

Synthesis and reactivity of substituted cyclopentadienyl rhodium(I) and (III) complexes

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Abstract

New cyclopentadienyl derivatives of rhodium COD complexes [$\text{Cp}^* = \text{C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2$ (**1**); $\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (**2**); $\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_4$ (**3**)] and carbonyl complex [$\text{Cp}^* = \text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_4$ (**4**)] were synthesized from $[\text{RhCl}(\text{COD})]_2$ and $[\text{RhCl}(\text{CO})_2]_2$. **1**, **2** and **3** oxidized by iodine gave iodine bridged dimers **5**, **6** and **7**, respectively. Triphenyl phosphine, carbon monoxide and carbon disulfide molecules broke down the iodine bridged structure easily and produced monomer products $\text{Cp}^*\text{RhI}_2\text{L}$ [$\text{Cp}^* = \text{C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2$, $\text{L} = \text{CS}_2$ (**8**); $\text{L} = \text{PPh}_3$ (**9**). $\text{Cp}^* = \text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_4$, $\text{L} = \text{CO}$ (**10**)]. All of these new compounds were characterized by elemental analysis, ^1H NMR, IR, UV–Vis and mass spectroscopy. The crystal structure of **1** was solved in the triclinic space group $P\bar{1}$ with one molecule in the unit cell, the dimensions of which are $a = 7.082(9)$ Å, $b = 8.392(3)$ Å, $c = 13.889(5)$ Å, $\alpha = 101.19(3)^\circ$, $\beta = 99.06(6)^\circ$, $\gamma = 105.11(5)^\circ$, and $V = 763(1)$ Å³. The crystal structure of **3** was solved in the orthorhombic space group $Pn21a$ with four molecules in the unit cell, the dimensions of which are $a = 9.748(3)$ Å, $b = 16.054(5)$ Å, $c = 14.816(4)$ Å and $V = 2319(1)$ Å³. Least squares refinement leads to values for the conventional R_1 of 0.0251 for **1** and 0.0558 for **3**, respectively. Compared to that in **1**, a shorter metal–ligand bond length in **3** was observed and this is attributed to the rich electron density on Rh(I) metal center piled up by the $\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_4$ ligand.

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1. Introduction

Organometallic compound of the transition metals with one or more cyclopentadienyl ligands is one of the most important classes of organometallic complexes. Over 80% of the known organometallic complexes contain the cyclopentadienyl ligand or a derivative of it [1]. The cyclopentadienyl ligand has been modified to improve the properties of the complex towards its specific applications. Alkylation on the cyclopentadienyl ring can improve the solubility of the complexes in organic solvent [2]. A pendant substituent with an electron donating functional group to the cyclopentadienyl ligand can be designed to change the properties of the

complexes during substitution that is important in catalytic process [3]. Such pendant side chain can temporarily and reversibly coordinate to a metal, acts as an intramolecular solvent, thus stabilizes reactive intermediates. The electron density of the cyclopentadienyl ring can be changed by its ring substituent or by introducing a hetero-atom into the ring structure [4]. Such structural modifications to the cyclopentadienyl ligand have received much attention by numerous research groups. Our interest is in the study of the influences of the chemical properties of an organometallic compound by electronic or stereo modifications to its cyclopentadienyl ligand [5]. Here we report the synthesis and the reactivity of some rhodium complexes with structural modifications to their cyclopentadienyl ligand. The pendant substituents to the cyclopentadienyl ligand include butenyl, tetraisopropanyl and allyloxycarbonyl groups, which varying from electron-donating to

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electron-withdrawing in nature, or may create steric hindrance around the metal center.

2. Experimental

2.1. General procedures

All reactions were carried out by standard Schlenk techniques under an inert atmosphere of dinitrogen. Solvents were deoxygenated and dried by standard methods and distilled under dinitrogen before use [6]. $\text{Na}(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)$ [7], $\text{C}_5\text{H}_2(i\text{-C}_3\text{H}_7)_4$, $[\text{RhCl}(\text{CO})_2]_2$ and $[\text{RhCl}(\text{COD})]_2$ (COD = C_8H_{12}) were prepared according to the literature methods [8]. Elemental analyses were performed on a Rapid CHN-O 240C Analyzer (Heraeus, Germany) at the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. IR spectra were recorded on a Nicolet AVATAR-360IR spectrophotometer in KBr pellets. ^1H NMR spectra were recorded on a Bruker A VAVCE-DMX 500 NMR spectrometer and the chemical shifts are reported in ppm referenced to tetramethylsilane. UV–Vis spectra were recorded on a HP diode-array model 8453 spectrometer in CH_2Cl_2 . Mass spectra were recorded on HP 5989A spectrometer with EI source.

The crystal structure was determined on an ENRAF-Nonius CAD4 X-ray diffractometer equipped with a graphite monochromator. Data collection was performed with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ω – 2θ scan technique to a maximum 2θ value of 29.77° at the room temperature. The structure of the crystal was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically with full-matrix least-squares. Hydrogen atoms were not included in refinement. The final agreement factors are described with R_1 and wR_2 values for observed reflections. All calculations were performed on a PC computer using SHELX-97 (Sheldrick, 1997).

2.2. $\text{Li}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)$

0.496 g (21.6 mmol) of sodium sand was reacted with 2.6 ml of freshly distilled cyclopentadiene in 15 ml of THF under ice water bath. When sodium sand disappeared, the solvent was evaporated under vacuum. The white residue was re-dissolved in 35 ml of THF and cooled to -40°C . 2.2 ml (21.7 mmol) of 4-bromo-1-butene was added slowly. After 2 h stirring under -40°C , the orange yellow solution was filtered through a pad of Celite. The solvent was removed from the filtrate by distillation under atmosphere and 0.5145 g of $\text{C}_5\text{H}_5\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ was obtained by distillation under reduced pressure. The distillate was dissolved in 10 ml of hexane and cooled to -45°C . 4.28 ml of *n*-butyllithium (1.6 M in hexane) was added in the period

of 40 min. The reaction mixture was continuously stirred for another 3 h. The precipitate was separated by centrifuge and washed with hexane for 3 times, then dried under vacuum. 0.2484 g of solid as pale pink powder was obtained, yield 46%.

2.3. $\text{K}(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)$

2.10 g (8.96 mmol) $\text{C}_5\text{H}_2(i\text{-C}_3\text{H}_7)_4$ was dissolved in 30 ml of THF, the solution was transferred slowly into a 125 ml of Schlenk tube containing 0.333 g (8.52 mmol) of metallic potassium. The reaction mixture was heated to reflux overnight. The metallic potassium disappeared and a lot of white crystals precipitated. The white crystals were filtered and washed with hexane until the washings was colorless. The precipitate was dried under vacuum. 2.33 g of white crystalline of solid was obtained, yield 99%.

2.4. Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{Rh}(\text{C}_8\text{H}_{12})$ (1)

$[\text{RhCl}(\text{COD})]_2$ (0.728 g, 1.48 mmol) was dissolved in 30 ml of THF in a 150 ml Schlenk tube under stirring, and added slowly 25 ml of THF solution containing $\text{Na}(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)$ (0.483 g, 2.81 mmol). The reaction mixture was allowed to stir overnight under room temperature. The solvent was evaporated to dryness in vacuo and the residue was added 25 ml of hexane. The yellow turbid hexane solution was filtered through a pad of Celite. The yellow clear filtrate was adsorbed by 2 g of alumina and then loaded on an alumina column. The column was rinsed with a mixed solvent of hexane and THF in the ratio of 25–1. The yellow band was collected and the eluent was evaporated in vacuo. 0.41 g of yellow solid was obtained. Yield: 40%. Anal. Found: C, 56.7; H, 6.10. Calc. for: $\text{C}_{17}\text{H}_{21}\text{O}_2\text{Rh}$ (360.25 g/mol): C, 56.7; H, 5.88%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3115 ($=\text{CH}$ of C_5H_4 ring), 2989, 2971, 2933 ($-\text{CH}$ aliphatic), 2875, 2827, 1691 ($\text{C}=\text{O}$), 1649 ($\text{C}=\text{C}$), 1470 ($\text{C}-\text{C}$), 1374, 1323 (COD), 1272, 1127, 968 (COD), 867 (COD), 804 (COD). UV–Vis $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 236 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} 1.51 \times 10^4$), 306 (0.41×10^4). Mass spectrum (EI) m/e : 360 (100, M^+), 319 (24.2, $\text{C}_5\text{H}_4\text{COORhCOD}^+$), 275 (38.5, $\text{C}_5\text{H}_4\text{RhCOD}^+$), 210 (6.9, $\text{C}_5\text{H}_4\text{COORh}^+$), 168 (39.8, $\text{C}_5\text{H}_5\text{Rh}^+$). δ_{H} ($(\text{CD}_3)_2\text{CO}$): 5.48 (t, 2H, Cp, $J=2.1$ Hz), 5.44 (t, 2H, Cp, $J=2.1$ Hz), 6.04 (m, 1H, $-\text{CH}=\text{}$), 5.42 (d, 1H, $=\text{CH}_2$ trans, $J=17.4$ Hz), 5.23 (d, 1H, $=\text{CH}_2$ cis, $J=10.5$ Hz), 4.71 (m, 2H, $-\text{OCH}_2-$), 4.03 (br s, 4H, COD, vinylic), 2.14 (m, 4H, CH_2 of COD), 1.92 (m, 4H, CH_2 of COD). The yellow solid product was redissolved in hexane and cooled under -28°C . Yellow crystals suitable for X-ray crystallographic analysis were obtained. The crystal data and structure refinement parameters are given in Tables 1 and 2.

Table 1
Crystal data and structure refinement for $(\eta^5\text{-C}_5\text{H}_4\text{CO-OCH}_2\text{CH=CH}_2)\text{Rh}(\text{COD})$ (1)

Empirical formula	$\text{C}_{34}\text{H}_{42}\text{O}_4\text{Rh}_2$
Formula weight	720.50
T (K)	295(2)
λ (Å)	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	7.082(9)
b (Å)	8.392(3)
c (Å)	13.889(5)
α (°)	101.19(3)
β (°)	99.06(6)
γ (°)	105.11(5)
V (Å ³)	763(1)
Z	1
ρ_{calc} (Mg/m ³)	1.569
Absorption coefficient (mm ⁻¹)	1.118
$F(000)$	368
Crystal size (mm)	0.50 × 0.20 × 0.10
θ range for data collection (°)	1.53–25.18
Index ranges	$-8 \leq h \leq 8, -10 \leq k \leq 9,$ $0 \leq l \leq 16$
Reflections collected/unique (R_{int})	2859/2738 (0.0140)
Completeness to $2\theta = 25.18$ (%)	99.8
Maximum and minimum transmission	0.8964 and 0.6048
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2738/0/182
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0251, wR_2 = 0.0664$
R indices (all data)	$R_1 = 0.0370, wR_2 = 0.0711$
Extinction coefficient	0.0005(9)
Largest diffraction peak and hole (e Å ⁻³)	0.360 and -0.316

2.5. Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH=CH}_2)\text{Rh}(\text{C}_8\text{H}_{12})$ (2)

[RhCl(COD)]₂ (0.408 g, 0.83 mmol) was dissolved in 25 ml of THF in a 150 ml Schlenk tube under stirring, and added slowly 25 ml of THF solution containing Li($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH=CH}_2$) (0.248 g, 1.97 mmol). The reaction mixture was stirred overnight under room temperature. The reaction mixture was evaporated to dryness in vacuo and the residue was added 25 ml of hexane. The yellow turbid hexane solution was filtered through a pad of Celite. The clear yellow filtrate was adsorbed by 2 g of alumina and then loaded on a silica column. The column was rinsed with hexane. The yellow band was collected and the solvent was evaporated in vacuo. 0.26 g of yellow oil was obtained. Yield: 47%. *Anal.* Found: C, 62.1; H, 7.08. Calc. for: $\text{C}_{17}\text{H}_{23}\text{Rh}$ (330.28 g/mol): C, 61.8; H, 7.02%. IR (neat), $\nu_{\text{max}}/\text{cm}^{-1}$: 3076, 2985, 2927, 2872 (–CH aliphatic), 1641 (C=C), 1472 (C–C), 1447 (COD), 1358, 1323 (COD), 1298, 1152, 960 (COD), 8137 (COD), 790 (COD). UV–Vis $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 242 ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$ 1.30×10^4), 280

(sh). Mass spectrum (EI) m/e : 330 (19.1, M^+), 289 (5.03, $\text{C}_5\text{H}_4\text{CH}_2\text{RhCOD}^+$), 275 (2.81, $\text{C}_5\text{H}_4\text{RhCOD}^+$), 222 (100, RhCOD^+), 182 (38.6, $\text{C}_5\text{H}_5\text{CH}_2\text{Rh}^+$), 168 (8.39, $\text{C}_5\text{H}_5\text{Rh}^+$). δ_{H} ($(\text{CD}_3)_2\text{CO}$): 5.15 (br s, 2H, Cp), 4.98 (br s, 2H, Cp), 5.86–5.93 (m, 1H, –CH=), 5.04 (d, 1H, =CH₂ *trans*, $J = 17.9$ Hz), 4.95 (d, 1H, =CH₂ *cis*, $J = 10.7$ Hz), 3.78 (br s, 4H, COD, vinylic), 2.32 (m, 2H, –CH₂C₂H₃–), 2.21 (m, 2H, –CH₂C₃H₅–), 2.18 (m, 4H, CH₂ of COD), 1.91 (m, 4H, CH₂ of COD).

2.6. Preparation of $(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)\text{Rh}(\text{C}_8\text{H}_{12})$ (3)

To an orange red solution of [RhCl(COD)]₂ (0.20 g, 0.41 mmol) in 30 ml of THF was added slowly a solution of K($\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4$) (0.35 g, 1.3 mmol) in 15 ml of THF. The reaction mixture was stirred overnight under room temperature and was then filtered through a pad of Celite. The orange red clear filtrate was adsorbed by 2 g of alumina and then loaded on an alumina column. The column was rinsed with hexane. The yellow band was collected and the eluant was evaporated in vacuo. 0.17 g of orange red oil was obtained. Yield: 47%. *Anal.* Found: C, 67.5; H, 9.70. Calc. for: $\text{C}_{25}\text{H}_{41}\text{Rh}$ (444.51 g/mol): C, 67.6; H, 9.30%. IR (neat), $\nu_{\text{max}}/\text{cm}^{-1}$: 2960, 2929, 2871 (–CH aliphatic), 1460 (C–C), 1380, 1364, 1321 (COD), 1179, 1100, 964 (COD), 858 (COD), 810 (COD). Mass spectrum (EI) m/e : 444 (100, M^+), 401 (7.18, $\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_3\text{RhCOD}^+$), 370 (23.0, $\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_2\text{CRhCOD}^+$), 315 (7.73, $\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)\text{RhCOD}^+$). δ_{H} ($(\text{CD}_3)_2\text{CO}$): 4.99 (s, 1H, ring-CH), 3.73 (br s, 4H, COD vinylic), 2.73–2.86 (m, 4H, CHMe₂), 2.22 (m, 4H, CH₂ of COD), 1.90 (m, 4H, CH₂ of COD), 1.33 (d, 6H, CH₃, $J = 7.12$ Hz), 1.27 (d, 6H, CH₃, $J = 7.17$ Hz), 1.14 (d, 6H, CH₃, $J = 2.84$ Hz), 1.13 (d, 6H, CH₃, $J = 2.78$ Hz). The yellow oil was dissolved in 1 ml of hexane and cooled under –28 °C. The yellow crystals suitable for X-ray crystallographic analysis were obtained. The crystal data and structure refinement parameters are given in Tables 3 and 4.

2.7. Preparation of $(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)\text{Rh}(\text{CO})_2$ (4)

To an orange red solution of [RhCl(CO)₂]₂ (0.324 g, 0.833 mmol) in 25 ml of THF was added slowly a solution of K($\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4$) (0.549 g, 2.01 mmol) in 25 ml of THF. The reaction mixture was stirred overnight under room temperature. The reaction mixture was filtered through a pad of Celite and the filtrate was adsorbed by 2 g of alumina, loaded on an alumina column. The column was rinsed with hexane. Two bands of different colors on the column were resulted. The first band was orange red and the second band was blue. The orange red band was collected. The eluant was evaporated in vacuo. 0.20 g of nacarat oil was obtained. Yield: 31%. *Anal.* Found: C, 58.7; H, 8.04. Calc. for: $\text{C}_{19}\text{H}_{29}\text{O}_2\text{Rh}$ (392.35 g/mol): C, 58.2; H, 7.45%. IR (neat), $\nu_{\text{max}}/\text{cm}^{-1}$:

Table 2

Selected bond lengths (Å) and angles (°) for $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{Rh}(\text{COD})$ (1)

Rh(1)–C(1)	2.221(3)	C(5)–C(6)	1.455(5)
Rh(1)–C(2)	2.294(4)	C(6)–O(1)	1.197(5)
Rh(1)–C(3)	2.301(4)	C(6)–O(2)	1.330(4)
Rh(1)–C(4)	2.231(3)	O(2)–C(7)	1.447(5)
Rh(1)–C(5)	2.255(3)	C(7)–C(8)	1.35(1)
Rh(1)–C(10)	2.114(4)	C(8)–C(9)	0.98(1)
Rh(1)–C(11)	2.127(3)	C(10)–C(11)	1.393(6)
Rh(1)–C(14)	2.128(3)	C(10)–C(17)	1.533(7)
Rh(1)–C(15)	2.114(4)	C(11)–C(12)	1.501(6)
C(1)–C(2)	1.409(5)	C(12)–C(13)	1.467(6)
C(1)–C(5)	1.427(5)	C(13)–C(14)	1.506(5)
C(2)–C(3)	1.390(6)	C(14)–C(15)	1.378(6)
C(3)–C(4)	1.419(6)	C(15)–C(16)	1.495(7)
C(4)–C(5)	1.417(5)	C(16)–C(17)	1.445(8)
C(10)–Rh(1)–C(1)	101.1(2)	O(1)–C(6)–C(5)	124.8(4)
C(15)–Rh(1)–C(4)	100.5(2)	O(2)–C(6)–C(5)	111.7(3)
C(15)–Rh(1)–C(5)	112.6(2)	C(6)–O(2)–C(7)	116.4(4)
C(10)–Rh(1)–C(5)	114.2(2)	C(8)–C(7)–O(2)	112.1(6)
C(11)–Rh(1)–C(2)	103.3(2)	C(9)–C(8)–C(7)	143(2)
C(14)–Rh(1)–C(3)	105.9(2)	C(11)–C(10)–C(17)	122.4(4)
C(3)–C(2)–C(1)	108.3(3)	C(10)–C(11)–C(12)	124.5(4)
C(2)–C(3)–C(4)	108.1(3)	C(13)–C(12)–C(11)	115.4(3)
C(5)–C(4)–C(3)	108.6(3)	C(12)–C(13)–C(14)	114.9(3)
C(4)–C(5)–C(1)	106.2(3)	C(15)–C(14)–C(13)	123.8(4)
C(4)–C(5)–C(6)	124.6(3)	C(14)–C(15)–C(16)	125.0(4)
C(1)–C(5)–C(6)	129.0(3)	C(17)–C(16)–C(15)	115.7(4)
O(1)–C(6)–O(2)	123.4(4)	C(16)–C(17)–C(10)	115.1(4)

2964, 2931, 2871 (–CH aliphatic), 2025 (C=O), 1960 (C=O), 1463 (C–C), 1380, 1365, 1312, 1182 and 1099. Mass spectrum (EI) m/e : 392 (14.8, M^+), 364 (20.4, $\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_4\text{RhCO}^+$), 336 (100, $\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_4\text{Rh}^+$). δ_{H} ($(\text{CD}_3)_2\text{CO}$): 5.05 (s, 1H, ring-CH), 2.87–3.01 (m, 4H, CHMe_2), 1.19 (d, 12H, CH_3 , $J = 7.2$ Hz), 1.13 (d, 12H, CH_3 , $J = 6.8$ Hz). The eluant was changed to ether to rinse the second blue band. The eluant was evaporated to give blue oil, which was very air sensitive. The IR spectrum of it showed a very strong absorption at 1730 cm^{-1} , which is a characteristic band for metal-bridged carbonyl stretching frequency. Thus the blue oil was assigned to $[\text{C}_5\text{H}(i\text{-C}_3\text{H}_7)_4\text{Rh}-\mu\text{-(CO)}_2\text{-RhC}_5\text{H}(i\text{-C}_3\text{H}_7)_4]$ dimer [9].

2.8. Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{RhI}_2]_2$ (5)

To a solution of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{Rh}(\text{C}_8\text{H}_{12})$ (0.205 g, 0.569 mmol) in 15 ml of ether was added slowly a solution of iodine (0.159 g, 0.626 mmol) in 5 ml of ether. Red purple precipitate appeared immediately. The reaction mixture was continuously stirred for another 2 h. The precipitate was filtered, washed with 3×5 ml of ether and dried in vacuo. 0.26 g of red purple solid was obtained. Yield: 90%. Anal. Found: C, 20.8; H, 2.04. Calc. for: $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Rh}_2\text{I}_4$ (1011.77 g/mol): C, 21.4; H, 1.79%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3086, 3065, 2971 (–CH aliphatic), 1723 (C=O), 1649 (C=C), 1460 (C–C), 1396, 1368, 1270, and 1152. UV–Vis $\nu_{\text{max}}/$

nm (CH_2Cl_2): 229 ($\epsilon/\text{dm}^3\text{ mol}^{-1}$ 4.2×10^4), 254 (4.03×10^4), 315 (1.73×10^4), 510 (0.8×10^4). Mass spectrum (EI) m/e : 757 (3.770, $\text{M}-2\text{I}^+$), 493 (1.72, $\text{C}_5\text{H}_4\text{COOCH}_2\text{CH}_2\text{RhI}_2^+$), 367 (7.36, $\text{C}_5\text{H}_4\text{COOCH}_2\text{CH}_3\text{RhI}^+$), 338 (10.69, $\text{C}_5\text{H}_4\text{COORhI}^+$), 168 (30.41, $\text{C}_5\text{H}_5\text{Rh}^+$). δ_{H} (CDCl_3): 6.07 (m, 4H, ring-CH), 5.71 (m, 4H, ring-CH), 6.00 (m, 2H, –CH=), 5.42 (d, 2H, = CH_2 *trans*, $J = 17.2$ Hz), 5.31 (d, 2H, = CH_2 *cis*, $J = 10.4$ Hz), 4.83 (d, 4H, – OCH_2 –, $J = 5.83$).

2.9. Preparation of $[(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)\text{RhI}_2]_2$ (6)

To a solution of $(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)\text{Rh}(\text{C}_8\text{H}_{12})$ (0.10 g, 0.22 mmol) in 15 ml of ether was added slowly a solution of iodine (0.063 g, 0.25 mmol) in ether. Red purple precipitate occurred immediately. The reaction mixture was continuously stirred for another 2 h. The precipitate was filtered and washed with 3×5 ml of ether and dried in vacuo. 0.113 g of red purple solid was obtained. Yield: 85%. Anal. Found: C, 34.2; H, 4.70. Calc. for: $\text{C}_{34}\text{H}_{58}\text{Rh}_2\text{I}_4$ (1180.3 g/mol): C, 34.6; H, 4.95%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 2958, 2928, 2871 (–CH aliphatic), 1462, 1384, 1366, 1172, 1101, 963, 868. UV–Vis $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 229 ($\epsilon/\text{dm}^3\text{ mol}^{-1}$ 5.17×10^4), 274 (4.6×10^4), 336 (2.02×10^4), 574 (0.81×10^4). Mass spectrum (EI) m/e : 1053 (20.9, $\text{M}-\text{I}^+$), 926 (2.27, $\text{M}-2\text{I}^+$), 590 (11.41, $\text{M}/2^+$), 463 (100, $\text{M}/2-\text{I}^+$). δ_{H} (CDCl_3): 5.50 (s, 2H, HC_5R_4), 3.03 (br, 4H, CHMe_2), 2.91 (br, 4H, CHMe_2), 1.56 (m, 12H, CH_3), 1.47 (m, 24H, CH_3), 1.27 (m, 12H, CH_3).

Table 3
Crystal data and structure refinement for $(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)\text{Rh}(\text{COD})$ (3)

Empirical formula	$\text{C}_{25}\text{H}_{41}\text{Rh}$
Formula weight	444.49
T (K)	293(2)
λ (Å)	0.71073
Crystal system	orthorhombic
Space group	$Pn21a$
Unit cell dimensions	
a (Å)	9.748(3)
b (Å)	16.054(5)
c (Å)	14.816(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å ³)	2319(1)
Z	4
ρ_{calc} (Mg/m ³)	1.273
Absorption coefficient (mm ⁻¹)	0.742
$F(000)$	368
Crystal size (mm)	0.40 × 0.20 × 0.20
θ range for data collection (°)	1.87–29.77
Index ranges	$-5 \leq h \leq 12$, $-18 \leq k \leq 19$, $-20 \leq l \leq 20$
Reflections collected/unique (R_{int})	11 838/5275 (0.0466)
Completeness to $2\theta = 29.77$ (%)	81.0
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	5275/0/243
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0558$, $wR_2 = 0.1174$
R indices (all data)	$R_1 = 0.0898$, $wR_2 = 0.1328$
Absolute structure parameter	0.41(12)
Largest diffraction peak and hole (e Å ⁻³)	1.100 and -0.334

2.10. Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{RhI}_2]_2$ (7)

To a solution of $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)\text{Rh}(\text{C}_8\text{H}_{12})$ (0.10 g, 0.30 mmol) in 15 ml of ether was added slowly a solution of iodine (0.078 g, 0.31 mmol) in ether. Black purple precipitate occurred immediately. The reaction mixture was continuously stirred for another 2 h. The precipitate was filtered and washed with 3×5 ml of ether and dried in vacuo. 0.115 g of red purple solid was obtained. Yield: 80%. *Anal.* Found: C, 22.7; H, 2.47. Calc. for: $\text{C}_{18}\text{H}_{22}\text{Rh}_2\text{I}_4$ (951.8 g/mol): C, 22.7; H, 2.33%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3088, 3070 (–CH aliphatic), 2985, 1640 (C=C), 1470 (C–C), 1393, 1107, 915. UV–Vis $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 230 ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$ 5.66×10^4), 345 (1.02×10^4), 488 (0.91×10^4). Mass spectrum (EI) m/e : 476 (18.33, $\text{M}/2^+$), 349 (83.94, $\text{M}/2\text{-I}^+$), 230 (14.25, RhI^+), 222 (17.42, $\text{M}/2\text{-2I}^+$), 181 (17.42, $\text{C}_5\text{H}_4\text{CH}_2\text{Rh}^+$). δ_{H} (CDCl_3): 5.78 (m, 2H, –CH=), 5.49 (m, 4H, ring-CH), 5.46 (m, 4H, ring-CH), 5.07 (d, 2H, =CH₂ *cis*, $J = 11.6$ Hz), 5.06 (d, 2H, =CH₂ *trans*, $J = 17.2$ Hz), 2.66 (m, 4H, –CH₂C₂H₃), 2.37 (m, 4H, –CH₂C₃H₅).

2.11. Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{RhI}_2\text{CS}_2$ (8)

To a deep red solution of $[(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{RhI}_2]_2$ (0.0791 g, 0.078 mmol) in 8 ml of methylene chloride was added slowly 0.020 ml (0.33 mmol) of CS₂ under stirring. The reaction mixture was stirred overnight under ambient temperature. The volume of the reaction mixture was reduced to about 1 ml under vacuum and the resulting solution was loaded on a silica column, rinsed with a mixed solvent of THF and hexane in 1.25–1 ratios. The deep red band was collected and the solvent was evaporated in vacuo. 0.055 g of black purple solid was obtained. Yield: 60%. *Anal.* Found: C, 20.8; H, 1.70. Calc. for: $\text{C}_{10}\text{H}_9\text{S}_2\text{O}_2\text{RhI}_2$ (582.01 g/mol): C, 20.6; H, 1.56%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3088, 3067, 2975 (–CH aliphatic), 1724 (C=O), 1649 (C=C), 1460 (C–C), 1393, 1369, 1274, 1156, 1026 (C=S). UV–Vis $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 229 ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$ 0.95×10^4), 254 (0.94×10^4), 313 (0.37×10^4). δ_{H} (CDCl_3): 6.08 (m, 2H, ring-CH), 6.01 (m, 1H–CH=), 5.71 (m, 2H, ring-CH), 5.42 (d, 1H, =CH₂ *trans*, $J = 16.5$ Hz), 5.31 (d, 1H, =CH₂ *cis*, $J = 11.0$ Hz), 4.82 (d, 2H, –OCH₂–, $J = 5.56$ Hz).

2.12. Preparation of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{RhI}_2\text{PPh}_3$ (9)

To a deep red solution of $[(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{RhI}_2]_2$ (0.10 g, 0.099 mmol) in 15 ml of methylene chloride was added slowly a solution of PPh₃ (0.049 g, 0.19 mmol) in methylene chloride. The reaction mixture was stirred overnight under ambient temperature and was then evaporated to dryness. The solid residue was washed with hexane for several times and was then recrystallized in the mixed solution of THF and hexane to give 0.055 g of red purple solid. Yield: 36%. *Anal.* Found: C, 41.9; H, 3.01. Calc. for: $\text{C}_{27}\text{H}_{24}\text{O}_2\text{RhPI}_2$ (768.17 g/mol): C, 42.2; H, 3.15%. IR (KBr pallet), $\nu_{\text{max}}/\text{cm}^{-1}$: 3085, 3056, 2970 (–CH aliphatic), 1718 (C=O), 1655 (C=C), 1580 (Ph), 1480 (C–C), 1433, 1399, 1278, 1150, 1092. UV–Vis $\lambda_{\text{max}}/\text{nm}$ (CH_2Cl_2): 230 ($\epsilon/\text{dm}^3 \text{ mol}^{-1}$ 5.79×10^4), 300 (1.98×10^4), 444 (0.49×10^4). δ_{H} (CDCl_3): 7.6 (br, 15H, PPh₃), 6.05 (m, 2H, ring-CH), 6.01 (m, 1H–CH=), 5.69 (m, 2H, ring-CH), 5.46 (d, 1H, =CH₂ *trans*, $J = 16.1$ Hz), 5.33 (d, 1H, =CH₂ *cis*, $J = 10.8$ Hz), 4.85 (d, 2H, –OCH₂–, $J = 5.7$ Hz).

2.13. Preparation of $(\eta^5\text{-C}_5\text{H}(\text{C}_3\text{H}_7)_4)\text{RhI}_2\text{CO}$ (10)

A 100 ml Schlenk tube with $[(\eta^5\text{-C}_5\text{H}(\text{C}_3\text{H}_7)_4)\text{RhI}_2]_2$ (0.10 g, 0.085 mmol) in it was evacuated, flushed with N₂ and then filled with 1 atm of carbon monoxide. 20 ml of THF was injected into the Schlenk tube. The reaction mixture was stirred overnight under ambient temperature. The solvent was removed in vacuo and the residue

Table 4
Bond lengths (Å) and angles (°) for $(\eta^5\text{-C}_5\text{H}(\textit{i}\text{-C}_3\text{H}_7)_4)\text{Rh}(\text{COD})$ (3)

Rh(1)–C(1)	2.308(5)	C(2)–C(3)	1.498(19)
Rh(1)–C(2)	2.110(11)	C(3)–C(4)	1.343(8)
Rh(1)–C(3)	2.308(10)	C(4)–C(5)	1.521(18)
Rh(1)–C(4)	2.208(12)	C(18)–C(25)	1.23(2)
Rh(1)–C(5)	2.317(9)	C(18)–C(19)	1.55(2)
Rh(1)–C(18)	2.159(9)	C(19)–C(20)	1.43(2)
Rh(1)–C(19)	1.977(12)	C(20)–C(21)	1.520(19)
Rh(1)–C(22)	2.172(9)	C(21)–C(22)	1.353(17)
Rh(1)–C(23)	2.048(11)	C(22)–C(23)	1.57(3)
C(1)–C(2)	1.344(15)	C(23)–C(24)	1.43(2)
C(1)–C(5)	1.411(12)	C(24)–C(25)	1.69(3)
C(19)–Rh(1)–C(18)	43.7(7)	C(2)–C(6)–C(8)	113(1)
C(23)–Rh(1)–C(18)	73.5(8)	C(2)–C(6)–C(7)	112(1)
C(19)–Rh(1)–C(22)	75.8(6)	C(11)–C(9)–C(3)	124(1)
C(23)–Rh(1)–C(22)	43.5(7)	C(3)–C(9)–C(10)	112(1)
C(1)–C(2)–C(3)	120.5(9)	C(14)–C(12)–C(4)	112(1)
C(1)–C(2)–C(6)	111(1)	C(13)–C(12)–C(4)	117(1)
C(3)–C(2)–C(6)	125(1)	C(5)–C(15)–C(17)	112(1)
C(4)–C(3)–C(9)	129(1)	C(5)–C(15)–C(16)	120(1)
C(4)–C(3)–C(2)	98(1)	C(25)–C(18)–C(19)	115(1)
C(9)–C(3)–C(2)	133(1)	C(20)–C(19)–C(18)	124(1)
C(3)–C(4)–C(5)	111(1)	C(19)–C(20)–C(21)	114(1)
C(3)–C(4)–C(12)	113(1)	C(22)–C(21)–C(20)	109.4(9)
C(5)–C(4)–C(12)	133.4(9)	C(21)–C(22)–C(23)	120(1)
C(15)–C(5)–C(1)	118(1)	C(24)–C(23)–C(22)	121(1)
C(15)–C(5)–C(4)	133(1)	C(23)–C(24)–C(25)	111(1)
C(1)–C(5)–C(4)	108.7(8)	C(18)–C(25)–C(24)	105(1)

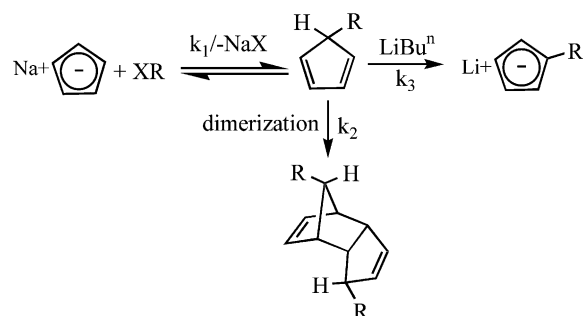
was recrystallized in a mixed solvent of THF and hexane to give 0.042 g of black purple solid. Yield: 40%. *Anal.* Found: C, 34.6; H, 4.50. Calc. for: $\text{C}_{18}\text{H}_{29}\text{ORhI}_2$ (618.14 g/mol): C, 35.0; H, 4.73%. IR (KBr pallet): $\nu_{\text{max}}/\text{cm}^{-1}$: 2964, 2922, 2869 (–CH aliphatic), 2050 (CO), 1467 (C–C), 1368, 1261 and 1103. δ_{H} (CDCl_3): 5.48 (s, 1H, $\text{HC}_5(\textit{i}\text{-propanyl})_4$), 3.01 (br, 2H, CHMe_2), 2.84 (br, 2H, CHMe_2), 1.56 (m, 6H, CH_3), 1.48 (m, 12H, CH_3), 1.28 (m, 6H, CH_3).

3. Results and discussion

The way to synthesis a functionally substituted cyclopentadienyl metal complex is versatile. Usually a functionalized cyclopentadienyl salt is prepared as the reaction precursor. This salt reacts with a metal chloride can lead to the aimed products. Direct modification of the cyclopentadienide with formyl-, acetyl- or methoxycarbonyl substituent was reported [10]. These functionalized cyclopentadienyl ligand were convenient precursors for the functionally substituted half-sandwich cobalt complexes. The synthetic method could be easily extended to other metals like Rh, Ir, Mn, Tc, Re, Cr, Mo, W or Ti. Direct functionalization with the cyclopentadienyl metal carbonyl complexes through Friedel–Crafts reaction was also reported [11]. Indirect modification through halogenation of the cyclopentadienide was reported as another way to the synthesis of

the functionally substituted cyclopentadienyl metal complexes [12]. The halogenated cyclopentadienyl metal complexes are useful reaction precursors for halogen–lithium exchange reaction, which could be further transferred to the desired metal complexes. In our experiments, the functionalized cyclopentadienyl salts were the desired reaction precursor. During the synthetic procedure, the electronic property of the substituent displayed great impact to the reaction. The influence of the substituent to the reaction is depicted by Scheme 1.

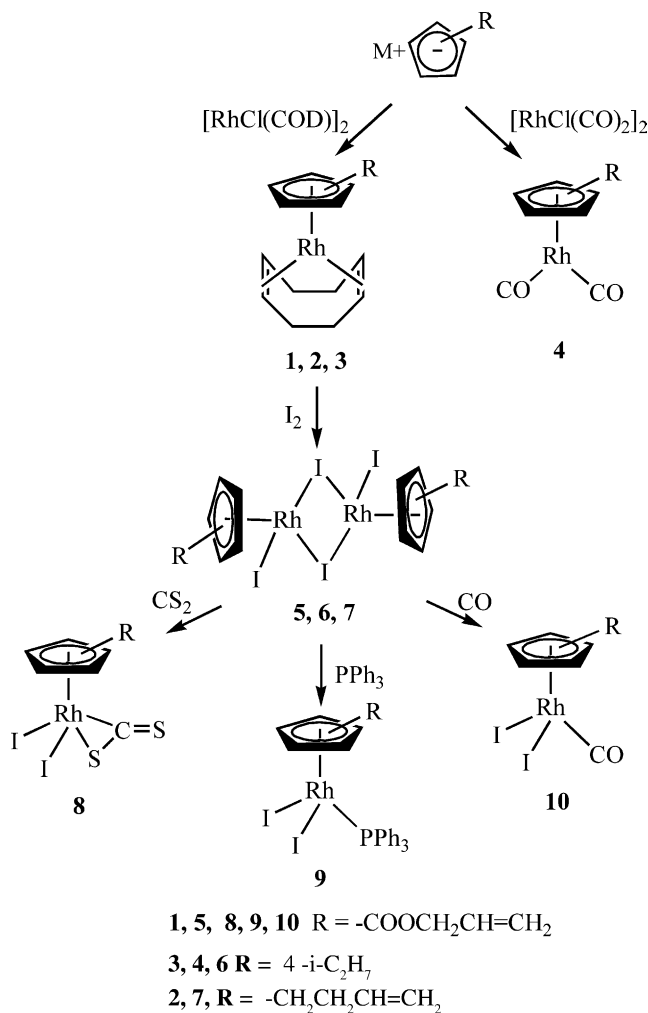
Scheme 1 illustrates that the major side-reaction is dimerization. In order to reduce the influence from side-reaction, faster functionization k_1 and deprotonation k_3 are both appreciated. Faster k_1 and k_3 can reduce the reaction time take by the dimerization before and after



Scheme 1.

deprotonation. The ω -butenyl is an electron-donating substituent. ω -Butenyl cyclopentadiene dimerizes easily even under the temperature of $-40\text{ }^\circ\text{C}$. The dimerization began as soon as the substituted cyclopentadiene was formed. Choosing 4-bromide-1-butene instead of 4-chloride-1-butene was favored the functionalization reaction k_1 owing to the activity of bromide. Compared to its bromide analogue, chloride usually gave poorer yield only because of its relatively inertness, which required longer time to finish the functionalization, therefore more dimerized side products resulted. The deprotonation of the functionalized cyclopentadiene was also competed by its dimerization. Metallic sodium is a clean deprotonation reagent, but its reaction rate is too slow. We chose sodium ethoxide as the deprotonation reagent, the yield was less than 30%. With the more reactive *n*-butyllithium as the deprotonation reagent, the yield was increased to 46%. Proper reaction concentration was also desired. If the concentration of the substrate was too low, it needed longer time to finish the synthetic reaction, and more dimerization resulted. However, higher reaction concentration would increase the rate of dimerization and was also disadvantageous. A proper reaction concentration for the substrate was found about 0.3 M, which was balanced by k_2 and k_3 . Allyl chloroformate has an active acyl chloride and an electron-withdrawing group of allyloxycarbonyl. With allyl chloroformate as the functionalization reagent, k_1 was increased and the time for dimerization was decreased. The yield of allyloxycarbonyl cyclopentadienide was 85% even though sodium ethoxide was used as the deprotonation reagent. This result supported the fact that the electron-withdrawing substituent disfavored the dimerization. A general atom-economizing method for the synthesis of hydroxyalkoxycarbonylcyclopentadienide was reported recently by Busetto and Albano [13]. High yields of over 90% were achieved through the reaction of the easily obtained sodium cyclopentadienide and cyclic carbornates with a mechanism in which the deprotonation of the 1-substituted cyclopentadiene intermediate occurs intramolecularly. This synthesis method avoid the transesterification type reaction between two alkoxy carbonylcyclopentadiene molecules [14], although the dimers derived from a transesterification type reaction between two molecules of the corresponding mononuclear complexes was also found during the synthesis of the metal complexes.

The reactions with the substituted cyclopentadienide as the starting material leading to the metal complexes are presented in Scheme 2. Rh(I) complexes were prepared through the reactions of substituted cyclopentadienide and rhodium chloride dimer $[\text{RhCl}(\text{COD})]_2$ or $[\text{RhCl}(\text{CO})_2]_2$ in THF solution, thus the corresponding half-sandwich type complexes of **1**, **2**, **3** and **4** were obtained in moderate yields. These complexes have pretty good solubility in organic solvent, either in polar solvent



Scheme 2.

as THF, diethyl ether and dichloromethane, or in non-polar solvent as benzene and hexane. The analytically pure products were obtained through column chromatography. The COD complexes of **1**, **2** and **3** were yellow, a typical color for Rh(I) compound; while **4** was nacarat, which is the typical color for Rh(I) carbonyl compound. The IR spectrum of **1** showed typical skeletal vibrations of cyclopentadienyl ring at 3084, 2933, 1470, 1374, 1272, 1127 cm^{-1} and typical COD skeletal vibrations at 2875, 2827, 1323, 968, 867 and 804 cm^{-1} . Vibrational frequency of a free terminal alkene group $\nu(\text{C}=\text{C})$ is found at 1649 cm^{-1} . Frequency of $\nu(\text{C}=\text{O})$ is found at 1692 cm^{-1} , apparently red shifted comparing to the ordinary ester $\nu(\text{C}=\text{O})$ value that is around 1750–1735 cm^{-1} , indicating a conjugating effect to the cyclopentadienyl ring system. The yield of the carbonyl compound **4** was lower than that of the COD complexes. During the separation of **4** on alumina column, a blue band was found and was collected to give blue oil. It was very air-sensitive and did not obtain analytically pure substance. It showed a very strong absorption at

1730 cm^{-1} in IR spectrum, which was considered the vibrational frequency of a bridged metal carbonyl group [9]. So the most possibility about the composition of the blue oil should be a carbonyl bridged dimer product $[\text{Cp}^{\text{4i}}\text{Rh}(\text{CO})]_2$.

The conjugation system between the ring and the oxycarbonyl group in the substituent is confirmed by the crystal structure of **1** (see Fig. 1). In the crystal structure of **1**, the average metal–ring carbon distance is found 2.260 Å. Among the five metal–ring carbon bonds, Rh(1)–C(2) and Rh(1)–C(3) have longer bond length [2.294(4) and 2.301(4) Å], while Rh(1)–C(1) and Rh(1)–C(4) have shorter bond length [2.221(3) and 2.231(3) Å]. The length of Rh(1)–C(5) [2.255(3) Å] is in between. Thus the cyclopentadienyl ring is found in a slightly puckered form. The C–C bond lengths in the cyclopentadienyl ring are in the range of 1.390(6)–1.427(5) Å. Among them, C(2)–C(3) band was located furthest from the ring substituent and has the shortest bond length [1.390(6) Å], showing more double bond character than other C–C bonds. The strong electron-withdrawing substituent of allyloxycarbonyl group is attached to C(5), resulting in a relatively electronic deficient situation on it. A longer metal–carbon bond length of Rh(1)–C(5) was found compared to its neighboring metal–carbon bond length of Rh(1)–C(1) and Rh(1)–C(4). The oxycarbonyl group is found coplanar with the cyclopentadienyl ring and forms a large π conjugating system. Similar bonding character was also found in the crystal structure of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_3)\text{Co}(\text{COD})$ [15], $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{C}_6\text{H}_5)\text{Co}(\text{PPh}_3)_2$ [5c] and the recently reported β -hydroxyalkoxycarbonylcyclopentadienyl rhodium complexes [13], respectively. In these complexes, the shortest metal–carbon bond was also found linking to the strong electron-withdrawing substituent. In **1**, the distances between rhodium atom and

the coordinated carbon atoms of the double bonds in the COD ring are also not the same. The bond lengths of Rh(1)–C(10) and Rh(1)–C(15) [both are 2.114(4) Å] are comparatively shorter than that of Rh(1)–C(11) [2.127(3) Å] and Rh(1)–C(14) [2.128(3) Å]. Opposite to the shorter rhodium–carbon bonds with COD are the longer rhodium–carbon bonds with Cp, and longer rhodium–carbon bonds with COD are opposite to the shorter rhodium–carbon bonds with Cp. The phenomena may be due to the trans effect. The bond lengths of C(10)–C(11) and C(14)–C(15) are 1.393(6) and 1.378(6) Å, respectively, showing the normal characteristic of the coordinated double bond [16].

^1H NMR spectrum of **1** in $(\text{CD}_3)_2\text{CO}$ shows one set of multiplet at 6.04 ppm and two sets of doublets at 5.42 and 5.23 ppm for the allyl protons, similar to the values found in its cobalt(I) analogue $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{Co}(\text{C}_6\text{O})_2$ [7]. However, the split of the two sets of the pseudo triplet for Cp ring protons at 5.48 and 5.44 ppm is only 0.04 ppm in **1**, smaller than the value of 0.15 ppm found in its cobalt(I) carbonyl analogue. In $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_3)\text{Co}(\text{COD})$, the corresponding value is found 0.70 ppm. On the contrary, the split of the ring protons in **2** is 0.17 ppm, although the substituent of ω -butenyl in **2** is electron-donating in nature. The electron-withdrawing substituent –COR to the Cp ring causes a split of the chemical shift of the ring protons about 0.60 ppm for cymantrene derivatives and about 0.15 ppm for cobalt(I) carbonyl analogues were reported [14]. In the case of electron-donating substituent as $-\text{CH}_2\text{CH}_2\text{CO}_2\text{R}$ and $-\text{CH}_2\text{CO}_2\text{R}$ to the Cp ring of cymantrene derivatives, the corresponding values were found only 0.02 and 0.15 ppm, respectively. The small split of the chemical shift of the ring protons is considered a hint that the Rh(I) atom in **1** is a more electron-rich metal center compared with Co(I) and Mn(I) complexes mentioned above.

Usually an electron-rich metal compound like Rh(I) complex is air sensitive, but **3** is air stable. Even the carbonyl compound **4** can stay in air for a reasonable long period of time. The probable explanation on this may be drawn from the crystal structure of **3** (see Fig. 2). The average metal and Cp ring–carbon distance in **3** is 2.250 Å. And the average metal and COD–carbon distance is 2.089 Å. Both of them are shorter than the corresponding values found in **1**. It is considered that part of the electron density on the metal center of **1** is dispersed into its π system, therefore leads a weaker bonding ability of the metal with its circumambient ligands. On the contrary, the four isopropanyl groups in $\text{C}_5\text{H}(\textit{i}\text{-C}_3\text{H}_7)_4$ ligand are electron-donating. The metal center of **3** is more electron-rich than **1**. The shorter metal–carbon bond distances reflect the stronger bonding ability of the metal with its circumambient ligands. In spite of such an electron-rich metal center, the four steric bulky isopropanyl groups are arrayed parallel to

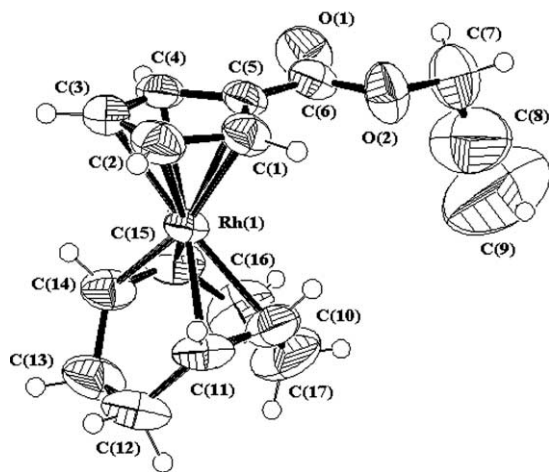


Fig. 1. Molecular structure of $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{Rh}(\text{COD})$ (**1**). Ellipsoids are drawn at 50% probability level.

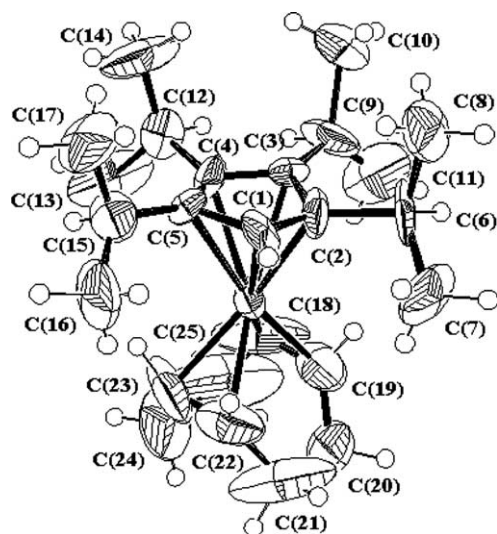


Fig. 2. Molecular structure of $(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)\text{Rh}(\text{COD})$ (**3**). Ellipsoids are drawn at 50% probability level.

each other and perpendicularly to the Cp ring, therefore they enwrapped the metal atom and protect it from being oxidized when exposed to air.

The addition of a solution of iodine in ether to the solutions of COD complexes of **1**, **2** and **3** in ether resulted in the loss of COD ligand and yielded the iodine bridged dimer products of **5**, **6** and **7**, respectively, in high yields. The IR spectrum of **5** showed typical skeletal vibrations of cyclopentadienyl ring at 3067, 1460, 1275, 1157 and 1026 cm^{-1} , very similar to its parent compound **1**. However, the frequency of $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{H}$ of Cp ring) are now 1724 and 2962 cm^{-1} , respectively, considerable blue shifted compared to the values of 1691 and 2933 cm^{-1} , respectively, found in its parent compound **1**, reflecting the electronic effect from a less electron-rich metal center of Rh(III) in **5** compare to Rh(I) in **1**. Frequency of $\nu(\text{C}=\text{C})$ at 1649 cm^{-1} is unchanged, indicating the existence of an untouched free terminal alkene group. The IR spectrum of **7** shows typical skeletal vibrations of cyclopentadienyl ring at 3088, 3070, 1470, 1393, 1107 and 1031 cm^{-1} , similar to its parent compound **2**. Vibrational frequency of a free terminal alkene group of $\nu(\text{C}=\text{C})$ at 1640 cm^{-1} is also found unchanged in its IR spectrum. In the ^1H NMR spectrum, the chemical shift of the ring protons of **5** (a derivative from **1**) in CDCl_3 are at 6.07 and 5.71 ppm, respectively, giving a split of 0.36 ppm. The corresponding chemical shifts of **7** (a derivative from **2**) are 5.49 and 5.46, with a split of only 0.03 ppm. These situations match the cases found in the substituted cyclopentadienyl Co(I) and Mn(I) complexes reported in the literatures mentioned above. Although **5**, **6** and **7** did not give molecular ion peaks for their dimer structures in mass spectra, the peaks of the molecular fragments of these complexes supported

their dimer structures. Hadjiliadis reported that the 2-(dimethylamino)ethyl cyclopentadienyl Rh(I) COD compound or carbonyl compound gave chelated halogenide monomer after treated with iodine or chlorine. However, after the nitrogen atom in the side chain was protonated, the amino group lost its donating ability. The addition of the halogen to the 2-(dimethylamino)ethyl cyclopentadienyl Rh(I) COD compound resulted in the iodine or chlorine bridged dimer product then [17]. The alkene group in the side chain of **5** and **7** has very weak donating ability. It cannot compete with halogen atom. The formation of the iodine bridged dimer of **5** and **7** will not be affected by their chelatable substituent.

When stronger electron donating molecule existed, the iodine bridged dimer structure was destroyed. Thus **5** treated with triphenyl phosphine or carbon monoxide resulted the corresponding monomer **9** or **10**. Carbon disulfide could also break down the iodine bridged structure. About two equivalent of carbon disulfide was added to the solution of **5** in CH_2Cl_2 , one of the coordination site on the Rh(III) was occupied by CS_2 and resulted the CS_2 substituted product of monomer **8**. The IR spectrum of **8** shows a medium strong stretching frequency at 1026 cm^{-1} , which is the characteristic frequency for the $\nu(\text{C}=\text{S})$ of a π bonded CS_2 molecule [18].

4. Supplementary data

Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition numbers 196053 for $(\eta^5\text{-C}_5\text{H}_4\text{COOCH}_2\text{CH}=\text{CH}_2)\text{Rh}(\text{COD})$ (**1**) and 196052 for $(\eta^5\text{-C}_5\text{H}(i\text{-C}_3\text{H}_7)_4)\text{Rh}(\text{COD})$ (**3**), respectively.

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