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Synthesis and structures of cycloalkylidene-bridged mixed cyclopentadienyl-indenyl tetracarbonyl diruthenium complexes

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A series of cycloalkylidene-bridged mixed cyclopentadienyl-indenyl tetracarbonyl diruthenium complexes (η^5:η^5-$RC_5H_3CR'_2C_9H_6$)$Ru_2(CO)_2(\mu\text{-}CO)_2$ [R = H, R′, R′ = Me_2 (1), $(CH_2)_4$ (2), $(CH_2)_5$ (3), $(CH_2)_6$ (4); R = ^{t}Bu, R′, R′ = Me_2 (5), $(CH_2)_4$ (6), $(CH_2)_5$ (7)] have been synthesized by reactions of the corresponding ligands $RC_5H_4CR'_2C_9H_7$ with $Ru_3(CO)_{12}$ in refluxing xylene. The molecular structures of 2, 6 and 7 have been determined by X-ray diffraction. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: cycloalkylidene-bridge; cyclopentadienyl; indenyl; M–M bond; ruthenium carbonyl

INTRODUCTION

Dinuclear metal complexes are often postulated as simple models with which to study the interactions of organic molecules with metal surfaces.[1–3] Cyclopentadienyl metal carbonyl dimers were reported to catalyze the allylic amination of olefins[4,5] and indolization of alkynes,[6,7] and the living polymerization of vinyl monomer.[8–10] All of these applications are on the basis of the reactivities of the metal–metal bonds.

The bridged bis(cyclopentadienyl) ligands 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.[11–16] Among the group 6 and 8 metal carbonyl dimers with bridged bis(cyclopentadienyl) ligands, diruthenium complexes received attention for their special reactivity.[17–26] 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.[17,18] For the Me_2Si-bridged bis(tetramethylcyclopentadienyl) tetracarbonyl diruthenium complex $(Me_2Si)[C_5Me_4Ru(CO)]_2(\mu\text{-}CO)_2$, a photochemical albeit thermally irreversible rearrangement by Si-C bond cleavage was also observed.[19] 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.[20,21] The tetramethyldisilylene- or digermylene-bridged bis(cyclopentadienyl) tetracarbonyl diruthenium complexes $(Me_2EEMe_2)[Cp'Ru(CO)]_2(\mu\text{-}CO)_2$ (E = Si, Ge; Cp′ = C_5H_4, C_5Me_4) can thermally rearrange with metathesis between the E–E and Ru–Ru bonds.[23–25]

As a part of systematic study of the structure–reactivity relationship of the bridged bis(cyclopentadienyl) metal carbonyl dimers, especially the effect of the bridge on the metal–metal bond length and its reactivity,[23–35] further applications of these complexes are being developed. In this work a series of cycloalkylidene-bridged mixed cyclopentadienyl-indenyl tetracarbonyl diruthenium complexes were synthesized, and three of their crystal structures were determined by X-ray diffraction analysis.

EXPERIMENTAL

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

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recorded on a Bruker AV 300 or Varian 400 instrument, while IR spectra were recorded as KBr disks on a Nicolet 560 ESP FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The ligands $C_5H_5CR_2C_9H_7$ [R, R = Me_2, $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$] and $^tBuC_5H_4CR_2C_9H_7$ [R, R = Me_2, $(CH_2)_4$, $(CH_2)_5$] were synthesized according to the literature.[36–38]

Synthesis of (η^5:η^5-$C_5H_4CMe_2C_9H_6$)$Ru_2(CO)_2(\mu\text{-}CO)_2$ (1)

A solution of $C_5H_5CMe_2C_9H_7$ (0.156 g, 0.7 mmol) and $Ru_3(CO)_{12}$ (0.3 g, 0.47 mmol) in 30 ml of xylene was refluxed for 12 h. After removal of solvent the residue was chromatographed on an alumina column using petroleum ether–CH_2Cl_2 as eluent. The orange band afforded 96 mg (26%) of **1** as red crystals; m.p. 163 °C (dec.). ^1H NMR (300 M Hz, $CDCl_3$): δ 7.55 (d, 1H, $J = 8.37$ Hz, C_9H_6), 7.49 (d, 1H, $J = 9.32$ Hz, C_9H_6), 7.41 (t, 1H, C_9H_6), 7.24 (m, 1H, C_9H_6), 6.20 (d, 1H, $J = 3.00$ Hz, C_9H_6), 5.65 (m, 1H, C_5H_4), 5.60 (d, 1H, J = 3.00 Hz, C_9H_6), 5.52 (m, 1H, C_5H_4), 5.46 (m, 1H, C_5H_4), 5.37 (m, 1H, C_5H_4), 1.83 (s, 3H, CH_3), 1.69 (s, 3H, CH_3). IR (ν_{CO}, cm^{-1}): 1982 (s), 1945 (s), 1824 (m), 1773 (s). Elemental analysis (%). Found: C, 47.10; H, 3.25. Calcd for $C_{21}H_{16}O_4Ru_2$: C, 47.19; H, 3.02.

Synthesis of [η^5:η^5-$C_5H_4C(CH_2)_4C_9H_6$]$Ru_2(CO)_2(\mu\text{-}CO)_2$ (2)

Using a procedure similar to that described above, reaction of $C_5H_5C(CH_2)_4C_9H_7$ with $Ru_3(CO)_{12}$ gave complex **2** as red crystals in 46% yield; m.p. 206–207 °C. ^1H NMR (300 M Hz, $CDCl_3$): δ 7.55 (d, 1H, $J = 8.38$ Hz, C_9H_6), 7.41 (m, 2H, C_9H_6), 7.22 (m, 1H, C_9H_6), 6.21 (d, 1H, $J = 2.95$ Hz, C_9H_6), 5.67 (m, 1H, C_5H_4), 5.56 (m, 1H, C_5H_4), 5.44 (d, 1H, $J = 2.96$ Hz, C_9H_6), 5.39 (m, 1H, C_5H_4), 5.29 (m, 1H, C_5H_4), 2.52 [m, 1H, $C(CH_2)_4$], 2.30 (m, 1H, $C(CH_2)_4$), 2.17 (m, 1H, $C(CH_2)_4$), 2.05 (m, 1H, $C(CH_2)_4$), 1.78–1.49 [m, 4H, $C(CH_2)_4$]. IR (ν_{CO}, cm^{-1}): 1977 (s), 1956 (s), 1809 (m), 1775 (s). Elemental analysis (%). Found: C, 48.99; H, 3.16. Calcd for $C_{23}H_{18}O_4Ru_2$: C, 49.28; H, 3.24.

Synthesis of [η^5:η^5-$C_5H_4C(CH_2)_5C_9H_6$]$Ru_2(CO)_2(\mu\text{-}CO)_2$ (3)

Using a procedure similar to that described above, reaction of $C_5H_5C(CH_2)_5C_9H_7$ with $Ru_3(CO)_{12}$ gave complex **3** as red crystals in 32% yield; m.p. 263 °C (dec.). ^1H NMR (400M Hz, $CDCl_3$): δ 7.55 (d, 1H, $J = 8.35$ Hz, C_9H_6), 7.42 (d, 1H, $J = 8.70$ Hz, C_9H_6), 7.35 (t, 1H, C_9H_6), 7.21 (t, 1H, C_9H_6), 6.25 (d, 1H, $J = 2.92$ Hz, C_9H_6), 5.68 (s, 1H, C_5H_4), 5.56 (s, 1H, C_5H_4), 5.43 (d, 1H, $J = 2.92$ Hz, C_9H_6), 5.34 (s, 1H, C_5H_4), 5.22 (s, 1H, C_5H_4), 2.27 (m, 2H, $C(CH_2)_5$), 2.00 (m, 2H, $C(CH_2)_5$), 1.60 (m, 2H, $C(CH_2)_5$), 1.47–1.16 [m, 4H, $C(CH_2)_5$]. IR (ν_{CO}, cm^{-1}): 1977 (s), 1942 (s), 1811 (s), 1774 (s). Elemental analysis (%). Found: C, 50.43; H, 3.70. Calcd for $C_{33}H_{34}O_4Ru_2$: C, 50.17; H, 3.51.

Synthesis of [η^5:η^5-$C_5H_4C(CH_2)_6C_9H_6$]$Ru_2(CO)_2(\mu\text{-}CO)_2$ (4)

Using a procedure similar to that described above, reaction of $C_5H_5C(CH_2)_6C_9H_7$ with $Ru_3(CO)_{12}$ gave complex **4** as red crystals in 32% yield; m.p. 250 °C (dec.). ^1H NMR (300 M Hz, $CDCl_3$): δ 7.41 (d, 1H, $J = 8.45$ Hz, C_9H_6), 7.31 (t, 1H, C_9H_6), 7.24 (d, 1H, $J = 8.33$ Hz, C_9H_6), 7.12 (t, 1H, C_9H_6), 5.95 (d, 1H, $J = 3.00$ Hz, C_9H_6), 5.39 (d, 1H, $J = 9.08$ Hz, C_5H_4), 5.34 (d, 1H, $J = 3.00$ Hz, C_9H_6), 4.88 (m, 1H, C_5H_4), 4.75 (m, 1H, C_5H_4), 4.71 (m, 1H, C_5H_4), 3.24–3.13 [m, 1H, $C(CH_2)_6$], 2.57–2.37 [m, 2H, $C(CH_2)_6$], 2.31–2.07 [m, 4H, $C(CH_2)_6$], 1.83–1.28 [m, 5H, $C(CH_2)_6$]. IR (ν_{CO}, cm^{-1}): 1991 (s), 1952 (s), 1811 (m), 1771 (s). Elemental analysis (%). Found: C, 51.10; H, 3.49. Calcd for $C_{34}H_{36}O_4Ru_2$: C, 51.02; H, 3.77.

Synthesis of (η^5:η^5-$^tBuC_5H_3CMe_2C_9H_6$)$Ru_2(CO)_2(\mu\text{-}CO)_2$ (5)

Using a procedure similar to that described above, reaction of $^tBuC_5H_5CMe_2C_9H_7$ with $Ru_3(CO)_{12}$ gave complex **5** as red crystals in 32% yield; m.p. 140 °C (dec.). ^1H NMR (300 M Hz, $CDCl_3$): δ 7.55 (d, 1H, $J = 8.34$ Hz, C_9H_6), 7.47–7.42 (m, 2H, C_9H_6), 7.24–7.21 (m, 1H, C_9H_6), 6.20 (d, 1H, $J = 2.86$ Hz, C_9H_6), 5.63–5.57 (m, 2H, C_9H_6 and C_5H_3), 5.45, 5.35, 5.28 (m, m, m, 2H, C_5H_3), 1.82, 1.81 [s, s, 3H, $C(CH_3)_2$], 1.66 [s, 3H, $C(CH_3)_2$], 1.32, 1.31 [s, s, 9H, $C(CH_3)_3$] (two isomers with ratio of about 1.6 : 1). IR (ν_{CO}, cm^{-1}): 1977 (s), 1942 (s), 1810 (w), 1778 (s). Elemental analysis (%). Found: C, 50.72; H, 4.17. Calcd for $C_{25}H_{24}O_4Ru_2$: C, 50.84; H, 4.10.

Synthesis of [η^5:η^5-$^tBuC_5H_3C(CH_2)_4C_9H_6$]$Ru_2(CO)_2(\mu\text{-}CO)_2$ (6)

Using a procedure similar to that described above, reaction of $^tBuC_5H_4C(CH_2)_4C_9H_7$ with $Ru_3(CO)_{12}$ gave complex **6** as red crystals in 46% yield; m.p. 173–174 °C. ^1H NMR (300 M Hz, $CDCl_3$): δ 7.56 (d, 1H, $J = 8.40$ Hz, C_9H_6), 7.45–7.33 (m, 2H, C_9H_6), 7.22 (m, 1H, C_9H_6), 6.21 (d, 1H, $J = 2.95$ Hz, C_9H_6), 5.41 (m, 1H, C_9H_6), 5.62 (q), 5.49 (q), 5.26 (t) 5.22–5.15 (m), (total 3H, C_5H_3), 2.54–2.42 [m, 1H, $C(CH_2)_4$], 2.36–2.24 [m, 1H, $C(CH_2)_4$], 2.24–2.12 [m, 1H, $C(CH_2)_4$], 2.10–1.97 [m, 1H, $C(CH_2)_4$], 1.76–1.47 [m, 4H, $C(CH_2)_4$], 1.32, 1.31 [s, s, 9H, $C(CH_3)_3$] (two isomers with ratio of 1 : 1). IR (ν_{CO}, cm^{-1}): 1983 (s), 1940 (s), 1817 (m), 1775 (s). Elemental analysis (%). Found: C, 52.75; H, 3.89. Calcd for $C_{27}H_{26}O_4Ru_2$: C, 52.59; H, 4.25.

Synthesis of [η^5:η^5-$^tBuC_5H_3C(CH_2)_5C_9H_6$]$Ru_2(CO)_2(\mu\text{-}CO)_2$ (7)

Using a procedure similar to that described above, reaction of $^tBuC_5H_4C(CH_2)_5C_9H_7$ with $Ru_3(CO)_{12}$ gave complex **7** as red crystals in 36% yield; m.p. 208–209 °C. ^1H NMR (300 M Hz, $CDCl_3$): δ 7.56 (d, 1H, $J = 8.34$ Hz, C_9H_6), 7.39 (d, 2H, C_9H_6), 7.21 (m, 1H, C_9H_6), 6.26 (d, 1H, $J = 2.98$ Hz, C_9H_6), 5.65 (m, 1H, C_5H_3), 5.42 (d, 1H, $J = 2.98$ Hz, C_9H_6), 5.23 (m, 1H, C_5H_3), 5.11 (m, 1H, C_5H_3), 2.38–2.25 [m, 1H, $C(CH_2)_5$], 2.24–2.12 [m, 1H, $C(CH_2)_5$], 2.09–1.90 (m, 2H, $C(CH_2)_5$), 1.67–1.49 [m, 4H, $C(CH_2)_5$], 1.46–1.35 [m, 2H, $C(CH_2)_5$], 1.32 [s, 9H, $C(CH_3)_3$].

IR (ν_{CO}, cm^{-1}): 1983 (s), 1944 (s), 1815 (m) 1780 (s). Elemental analysis (%). Found: C, 53.18; H, 4.25. Calcd for $C_{28}H_{28}O_4Ru_2$: C, 53.30; H, 4.47.

Crystal structure determinations

Crystals of complexes **2**, **6** and **7** suitable for X-ray diffraction were obtained from hexane–CH_2Cl_2 solution. Data collection was performed on a Bruker SMART 1000 CCD detector, using graphite-monochromated Mo Kα radiation ($\omega - 2\theta$ scans, $\lambda = 0.71073$ Å) at room temperature. Semiempirical absorption corrections were applied using the SADABS program.[39] The structures were solved by direct methods and refined by full-matrix least squares. All calculations were performed using the SHELXTL-97 program system. The crystal data and summary of X-ray data collection are presented in Table 1. Selected bond lengths and angles are listed in Tables 2–4. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 288 226–288 228.

RESULTS AND DISCUSSION

When ligands $RC_5H_4CR'_2C_9H_7$ reacted with $Ru_3(CO)_{12}$ under refluxing xylene for 12 h, the corresponding

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

Bond distances			
Ru(1)–Ru(2)	2.6746(4)	Ru(2)–C(2)	2.054(3)
Ru(1)–C(2)	2.019(3)	Ru(2)–C(3)	2.021(3)
Ru(1)–C(3)	2.057(3)	Ru(2)–C(19)	2.284(3)
Ru(1)–C(5)	2.296(3)	Ru(2)–C(20)	2.269(3)
Ru(1)–C(6)	2.262(3)	Ru(2)–C(21)	2.249(3)
Ru(1)–C(7)	2.215(3)	Ru(2)–C(22)	2.243(3)
Ru(1)–C(8)	2.328(3)	Ru(2)–C(23)	2.283(3)
Ru(1)–C(13)	2.394(3)	C(8)–C(9)	1.417(4)
C(5)–C(6)	1.424(4)	C(9)–C(10)	1.357(5)
C(5)–C(13)	1.457(4)	C(10)–C(11)	1.398(5)
C(6)–C(7)	1.398(4)	C(11)–C(12)	1.367(4)
C(7)–C(8)	1.446(4)	C(12)–C(13)	1.412(4)
C(8)–C(13)	1.440(4)	C(5)–C(14)	1.526(4)
C(14)–C(19)	1.527(4)	Ru(1)–CEN(1)[a]	1.951
Ru(2)–CEN(2)	1.916		
Bond angles			
C(5)–Ru(1)–Ru(2)	88.20(7)	C(19)–Ru(2)–Ru(1)	88.00(7)
Ru(1)–C(2)–Ru(2)	82.11(11)	Ru(2)–C(3)–Ru(1)	81.97(12)
C(14)–C(5)–Ru(1)	123.70(18)	C(5)–C(14)–C(19)	111.7(2)
C(14)–C(19)–Ru(2)	125.05(18)	PL(1)–PL(2)[b]	117.1

[a] CEN, centroid of the cyclopentadienyl ring.

[b] PL, plane of the cyclopentadienyl ring.

Table 1. Crystal data and summary of X-ray data collection for **2**, **6** and **7**

	2	**6**	**7**
Formula	$C_{23}H_{18}O_4Ru_2$	$C_{27}H_{26}O_4Ru_2$	$C_{28}H_{28}O_4Ru_2$
Formula weight	560.51	616.62	630.64
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*P*bca	$P2_1/c$	*P*-1
a (Å)	16.5815(15)	14.1682(17)	10.8270(14)
b (Å)	14.0971(13)	10.1714(12)	11.0239(14)
c (Å)	16.9676(16)	17.659(2)	12.6293(17)
α (°)	90	90	100.686(2)
β (°)	90	108.461(2)	99.378(2)
γ (°)	90	90	118.100(2)
V (Å^3)	3966.2(6)	2413.9(5)	1251.0(3)
Z	8	4	2
D_{calc} (g cm^{-3})	1.877	1.697	1.674
μ (mm^{-1})	1.550	1.282	1.239
F(000)	2208	1232	632
Crystal size (mm)	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.16	0.26 × 0.24 × 0.20
Max. 2θ (°)	52.72	52.72	50.02
Reflections collected	21 081	13 278	6418
Unique reflections/R_{int}	4033/0.0351	4897/0.0318	4378/0.0191
No. of parameters	262	301	310
Goodness-of-fit on F^2	1.033	1.031	1.009
R_1, wR_2 [$I > 2\sigma(I)$]	0.0230, 0.0456	0.0294, 0.0594	0.0253, 0.0566
R_1, wR_2 (all data)	0.0410, 0.0525	0.0497, 0.0672	0.0367, 0.0617

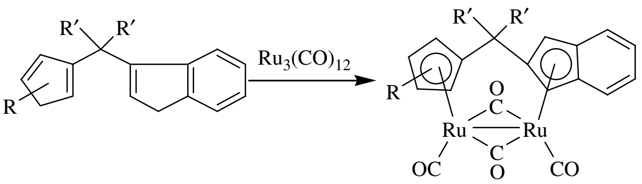
Table 3. Selected bond distances (Å) and selected bond angles (deg) for **6**

Bond distances			
Ru(1)–Ru(2)	2.6727(4)	Ru(2)–C(2)	2.024(3)
Ru(1)–C(2)	2.037(3)	Ru(2)–C(3)	2.044(3)
Ru(1)–C(3)	2.043(3)	Ru(2)–C(19)	2.286(3)
Ru(1)–C(5)	2.271(3)	Ru(2)–C(20)	2.372(3)
Ru(1)–C(6)	2.224(3)	Ru(2)–C(25)	2.321(4)
Ru(1)–C(7)	2.253(3)	Ru(2)–C(26)	2.212(4)
Ru(1)–C(12)	2.262(3)	Ru(2)–C(27)	2.254(4)
Ru(1)–C(13)	2.279(3)	C(13)–C(14)	1.537(4)
C(14)–C(19)	1.526(5)	C(20)–C(21)	1.420(5)
C(19)–C(20)	1.452(5)	C(21)–C(22)	1.356(6)
C(20)–C(25)	1.428(5)	C(22)–C(23)	1.411(8)
C(25)–C(26)	1.440(6)	C(23)–C(24)	1.348(8)
C(26)–C(27)	1.398(5)	C(24)–C(25)	1.430(6)
C(19)–C(27)	1.433(5)	Ru(1)–CEN(1)	1.906
Ru(2)–CEN(2)	1.940		
Bond angles			
Ru(2)–C(3)–Ru(1)	81.68(12)	Ru(1)–C(2)–Ru(2)	82.32(13)
C(13)–Ru(1)–Ru(2)	89.16(8)	C(14)–C(13)–Ru(1)	124.3(2)
C(19)–Ru(2)–Ru(1)	87.49(8)	C(13)–C(14)–C(19)	112.0(3)
C(14)–C(19)–Ru(2)	126.1(2)	PL(1)–PL(2)	116.0

Table 4. Selected bond distances (Å) and selected bond angles (deg) for **7**

Bond distances			
Ru(1)–Ru(2)	2.6739(4)	Ru(2)–C(2)	2.065(3)
Ru(1)–C(2)	2.006(3)	Ru(2)–C(3)	2.039(3)
Ru(1)–C(3)	2.065(3)	Ru(2)–C(20)	2.283(3)
Ru(1)–C(5)	2.375(3)	Ru(2)–C(21)	2.281(3)
Ru(1)–C(10)	2.322(3)	Ru(2)–C(22)	2.237(3)
Ru(1)–C(11)	2.210(3)	Ru(2)–C(23)	2.255(3)
Ru(1)–C(12)	2.260(3)	Ru(2)–C(24)	2.270(3)
Ru(1)–C(13)	2.297(3)	C(5)–C(6)	1.422(4)
C(5)–C(10)	1.434(4)	C(6)–C(7)	1.364(4)
C(10)–C(11)	1.450(4)	C(7)–C(8)	1.402(5)
C(11)–C(12)	1.398(4)	C(8)–C(9)	1.354(5)
C(12)–C(13)	1.428(4)	C(9)–C(10)	1.409(4)
C(5)–C(13)	1.461(4)	C(13)–C(14)	1.533(4)
C(14)–C(20)	1.533(4)	Ru(1)–CEN(1)	1.942
Ru(2)–CEN(2)	1.913		
Bond angles			
Ru(2)–C(3)–Ru(1)	81.30(12)	Ru(1)–C(2)–Ru(2)	82.11(12)
C(13)–Ru(1)–Ru(2)	88.11(7)	C(20)–Ru(2)–Ru(1)	88.28(7)
C(14)–C(13)–Ru(1)	124.50(18)	C(20)–C(14)–C(13)	111.4(2)
C(14)–C(20)–Ru(2)	125.4(2)	PL(1)–PL(2)	116.0

cycloalkylidene-bridged mixed cyclopentadienyl-indenyl diruthenium complexes ($(\eta^5{:}\eta^5\text{-RC}_5\text{H}_3\text{CR}'_2\text{C}_9\text{H}_6)\text{Ru}_2(\text{CO})_2(\mu\text{-CO})_2$ [R = H, R′, R′ = Me_2 (**1**), $(\text{CH}_2)_4$ (**2**), $(\text{CH}_2)_5$ (**3**), $(\text{CH}_2)_6$ (**4**); R = ^{t}Bu, R′, R′ = Me_2 (**5**), $(\text{CH}_2)_4$ (**6**), $(\text{CH}_2)_5$ (**7**)] were obtained in 26–46% yields, respectively (Scheme 1). In contrast, reaction of the mixed ligand $\text{C}_5\text{H}_5\text{CMe}_2\text{C}_9\text{H}_7$ with $\text{Fe}_2(\text{CO})_9$ or $\text{Mo(CO)}_3(\text{CH}_3\text{CN})_3$ in refluxing THF only gave the dimer $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_9\text{H}_7)\text{Fe(CO)}_2]_2$ or $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_9\text{H}_7)\text{Mo(CO)}_3]_2$, in which the indenyl ring was unmetallated.[40,41] All these complexes are air stable and soluble in most organic solvents except for alkanes. The solubility and melting points of complexes increased with the introduction of a cycloalkylidene bridge and increasing the size of the cycloalkylidene bridge. The cyclohexylidene-bridged complexes (**3, 7**) showed higher melting points than the corresponding Me_2C, cyclopentylidene and cycloheptylidene-bridged complexes, indicating the higher thermal stability. Introduction of a tert-butyl on the cyclopentadienyl ring further increased the solubility but decreased the melting points of complexes. The ^{1}H NMR spectra of complexes **1–4** are very similar and all show three or four groups of peaks for the six-membered ring protons of indenyl groups, two doublets for the five-membered ring protons of indenyl groups, and four groups of peaks for the cyclopentadienyl protons. The ^{1}H NMR spectra of complexes **5** and **6** are more complex due to the presence of a mixture of *racemic* and *meso* isomers. However, the ^{1}H NMR spectrum of complex **7** is similar to that of complexes **1–4**, indicating the presence of only one isomer. The single X-ray diffraction analysis shows that it is a *racemic* isomer. The IR spectra of complexes **1–7** show two terminal carbonyl absorptions at 1900–2000 cm^{-1} and two bridging carbonyl absorptions at about 1800 cm^{-1}, in consistent with their structures (Scheme 1).



R = H, R′, R′ = Me_2(**1**), $(\text{CH}_2)_4$(**2**), $(\text{CH}_2)_5$(**3**), $(\text{CH}_2)_6$(**4**)
R = ^{t}Bu, R′, R′ = Me_2(**5**), $(\text{CH}_2)_4$(**6**), $(\text{CH}_2)_5$(**7**)

Scheme 1.

The crystal structures of complexes **2, 6** and **7** were determined by X-ray diffraction analysis. The molecular structures of **2, 6** and **7** are presented in Figs 1–3, respectively. The cycloalkylidene rings, C(14)–C(15)–C(16)–C(17)–C(18) for **2**, C(14)–C(15)–C(16)–C(17)–C(18) for **6**, and C(14)–C(15)–C(16)–C(17)–C(18)–C(19) for **7**, all take the standard envelope or chair conformation. As to be expected, the presence of different alkyl substituents at the bridging carbon

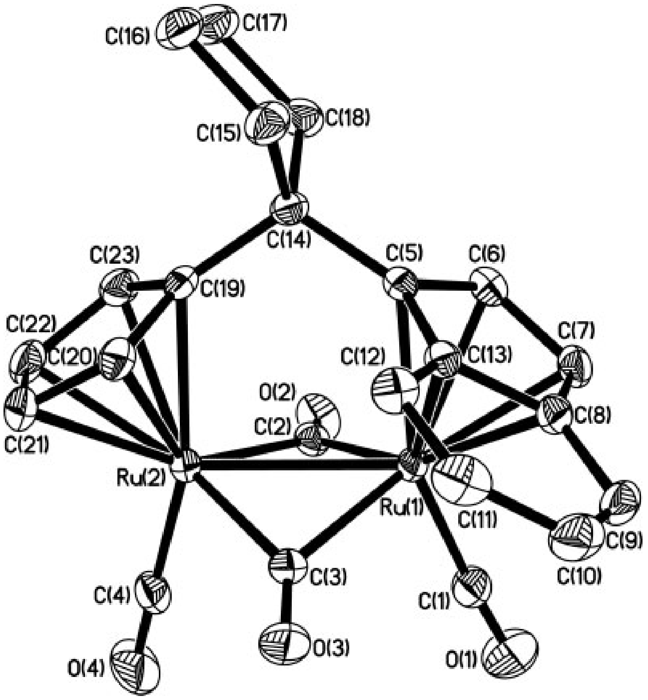


Figure 1. Molecular structure of **2**. Thermal ellipsoids are shown at the 30% level.

atom has effectively no influence on the molecular structures. The Ru–Ru bond distances [2.6746(4) Å (**2**), 2.6727(4) Å (**6**) and 2.6739(4) Å (**7**)] are very similar, and much shorter than that in the single carbon bridged biscyclopentadienyl diruthenium complexes $(CH_2)[(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ [2.767(1) Å],[42] $(Me_2C)[(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ [2.788 Å],[20] but slightly longer than that in the single carbon bridged bis(indenyl) diruthenium complex *trans*-$(MeCH)[(\eta^5\text{-}C_9H_6)Ru(CO)_2]_2$ [2.656(2) Å].[43] In the cycloalkylidene-bridged biscyclopentadienyl diiron complexes, it was found that introduction of a cycloalkylidene bridge made the Fe–Fe bond distance smaller than that of the Me_2C-bridged analog $(Me_2C)[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ due to the nonbonding interaction between the cycloalkylidene bridge and two cyclopentadienyl groups. The Fe–Fe bond of $(CH_2)_5C)[(\eta^5\text{-}C_5H_4)Fe(CO)_2]_2$ [2.466(1) Å] is also the shortest among the biscyclopentadienyl tetracarbonyl diiron complexes.[44] However, this was not found for the diruthenium complexes **2, 6** and **7**. The dihedral angles between the cyclopentadienyl ring and indenyl ring [117.1° (**2**), 116.0° (**6**) and 116.0° (**7**)], are also larger than that in the single carbon-bridged biscyclopentadienyl diruthenium complex $(CH_2)[(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ (112.9°).[42] The shorter Ru–Ru bond distances in **2, 6** and **7** than in $(CH_2)[(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ and $(Me_2C)[(\eta^5\text{-}C_5H_4)Ru(CO)_2]_2$ can be attributed to the presence of the bridging carbonyl groups, which tend to shorten metal–metal distances.[45,46] The presence of an indenyl group may also tend to form the complex with the bridging carbonyl groups.[22,43] The distances of ruthenium atom to the centroid of the indenyl rings (Ru–CEN: 1.951, 1.940, 1.942 Å for **2, 6** and **7**, respectively) are significantly longer than that to the centroid of the cyclopentadienyl rings (Ru–CEN: 1.916, 1.906, 1.913 Å for **2, 6** and **7**, respectively). Introduction of a bulky tert-butyl group to the cyclopentadienyl ring also seems to have effectively no influence on the molecular structures

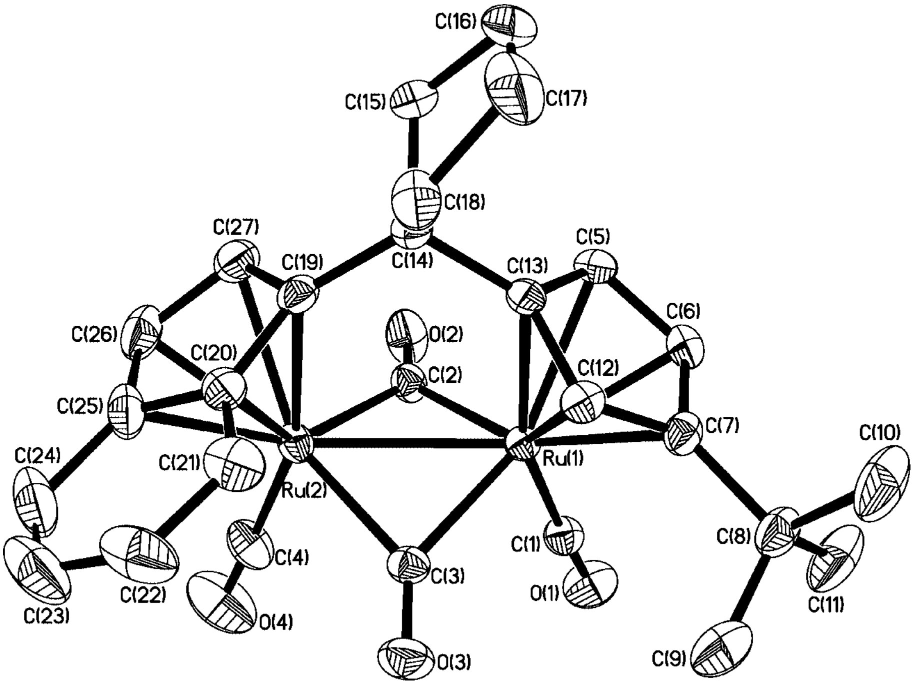


Figure 2. Molecular structure of **6**. Thermal ellipsoids are shown at the 30% level.

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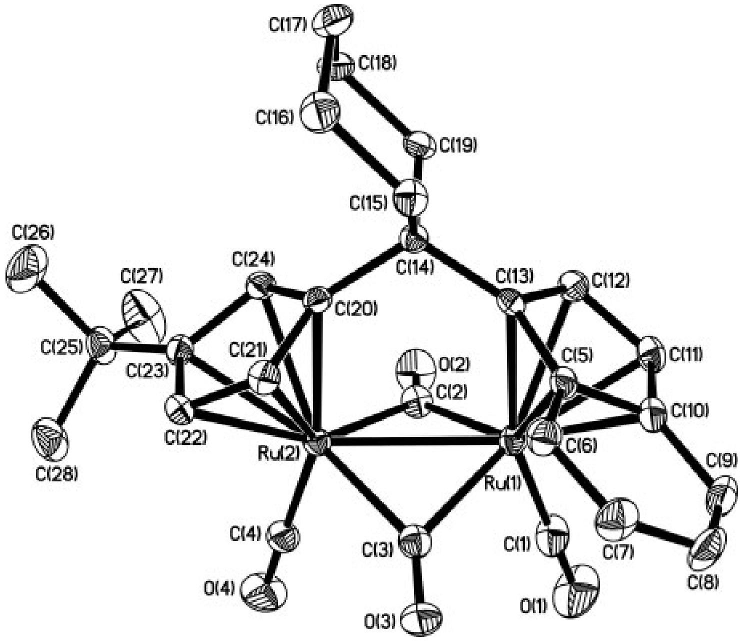

Figure 3. Molecular structure of **7**. Thermal ellipsoids are shown at the 30% level.

because it could extend outside to reduce the intramolecular nonbonding interaction.

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