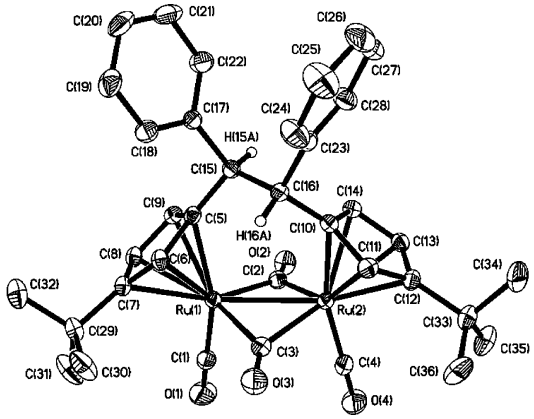

Figure 9. ORTEP diagram of **14**. Thermal ellipsoids are shown at the 30% level. All hydrogen atoms except for the bridging-carbon protons have been omitted for clarity.

Scheme 4

15 **16**

rearrangement) may take place. Indeed, the analogous compound 2,3-dimethyl-2,3-di(cyclopentadienyl)butane (**15**) was reported to be quite unstable even in dilute solution at room temperature and nearly quantitatively isomerizes to 1,1′-bi(2-isopropylidenecyclopent-3-enyl) (**16**) by Cope rearrangement (Scheme 4).[20] However, when ligand **1** was heated in refluxing $CDCl_3$ for 50 h or in refluxing xylene for 12 h, no new compound was monitored. So the easy rearrangement of **15** may come from the crowded substituents at the 2- and 3-carbons. Both kinetics and thermodynamics apparently favor this reaction. In contrast, the Cope rearrangement is not observed for **1** alone, but with $Ru_3(CO)_{12}$ present this does occur. This indicates that the less crowded nature of ligand **1** does not favor the thermal rear-

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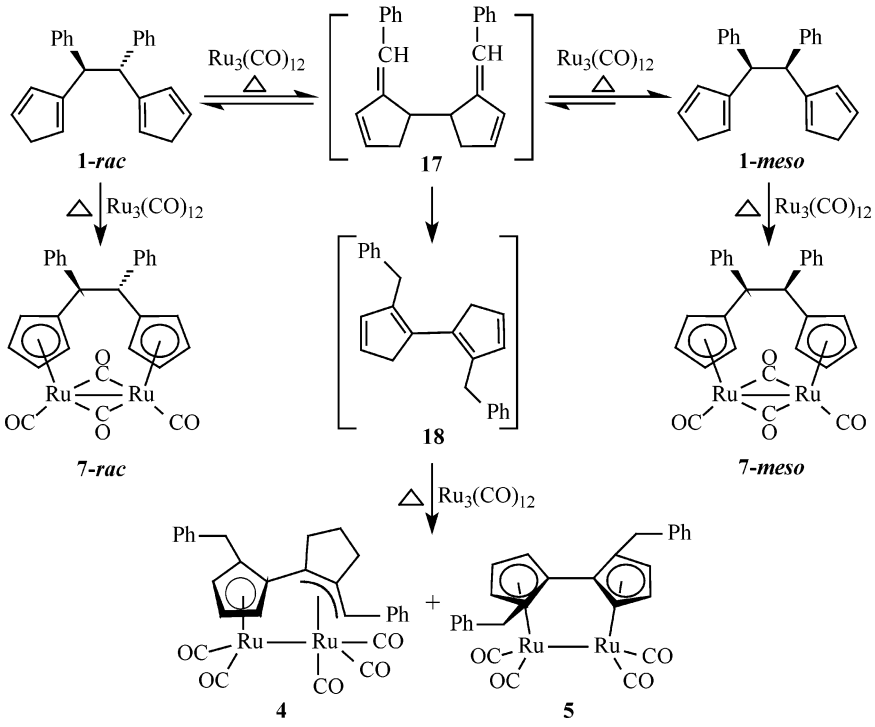
Scheme 5



rangement, but $Ru_3(CO)_{12}$ in some way catalyzes the reaction. The conversion of **1**-*rac* to **7**-*meso* opens up the possibility that the reaction itself has led to some sort of equilibration between the two stereochemistries and would suggest some equilibrium processes within the mechanism. So the reaction may be through a reversible nonconcerted Cope rearrangement, involving either a biradical intermediate or a spectrum of transition states ranging from a six-center structure, representing interacting allyl radicals, to the biradical.[21]

The rearrangement of **1**-*meso* (we cannot separate enough of pure **1**-*meso* for the reaction) may vary from that of the *racemic* isomer, as the *meso* and *racemic* isomers of 3,4-diphenylhexa-1,5-diene rearrange to give different products through different transition states.[22] However, from the reaction results of the pure **1**-*rac* and the mixture of *racemic* and *meso* isomers of ligand **1**, it can be concluded that the reactions are similar, and the reactivity of the *meso* isomer of ligand **1** with $Ru_3(CO)_{12}$ is much better than that of the *racemic* isomer. The poorer reactivity of the *racemic* isomer than that of the *meso* isomer of the ligand was also observed for ligand **2** and some bridged indenyl ligands.[8b,14] On the basis of these results, the possible mechanism of the reaction may be as shown in Scheme 5.

The Cope rearrangement of ligand **1** to the intermediate **17** is promoted by coordination of the double bonds of the ligand to $Ru_3(CO)_{12}$ instead of carbonyls. Then **17** can further isomerize to the benzyl-substituted dihydrofulvalene **18** and react with $Ru_3(CO)_{12}$ to form complexes **4** and **5**. The rearrangement is reversible and nonconcerted. So **1**-*rac* can rearrange to **17**, and the *meso* isomer **1**-*meso* can be formed from **17** by the reverse rearrangement.

The reaction of **15** with $Ru_3(CO)_{12}$ gave only a trace of complex, which was too small to identify, and the rearrangement product **16** did not react with $Ru_3(CO)_{12}$ at all. So the aromatic substituents at the 2- and 3-positions of the ligand may be necessary for both the Cope rearrangement and the further isomerization from **17** to **18**. The new double bonds in **17** conjugate with the aromatic rings, which makes the rearrangement product higher in energy. On the contrary, reactions of the CH_2CH_2-bridged bis(cyclopentadiene or indene) with $Ru_3(CO)_{12}$ gave only the normal bridged bis(cyclopentadienyl or indenyl) diruthenium complexes.[8]

Conclusions

Reaction of CpPhCHCHPhCp with $Ru_3(CO)_{12}$ in refluxing xylene afforded the unexpected bridging C−C cleavage and cyclopentadienyl coupling products: the 2,2′-bisubstituted fulvalene diruthenium complex **5** and the partially hydrogenated product **4**, in addition to the normal bridged bis(cyclopentadienyl) tetracarbonyl diruthenium **7**. Introduction of a methoxyl to the 4-position of the phenyl or a *tert*-butyl to the cyclopentadienyl ring did not affect the bridging C−C cleavage and cyclopentadienyl coupling. This provides a new method to synthesize the *ortho*-benzyl-substituted fulvalene diruthenium complexes. The mechanism may involve the $Ru_3(CO)_{12}$-promoted nonconcerted reversible Cope rearrangement.

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Supporting Information Available: X-ray structural information for complexes **4**, **5**, **7**-*meso*, **7**-*rac*, **8**, **10**-*meso*, **11**, **12**, **13**, and **14**, including the ORTEP figures of **8** and **10**-*meso*, the full $^1H-^1H$ COSY spectrum of complex **4**, the ^1H NMR spectra of ligand **1** as a mixture of *racemic* and *meso* isomers with a ratio of about 1:0.9 and as a pure *racemic* isomer. This material is available free of charge via the Internet at http://pubs.acs.org.

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