Reactions of SiH-Functionalized Cyclopentadienes with Metal Carbonyls

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Thermal treatment of the SiH-functionalized cyclopentadienes (RC_5H_4)SiHMeR′ [R = H, R′ = Ph (**1**), $PhCH_2$ (**2**); R = *t*-Bu, R′ = Ph (**3**), $PhCH_2$ (**4**)] with $Ru_3(CO)_{12}$ gave the cyclic dinuclear metal complexes *trans*-[(R′MeSi)(η^5-RC_5H_3)Ru$(CO)_2$]$_2$ [R = H, R′ = Ph (**7**), $PhCH_2$ (**8**); R = *t*-Bu, R′ = Ph (**10**), $PhCH_2$ (**11**)] containing two Si−Ru bonds via Si−H activation. A cyclopentenyl complex, [(η^2-C_5H_7)SiMe(CH_2Ph)Ru$(CO)_3$]$_2$ (**9**), bridged by a vinylsilyl ligand was also obtained from the reaction, but reactions of the SiH-functionalized tetramethylcyclopentadienes (C_5Me_4H)SiHMeR′ [R′ = Ph (**5**), $PhCH_2$ (**6**)] with $Ru_3(CO)_{12}$ only gave the cyclic diruthenium complex [(PhMeSi)(η^5-C_5Me_4)]$Ru_2(CO)_6$ (**12**) with one Si−Ru bond and the desilylation product [(η^5-C_5Me_4H)Ru(CO)]$_2$(μ-CO)$_2$ (**13**). When **2** and **4** reacted with M$(CO)_6$, the similar cyclic dinuclear complexes *trans*-[($PhCH_2$MeSi)(η^5-RC_5H_3)M$(CO)_3$]$_2$ [R = H, M = W (**18**); R = *t*-Bu, M = Mo (**15**), W (**20**)] were obtained, in addition to the desilylation products [(η^5-RC_5H_4)M$(CO)_3$]$_2$ [R = H, M = Mo (**14**), W (**19**); R = *t*-Bu, M = Mo (**16**), W (**21**)], but reactions of **6** with M$(CO)_6$ only gave the desilylation products [(η^5-C_5Me_4H)M$(CO)_3$]$_2$ [M = Mo (**17**); M = W (**22**)]. The molecular structures of **7**, **9**, **12**, **13**, **15**, **18**, and **20** were determined by X-ray diffraction.

Introduction

Since the first complex containing an M−Si bond was synthesized by Wilkinson and co-workers in 1956,[1] silyl transition-metal chemistry has grown enormously and a large number of new complexes have been prepared due to their broad applications in industry.[2] One of the most effective methods for the preparation of these complexes is by the reactions of transition-metal complexes with hydrosilanes via Si−H activation.[2,3] Furthermore, activation of Si−H bonds is also very important in industrial processes such as hydrosilylation, dehydrogenative silylation, and polysilane production.[2,4] It is widely considered that oxidative addition of the Si−H bond to a metal center is one of the crucial steps in these processes.[2−5]

Metal carbonyl, especially $Ru_3(CO)_{12}$, has been extensively used to catalyze multiple-component addition reactions, generally involving activation of C−H and other bonds.[6] These reactions are very useful in organic synthesis and in industry; however, the mechanisms for most reactions are still unclear. Our initial idea is to link the functional group, one of the multiple components of the addition reaction, to a cyclopentadienyl ring as a functionalized side chain and then to study the reactions of the side-chain-functionalized cyclopentadienes with metal carbonyls. Because the cyclopentadienyl ligand is a strong

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ligand to complex with a metal, it can be used as a trapping tool to catch the possible intermediate for the metal carbonyl catalyzed multiple-component addition reaction. The structures and reactions of the possible intermediate may help us to deeply understand the reaction mechanism. In recent studies we have shown the reactions of pyridyl side-chain-functionalized cyclopentadienes with metal carbonyl, which gave some novel intramolecular C−H-activated products.[7] Because hydrosilanes are also one of the important components for the metal carbonyl catalyzed multiple-component addition reaction,[6a,c,8] and as part of a systematic study of the reactions of functionalized cyclopentadienes with metal carbonyls,[7] in this work we studied the reactions of the SiH-functionalized cyclopentadienes with metal carbonyls, and a series of cyclic dinuclear metal complexes with two Si−M bonds were obtained via Si−H activation.

Experimental Section

General Considerations. Schlenk and vacuum line techniques were employed for all manipulations of air- and moisture-sensitive compounds. All solvents were distilled from appropriate drying agents under argon before use. ^{1}H NMR spectra and mass spectra were recorded on a Bruker AV300 and TRACE DSQ, respectively, while IR spectra were recorded as KBr disks on a Nicolet 5DX FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer.

Preparation of SiH-Functionalized Cyclopentadienes. The SiH-functionalized cyclopentadienes **1**−**6** were prepared using methods similar to those described in the literature.[9] A 12.5 g (80 mmol) sample of PhMeSiHCl was quickly added to the suspension of CpLi in THF at 0 °C, which was prepared from C_5H_6 (5.8 g, 88 mmol) in 100 mL of THF and *n*-BuLi (40 mL, 80 mmol) in *n*-hexane. The mixture was stirred overnight. After filtration the volatiles were removed under reduced pressure. The resulting oil was distilled, and the yellow fraction at 57−60 °C/0.07 mmHg was collected (10.0 g, yield 67%), which was characterized as **1**. ^{1}H NMR ($CDCl_3$): δ 7.42−7.32 (m, 2H, ArH), 7.25−7.12 (m, 3H, ArH), 6.80−6.20 (m), 3.61−3.42 (m), 2.89 (m) (total 5H, CpH), 4.61, 3.94 (q, q, total 1H, SiH), 0.31 (d, J = 3.73 Hz), 0.00 (d, J = 3.73 Hz) (total 3H, SiMe). EI-MS: *m/z* 186 (63, M^+).

Compound 2. Using a procedure similar to that described above, compound **2** (15.0 g, 75 mmol) was synthesized from ($PhCH_2$)-MeSiHCl (13.6 g, 80 mmol) and CpLi (80 mmol) in 94% yield as a yellow oil (bp 64−66 °C/0.07 mmHg). ^{1}H NMR ($CDCl_3$): δ 7.40−7.27 (m, 2H, ArH), 7.24−7.10 (m, 3H, ArH), 7.00−6.55 (m), 3.04 (m), 2.48−2.30 (m), 2.21 (d, J = 3.60 Hz) (total 5H, CpH), 4.42, 3.83 (q, q, total 1H, SiH), 2.26 (t, 2H, $SiCH_2$), 0.31 (d, J = 3.63 Hz), 0.00 (d, J = 3.20 Hz) (total 3H, SiMe). EI-MS: *m/z* 200 (35, M^+).

Compound 3. Using a procedure similar to that described above, compound **3** (9.87 g, 41 mmol) was synthesized from PhMeSiHCl (12.5 g, 80 mmol) and (t-BuC_5H_4)Li (80 mmol) in 51% yield as a yellow oil (bp 89−92 °C/0.5 mmHg). ^{1}H NMR ($CDCl_3$): δ 7.42−7.34 (m, 2H, ArH), 7.26−7.08 (m, 3H, ArH), 6.84 (m), 6.66 (m), 6.55−5.86 (m), 3.38 (m), 2.88 (m) (total 4H, CpH), 4.98, 4.62, 4.09 (q, q, q, total 1H, SiH), 1.02, 0.98 (s, s, total 9H, CMe_3), 0.34 (m), 0.27 (d, J = 3.00 Hz), 0.01 (d, J = 3.56 Hz) (total 3H, SiMe). EI-MS: *m/z* 242 (11, M^+).

Compound 4. Using a procedure similar to that described above, compound **4** (11.3 g, 44 mmol) was synthesized from ($PhCH_2$)-MeSiHCl (13.6 g, 80 mmol) and (t-BuC_5H_4)Li (80 mmol) in 55% yield as a yellow oil (bp 90−100 °C/0.3 mmHg). ^{1}H NMR ($CDCl_3$): δ 7.40−7.30 (m, 2H, ArH), 7.27−7.12 (m, 3H, ArH), 7.05−6.06 (m), 3.48 (m), 3.13−2.97 (m), 2.48−2.30 (m) (total 4H, CpH), 4.73, 4.41, 3.91 (m, m, m, total 1H, SiH), 2.30−2.19 (m, 2H, $SiCH_2$), 1.35−1.27 (m, 9H, CMe_3), 0.32 (m), 0.18 (d, J = 2.84 Hz), −0.03 (d, J = 3.61 Hz) (total 3H, SiMe). EI-MS: *m/z* 256 (15, M^+).

Compound 5. Using a procedure similar to that described above, compound **5** (5.03 g, 21 mmol) was synthesized from PhMeSiHCl (12.5 g, 80 mmol) and (C_5Me_4H)Li (80 mmol) in 26% yield as a yellow oil (bp 88−96 °C/0.25 mmHg). ^{1}H NMR ($CDCl_3$): δ 7.50−7.15 (m, 5H, ArH), 5.05, 4.44 (m, m, total 1H, SiH), 3.04, 2.61 (s, s, total 1H, CpH), 1.88−1.58 (m, total 12H, CpMe), 0.33 (m), 0.00 (m) (total 3H, SiMe). EI-MS: *m/z* 242 (100, M^+).

Compound 6. Using a procedure similar to that described above, compound **6** (15.2 g, 59 mmol) was synthesized from ($PhCH_2$)-MeSiHCl (13.6 g, 80 mmol) and (C_5Me_4H)Li (80 mmol) in 74% yield as a yellow oil (bp 94−98 °C/0.08 mmHg). ^{1}H NMR ($CDCl_3$): δ 7.39−7.29 (m, 2H, ArH), 7.26−7.08 (m, 3H, ArH), 4.74, 4.19 (m, m, total 1H, SiH), 3.07, 2.26 (s, s, total 1H, CpH), 2.18−1.88 (m, total 14H, $SiCH_2$ and CpMe), 0.20 (d, J = 2.77 Hz), 0.01 (d, J = 3.50 Hz) (total 3H, SiMe). EI-MS: *m/z* 256 (52, M^+).

Reaction of 1 with $Ru_3(CO)_{12}$. A solution of 0.300 g (0.469 mmol) of $Ru_3(CO)_{12}$ and 0.262 g (1.41 mmol) of **1** in 30 mL of heptane was refluxed for 12 h. The solvent was removed under reduced pressure, and the residue was placed in an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed a colorless band, which gave 0.050 g (0.070 mmol, 10%) of **7** as colorless crystals. Mp: >300 °C. Anal. Calcd for $C_{28}H_{24}O_4Ru_2Si_2$: C, 49.25; H, 3.54. Found: C, 49.50; H, 3.71. ^{1}H NMR ($CDCl_3$): δ 7.50−7.40 (m, 4H, ArH), 7.33−7.23 (m, 6H, ArH), 5.62 (m, 2H, CpH), 5.60−5.55 (m, 4H, CpH), 5.39 (m, 2H, CpH), 0.83 (s, 6H, SiMe). IR (ν_{CO}, cm^{-1}): 1999(s), 1946(s).

Reaction of 2 with $Ru_3(CO)_{12}$. Using a procedure similar to that described above, reaction of **2** (0.282 g, 1.41 mmol) with $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) gave **8** (0.050 g, 0.063 mmol, 9%) and **9** (0.060 g, 0.077 mmol, 11%) as colorless and yellow crystals, respectively. The following are data for **8**. Mp: 190−192 °C dec. Anal. Calcd for $C_{30}H_{28}O_4Ru_2Si_2$: C, 50.69; H, 3.97. Found: C, 51.10; H, 4.23. ^{1}H NMR ($CDCl_3$): δ 7.10 (t, 4H, ArH), 7.01 (t, 2H, ArH), 6.73 (d, J = 7.53 Hz, 4H, ArH), 5.38 (m, 2H, CpH), 5.27 (m, 4H, CpH), 5.06 (t, 2H, CpH), 2.43 (d, J = 7.13 Hz, 4H, $SiCH_2$), 0.38 (s, 6H, SiMe). IR (ν_{CO}, cm^{-1}): 2006(s), 1950(s). The following are data for **9**. Mp: 98−99 °C. Anal. Calcd for $C_{32}H_{34}O_6Ru_2Si_2$: C, 49.73; H, 4.43. Found: C, 49.51; H, 4.52. ^{1}H NMR ($CDCl_3$): δ 7.27−6.85 (m, 10H, ArH), 6.14 (m), 5.66 (m), 5.54 (s). 5.41 (s), 5.19 (s), 5.10 (s), 5.02 (s), 4.86 (s), 4.76 (s) (total 2H, vinyl H), 2.81−1.24 (m, 16H, $(CH_2)_3$ and $PhCH_2$), 0.60 (s), 0.50 (s), 0.42 (s), 0.38 (s), 0.31 (s), 0.26 (s), 0.24 (s), 0.21 (s), 0.19 (s), 0.07 (s) (total 6H, SiMe). IR (ν_{CO}, cm^{-1}): 2018(s), 1987(s), 1965(s), 1952(m).

Reaction of 3 with $Ru_3(CO)_{12}$. A solution of 0.300 g (0.469 mmol) of $Ru_3(CO)_{12}$ and 0.341 g (1.41 mmol) of **3** in 30 mL of heptane was refluxed for 12 h. Monitored by TLC, a little **3** still

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Table 1. Crystal Data and Summary of X-ray Data Collection for 7, 9, 12, 13, and 15

	7	**9**	**12**	**13**	**15**
empirical formula	$C_{28}H_{24}O_4Ru_2Si_2$	$C_{32}H_{34}O_6Ru_2Si_2$	$C_{22}H_{20}O_6Ru_2Si$	$C_{22}H_{26}O_4Ru_2$	$C_{40}H_{44}Mo_2O_6Si_2$
fw	684.81	772.91	610.61	556.57	868.81
T, K	294(2)	294(2)	294(2)	293(2)	294(2)
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$	$P2(1)/n$	$P\bar{1}$
a, Å	12.478(2)	8.574(2)	9.438(4)	7.472(2)	9.7330(15)
b, Å	8.4064(13)	12.807(3)	11.766(4)	14.960(4)	9.9833(16)
c, Å	13.557(2)	16.875(4)	21.820(8)	9.964(3)	10.5532(17)
α, deg	90	70.257(4)	90	90	80.329(2)
β, deg	109.067(2)	79.676(4)	92.076(6)	107.405(4)	86.341(3)
γ, deg	90	71.357(4)	90	90	74.622(2)
V, Å^3	1344.0(4)	1647.2(7)	2421.5(16)	1062.7(5)	974.5(3)
Z	2	2	4	2	1
D_{calcd}, g·cm^{-3}	1.692	1.558	1.675	1.739	1.481
μ, mm^{-1}	1.245	1.030	1.330	1.445	0.749
F(000)	684	780	1208	556	444
cryst size, mm	0.20 × 0.14 × 0.12	0.24 × 0.20 × 0.12	0.24 × 0.20 × 0.16	0.20 × 0.18 × 0.14	0.40 × 0.22 × 0.20
θ range, deg	1.93−26.39	1.29−25.01	1.87−26.69	2.54−26.42	1.96−26.34
no. of reflns collected	7325	8338	13268	6058	5509
no. of independent reflns/R_{int}	2735/0.0394	5760/0.0336	4952/0.0298	2179/0.0223	3909/0.0160
no. of params	164	389	285	131	230
GOF on F^2	0.998	1.029	1.057	1.072	1.071
R1, wR2 [$I > 2\sigma(I)$]	0.0308, 0.0669	0.0434, 0.0823	0.0265, 0.0568	0.0205, 0.0486	0.0283, 0.0676
R1, wR2 (all data)	0.0552, 0.0768	0.0955, 0.1022	0.0412, 0.0622	0.0281, 0.0514	0.0359, 0.0724

remained in the solvent. The solvent was removed under reduced pressure. The residue was washed with hexane to give 0.080 g of a white solid (**10a**). The filtrate was removed under reduced pressure and then placed in an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed a colorless band, which gave 0.050 g (0.063 mmol, 9%) of **10** as colorless crystals. The following are data for **10**. Mp: 225−226 °C. Anal. Calcd for $C_{36}H_{40}O_4Ru_2Si_2$: C, 54.39; H, 5.07. Found: C, 54.10; H, 5.10. ^1H NMR ($CDCl_3$): δ 7.50−7.40 (m, 4H, ArH), 7.32−7.23 (m, 6H, ArH), 5.44 (m, 4H, CpH), 5.36 (t, 2H, CpH), 1.20 (s, 18H, CMe$_3$), 0.81 (s, 6H, SiMe). IR (ν_{CO}, cm^{-1}): 2000(s), 1943(s). The following are data for **10a**. ^1H NMR ($CDCl_3$): δ 7.56−7.48 (m, 2H, C_6H_5), 7.38−7.28 (m, 3H, C_6H_5), 5.50 (br s, 1H, CpH), 5.34 (m, 1H, CpH), 5.32 (m, 1H, CpH), 1.280 (s, 9H, CMe$_3$), 0.81 (s, 3H, SiMe). IR (ν_{CO}, cm^{-1}): 1999(s), 1948(s), 1940(s), 1913(m).

Reaction of 4 with $Ru_3(CO)_{12}$. Using a procedure similar to that described above, reaction of **4** (0.361 g, 1.41 mmol) with $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) gave **11** (0.052 g, 0.063 mmol) as colorless crystals in 9% yield. Mp: 245−247 °C dec. Anal. Calcd for $C_{38}H_{44}O_4Ru_2Si_2$: C, 55.45; H, 5.39. Found: C, 55.80; H, 5.10. ^1H NMR ($CDCl_3$): δ 7.08 (t, 4H, ArH), 6.98 (t, 2H, ArH), 6.69 (d, J = 7.02 Hz, 4H, ArH), 5.23 (t, 2H, CpH), 5.10 (t, 2H, CpH), 4.88 (t, 2H, CpH), 2.41 (d, J = 1.42 Hz, 4H, SiCH$_2$), 1.17 (s, 18H, CMe$_3$), 0.33 (s, 6H, SiMe). IR (ν_{CO}, cm^{-1}): 1997(s), 1940(s).

Reaction of 5 with $Ru_3(CO)_{12}$. Using a procedure similar to that described above, reaction of **5** (0.341 g, 1.41 mmol) with $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) gave **12** (0.082 g, 0.134 mmol, 19%) and **13** (0.012 g, 0.021 mmol, 3%) as yellow and orange crystals, respectively. The following are data for **12**. Mp: 130−132 °C dec. Anal. Calcd for $C_{22}H_{20}O_6Ru_2Si$: C, 43.27; H, 3.30. Found: C, 42.90; H, 3.05. ^1H NMR ($CDCl_3$): δ 7.70 (m, 2H, ArH), 7.37 (m, 3H, ArH), 2.24 (s, 3H, CpMe), 2.13 (s, 3H, CpMe), 1.95 (s, 3H, CpMe), 1.23 (s, 3H, CpMe), 0.81 (s, 3H, SiMe). IR (ν_{CO}, cm^{-1}): 2082(m), 2042(m), 2006(s), 1991(s), 1969(m), 1924(m). The following are data for **13**. Mp: 210−211 °C dec. Anal. Calcd for $C_{22}H_{26}O_4Ru_2$: C, 47.48; H, 4.71. Found: C, 46.93; H, 5.11. ^1H NMR ($CDCl_3$): δ 4.66 (s, 2H, CpH), 1.90 (s, 12H, CpMe), 1.85 (s, 12H, CpMe). IR (ν_{CO}, cm^{-1}): 1929(s), 1755(s).

Reaction of 6 with $Ru_3(CO)_{12}$. Using a procedure similar to that described above, reaction of **6** (0.361 g, 1.41 mmol) with $Ru_3(CO)_{12}$ (0.300 g, 0.469 mmol) only gave **13** (0.024 g, 0.042 mmol) in 6% yield.

Reaction of 2 with $Mo(CO)_6$. A solution of 0.500 g (1.89 mmol) of $Mo(CO)_6$ and 0.379 g (1.89 mmol) of **2** in 30 mL of xylene was refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was placed in an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed a red band, which gave 0.040 g (0.081 mmol, 9%) of the known complex **14**.[10] Mp: 215 °C dec. ^1H NMR ($CDCl_3$): δ 5.30 (s, 10H, CpH). IR (ν_{CO}, cm^{-1}): 1952(s), 1917(m), 1887(s).

Reaction of 4 with $Mo(CO)_6$. Using a procedure similar to that described above, reaction of **4** (0.484 g, 1.89 mmol) with $Mo(CO)_6$ (0.500 g, 1.89 mmol) gave **15** (0.050 g, 0.057 mmol, 6%) and **16** (0.065 g, 0.107 mmol, 12%) as colorless and red crystals, respectively. The following are data for **15**. Mp: 242 °C dec. Anal. Calcd for $C_{40}H_{44}Mo_2O_6Si_2$: C, 55.30; H, 5.10. Found: C, 55.78; H, 4.99. ^1H NMR ($CDCl_3$): δ 7.13 (t, 4H, ArH), 7.03 (t, 2H, ArH), 6.75 (d, J = 6.90 Hz, 4H, ArH), 5.55 (t, 2H, CpH), 5.38 (t, 2H, CpH), 4.53 (t, 2H, CpH), 2.48 (q, 4H, CH$_2$), 1.18 (s, 18H, CMe$_3$), 0.53 (s, 6H, SiMe). IR (ν_{CO}, cm^{-1}): 1992(s), 1922(s), 1889(s). The following are data for **16**. Mp: 155 °C dec. Anal. Calcd for $C_{24}H_{26}Mo_2O_6$: C, 47.86; H, 4.35. Found: C, 48.10; H, 4.80. ^1H NMR ($CDCl_3$): δ 5.27 (br s, 4H, CpH), 5.10 (br s, 4H, CpH), 1.25 (s, 18H, CMe$_3$). IR (ν_{CO}, cm^{-1}): 1940(s), 1893(s).

Reaction of 2 with $W(CO)_6$. A solution of 0.500 g (1.42 mmol) of $W(CO)_6$ and 0.285 g (1.42 mmol) of **2** in 30 mL of xylene was refluxed for 5 days. The solvent was removed under reduced pressure, and the residue was placed in an Al_2O_3 column. Elution with CH_2Cl_2/petroleum ether developed two bands. The first band (red) gave 0.035 g (0.053 mmol, 9%) of the known complex **19**.[11] The second band (colorless) gave 0.045 g of **18** (0.048 mmol, 7%) as colorless crystals. The following are data for **18**. Mp: 270 °C dec. Anal. Calcd for $C_{32}H_{28}W_2O_6Si_2$: C,41.22; H, 3.03. Found: C, 41.40; H, 3.15. ^1H NMR ($CDCl_3$): δ 7.11 (t, 4H, ArH), 7.02 (t, 2H, ArH), 6.73 (d, J = 7.09 Hz, 4H, ArH), 5.77 (d, J = 1.68 Hz, 2H, CpH), 5.53 (br s, 4H, CpH), 4.54 (d, J = 1.68 Hz, 2H, CpH), 2.52 (q, 4H, CH$_2$), 0.54 (s, 6H, SiMe). IR (ν_{CO}, cm^{-1}): 2000(s), 1925(s), 1883(s). The following are data for **19**.[11] Mp: 238−240 °C.

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(10) Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85.

(11) (a) Abrahamson, H. B.; Heeg, M. J. *Inorg. Chem.* **1984**, *23*, 2281. (b) Verdonck, L.; Bossuyt, A. R.; Verpoort, P. F.; Geeraert, J.; Van de Vondel, D.; Van der Kelen, G. P. *J. Mol. Catal.* **1992**, *76*, 319. (c) Aime, S.; Cordero, L.; Gobetto, R.; Szalontai, G. *Spectrochim. Acta* **1993**, *49A*, 1307.

Table 2. Crystal Data and Summary of X-ray Data Collection for 18 and 20

	18	**20**
empirical formula	$C_{32}H_{28}W_2O_6Si_2$	$C_{40}H_{44}W_2O_6Si_2$
fw	932.42	1044.63
T, K	294(2)	294(2)
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)
cryst syst	monoclinic	triclinic
space group	$P2(1)/c$	$P\bar{1}$
a, Å	11.111(3)	9.7235(19)
b, Å	13.783(3)	10.012(2)
c, Å	11.075(3)	10.540(2)
α, deg	90	80.436(3)
β, deg	107.598(4)	86.223(3)
γ, deg	90	74.183(3)
V, Å^3	1616.6(6)	973.3(3)
Z	2	1
D_{calcd}, g·cm^{-3}	1.915	1.782
μ, mm^{-1}	7.225	6.011
F(000)	888	508
cryst size, mm	0.22 × 0.20 × 0.18	0.28 × 0.24 × 0.20
θ range, deg	2.43−26.36	1.96−25.01
no. of reflns collected	8850	4970
no. of independent reflns/R_{int}	3280/0.0295	3399/0.0243
no. of params	216	230
GOF on F^2	1.012	1.041
R1, wR2 [$I > 2\sigma(I)$]	0.0226, 0.0436	0.0312, 0.0721
R1, wR2 (all data)	0.0388, 0.0481	0.0382, 0.0756

^{1}H NMR ($CDCl_3$): δ 5.38 (s, 10H, CpH). IR (ν_{CO}, cm^{-1}): 1948(s), 1910(m), 1875(s).

Reaction of 4 with $W(CO)_6$. Using a procedure similar to that described above, reaction of **4** (0.364 g, 1.42 mmol) with $W(CO)_6$ (0.500 g, 1.42 mmol) gave **20** (0.030 g, 0.029 mmol, 4%) and **21** (0.040 g, 0.051 mmol, 7%) as colorless and red crystals, respectively. The following are data for **20**. Mp: 275 °C dec. Anal. Calcd for $C_{40}H_{44}W_2O_6Si_2$: C,45.99; H, 4.25. Found: C, 46.47; H, 4.58. ^{1}H NMR ($CDCl_3$): δ 7.13 (t, 4H, ArH), 7.03 (t, 2H, ArH), 6.77 (d, J = 6.90 Hz, 4H, ArH), 5.66 (t, 2H, CpH), 5.47 (t, 2H, CpH), 4.53 (t, 2H, CpH), 2.50 (q, 4H, CH_2), 1.19 (s, 18H, CMe_3), 0.55 (s, 6H, SiMe). IR (ν_{CO}, cm^{-1}): 1992(s), 1919(s), 1887(s). The following are data for **21**. Mp: 194 °C dec. Anal. Calcd for $C_{24}H_{26}W_2O_6$: C, 37.04; H, 3.37. Found: C, 37.11; H, 3.57. ^{1}H NMR ($CDCl_3$): δ 5.71 (t, 4H, CpH), 5.40 (t, 4H, CpH), 1.31 (s, 18H, CMe_3). IR (ν_{CO}, cm^{-1}): 1935(s), 1885(s).

Reaction of 6 with $Mo(CO)_6$. Using a procedure similar to that described above, reaction of **6** (0.484 g, 1.89 mmol) with $Mo(CO)_6$ (0.500 g, 1.89 mmol) only gave the desilylation complex **17** (0.040 g, 0.066 mmol, 7%) as red crystals. Mp: 159 °C dec. Anal. Calcd for $C_{24}H_{26}Mo_2O_6$: C,47.86; H, 4.35. Found: C, 48.31; H, 4.85. ^{1}H NMR ($CDCl_3$): δ 4.89 (s, 2H, CpH), 2.01 (s, 12H, CpMe), 1.94 (s, 12H, CpMe). IR (ν_{CO}, cm^{-1}): 1920(s), 1889(s).

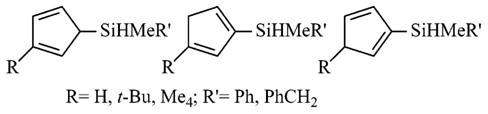
Reaction of 6 with $W(CO)_6$. Using a procedure similar to that described above, reaction of **6** (0.364 g, 1.42 mmol) with $W(CO)_6$ (0.500 g, 1.42 mmol) only gave the desilylation complex **22** (0.050 g, 0.064 mmol, 9%) as red crystals. Mp: 205 °C dec. Anal. Calcd for $C_{24}H_{26}W_2O_6$: C, 37.05; H, 3.37. Found: C, 37.43; H, 3.40. ^{1}H NMR ($CDCl_3$): δ 5.26 (s, 2H, CpH), 2.06 (s, 12H, CpMe), 2.03 (s, 12H, CpMe). IR (ν_{CO}, cm^{-1}): 1920(s), 1882(s).

Crystallographic Studies. Single crystals of complexes **7**, **9**, **12**, **13**, **15**, **18**, and **20** 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 (ω−2θ 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 SHELXL-97 program system. The crystal data and summary of X-ray data collection are presented in Tables 1 and 2. Selected bond lengths and angles are listed in Table 3.

Table 3. Selected Bond Distances (Å) and Angles (deg)

Compound **7**			
Ru(1)−Si(1)	2.4001(11)	Ru(1)−C(3)	2.261(4)
C(3)−Si(1A)	1.907(4)	Si(1)−C(9)	1.895(4)
Si(1)−C(8)	1.882(4)		
C(3)−Ru(1)−Si(1)	100.48(9)	C(3A)−Si(1)−Ru(1)	122.43(11)
Si(1A)−C(3)−Ru(1)	128.76(17)		
Compound **9**			
Ru(1)−Ru(2)	2.8875(8)	Ru(1)−Si(1)	2.4178(18)
Ru(2)−Si(2)	2.4195(17)	Ru(1)−C(28)	2.475(5)
Ru(1)−C(29)	2.477(6)	Ru(2)−C(15)	2.493(6)
Ru(2)−C(16)	2.471(5)	Si(1)−C(15)	1.894(6)
Si(1)−C(7)	1.911(6)	Si(1)−C(14)	1.879(6)
Si(2)−C(28)	1.869(6)	Si(2)−C(20)	1.899(6)
Si(2)−C(27)	1.870(6)	C(15)−C(16)	1.364(8)
C(28)−C(29)	1.385(8)		
C(28)−Ru(1)−Ru(2)	81.22(14)	Si(2)−Ru(2)−Ru(1)	73.58(4)
C(28)−Si(2)−Ru(2)	108.93(18)	Si(2)−C(28)−Ru(1)	93.9(2)
C(28)−Ru(1)−C(29)	32.48(19)	Si(1)−Ru(1)−Ru(2)	74.22(5)
C(15)−Ru(2)−Ru(1)	81.33(14)	Si(1)−C(15)−Ru(2)	93.5(2)
C(15)−Si(1)−Ru(1)	108.75(19)	C(16)−Ru(2)−C(15)	31.89(19)
Compound **12**			
Ru(1)−Ru(2)	2.8628(9)	Ru(1)−C(13)	2.253(3)
Ru(2)−Si(1)	2.4834(11)	Si(1)−C(13)	1.897(3)
Si(1)−Ru(2)−Ru(1)	74.50(2)	C(13)−Ru(1)−Ru(2)	82.06(6)
C(13)−Si(1)−Ru(2)	100.55(8)	Si(1)−C(13)−Ru(1)	102.75(11)
Compound **15**			
Mo(1)−Si(1A)	2.6294(8)	Mo(1)−C(4)	2.342(2)
C(4)−Si(1)	1.890(2)	Si(1)−C(13)	1.882(3)
Si(1)−C(14)	1.907(3)		
C(4)−Mo(1)−Si(1A)	93.24(6)	C(4)−Si(1)−Mo(1A)	116.09(8)
Si(1)−C(4)−Mo(1)	131.64(12)		
Compound **18**			
W(1)−Si(1)	2.6252(12)	W(1)−C(4)	2.362(4)
C(4)−Si(1A)	1.895(4)	Si(1)−C(9)	1.877(5)
Si(1)−C(10)	1.900(4)		
C(4)−W(1)−Si(1)	93.67(10)	C(4A)−Si(1)−W(1)	114.80(14)
Si(1A)−C(4)−W(1)	133.0(2)		
Compound **20**			
W(1)−Si(1A)	2.6235(16)	W(1)−C(4)	2.331(5)
Si(1)−C(4)	1.903(6)	Si(1)−C(13)	1.883(6)
Si(1)−C(14)	1.908(6)		
C(4)−W(1)−Si(1A)	93.49(14)	C(4)−Si(1)−W(1A)	115.97(17)
Si(1)−C(4)−W(1)	131.1(3)		

Chart 1

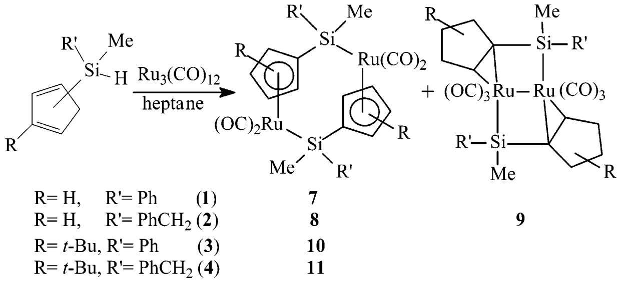


A **B** **C**

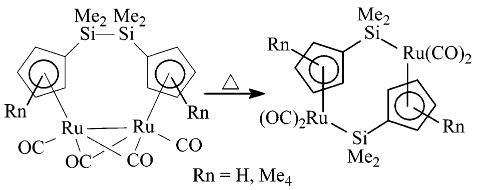
Results and Discussion

The SiH-functionalized cyclopentadienes **1**−**6** were prepared from the corresponding Cp′Li (Cp′ = C_5H_5, t-BuC_5H_4, C_5Me_4H) and RMeSiHCl (R = Ph, $PhCH_2$) in 26−94% yields. **1**, **2**, **5**, and **6** exist mainly as a mixture of two isomers (**A** and **B** in Chart 1) with ratios of about 2.9:1, 2.5:1, 12.5:1, and 2.3:1, respectively, while **3** and **4** exist mainly as a mixture of three isomers (**A**, **B**, and **C** in Chart 1) with ratios of about 2.5:1:0.5 and 2:1:0.7, respectively, based on the characteristic peaks of SiH (quadriplex or multiplet) and SiMe (doublet) protons in their ^{1}H NMR spectra (Supporting Information). All the EI mass spectra of **1**−**6** show the molecular ion peaks; among them the molecular ion peak of **5** appears as the basic peak. However, no satisfied elemental analysis for **1**−**6** was obtained. This is probably due to the fact that the SiH-containing compounds **1**−**6** cannot be combusted completely, which leads to the formation of SiC and makes the found values of carbon much lower than the calculated values.

Scheme 1



Scheme 2



Thermal treatment of CpSiHMePh (**1**) with $Ru_3(CO)_{12}$ in refluxing heptane afforded the cyclic dinuclear complex *trans*-$[(PhMeSi)(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ (**7**) in 10% yield (Scheme 1). The Si−H bond was activated, and two Si−Ru bonds were formed in the molecule. This kind of complex was reported to be prepared by the thermal rearrangement reactions of the corresponding disilyl-bridged biscyclopentadienyltetracarbonyldiruthenium complexes in very low yields (2−6%) (Scheme 2).[12] Therefore, this work provided a new synthetic route for this kind of complex, especially with different substituents at the silicon atom. The ^{1}H NMR spectrum of **7** shows three groups of peaks for the Cp protons at 5.62, 5.57, and 5.39 ppm and one singlet for the SiMe protons at 0.83 ppm, indicating the existence of only one isomer. Single-crystal X-ray diffraction analysis showed that it is a *trans* isomer (Figure 1). The IR spectrum of **7** shows two terminal carbonyl absorptions at 1999 and 1946 cm^{-1}.

Similarly, reactions of (t-BuC_5H_4)SiHMePh (**3**) and (t-BuC_5H_4)SiHMe(CH_2Ph) (**4**) with $Ru_3(CO)_{12}$ also gave the cyclic dinuclear complexes *trans*-$[(PhMeSi)(\eta^5\text{-}t\text{-}BuC_5H_3)Ru(CO)_2]_2$ (**10**) and *trans*-$[(PhCH_2)MeSi(\eta^5\text{-}t\text{-}BuC_5H_3)Ru(CO)_2]_2$ (**11**) both in 9% yield, but the reaction of $CpSiHMe(CH_2Ph)$ (**2**) with $Ru_3(CO)_{12}$ afforded a yellow complex, $[(\eta^2\text{-}C_5H_7)SiMe(CH_2Ph)Ru(CO)_3]_2$ (**9**) (11%), in addition to the analogous cyclic dinuclear complex *trans*-$[(PhCH_2)MeSi(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ (**8**) (9%) (Scheme 1). The ^{1}H NMR spectrum of **9** (Supporting Information) shows at least nine groups of peaks at 6.14−4.76 ppm for the vinyl protons and ten groups of peaks at 0.60−0.07 ppm for the SiMe protons, indicating that **9** exists as a mixture of several isomers. However, the isomers cannot be separated by TLC due to the almost equal R_f values or by recrystallization. Single-crystal X-ray analysis revealed the structure of one isomer, in which the cyclopentadienyl rings were partially hydrogenated (Figure 2). In the ^{1}H NMR spectrum of **9**, signals for the vinyl protons appeared at 6.14−4.76 ppm. Their shifts were significantly downfield from those of the bridged vinylsilyl ligands in $[Cp^*Ru(\mu\text{-}H)]_2[\mu\text{-}\eta^2\text{:}\eta^2\text{-}HSiMe_2\text{-}(CH{=}CH_2)$ (**23**) (4.50−3.72 ppm)[15a] and $Cp^*{}_2Ru_2(SiPh_2CH{=}CH_2)(\mu\text{-}\eta^2\text{-}HSiPh_2)(\mu\text{-}H)(H)$ (**24**) (1.89−1.44 ppm),[15b] suggesting the reduced back-donation from the ruthenium center and the weakened coordination of the C═C bond to the ruthenium center. This is further supported by the single-crystal X-ray diffraction analysis. The IR spectrum of **9** shows four terminal carbonyl absorptions at 2018, 1987, 1965, and 1952 cm^{-1}. The ^{1}H NMR and IR spectra of complexes **8**, **10**, and **11** are similar to those of **7** indicated similar structures.

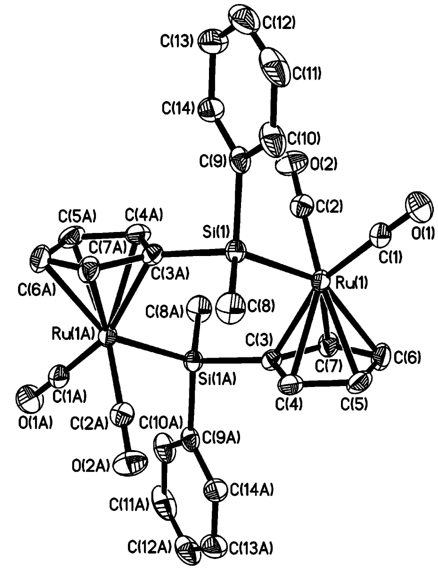


Figure 1. ORTEP diagram of **7**. Thermal ellipsoids are shown at the 30% level.

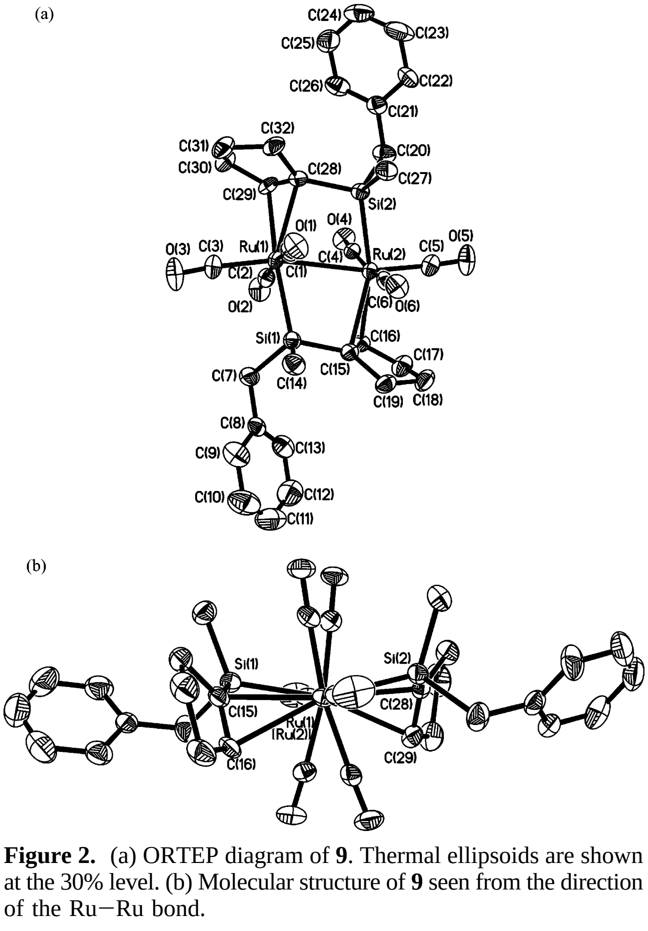


Figure 2. (a) ORTEP diagram of **9**. Thermal ellipsoids are shown at the 30% level. (b) Molecular structure of **9** seen from the direction of the Ru−Ru bond.

The yields of all the products are low. The main reasons are the formation of the polymeric products and the decomposition of $Ru_3(CO)_{12}$ (the unreacted ligand precursors were monitored

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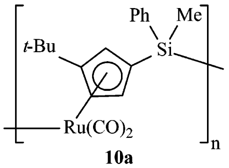
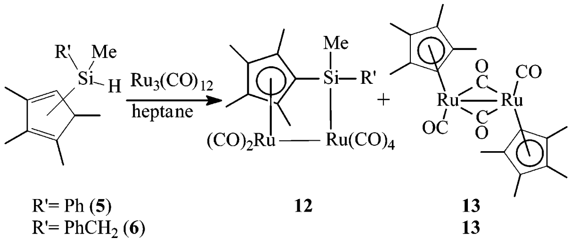
[12] (a) Zhang, Y.; Xu, S.; Zhou, X. *Organometallics* **1997**, *16*, 6017. (b) Zhang, Y.; Wang, B.; Xu, S.; Zhou, X.; Sun, J. *J. Organomet. Chem.* **1999**, *584*, 356. (c) Zhang, Y.; Wang, B.; Xu, S.; Zhou, X. *Organometallics* **2001**, *20*, 3829. (d) Zhang, Y.; Wang, B.; Xu, S.; Zhou, X. *Chin. J. Chem.* **2002**, *20*, 1388. (e) Chen, D.; Mu, B.; Xu, S.; Wang, B. *J. Organomet. Chem.* **2006**, *691*, 3823.

Chart 2



10a

Scheme 3



at the end of the reaction). For the reaction of **3** with $Ru_3(CO)_{12}$, the polymeric product **10a** (Chart 2) was obtained as a white solid. It is insoluble in hexane and slightly soluble in $CHCl_3$ and cannot be developed by Al_2O_3 column. For other reactions, the polymeric products were more insoluble and filtered off by an Al_2O_3 column. The ^1H NMR spectrum of **10a** shows two groups of multiplets at 7.56−7.48 (2H) and 7.38−7.28 (3H) ppm for the phenyl protons, a broad singlet at 5.50 (1H) and two multiplets at 5.34 (1H) and 5.32 (1H) ppm for the Cp protons, a singlet at 1.28 (9H) for the *t*-butyl protons, and a singlet at 0.81 (3H) ppm for the SiMe protons (Supporting Information). Its IR spectrum shows four terminal carbonyl absorptions at 1999(s), 1948(s), 1940(s), and 1913(m) cm^{-1}. Its ^1H NMR and IR data are similar to those of **10** but with a little difference. The mass spectrum (ESI) shows complicated peaks up to 2000 (the limit of the instrument), indicating the polymeric structure.

When $(C_5Me_4H)SiHMePh$ (**5**) reacted with $Ru_3(CO)_{12}$, a yellow complex, $[(PhMeSi)(\eta^5\text{-}C_5Me_4)]Ru_2(CO)_6$ (**12**), was obtained, in addition to the desilylation product $[(\eta^5\text{-}C_5Me_4H)Ru(CO)]_2(\mu\text{-}CO)_2$ (**13**) (Scheme 3). The ^1H NMR spectrum of **12** showed two groups of multiplets for the phenyl protons, four singlets for CpMe protons at 2.24, 2.13, 1.95, and 1.23 ppm, and a singlet for the SiMe protons at 0.81 ppm. The IR spectrum of **12** showed six terminal carbonyl absorptions at 2082, 2042, 2006, 1991, 1969, and 1924 cm^{-1}. Single-crystal X-ray analysis revealed that it is a (tetramethylcyclopentadienyl)diruthenium complex with a Si−Ru bond (Figure 3). However, reaction of $(C_5Me_4H)SiHMe(CH_2Ph)$ (**6**) with $Ru_3(CO)_{12}$ only gave the desilylation product **13**.

Considering the similarity of iron with ruthenium, reactions of **1**−**6** with $Fe(CO)_5$ and $Fe_2(CO)_9$ were also studied. However, no product was monitored by TLC. This may be attributed to the lower activity of iron carbonyl compared to $Ru_3(CO)_{12}$.[13]

When **4** reacted with $Mo(CO)_6$ in refluxing xylene, the analogous cyclic complex *trans*-$[(PhCH_2MeSi)(\eta^5\text{-}t\text{-}BuC_5H_3)Mo(CO)_3]_2$ (**15**) (6%) was also given, besides the desilylation product $[(\eta^5\text{-}t\text{-}BuC_5H_4)Mo(CO)_3]_2$ (**16**) (12%) (Scheme 4), while reaction of **2** or $(C_5Me_4H)SiHMe(CH_2Ph)$ with $Mo(CO)_6$ only gave the desilylation product $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ (**14**) (9%) or $[(\eta^5\text{-}C_5Me_4H)Mo(CO)_3]_2$ (**17**) (7%). Similarly, the cyclic dinuclear complexes *trans*-$[(PhCH_2MeSi)(\eta^5\text{-}C_5H_4)W(CO)_3]_2$ (**18**) (7%) and *trans*-$[(PhCH_2MeSi)(t\text{-}BuC_5H_3)W(CO)_3]_2$ (**20**) (4%) were also obtained by reactions of **2** and **4** with $W(CO)_6$, in addition to the desilylation complexes $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ (**19**) (9%) and $[(\eta^5\text{-}t\text{-}BuC_5H_4)Mo(CO)_3]_2$ (**21**) (7%) (Scheme 4), but reaction of $(C_5Me_4H)SiHMe(CH_2Ph)$ with $W(CO)_6$ only gave the desilylation product $[(\eta^5\text{-}C_5Me_4H)W(CO)_3]_2$ (**22**) (9%).

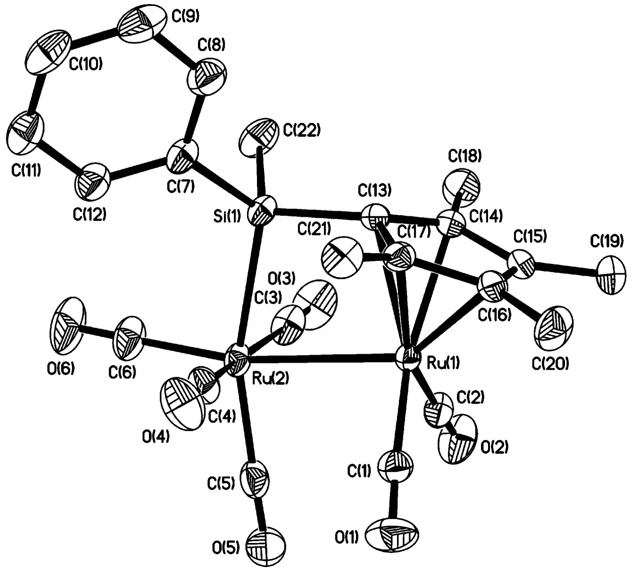


Figure 3. ORTEP diagram of **12**. Thermal ellipsoids are shown at the 30% level.

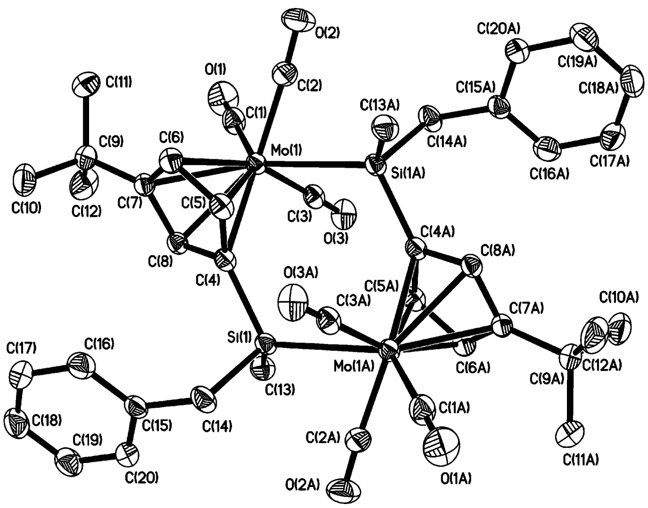
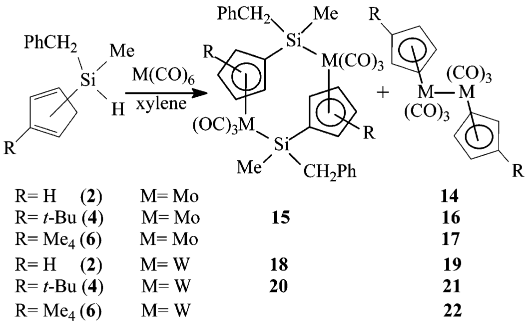


Figure 4. ORTEP diagram of **15**. Thermal ellipsoids are shown at the 30% level.

Scheme 4



The molecular structures of **7**, **9**, **12**, **13**, **15**, **18**, and **20** were determined by X-ray diffraction analysis (Figures 1−5 and Supporting Information). The molecule of **7** consists of two $[PhMeSi(\eta^5\text{-}C_5H_4)Ru(CO)_2]$ moieties linked to each other by two Si−Ru bonds. Like many analogues,[12] **7** has C_i symmetry.

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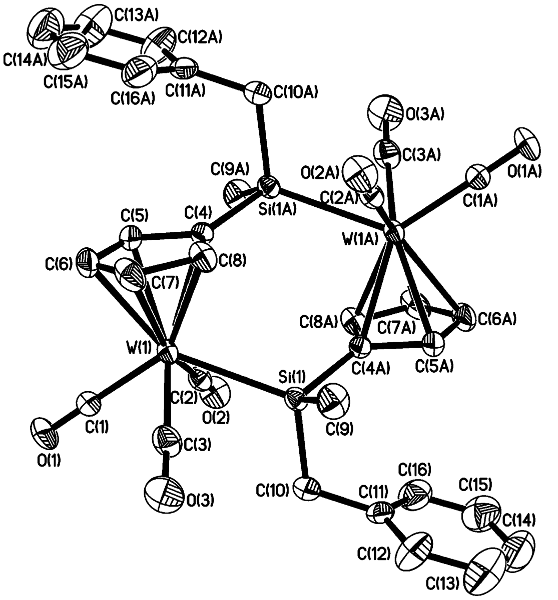

Figure 5. ORTEP diagram of **18**. Thermal ellipsoids are shown at the 30% level.

The six-membered ring Ru(1)−Si(1)−C(3A)−Ru(1A)−Si(1A)−C(3), constituting its molecular framework, adopts precisely a standard chair conformation. The Ru−Si distance [2.4001(11) Å] is slightly shorter than that of the analogues [$Me_2Si(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ [2.4074(9) Å][12a] and [$Me_2Si(\eta^5\text{-}C_5Me_4)Ru(CO)_2]_2$ [2.424(1) Å][12b] and much shorter than those in acyclic analogues [2.452(3)−2.507(8) Å].[14]

The structure of **9** (Figure 2a) shows that a double bond of the cyclopentadienyl ring was hydrogenated. The two Ru atoms are bridged by two vinylsilyl ligands, and the Ru−Ru distance is 2.8875(8) Å. The Ru(1)−Si(1) and Ru(2)−Si(2) distances [2.4178(18) and 2.4195(17) Å] are comparable with those in the bridged silyl complexes **23** and **24** [2.421(2)−2.384(2) Å].[15a,b] The C(15)−C(16) and C(28)−C(29) distances [1.364(8) and 1.385(8) Å] are in the range of normal C═C double bonds, but shorter than those in the bridged silyl complexes **23** and **24** [1.406(9)−1.39(1) Å][15a,b] and in the coordinated ethylene in [$Cp^*Ru(\mu\text{-}\eta^2\text{-}CH{=}CH_2)]_2(\eta^2\text{-}CH_2{=}CH_2)$ [1.389(13) Å] and $Cp^*_2Ru_2(\mu\text{-}CMe{=}CHCH{=}CMe)(\eta^2\text{-}CH_2{=}CH_2)$ [1.389(13) Å].[15c] The Ru−C bond lengths [Ru(2)−C(15), Ru(2)−C(16), Ru(1)−C(28), and Ru(1)−C(29)], varying from 2.471(5) to 2.493(6) Å, are much longer than the corresponding Ru−C distances of the bridged silyl complexes **23** [2.218(6) and 2.228(6) Å][15a] and **24** [2.243(7) and 2.270(7) Å].[15b] These results and the NMR data for the coordinated vinyl group strongly suggest that the π-coordination of the vinyl group in methylphenylcyclopentenylsilane to the Ru atom was considerably weakend. The structure of **9** has C_2 symmetry. The C_2 axis passes through the midpoint of Ru(1)−Ru(2) and perpendicular with it. The structure of **9** has a *cis* geometry with the two η^2-cyclopentene rings, and the substitution at the two silicon atoms is also of *cis* geometry. However, **9** should have three *cis* isomers [*cis*-η^2-cyclopentene rings, *cis* (two isomers) or *trans* (one isomer) substitution at the two silicon atoms] and three *trans* isomers [*trans*-η^2-cyclopentene rings, *cis* (one isomer) or *trans* (two isomers) substitution at the two silicon atoms]. This agrees with the ^1H NMR data of **9**, though only one isomer was determined by X-ray diffraction analysis.

The structure of complex **12** is similar to that of [$(Me_2Ge)(\eta^5\text{-}C_5Me_4)]Ru_2(CO)_6$, synthesized by the reaction of $C_5Me_4HMe_2GeGeMe_2C_5Me_4H$ with $Ru_3(CO)_{12}$.[12c] The Ru(2)−Si(1) bond length is 2.4834(11) Å, much longer than those of **7** [2.4001(11) Å] and **9** [2.4178(18) and 2.4195(17) Å]. The Ru−Ru distance is 2.8628(9) Å, close to that of [$(Me_2Ge)(\eta^5\text{-}C_5Me_4)]Ru_2(CO)_6$] [2.861(1) Å][11c] and slightly longer than those found in $Ru_3(CO)_{12}$ [2.854(1) Å].[15] The four-membered ring Ru(1)−Ru(2)−Si(1)−C(13) is almost coplanar, and the plane is nearly perpendicular to the cyclopentadienyl plane (dihedral angle 86.9°).

The structure of **13** is a *trans* form and has C_i symmetry, similar to the cyclopentadienyl and pentamethylcyclopentadienyl analogues.[16,17] The two cyclopentadienyl ring planes are parallel. Two carbonyls are bridged, and two carbonyls are terminal. The Ru−Ru bond distance [2.7458(7) Å] is slightly longer than that in *trans*-[$\eta^5\text{-}CpRu(CO)(\mu\text{-}CO)]_2$ [2.735(2) Å][16] and comparable with the value in [$(\eta^5\text{-}C_5Me_5)Ru(CO)(\mu\text{-}CO)]_2$ [2.752(1) Å].[17]

Similar to that of **7**, the structures of **15**, **18**, and **20** also have C_i symmetry and consist of two [$(PhCH_2)MeSi(RC_5H_3)M(CO)_3$] moieties linked to each other by two Si−M bonds. The six-membered rings (two Si atoms, two metal atoms, and two bridgehead carbons), constituting their molecular frameworks, also adopt standard chair conformations. The Mo−Si distance [2.6294(8) Å] in **15** is close to those of [$\{Mo(\mu\text{-}\eta^2\text{-}HSiEt_2)(CO)_4\}_2$] [2.6152(6) and 2.7093(6) Å].[18] The W−Si distances [2.6252(12) Å for **18**, 2.6235(16) Å for **20**] are in the range of the tungsten−silyl bond distances (2.533−2.633 Å) in the structurally related silyltungsten complexes $Cp^*(CO)_2(L)WSiR_3$ (L = PR′$_3$, pyridine).[2d,3c,l,o,19] This is the first report for this kind of cyclic dinuclear molybdenum and tungsten complex, although there are many examples for the iron and ruthenium analogues.[12,20]

Conclusions

Reactions of the SiH-functionalized cyclopentadienes with $Ru_3(CO)_{12}$, $Mo(CO)_6$, and $W(CO)_6$ were studied. A series of

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cyclic dinuclear metal complexes with one or two Si−M bonds were obtained via Si−H activation. A novel cyclopentenyl complex, $[(\eta^2\text{-}C_5H_7)SiMe(CH_2Ph)Ru(CO)_3]_2$ (**9**), bridged by a vinylsilyl ligand was also obtained and characterized.

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Supporting Information Available: X-ray structural information for complexes **7**, **9**, **12**, **13**, **15**, **18**, and **20**, ORTEP figures of **13** and **20**, and ^{1}H NMR spectra of **1**−**6**, **9**, and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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