烃基取代茚基钌羰基化合物的合成及晶体结构

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摘要: 配体 $C_9H_7R(R=CH_2CH_2CH_3$ (**1**)$,CH(CH_3)_2$ (**2**)$,C_5H_9$ (**3**)$,CH_2C_6H_5$ (**4**)$,CH_2CH=CH_2$ (**5**))分别与 $Ru_3(CO)_{12}$ 在二甲苯或庚烷中加热回流,得到了 6 个双核配合物$[(\eta^5-C_9H_6R)Ru(CO)(\mu-CO)]_2(R=CH_2CH_2CH_3$ (**6**)$,CH(CH_3)_2$ (**7**)$,C_5H_9$ (**8**)$,CH_2C_6H_5$ (**9**)$,CH_2CH=CH_2$ (**10**))和$[(\eta^5-C_9H_6)(H_3CH_2C)CHCH(CH_2CH_3)(\eta^5-C_9H_6)][Ru(CO)(\mu-CO)]_2$ (**11**)。通过元素分析、红外光谱、核磁共振氢谱对配合物的结构进行了表征,并用 X-射线单晶衍射法测定了配合物 **6**,**9**,**10** 和 **11** 的结构。

关键词: 茚基;羰基钌;X-射线衍射;结构

Ruthenium Carbonyl Complexes Containing Alkyl-Substituted Indenyl Ligands: Syntheses and Structures

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Abstract: Reactions of the alkyl-substituted indenyl ligands $[C_9H_7R]$ (R=$CH_2CH_2CH_3$ (**1**), $CH(CH_3)_2$ (**2**), C_5H_9 (**3**), $CH_2C_6H_5$ (**4**), $CH_2CH=CH_2$ (**5**)) with $Ru_3(CO)_{12}$ in refluxing xylene or heptane gave the responding dinuclear metal carbonyl complexes $[(\eta^5-C_9H_6R)Ru(CO)(\mu-CO)]_2$ (R=$CH_2CH_2CH_3$ (**6**), $CH(CH_3)_2$ (**7**), C_5H_9 (**8**), $CH_2C_6H_5$ (**9**), $CH_2CH=CH_2$ (**10**)), respectively, as well as the bridged diruthenium complex $[(\eta^5-C_9H_6)(H_3CH_2C)CHCH(CH_2CH_3)(\eta^5-C_9H_6)]$ $[Ru (CO) (\mu-CO)]_2$ (**11**). These complexes have been characterized by elemental analysis, IR, and ^{1}H NMR spectroscopy. The molecular structures of **6**, **9**, **10** and **11** were determined by X-ray diffraction analysis. CCDC: 937499, **6**; 972340, **9**; 944111, **10**; 970734, **11**.

Key words: indenyl; ruthenium carbonyl; X-ray diffraction; structure

0　Introduction

Substituted cyclopentadienyl and related indenyl anions occupy a prominent role in organometallic chemistry, serving as versatile ligands for transition metals. Seemingly subtle changes in either cyclopentadienyl or indenyl ligand substitution can have profound consequences on chemical reactivity. The cyclopentadienyl or indenyl metal complexes have received increasing attention due to their diverse and

flexible hapticities and the enhanced reactivity both in stoichiometric and catalytic reactions[1-9]. The side chain functionalized cyclopentadienyl or indenyl ligands have usually been used to form intramolecular coordination to a Lewis acidic metal center or to construct oligonuclear metal complexes, which usually show different structures and reactivity[10]. In our previous work we studied the reactions of substituted cyclopentadienes with $Ru_3(CO)_{12}$ and obtained a series of ruthenium carbonyl complexes involving novel intramolecular C-H activation, allyl isomerization, bridged or normal and including different bonding modes of cyclopentadienyl ligands[11-18]. Considering the properties and the reactivity of transition-metal complexes are influenced by the electronic and steric properties of the surrounding ligands, we further studied the reactions of alkyl-substituted indenyl ligands [C_9H_7R] with $Ru_3(CO)_{12}$, and a series of diruthenium complexes with η^5-fashion were obtained.

1　Experimental

1.1　General considerations

All manipulations of air- and moisture-sensitive complexes were performed at an argon/vacuum manifold using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under an atmosphere of nitrogen prior to use. ^{1}H NMR spectra were recorded on a Bruker AV 500 instrument, while IR spectra were recorded as KBr disks on a FT IR 8900 spectrometer. X-ray measurements were made on a Bruker Smart APEX diffractometer with graphite monochromated Mo $K\alpha$ (λ=0.071 073 nm) radiation. Elemental analyses were performed on a Vario EL Ⅲ analyzer. The ligand precursors [C_9H_7R] (R=$CH_2CH_2CH_3$ (**1**), $CH(CH_3)_2$ (**2**), C_5H_9 (**3**), $CH_2C_6H_5$ (**4**), $CH_2CH=CH_2$ (**5**)) were synthesized according to the literature[19]. $Ru_3(CO)_{12}$ were purchased from J&K Scientific Ltd and used without further purification, other reagents were purchased from commercial suppliers.

1.2　Reaction of 1 with $Ru_3(CO)_{12}$ in xylene

A solution of ligand precursor $C_9H_7CH_2CH_2CH_3$ (**1**) (0.22 g, 1.41 mmol) and $Ru_3(CO)_{12}$ (0.30 g, 0.47 mmol) in 25 mL of xylene was refluxed for 12 h. After removal of solvent under reduced pressure, the residue was chromatographed on an alumina column using petroleum ether/CH_2Cl_2　(6∶1, *V/V*) as eluent. Only the yellow band was eluted and collected. After vacuum removal of the solvents from the above eluate, the residue was recrystallized from *n*-hexane/CH_2Cl_2 (1∶3, *V/V*) at room temperature to give complex **6** as orange-yellow crystals　(Yield: 0.343 g, 77.5%). m.p. 184 ℃ (dec.). Anal. Calcd.(%) for $C_{28}H_{26}Ru_2O_4$: C, 53.50; H, 4.17. Found　(%): C, 53.12; H, 4.33. ^{1}H NMR (500 MHz, $CDCl_3$): 7.23~7.32　(m, 6H, C_9H_6), 7.02 (d, 2H, *J*=8.0 Hz, C_9H_6), 5.47　(d, 2H, *J*=3.0 Hz, C_9H_6), 5.08　(d, 2H, *J*=2.5 Hz, C_9H_6), 2.65~2.83　(m, 4H, CH_2), 1.61~1.74 (m, 4H, CH_2), 0.98 (t, 6H, *J*=7.5 Hz, CH_3). IR (ν_{CO}, cm^{-1}): 1 938(s), 1 790(s).

1.3　Reaction of 2 with $Ru_3(CO)_{12}$ in xylene

By using a similar procedure to that described above, ligand precursor $C_9H_7CH(CH_3)_2$ (**2**) reacted with $Ru_3(CO)_{12}$ in refluxing xylene for 10 h, after chromatography and eluted with petroleum ether/CH_2Cl_2, complex **7** was obtained　(0.309 g, 69.7% yield) as orange-yellow solid. m.p. 212 ℃. Anal. Calcd.(%) for $C_{28}H_{26}Ru_2O_4$: C, 53.50; H, 4.17. Found(%): C, 53.83; H, 4.31. ^{1}H NMR (500 MHz, $CDCl_3$): 7.50 (d, 2H, *J*=8.0 Hz, C_9H_6), 7.37　(t, 2H, *J*=7.5 Hz, C_9H_6), 7.26 (t, 2H, *J*=7.5 Hz, C_9H_6), 6.98　(d, 2H, *J*=8.5 Hz, C_9H_6), 5.46 (d, 2H, *J*=2.5 Hz, C_9H_6), 4.72 (d, 2H, *J*=2.5 Hz, C_9H_6), 1.31　(d, 6H, *J*=6.8 Hz, CH_3), 1.52　(d, 6H, *J*=6.5 Hz, CH_3), 3.30~3.40 (m, 2H, CH). IR (ν_{CO}, cm^{-1}): 1 950(s), 1 772(s).

1.4　Reaction of 3 with $Ru_3(CO)_{12}$ in xylene

By using a similar procedure to that described above, ligand precursor $C_9H_7C_5H_9$ (**3**) reacted with $Ru_3(CO)_{12}$ in refluxing xylene for 10 h, after chromatography and eluted with petroleum ether/CH_2Cl_2, complex 8 was obtained　(0.383 g, 79.9% yield) as orange-red solid. m.p. 210 ℃. Anal. Calcd.(%) for $C_{32}H_{30}Ru_2O_4$: C, 56.46; H, 4.44. Found(%): C, 56.73; H, 4.20. ^{1}H NMR (500 MHz, $CDCl_3$): 7.51 (d, 2H, *J*=8.5 Hz, C_9H_6), 7.35　(t, 2H, *J*=7.5 Hz, C_9H_6), 7.25 (t, 2H, *J*=7.5 Hz, C_9H_6), 6.97　(d, 2H, J=8.5 Hz, C_9H_6), 5.44 (d, 2H, *J*=2.5 Hz, C_9H_6), 4.77 (d, 2H, *J*=2.5 Hz, C_9H_6), 3.43~3.49　(m, 2H, C_9H_6 CH), 1.71~1.97 (m,

16H, (CH$_2$)$_4$). IR (ν_{CO}, cm^{-1}): 1 944(s), 1 786(s).

1.5 Reaction of 4 with Ru$_3$(CO)$_{12}$ in xylene

By using a similar procedure to that described above, ligand precursor C$_9$H$_7$CH$_2$C$_6$H$_5$ (**4**) reacted with Ru$_3$(CO)$_{12}$ in refluxing xylene for 12 h, after chromatography and eluted with petroleum ether/CH$_2$Cl$_2$, complex **9** was obtained (Yield: 0.439 g, 86.1%) as orange-yellow solid. m.p. 228 ℃ (dec.). Anal. Calcd. (%) for C$_{36}$H$_{26}$Ru$_2$O$_4$: C, 59.66; H, 3.62. Found(%): C, 59.83; H, 3.48. ^{1}H NMR (500 MHz, CDCl$_3$): 7.27~7.35 (m, 8H, C$_9$H$_6$), 7.05~7.25 (m, 10H, C$_6$H$_5$), 5.52 (d, 2H, J=3.0 Hz, C$_9$H$_6$), 5.20 (d, 2H, J=3.0 Hz, C$_9$H$_6$), 4.05~4.15 (m, 4H, C$_6$H$_5$CH$_2$). IR (ν_{CO}, cm^{-1}): 1 952(s), 1 784(s).

1.6 Reaction of 5 with Ru$_3$(CO)$_{12}$ in xylene

By using a similar procedure to that described above, ligand precursor C$_9$H$_7$CH$_2$CH=CH$_2$ (**5**) reacted with Ru$_3$(CO)$_{12}$ in refluxing xylene for 12 h. The solvent was removed under reduced pressure, and the residue was placed in an Al$_2$O$_3$ column. Elution with CH$_2$Cl$_2$/petroleum ether developed two bands. The first band gave 0.268 g (60.9%) of 10 as orange-red crystals, and the second band yielded 0.047 g (10.7%) of **11** as orange-red crystals. Data for **10**: m.p. 174 ℃. Anal. Calcd.(%) for C$_{28}$H$_{22}$Ru$_2$O$_4$: C, 53.84; H, 3.55. Found (%): C, 53.50; H, 3.78. ^{1}H NMR (500 MHz, CDCl$_3$): 7.23~7.31 (m, 8H, C$_9$H$_6$), 5.79 (d, 2H, J=2.5 Hz, C$_9$H$_6$), 4.92 (d, 2H, J=2.5 Hz, C$_9$H$_6$), 5.67 (d, 4H, J=3.0 Hz, CH$_2$), 5.46~5.48 (m, 2H, CH), 2.73~2.87(m, 4H, CH$_2$). IR (ν_{CO}, cm^{-1}): 1 942 (s), 1 784 (s). Data for **11**: m.p. 225 ℃. Anal. Calcd.(%) for C$_{28}$H$_{24}$Ru$_2$O$_4$: C, 53.67; H, 3.86. Found (%): C, 53.95; H, 3.65. ^{1}H NMR (500 MHz, CDCl$_3$): 7.55 (d, 2H, J=8.5 Hz, C$_9$H$_6$), 7.42 (t, 2H, J=7.5 Hz, C$_9$H$_6$), 7.33 (d, 2H, J=8.5 Hz, C$_9$H$_6$), 7.22 (t, 2H, J=7.5 Hz, C$_9$H$_6$), 6.16 (d, 2H, J=3.0 Hz, C$_9$H$_6$), 5.46 (d, 2H, J=3.0 Hz, C$_9$H$_6$), 2.88 (s, 2H, CH), 1.75~1.61 (m, 4H, CH$_2$), 0.57 (d, 6H, J=7.5 Hz, CH$_3$). IR (ν_{CO}, cm^{-1}): 1 977(vs), 1 938(m), 1 776(s).

1.7 Crystal structure determination

Crystals of the complexes **6**, **9**, **10** and **11** suitable for X-ray diffraction were isolated from the slow evaporation of hexane-dichloromethane solution. Data collection were performed on a Bruker SMART APEX (Ⅱ)-CCD detector with graphite monochromated Mo $K\alpha$ (λ=0.071 073 nm) radiation using the φ-ω scan technique. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using the SHELX-97 program system[20]. Hydrogen atoms were included in calculated positions riding on the parent atoms and refined with fixed thermal parameters. Crystallographic data and experimental details of the structure determinations are given in Table 1.

CCDC: 937499, **6**; 972340, **9**; 944111, **10**; 970734, **11**.

Table 1 Crystal data and structure refinement parameters for complexes 6, 9, 10 and 11

Complex	6	9	10	11
Empirical formula	C$_{28}$H$_{26}$O$_4$Ru$_2$	C$_{36}$H$_{26}$O$_4$Ru$_2$	C$_{28}$H$_{22}$O$_4$Ru$_2$	C$_{28}$H$_{24}$O$_4$Ru$_2$
Formula weight	628.63	724.71	624.60	626.61
Temperature / K	298(2)	298(2)	298(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a / nm	0.872 9(4)	0.943 83(6)	0.938 7(3)	1.177 15(4)
b / nm	0.911 6(4)	1.953 85(16)	1.112 9(3)	1.623 86(6)
c / nm	0.938 6(4)	0.768 55(4)	1.273 6(4)	1.241 08(5)
α / (°)	93.968(6)	90	90	90
β / (°)	112.601(5)	90.303 0(10)	108.584(4)	102.367(4)
γ / (°)	114.606(5)	90	90	90
V / nm^3	0.603 0(5)	1.417 27(16)	1.261 1(6)	2.317 31(15)
Z	1	2	2	4

Continued Table 1

$F(000)$	314	724	620	1248
D_c / (g·cm^{-3})	1.731	1.698	1.645	1.796
Crystal dimensions / mm	0.47×0.27×0.03	0.40×0.21×0.13	0.25×0.20×0.04	0.35×0.17×0.10
θ range / (°)	2.44~25.50	2.85~25.02	2.29~25.50	2.97~25.50
Reflection collected	3 179	2 491	12 822	11 085
Independent reflection	2 205	2 491	2 343	4 305
R_{int}	0.041 7	0.000 0	0.032 0	0.023 0
Parameter	155	191	181	309
Goodness of fit on F^2	1.092	1.157	1.045	1.107
R_1, wR_2[a] ($I>2\sigma(I)$)	0.046 1, 0.120 5	0.050 0, 0.107 9	0.064 2, 0.154 9	0.025 5, 0.063 8
R_1, wR_2[a] (all data)	0.047 9, 0.122 9	0.060 1, 0.112 5	0.090 8, 0.174 0	0.031 2, 0.067 9

[a] Complex **6**: $w=1/[\sigma^2(F_o^2)+(0.097\ 7p)^2+0.000\ 0p]$, where $p=(F_o^2+2F_c^2)/3$; Complex **9**: $w=1/[\sigma^2(F_o^2)+(0.023\ 6p)^2+5.765\ 8p]$, where $p=(F_o^2+2F_c^2)/3$; Complex **10**: $w=1/[\sigma^2(F_o^2)+(0.077\ 0p)^2+5.763\ 6p]$, where $p=(F_o^2+2F_c^2)/3$; Complex **11**: $w=1/[\sigma^2(F_o^2)+(0.030\ 8p)^2+1.068\ 4p]$, where $p=(F_o^2+2F_c^2)/3$

2　Results and discussion

Reactions of ligand precursors C$_9$H$_7$R　(R=CH$_2$CH$_2$CH$_3$ (**1**), CH(CH$_3$)$_2$ (**2**), C$_5$H$_9$ (**3**), CH$_2$C$_6$H$_5$ (**4**)) with Ru$_3$(CO)$_{12}$ in refluxing xylene afforded the corresponding products **6** (77.5%), **7** (69.7%), **8** (79.9%) and **9** (86.1%), respectively (Scheme 1). When [C$_9$H$_7$R] (R=CH$_2$CH=CH$_2$ (**5**)) was treated with Ru$_3$(CO)$_{12}$ in refluxing xylene, the diruthenium complex **10** (60.9%) and the bridged product **11** (10.7%) were obtained (Scheme 2). When heptane was chosen as the solvent instead, the corresponding product was **6** (10.5%), **7** (9.21%), **8** (20.8%), **9** (22.3%) and **10** (14.1%), respectively. The products were the same, but the total yield was much lower

R=CH$_2$CH$_2$CH$_3$ (**6**); R=CH(CH$_3$)$_2$ (**7**);
R=C$_5$H$_9$ (**8**); R=CH$_2$C$_6$H$_5$ (**9**)
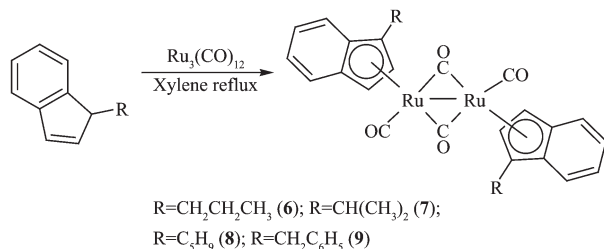
Scheme 1　Synthesis of complexes 6~9
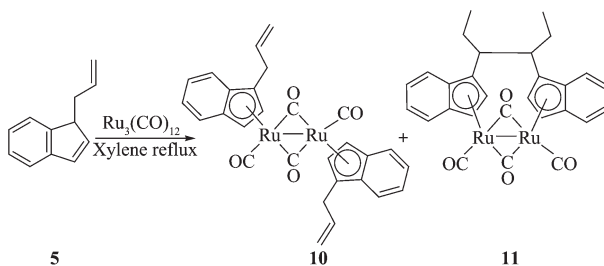
Scheme 2　Synthesis of complexes 10 and 11

than that in xylene.

Based on their ^{1}H NMR and IR spectra, 6~10 were assigned as the normal Ru-Ru single bonded dinuclear complexes. The IR spectra of **6~10** all exhibited a strong terminal carbonyl absorption at 1 938 ~1 952 cm^{-1} and a strong bridging carbonyl absorption at 1 772~1 790 cm^{-1}, which are comparable to other metal-metal bond spectra found in other single substituted indenyl ruthenium dimers. The ^{1}H NMR spectra of the normal indenyl diruthenium complexes **6~10** are similar, and they all show peaks at 7.55~6.97 for the C6-ring protons of the indenyl ligands and two doublets at 6.16~4.72 for the C5-ring protons of the indenyl ligands. Different from **6~10**, complex **11** shows two terminal and one bridging carbonyl absorptions at 1 977(vs), 1 938(m) and 1 776(s) cm^{-1} in its IR spectrum. The ^{1}H NMR spectra of **11** shows one singlet at 2.88 for the methyne protons, one multiplet at 1.75~1.61 for the methylene protons, and one doublet at 0.57 for the methyl protons. This illustrated that the coupling of the allyl pendant group took place, which agrees with the single crystal X-ray diffraction analysis results.

The crystal structures of **6**, **9**, **10** and **11** were determined by X-ray diffraction analysis. Selected bond lengths and angles are given in Table 2. The molecular structures of **6**, **9**, **10** and **11** are presented in Fig.1~4, respectively.
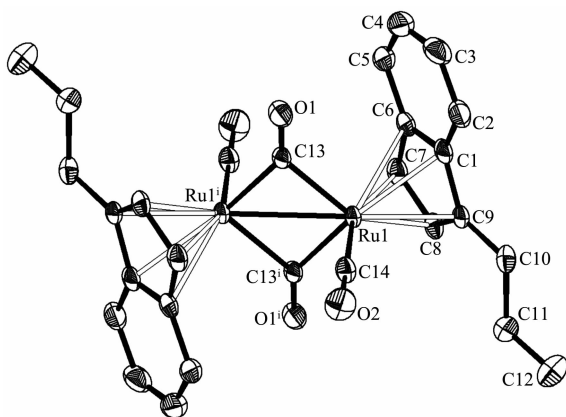
Complexes **6**, **9** and **10** are diruthenium complexes

Table 2　Selected bond distances (nm) and angles (°) for complexes 6, 9, 10 and 11

6					
Ru(1)-Ru(1^i)	0.273 99(10)	C(6)-Ru(1)	0.237 0(4)	C(8)-Ru(1)	0.225 3(4)
C(1)-Ru(1)	0.232 3(4)	C(7)-Ru(1)	0.226 6(4)	C(13)-Ru(1)	0.205 8(4)
C(6)-C(1)-Ru(1)	74.3(2)	C(9)-C(8)-Ru(1)	71.0(2)	Ru(1i)-C(13)-Ru(1)	85.10(16)
C(6)-C(7)-Ru(1)	76.3(3)	O(1)-C(13)-Ru(1)	134.7(4)	C(13i)-Ru(1)-Ru(1^i)	48.46(11)
9					
Ru(1)-Ru(1^i)	0.275 73(16)	C(3)-Ru(1)	0.226 9(8)	C(17)-Ru(1)	0.207 7(9)
C(1)-Ru(1)	0.223 8(8)	C(4)-Ru(1)	0.236 6(7)	C(18)-Ru(1)	0.186 1(8)
C(1)-Ru(1)-Ru(1^i)	169.1(2)	C(3)-Ru(1)-Ru(1^i)	108.3(2)	C(5)-Ru(1)-Ru(1^i)	140.4(2)
C(2)-Ru(1)-Ru(1^i)	133.8(3)	C(4)-Ru(1)-Ru(1^i)	111.2(2)	O(1)-C(17)-Ru(1)	134.3(7)
10					
Ru(1)-Ru(1^i)	0.273 54(14)	C(11)-C(12)	0.133 6(10)	C(7)-Ru(1)	0.226 8(9)
C(10)-C(11)	0.151 6(10)	C(6)-Ru(1)	0.237 8(8)	C(13)-Ru(1)	0.187 8(10)
C(2)-C(1)-Ru(1)	123.9(6)	O(2)-C(13)-Ru(1)	178.3(9)	Ru(1)-C(14)-Ru(1^i)	85.1(3)
C(7)-C(6)-Ru(1)	68.0(5)	O(1)-C(14)-Ru(1)	140.6(7)	C(14)-Ru(1)-Ru(1^i)	48.7(2)
11					
Ru(1)-Ru(2)	0.270 15(3)	C(9)-C(12)	0.154 8(4)	C(1)-Ru(1)	0.221 4(3)
C(9)-C(10)	0.155 2(4)	C(10)-C(11)	0.152 4(4)	C(2)-Ru(1)	0.233 2(3)
C(1)-C(2)-Ru(1)	67.01(16)	C(12)-C(15)-Ru(2)	130.53(18)	C(2)-Ru(1)-Ru(2)	143.31(7)
C(6)-C(7)-Ru(1)	127.37(19)	O(1)-C(27)-Ru(1)	178.8(3)	C(27)-Ru(1)-Ru(2)	101.66(9)

Symmetry codes: for **6**: ^{i} 2−x, 2−y, −z; for **9**: ^{i} 1−x, 1−y, 1−z; for **10**: ^{i} 1−x, 2−y, 2−z

and have similar structures, in which two indenyl ligands coordinate with two ruthenium atoms through their indenyl ring in η^5-bonding. Similar to the cyclopentadienyl analogue $trans$-[(η^5-Cp)Ru(CO)(μ-CO)]$_2$ (where Cp=cyclopentadienyl ligand), all the structures are $trans$ form, and all the complexes have two forms of coordinated carbonyl ligands, terminal and bridging CO. The two indenyl ring planes are parallel. The Ru-Ru bond distances (0.273 99(10) nm for **6**, 0.275 73(16) nm for **9** and 0.273 54(14) nm for **10**) are close to that of analogous complexes [{(η^5-C$_9$H$_7$)Ru(CO)$_2$}$_2$] (0.274 12(5) nm)[21], [η^5-(MeC$_5$H$_3$N)CH$_2$CMe$_2$(C$_9$H$_6$)Ru(CO)]$_2$(μ-CO)$_2$ (0.274 43(13) nm), [η^5-(C$_5$H$_4$N)CH$_2$(C$_9$H$_6$)
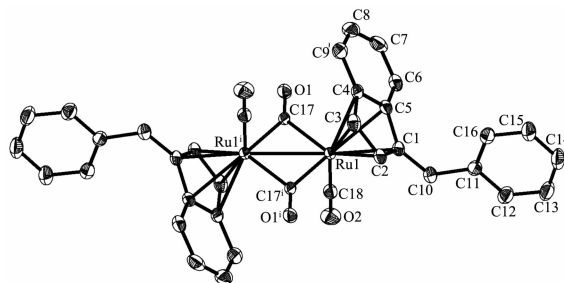
Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ^{i} 2−x, 2−y, −z

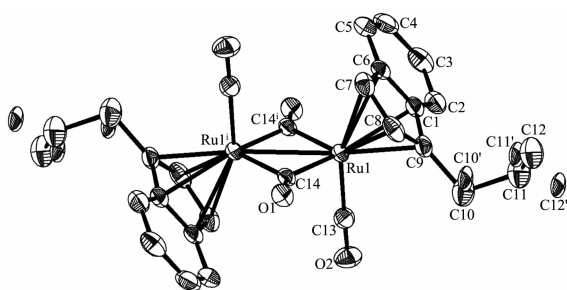Fig.1　Molecular structure of complex **6**

Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ^{i} 1−x, 1−y, 1−z

Fig.2　Molecular structure of complex **9**
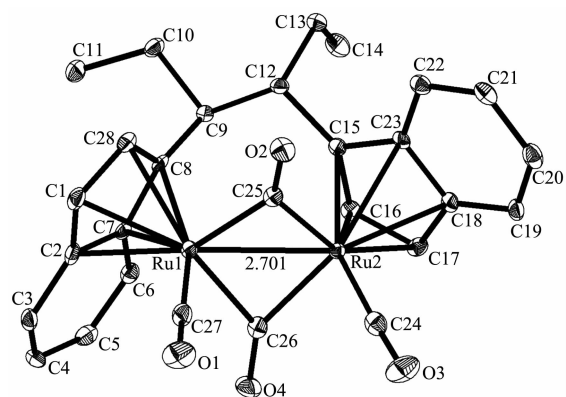
Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level; Symmetry code: ^{i} 1−x, 2−y, 2−z

Fig.3　Molecular structure of complex **10**

Hydrogen atoms are omitted for clarity; Displacement ellipsoids are drawn at the 30% probability level

Fig.4　Molecular structure of complex **11**

Ru(CO)]$_2$(μ-CO)$_2$ (0.273 89(15) nm)[22] and [(η^5-C$_9$H$_6$ ^{n}Bu)$_2$Ru$_2$(CO)$_4$ (0.275 5(2) nm)[23]. For **11**, single crystal X-ray diffraction analysis showed that C(8)-C(9), C(9)-C(10), C(10)-C(11), C(12)-C(13), C(13)-C(14), C(8)-C(9) and C(9)-C(12) are all single bonds, and this illustrated that the coupling of the allyl pendant group took place, which was evidenced by its ^{1}H NMR spectrum. Complex **11** is an unexpected product and the structure is unusual. We obtained the products of the allyl isomerization, but our team has never observed similar reaction of substituted tetramethylcyclopentadienes with metal carbonyl complex. After consulting some literatures[24-26], we proposed the following mechanistic pathway shown in Scheme 3. When ligand **5** reacted with Ru$_3$(CO)$_{12}$ under refluxing xylene for 12 h, the ruthenium hydride complex **a** was firstly obtained, then the isomerization of allyl pendant group took place to give the intermediate species **b**. Subsequent homolysis of the Ru-H formed the free

radical **c** and hydrogen free radical, then free radical addition created **d**. At last the coupling reaction of d generated the dinuclear species **11**.
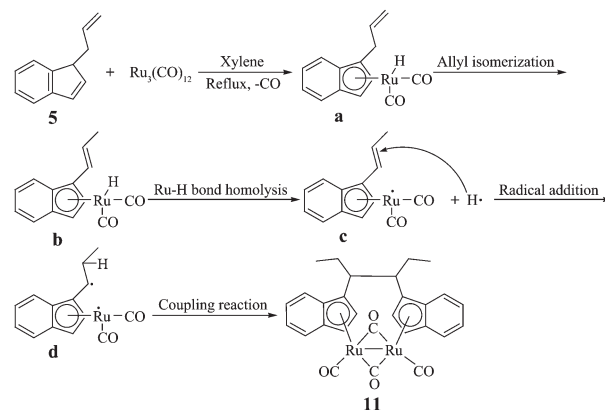
Scheme 3　Possible mechanistic pathway of **11**

3　Conclusions

Reactions of alkyl-substituted indenes with Ru$_3$(CO)$_{12}$ in refluxing xylene or heptane were investigated, respectively. Six new metal carbonyl complexes were obtained and the structures of four of them were determined by single-crystal X-ray diffraction. The results clearly reveal that the coordination mode of indenyl diruthenium complexes is η^5 and substituent group variations display some influence on the Ru-Ru bond length. The solvent also has a significant effect on the reaction yield.

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