

Half-sandwich cyclopentadienyl rhodium complexes bearing pendant sulfur or oxygen ligands and their catalytic behaviors in ethylene polymerization

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Received 20 November 2004; accepted 15 February 2005

Available online 11 March 2005

Abstract

Two half-sandwich rhodium complexes with sulfur or oxygen functionalized cyclopentadienyl ligands $[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{SCH}_2\text{CH}_3]\text{RhI}_2$ **3**, $\{[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{OCH}_3]\text{RhI}_2\}_2$ **4** have been synthesized and characterized by IR, $^1\text{H-NMR}$ spectra and Elemental analyses. The molecular structures of complexes **3** and **4** have been determined by X-ray crystallographic analysis. Complexes **3**, **4** with a pendent arm on cyclopentadienyl ligand have been tested as catalysts for ethylene and norbornene polymerization in the presence of MAO. Complexes **3** and **4** kept high activities of ca. 10^6 g PE mol $^{-1}$ Rh h $^{-1}$ with moderate molecular weight ($M_w \approx 10^5$ g mol $^{-1}$) of polyethylene in the ethylene polymerization. Catalytic activities, molecular weights of polyethylene have been investigated under the various reaction conditions.

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Keywords: Rhodium; Functional cyclopentadienyl group; Rhodium; Ethylene; Polymerization; Molecular structures

1. Introduction

Cyclopentadienyl chemistry has clearly attained a state of maturity now. Various organic substituents were used to create new chemistry. Among these chemistry, cyclopentadienyl ligands with a functionalized pendant arm have attracted great interest [1]. Many new developments on this so-called “constrained geometry catalyst” (CGC) system have been reported [2–8]. In comparison to related N-functionalized cyclopentadienyl complexes, where catalytic applications of such species have been remarkably successful [9], the use of O- and S-functionalized compounds in catalysis still seems underdeveloped.

Half-sandwich complexes of transition metals, such as titanium or chromium with functionalized cyclopentadienyl ligands show high activity as olefin polymerization catalysts [10]. But only few rhodium complexes are used in olefin polymerization due to their relatively low activity [11,12]. In our previous work, we have prepared late transition metal catalysts [13] and metallocenes catalysts [14] for ethylene polymerization. So we take interest into the synthesis, structure and ethylene polymerization of the half-sandwich cyclopentadienyl rhodium complexes bearing a sidearm with donor moiety. With the pendant arm coordinated to the metal center, it becomes bidentate ligand. The cyclopentadienyl ligand is rather tightly bound to the metal and we could make the other coordinated site to be hemilabile and such system can stabilize reactive metal–ligand fragments in a reversible way, which can be very useful for catalytic purposes.

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Here, we report an investigation of Rh(III) olefin polymerization catalysts derived from the cyclopentadienyl ligand with a sulfur or oxygen functionalized pendent arm. Both the less bulky cyclopentadienyl derivatives and the π -donor properties of the pendant arms were selected for enhancing the activity of olefin polymerization catalysts.

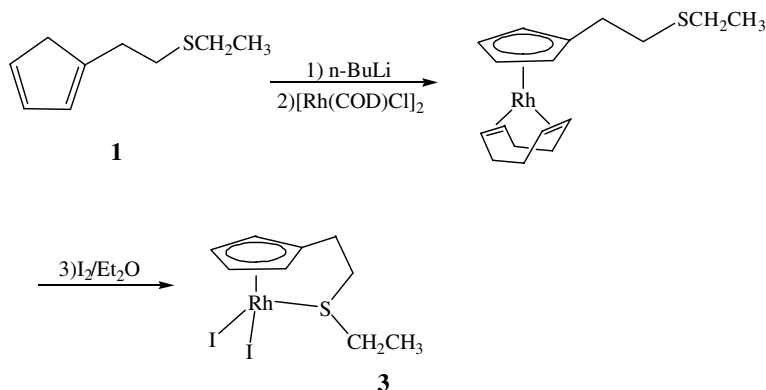
2. Results and discussion

2.1. Syntheses of the complexes

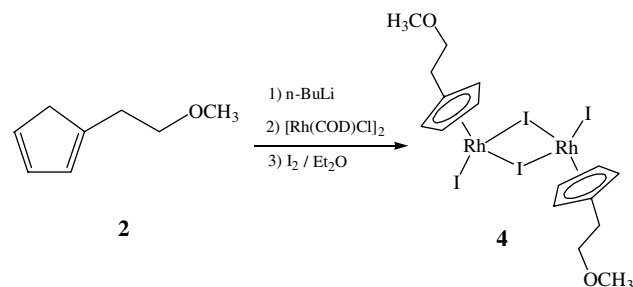
The sulfur-functionalized cyclopentadiene $C_5H_5(CH_2)_2SCH_2CH_3$ (**1**) reacts with *n*-BuLi and then $[Rh(COD)Cl]_2$ [15] in a THF solution to yield the cyclooctadiene (COD) rhodium complex, which, without isolation, was easily oxidized with elemental iodine in diethyl ether solutions to give the air-stable diiodo rhodium(III) complex $[\eta^5-C_5H_4(CH_2)_2SCH_2CH_3]RhI_2$ (**3**) in a good yield (Scheme 1). Infrared spectrum of **3** shows the skeletal vibrations [16] of the cyclopentadienyl ring at 3050, 1452, 1120 cm^{-1} .

In the 1H NMR spectrum of **3** in $CDCl_3$, the cyclopentadienyl triplets [17] are observed at 5.84 and 5.62 ppm, the ethylenic side-chain protons (CH_2S and CH_2CH_2S) appeared at 3.82, 2.96 and 2.65, 2.47 ppm, the SCH_2CH_3 multiplet is at 3.54 ppm, and the CH_2CH_3 triplet is at 1.35 ppm. A halogen-bridged dimer structure with a decoordinated sulfide arm can be excluded on the basis of the observation of two doublets of multiplet of the ethylenic protons by NMR spectroscopy [18]. The change in environment that caused the split in the 1H signals of the side-chain of the ligand must be that the sulfur is now coordinated to the rhodium atom.

The oxygen-functionalized cyclopentadienyl rhodium complex $\{[\eta^5-C_5H_4(CH_2)_2OCH_3]RhI_2\}_2$ (**4**) was prepared according to the similar method described above using ligand $C_5H_5(CH_2)_2OCH_3$ (**2**) (Scheme 2).



Scheme 1. Synthesis of **3**.



Scheme 2. Synthesis of **4**.

In the IR spectrum of **4**, the typical bands for cyclopentadienyl ring were observed at 2922, 1426, 1112 cm^{-1} . The 1H NMR spectrum of **4** showed an AA'BB' pattern for the C_5H_4 ring, and two triplets for the ring are observed at 5.58 and 5.47 ppm. Two triplets for the ethylenic side-chain protons (CH_2O and CH_2CH_2O) appeared at 3.67 and 2.78 ppm, and a singlet for the OCH_3 was at 3.35 ppm. The patterns and data of the side-chain protons are in agreement with the reported diiodo cobalt(III) complex (3.73 (t, 2H, OCH_2), 2.98 (t, 2H, CH_2), 3.40 (s, 3H, OCH_3)). [19] In accordance with the 18-electron rule, these data exclude the coordination of the OCH_3 group with the metal atom.

2.2. Molecular structure

The molecular structures of $[\eta^5-C_5H_4(CH_2)_2SCH_2CH_3]RhI_2$ (**3**) and $\{[\eta^5-C_5H_4(CH_2)_2OCH_3]RhI_2\}_2$ (**4**) were determined by single crystal X-ray diffraction. Suitable crystal was obtained by slow diffusion of hexane into a dichloromethane solution at low temperature.

As depicted in Fig. 1, complex **3** possesses basically a three-legged half-sandwich CpM structure, in which the sulfur atom was attached via an intramolecular coordination with the metal center and form an 18-electron complex. The structures of these two complexes are typical in this serial; the rhodium atom is not exactly

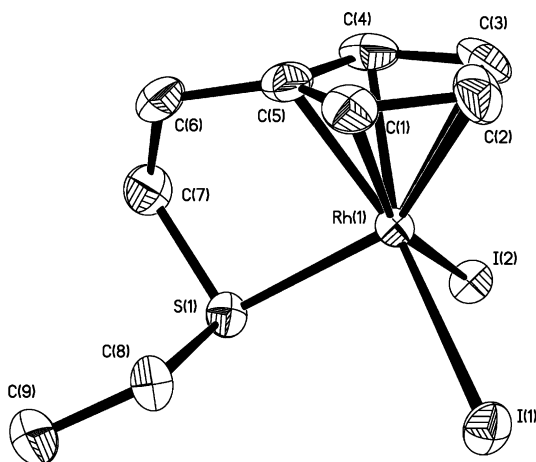


Fig. 1. Molecular structure of complex 3.

centered below the cyclopentadienyl unit but shifted by a small extent to the carbon atom which bears the pendent arm. The side-chain is coordinated to the metal center in a zigzag fashion in both cases [20]. The angles of the five-membered ring composed of metal and sulfur atom, part of the side-chain, and one of the carbon atoms in the cyclopentadienyl group are 116.1°, 112.1°, 111.7°, 96.7°, 85.1°. The bond length of Rh–S (1) is 2.348 Å which is a little shorter than the bond length of Rh–I (1) 2.6861 Å, or Rh–I (2) 2.6915 Å, due to the size difference between sulfur and iodine.

The molecule of **4** is dimer that has a central symmetry at the midpoint of two rhodium atoms. Complex **4** is composed of two $[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{OCH}_3]\text{RhI}_2$ units, which is very similar with the structure we reported before. [14] In each unit, the Rh atom is η^5 -bound to the cyclopentadienyl ring and σ -bound to two bridging-iodine atoms and to one terminal-iodine atom. The oxygen atom of side-chain is free of coordination with rhodium. The bridging iodine atom and two rhodium metals form a slightly distorted trigon. Two rhodium atoms and two bridging iodine atoms are coplanar. In complex **4**, the bond distances between the rhodium atoms and the bridging iodine atom are 2.6920(13) and 2.6959(15) Å, respectively, slightly longer than the Rh(1)–I(2) bond distance (2.6921(15) Å) between the rhodium atom and the non-bridging iodine atom. The distance between Rh(1) and Rh(1A) atoms indicates that direct rhodium–rhodium bonding interaction is absent in complex **4**. And due to the fact that the side-chain is not coordinated to the metal atom, the bond length of Rh(1)–C(1) is the longest among the bond lengths of rhodium and the five carbon atom in the cyclopentadienyl ligand. This may indicate that there is a slight repulsion between the side-chain and the iodine atom (see Fig. 2).

The relevant bond distances and angles are collected in Tables 1 and 2, respectively.

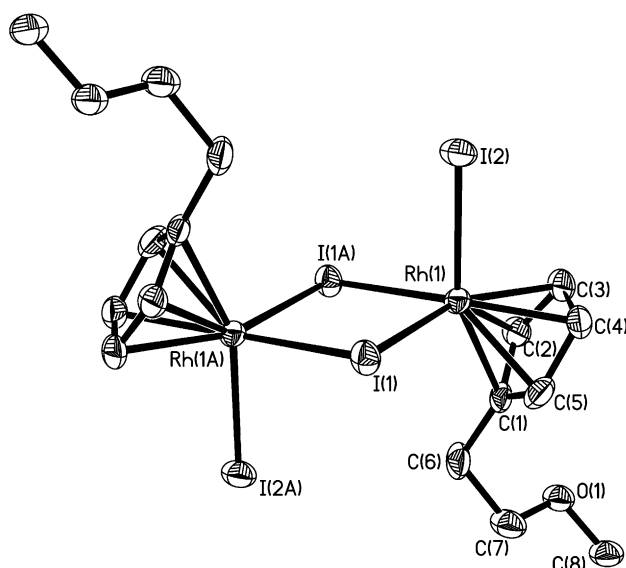


Fig. 2. Molecular structure of complex 4.

2.3. Catalytic activity

In the presence of a co-catalyst (MAO), the two functionalized cyclopentadienylmetal complexes as catalysts have been investigated for the polymerizations of ethylene.

2.3.1. Polymerization of ethylene

First, complex **3** and **4** were used as catalysts for ethylene polymerization under the condition of 30 °C, 1 atm and at the presence of 1000 equivalents of methylaluminumoxane MAO as co-catalyst. The results showed in Table 3, we got moderate catalytic activity (10^5 g PE mol^{-1} Rh h^{-1}). The results are rather satisfactory compared with other Group 9 catalysts.

Their catalytic activities are basically at the same level under this condition, though the environment around the metal atom is rather different.

For catalyst **3**, the detail data of ethylene polymerization are listed in Table 4. The results show that the increment of $n(\text{Al})/n(\text{Rh})$ leads to a curve in the reactivity (Fig. 3). When the $n(\text{Al})/n(\text{Rh})$ is 5000, its reactivity reach the maximum, but excess MAO may deactivate the active center, thus the activity will decrease. The effect of changing temperature is not very obvious, the reactivity decrease a little during the increase of the temperature. High temperature may deactivate the active center and decrease the solubility of ethylene in toluene. And compared run 4 and run 12, we find that the high ethylene pressure can decrease the activity a lot.

Catalyst **4** has the same metal center with the complex **3**, so we set the $n(\text{Al})/n(\text{Rh})$ at 5000:1. The detail data of ethylene polymerization are listed in Table 5.

Unlike complex **3**, the dimer sustains the increase in activity as we raise the temperature. When the reaction

Table 1
X-ray crystallographic data and processing parameters for **3** and **4**

Empirical formula	C ₉ H ₁₃ I ₂ RhS	C ₁₆ H ₂₂ I ₄ Rh ₂ O ₂
Formula weight	509.96	599.76
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>Unit cell dimensions</i>		
<i>a</i> (Å)	13.793(4)	7.3397(19)
<i>b</i> (Å)	7.887(2)	7.709(2)
<i>b</i> (Å)	13.454(4)	10.911(3)
α (°)	90	84.749(4)
β (°)	117.164(3)	70.512(4)
γ (°)	90	76.777(4)
Volume (Å ³)	1302.2(6)	566.5(3)
<i>Z</i>	4	1
Absorption coefficient (mm ⁻¹)	6.172	6.913
Crystal size (mm)	0.20 × 0.15 × 0.05	0.10 × 0.08 × 0.05
Calculated density (mg/m ³)	2.601	2.813
<i>F</i> (000)	936	436
θ range (°)	1.66–25.01	1.98–25.01
<i>h</i> , <i>k</i> , <i>l</i> collected	–10, 16; \pm 9; –15, 11	–8, 7; –9, 8; –12, 12
Reflections collected/unique [<i>R</i> (int)]	5238/2296 [0.0747]	2891/1952 [0.0291]
Data/restraints/parameters	2296/0/119	1952/0/109
Goodness-of-fit on <i>F</i> ²	1.026	0.997
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0557, <i>wR</i> ₂ = 0.1477	<i>R</i> = 0.0519, <i>wR</i> ₂ = 0.1078
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0633, <i>wR</i> ₂ = 0.1574	<i>R</i> ₁ = 0.0877, <i>wR</i> ₂ = 0.1192
Largest diff. peak and hole (e Å ⁻³)	1.679 and –1.990	1.148 and –0.872

Table 2
Selected bond distances (Å) and bond angles (°) for **3** and **4**

3		4	
Rh(1)–C(5)	2.124(9)	Rh(1)–C(1)	2.173(12)
Rh(1)–C(1)	2.153(8)	Rh(1)–C(3)	2.136(13)
Rh(1)–C(4)	2.154(9)	Rh(1)–C(2)	2.154(13)
Rh(1)–C(3)	2.178(9)	Rh(1)–C(4)	2.147(14)
Rh(1)–C(2)	2.183(9)	Rh(1)–C(5)	2.139(14)
Rh(1)–S(1)	2.348(2)	Rh(1)–S(1)	2.246(2)
Rh(1)–I(1)	2.6861(10)	I(1)–Rh(1)	2.6920(13)
Rh(1)–I(2)	2.6915(9)	I(2)–Rh(1)	2.6921(15)
S(1)–C(8)	1.806(9)	I(1a)–Rh(1)	2.6959(15)
S(1)–C(7)	1.820(10)	O(1)–C(7)	1.396(16)
C(1)–C(2)	1.401(14)	C(1)–C(5)	1.40(2)
C(1)–C(5)	1.414(13)	C(1)–C(2)	1.419(19)
C(2)–C(3)	1.413(15)	C(1)–C(6)	1.512(18)
C(3)–C(4)	1.441(15)	C(2)–C(3)	1.38(2)
C(4)–C(5)	1.422(12)	C(3)–C(4)	1.43(2)
C(5)–C(6)	1.502(14)	C(4)–C(5)	1.402(19)
C(6)–C(7)	1.520(14)	C(6)–C(7)	1.521(19)
C(8)–C(9)	1.533(14)	O(1)–C(8)	1.427(16)
I(1)–Rh(1)–I(2)	92.90(3)	I(1)–Rh(1)–I(2)	92.64(4)
S(1)–Rh(1)–I(2)	89.73(6)	I(1)–Rh(1)–I(1a)	94.76(4)
S(1)–Rh(1)–I(1)	93.42(6)	I(1a)–Rh(1)–I(2)	93.25(5)
C(7)–S(1)–Rh(1)	96.7(4)	C(7)–O(1)–C(8)	109.9(10)
C(8)–S(1)–Rh(1)	107.4(3)	C(6)–C(7)–O(1)	109.2(12)
C(8)–S(1)–C(7)	101.5(5)	C(6)–C(1)–Rh(1)	127.8(8)
C(6)–C(7)–S(1)	111.7(7)	C(2)–C(3)–Rh(1)	72.0(8)
C(9)–C(8)–S(1)	112.9(8)	C(4)–C(3)–Rh(1)	70.8(8)
C(6)–C(5)–Rh(1)	116.1(6)	C(1)–C(2)–Rh(1)	71.6(7)

Table 3
Ethylene polymerization results of catalyst **3** and **4**

Run	Catalyst	Activity ^a
1	[η^5 -C ₅ H ₄ (CH ₂) ₂ SCH ₂ CH ₃]RhI ₂ (3)	1.9
2	{[η^5 -C ₅ H ₄ (CH ₂) ₂ OCH ₃]RhI ₂ } ₂ (4)	2.2

^a 10⁵ g PE mol⁻¹ Rh h⁻¹; *T* = 30 °C, *n*(Al)/*n*(M) = 1000 (M = Co, Rh), *n*(M) = 5 μmol, pressure = 1 atm.

Table 4
Ethylene polymerization results of catalyst **3**

Run	<i>n</i> (Rh) (μmol)	<i>T</i> (°C)	<i>n</i> (Al)/ <i>n</i> (Rh)	Pressure (atm)	Activity ^a	<i>M</i> _w ^b (10 ⁵)
1	1.4	30	3000	1	0.60	3.24
2	1.4	30	3500	1	0.77	1.96
3	1.4	30	4000	1	0.87	2.28
4	1.4	30	5000	1	1.00	1.80
5	1.4	30	6000	1	0.93	2.25
6	0.4	20	5000	1	1.40	2.22
7	0.4	30	5000	1	1.24	2.53
8	0.4	40	5000	1	1.20	2.64
9	0.4	50	5000	1	1.09	3.81
10	0.4	30	5000	2	1.25	2.75
11	0.4	30	5000	3	1.21	3.85
12	0.4	30	5000	4	0.78	4.34

^a 10⁶ g PE mol⁻¹ Rh h⁻¹.

^b g mol⁻¹.

is heated to 65 °C, it reaches 1.4 × 10⁶ g PE mol⁻¹ Rh h⁻¹. Same as the complex **3** did at room temperature. We figure that the complex **4** may need the heat

to be decomposed into monomers, so that it can exhibit higher activity along with the co-catalyst MAO. But the activity is affected by the pressure easily, the results show that it drops to 10⁵ g PE mol⁻¹ Rh h⁻¹ at 4 atm.

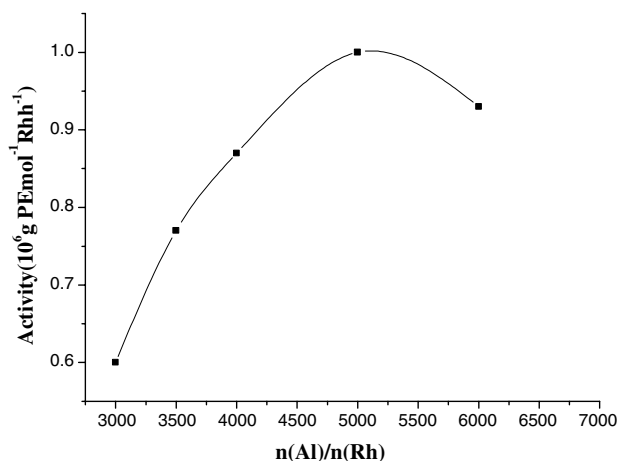


Fig. 3. effects on activity due to the increase of the $n(\text{Al})/n(\text{Rh})$.

Table 5
Ethylene polymerization results of catalyst **4**

Run	$n(\text{Rh})$ (μmol)	T ($^{\circ}\text{C}$)	$n(\text{Al})/n(\text{Rh})$	Pressure (atm)	Activity ^a	M_w^b
1	1.4	25	5000	1	1.05	2.76
2	1.4	45	5000	1	1.28	0.59
3	1.4	65	5000	1	1.4	0.38
4	1.4	25	5000	2	0.72	3.41
5	1.4	25	6000	4	0.31	4.57

^a 10^6 g PE mol⁻¹ Rh h⁻¹.

^b g mol⁻¹.

We have synthesized two half-sandwich rhodium complexes with sulfur or oxygen functionalized cyclopentadienyl ligands $[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{SCH}_2\text{CH}_3]\text{RhI}_2$ **3**, $\{[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{OCH}_3]\text{RhI}_2\}_2$ **4**. Preliminary study shows that new half-sandwich rhodium complexes **3** and **4** show highly active as catalyst precursor in ethylene polymerization in the presence of MAO. Although the detail mechanism of the catalytic olefin polymerization is not clear, we believe that a cationic methyl rhodium is formed in the presence of co-catalyst (MAO) and then a vacant site (active site) for coordination of olefin must be generated. To our best knowledge, it is the first report that this kind of half-sandwich rhodium complexes exhibits high activity toward ethylene polymerization. Further investigations into olefin polymerization of such kind of complexes and polymerization mechanism are ongoing.

3. Experimental

All operations were carried out under a nitrogen atmosphere using standard schlenk techniques. Tetrahydrofuran (THF), hexane and diethyl ether were distilled from sodium benzophenone; and dichloromethane (CH_2Cl_2) was distilled from calcium hydride. $n\text{-BuLi}$ (2.3 M in hexane, Aldrich). The $[\text{Rh}(\text{COD})\text{Cl}]_2$ was

synthesized via a literature procedure [8]. $\text{C}_5\text{H}_4(\text{CH}_2)_2\text{SCH}_2\text{CH}_3$ (**1**) and $\text{C}_5\text{H}_4(\text{CH}_2)_2\text{OCH}_3$ (**2**) were synthesized through the reported method [12]. Infrared spectra were recorded on Nicolet-FT-IR-50X spectrophotometer, only characteristic frequencies were listed. ^1H NMR spectra were obtained using a Bruker DMX-500 spectrophotometer in CDCl_3 . The element analyses were performed on Rapid CHN-O 240C Analyzer.

3.1. $[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{SCH}_2\text{CH}_3]\text{RhI}_2$ (**3**)

To a solution of **1** (1.54 g, 1.0 mmol) in 10 ml THF was added $n\text{-BuLi}$ (0.43 ml, 1.0 mmol) drop wise at -78 $^{\circ}\text{C}$. The suspension was stirred for 1 h at room temperature. The mixture was cooled to -78 $^{\circ}\text{C}$, and was added drop wise to a solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.25 g 0.5 mmol) in 15 ml THF. The resulting suspension was warmed to room temperature and kept over night and the solvent was removed under vacuum. The residue was extracted in 20 ml diethyl ether to remove LiCl salt. And to this obtained chrysoidine solution was added drop wise 15 ml diethyl ether containing I_2 (0.25 g, 1.0 mmol) at -78 $^{\circ}\text{C}$. After 12 h stirring at room temperature, the upper clear solution was removed, and after washed with diethyl ether twice afford **3** (0.292 g, 57%) as a red solid. Recrystallization of **3** from $\text{CH}_2\text{Cl}_2/\text{hexane}$ afforded dark red crystals. Anal. Calc. for $\text{C}_9\text{H}_{13}\text{RhSI}_2$ (509.98 g/mol) C, 21.20; H, 2.57. Found: C, 21.60; H, 2.56. IR (KBr, cm^{-1}): ν 3050, 2959, 2924, 1693, 1452, 1415, 1382, 1120, 1013, 910, 850, 819, 656, 562. ^1H NMR (500 Hz, CDCl_3 , ppm): δ 5.84(t, 2H, Cp), 5.62(t, 2H, Cp), 3.82, 2.96 (2 \times m, 2H, $\text{CH}_2\text{CH}_2\text{S}$), 2.65, 2.47 (2 \times m, 2H, SCH_2CH_3), 3.54 (m, 2H, CH_2CH_3), 1.34 (m, 3H, CH_3).

3.2. $\{[\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{OCH}_3]\text{RhI}_2\}_2$ (**4**)

Following the procedure described for **3**, $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.5 g, 1.0 mmol); **2** (0.25 g, 2.0 mmol); $n\text{-BuLi}$ (0.86 ml, 2.0 mmol); I_2 (0.54 g, 2.1 mmol) gave **4** (0.58 g, 60%) as a dark purple solid. Anal. Calc. for $\text{C}_{16}\text{H}_{22}\text{Rh}_2\text{O}_2\text{I}_4$ (959.78 g/mol) C, 20.02, H, 2.31, Found: C, 19.83, H, 2.22. IR (KBr, cm^{-1}) ν 3412, 2922, 1637, 1426, 1112, 838, 775. ^1H NMR (500 Hz, CDCl_3 , ppm): δ 5.58 (t, 2H, Cp), 5.47 (t, 2H, Cp), 3.68 (t, 2H, CH_2O), 2.78 (t, 2H, CH_2), 3.35 (s, 3H, CH_3).

3.3. X-ray crystal structure analysis

Single crystal was sealed in glass capillaries and was sequentially mounted on CCD-Bruker smart diffractometer. The determinations of unit and intensity data were performed with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature using the scan technique. The structure was solved by the direct methods expanded using Fourier

techniques and refined on F^2 by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included but not refined. Details of crystal data for **3** and **4** are summarized in Table 2.

3.4. Polymerization of ethylene

A 200 ml Schlenk-type glass reactor containing 50 ml toluene was equilibrated with the ethylene monomer. MAO was added as a solution in toluene. After stirred for 5 min, the certain catalyst solution in toluene was added. After reaction for half an hour, the polymerization was terminated with an ethanol solution containing 1% HCl. The mixture was filtered, washed and dried under vacuum at 40 °C for 24 h. The molecular weight of the polymer was measured by the Ubbelohde calibrated viscosimeter technique through the investigation of the intrinsic viscosity.

4. Supplementary material

Crystallographic data for the structures of complexes **3** and **4** reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-255014 and 255015. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1233/336 033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgment

Financial support by the National Nature Science Foundation of China for Distinguished Young Scholars (29925101) and by the special Funds for Major State Basic Research Projects (G 1999064800) and Youth Funds of Fudan University is gratefully acknowledged.

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