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Functionalized cyclopentadienyl rhodium(III) bipyridine complexes: synthesis, characterization, and catalytic application in hydrogenation of ketones†

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A series of highly functionalized cyclopentadienyl rhodium(III) complexes, [Cp′Rh(bpy)Br](ClO$_4$) (Cp′ = substituted cyclopentadienyl), was synthesized from various multi-substituted cyclopentadienes (Cp′H). [Rh(cod)Cl]$_2$ and Cp′H were firstly converted to [Cp′Rh(cod)] complexes, which were then treated with Br$_2$ to give the rhodium(III) dibromides [Cp′RhBr$_2$]$_2$. The novel complexes [Cp′Rh(bpy)Br](ClO$_4$) were obtained readily by the reaction of 2,2′-bipyridine with [Cp′RhBr$_2$]$_2$. These rhodium complexes [Cp′Rh(bpy)Br](ClO$_4$) were fully characterized and utilized in the hydrogenation of cyclohexanone and acetophenone with generally high yields, but they did not exhibit the same reactivity trends for the two substrate ketones. The different activity of these complexes for the different substrates may be due to the influence of the substituents on the Cp′ rings.

Introduction

Half-sandwich complexes, [Cp*M(L)X]$^+$ (Cp* = η^5-pentamethylcyclopentadienyl; M = Rh(III), Ir(III)), have recently attracted increasing attention due to their favourable thermal stability and water solubility, excellent catalytic activity in various transformations, and promising anticancer activity.[1–4] A large number of [Cp*M(L)X]$^+$ have been studied using different kinds of ligands (L), such as bpy (2,2′-bipyridine), phen (1,10-phenanthroline), cod (1,5-cyclooctadiene), diamines, NHC (*N*-heterocyclic carbenes), *etc*.[5–7] In contrast, functionalized complexes based on cyclopentadienes bearing multiple functional groups have been less investigated.[8–14] To a great extent, this is due to the inaccessibility of multi-substituted cyclopentadienes (Cp′H). Functionalized cyclopentadienes are generally limited to monosubstituted analogs[15–20] and/or confined functional groups.[8,9] Moreover, feasible and practical synthesis of multi-substituted cyclopentadienes is quite limited due to the use of complex substrates and/or expensive transition metals.[10,21–29] We have reported one-step synthesis of multi-substituted cyclopentadienes from 3-alkoxycarbonylallylidenephosphorane and α-halocarbonyl compounds *via* [3 + 2] annulation under mild conditions.[30–32] This convenient method has been employed by Takahashi and Onitsuka *et al.* to construct various chiral Cp′–Fe(II), –Rh(I), and –Ru(II) complexes which have been demonstrated to be effective catalysts for a series of enantioselective reactions.[11–14]

We have been interested in improving the catalytic activity of [Cp*M(L)Cl]$^+$ (M = Rh(III), Ir(III)) for a number of reactions such as the transfer hydrogenation of unsaturated organic substrates,[33] deuterogenation,[34,35] hydrogenation of carbon dioxide,[36–38] and dehydrogenation of formic acid.[39,40] By introducing electron-donating groups (OH, OMe, Me) into the bpy ligands, significantly improved activity was achieved. The multi-substituted cyclopentadienyl ligands have advantages to modulate their steric and electronic properties by varying the substituents on the ligand. Consequently, the physical properties and catalytic activity of the corresponding functionalized cyclopentadienyl complex can be readily fine-tuned.[10,19] Accordingly, we sought to develop complexes based on highly functionalized cyclopentadienyl ligands, which are accessible using our previously reported method, and to investigate the substituent effects thereof. Herein, we report a facile preparation of multi-substituted cyclopentadienyl rhodium complexes [Cp′RhBr(bpy)](ClO$_4$) and their application in the hydrogenation of ketones.

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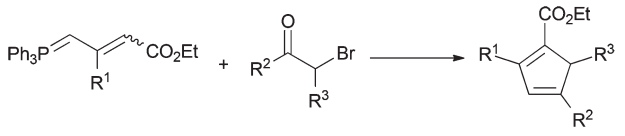
†Electronic supplementary information (ESI) available: HHCOSY, NOESY, HMBC spectra, cyclic voltammograms. CCDC 921223 (**6e**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50445j

Results and discussion

1. Synthesis of functionalized cyclopentadienes 1a–e

The substituted cyclopentadienes **1a–e** were synthesized from 3-alkoxycarbonylallylidenephosphoranes and α-bromocarbonyl



1a (Cp^1H): R^1 = Me, R^2 = Me, R^3 = H; Yield: 96%
1b (Cp^2H): R^1 = Me, R^2 = Ph, R^3 = H; Yield: 78%
1c (Cp^3H): R^1 = OEt, R^2 = Me, R^3 = H; Yield: 84%
1d (Cp^4H): R^1 = OEt, R^2 = SEt, R^3 = H; Yield: 72%
1e (Cp^5H): R^1 = OEt, R^2, R^3 = -C_4H_8-; Yield: 47%

1a-e

Scheme 1 Synthesis of multi-substituted cyclopentadienes **1a–e** (Cp′H). Reaction conditions: (1) for **1a–b**: aq. $NaHCO_3$, CH_2Cl_2, rt, 12 h, (2) for **1c–e**: 0.6 eq. Cs_2CO_3, CH_2Cl_2, 30 °C, 48–72 h.

compounds in one step with good to high yields (47–96%) according to our previously reported method (Scheme 1).[30–32]

2. Synthesis of the bipyridine complex (3) from 1a and rhodium chloride

In the same manner as the preparation of the pentamethylcyclopentadienyl analogue $[Cp^*RhCl_2]_2$,[41,42] the cyclopentadiene **1a** reacted with $RhCl_3{\cdot}3H_2O$ in ethanol at reflux for 5 h to give a dark red solid **2** (Scheme 2). The ^1H NMR spectrum of **2** showed the two broad peaks (5.75 and 5.20 ppm) due to the vinyl protons of the substituted cyclopentadienyl (Cp′) ring, suggesting the formation of the oligomer $[Cp'RhCl_2]_n$ **2**. Subsequently, addition of 2,2′-bipyridine to the ethanol suspension of **2** gave the bipyridine complex **3** as a yellow solid with a yield of 60%. The structure of **3** was fully confirmed by H–H COSY, NOESY, and HMBC (see ESI, Fig. S1–S3†). Fig. 1 shows partial ^1H and ^{13}C NMR spectra of **3** in CD_3CN. The 6,6′-protons on the bpy were observed at 9.23 and 9.09 ppm which are markedly downfield shifted compared with those (8.66 ppm) of $[Cp^*Rh(bpy)Cl]^+$ (Table 2).

The NOESY spectrum of complex **3** showed the cross peaks of 6′-H on the bpy with 2-Me on Cp^1, conversely, 6-H on the bpy with 3,5-H and 4-Me on Cp′. The ^{13}C NMR spectrum shows that the corresponding pairs of carbons on the bpy are magnetically nonequivalent (Table 2). It appears that these observations are attributable to the anisotropy of the unsymmetrical Cp′ ligand. In addition, **3** was racemic due to the planar chirality of the unsymmetrical Cp′ ligand,[13] but this subject will not be considered in this paper.

Unfortunately, all attempts to prepare the other substituted cyclopentadienyl complexes by the above method were unsuccessful. Therefore, we employed another route to prepare the rhodium complexes $[Cp'RhX(bpy)]^+$.

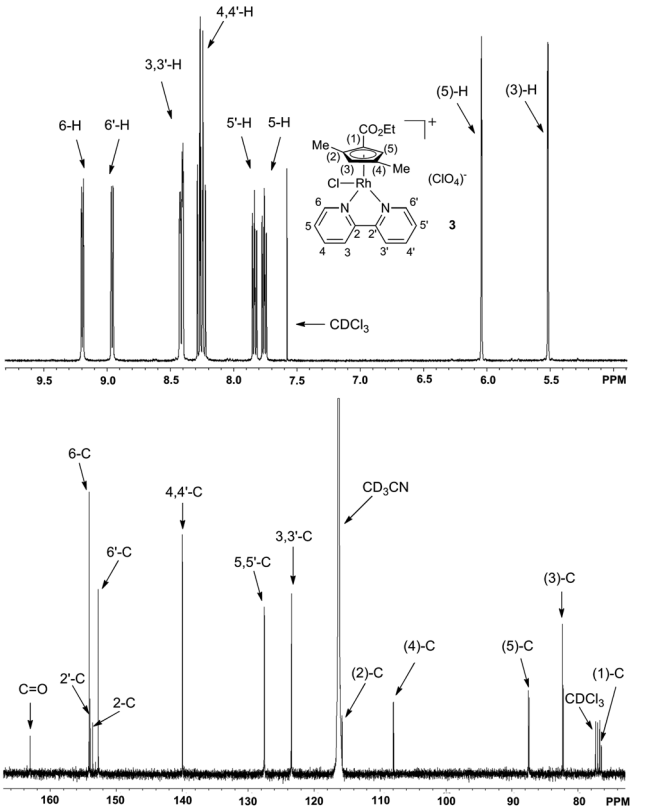
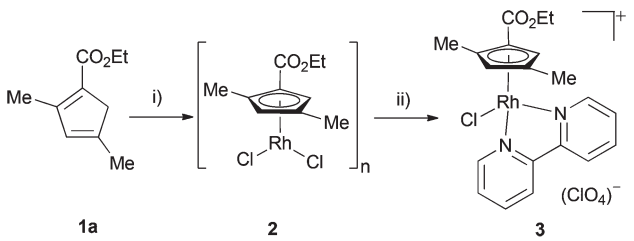


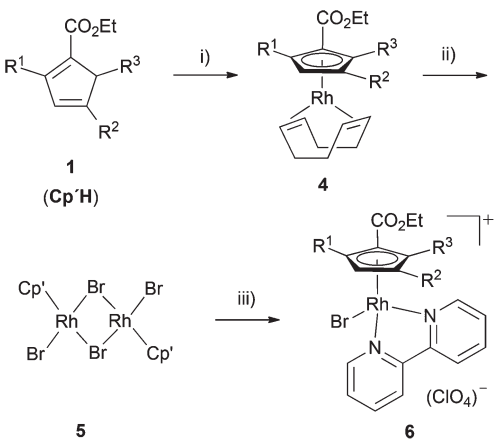
Fig. 1 Partial ^1H and ^{13}C NMR spectra of complex **3** in CD_3CN.

3. Synthesis of the bipyridine complexes (6a–e) from 1 and $[Rh(cod)Cl]_2$

An alternative procedure for the preparation of rhodium dihalides was performed by way of $[Cp'Rh(diene)]$ (Scheme 3).[43] The cod complexes $[Cp'Rh(cod)]$ **4** were prepared by the reaction of $[Rh(cod)Cl]_2$ with the corresponding cyclopentadienyl



Scheme 2 Synthesis of complex **3** from cyclopentadiene **1a**. Reaction conditions: (i) $RhCl_3{\cdot}3H_2O$, EtOH, reflux, 5 h; (ii) bpy then $LiClO_4$, EtOH, rt.



Scheme 3 Synthesis of complexes **6** from cyclopentadienes **1**. Reaction conditions: (i) $[Rh(cod)Cl]_2$, Na_2CO_3/MeOH or *n*-BuLi/THF; (ii) Br_2, Et_2O; (iii) bpy then $LiClO_4$, MeOH.

Table 1 Synthesis of rhodium complexes **4**, **5**, and **6** from cyclopentadiene **1**

Cp′H	Yield of **4**[a]/%	Yield of **5**/%	Yield of **6**/%
1a	92 (A)	88	92
1b	98 (A)	90	89
1c	87 (B)	94	81
1d	92 (B)	89	67
1e	70 (B)	85	80

[a] In parentheses are the reaction methods. Method A: using Na_2CO_3 in MeOH. Method B: using *n*-BuLi in THF.

anions, which were prepared by the treatment of 2-methylcyclopentadienes **1a**, **b** with Na_2CO_3 or 2-ethoxylcyclopentadienes **1c–e** with *n*-BuLi (Scheme 3). The addition of *ca.* 2 equivalent of Br_2 to a solution of **4** in diethyl ether in an ice bath gave rhodium dimers **5** as dark red powders in high yields (85–94%, Table 1). The FAB-MS spectra of **5** showed the parent peaks corresponding to the loss of one bromine from the dibromide dimer $[Cp'RhBr_2]_2$, which may be considered as a mixture of diastereoisomers.[13] Finally, the reaction of **5** with bpy in methanol, followed by addition of $LiClO_4$, gave complexes **6**, [Cp′Rh(bpy)Br](ClO_4), in good to high yields (67–92%, Table 1).

All the products and intermediates were fully characterized with NMR, IR, ESI-MS and elemental analysis (see Experimental section). The structure of complex **6e** has been confirmed by X-ray crystallography (Fig. 2). The average Rh–C distance (2.181 Å) and the distance between Rh and the centroid of the Cp ring (1.811 Å) are longer than those (2.151 and 1.776 Å, respectively) of $[Cp^*Rh(bpy)Cl]^+$.[44] The two pyridine rings in $[Cp^*Rh(bpy)Cl]^+$ are almost coplanar (dihedral angle: 0.38°). In contrast, the two pyridine rings of **6e** show a relatively larger dihedral angle of 8.07°. Apparently, the bulky substituents exhibited a remarkable influence on the molecular structure of the complex.

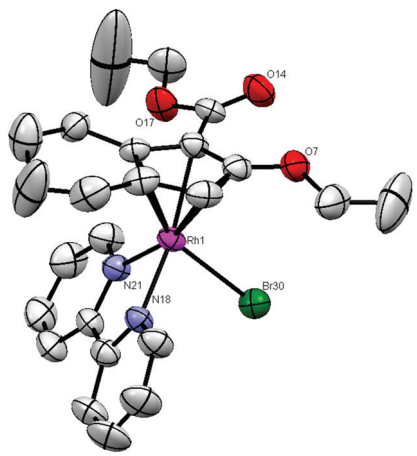


Fig. 2 ORTEP view of complex **6e**. The thermal ellipsoids are shown at 30% probability level. The perchlorate anion and all hydrogen atoms are omitted for clarity. Selected distances (Å): Rh–Br 2.534(6), Rh–N18 2.060(3), Rh–N21 2.081(3), Rh–C2 2.164(4), Rh–C3 2.165(5), Rh–C6 2.268(4), Rh–C30 2.150(4), Rh–C31 2.159(4), Rh–P3 1.809; selected angles (°): N–Rh–N 78.0(1), N21–Rh–Br 87.74(9), N18–Rh–Br 84.52(9), P1–P2 8.07, P2–P3 65.59, P1–P3 87.87 (P1: plane of first pyridine ring, P2: plane of second pyridine ring, P3: plane of Cp′ ring).

Table 2 Comparison of ^{1}H NMR data for 6,6′-H of bpy and ^{13}C NMR data for the Cp′ ring in the complexes

Complex	^{1}H NMR/δ 6,6′-H of bpy	^{13}C NMR/δ 1-C	2-C	3-C	4-C	5-C
$[Cp^*Rh(bpy)Cl]^+$	8.66	98.14	—	—	—	—
3	9.23, 9.09	76.45	115.73	82.27	107.97	87.44
6a	9.20, 9.06	76.80	115.47	83.13	107.44	88.30
6b	9.05, 8.53	76.12	115.86	81.57	103.82	86.31
6c	9.20, 8.96	61.45	147.04	83.53	101.78	64.08
6d	9.15, 9.06	60.36	144.73	74.73	114.25	61.77
6e	9.26, 8.96	59.49	152.56	59.54	103.88	99.22

The characteristic spectral data of **6** are summarized in Tables 2 and 3. The NMR spectrum of **6a** is in good agreement with that of **3**. It is interesting that an upfield shift of 6-H of the bpy in **6b** was observed, which may be due to the shielding effect of the phenyl group on the Cp′. In the ^{13}C NMR spectrum, the chemical shifts of the carbons of the Cp′ ring were found to be affected by the substituents (Table 2). To evaluate the electronic effect of the substituent on the rhodium center, we performed cyclic voltammetry (CV) measurements and the results are listed in Table 3. As shown in Fig. S4,† the cyclic voltammogram of $[Cp^*Rh(bpy)Cl]^+$ showed a quasi-reversible reduction peak at −0.78 V. The peaks observed in complex **6a–e** were positively shifted by 140–340 mV. When the potential was swept to −3.0 V *vs.* Ag/Ag^+, complex **6a–e** showed another quasi-reversible peak and irreversible peak which were observed at more positive potential than the second reduction peak of $[Cp^*Rh(bpy)Cl]^+$. The first reduction peaks correspond to the two-electron reduction of the metal, in which Rh^{III} is reduced to Rh^I with the release of a halide ligand (eqn (1)). And the following peaks correspond to reduction of the bipyridine ligand (eqn (2) and (3)).[45,46] The electron-withdrawing substituent (COOEt) introduced on the cyclopentadienyl increases the electron-accepting character of the ligand and stabilizes the low oxidation state of the metal, resulting in the positive shift of the reduction processes in complexes **6a–e**.

$$[Cp'Rh^{III}(bpy)X]^+ + 2e^- \rightarrow [Cp'Rh^{I}(bpy)]^0 + X^- \quad (1)$$

$$[Cp'Rh^{I}(bpy)]^0 + e^- \rightarrow [Cp'Rh^{I}(bpy^{\cdot -})]^- \quad (2)$$

$$[Cp'Rh^{I}(bpy^{\cdot -})]^- + e^- \rightarrow [Cp'Rh^{I}(bpy^{2-})]^{2-} \quad (3)$$

The electrochemical behavior and UV/Vis absorption spectra of all these complexes are similar to that of $[Cp^*Rh(bpy)Cl]^+$.[47,48] The $[Cp'Rh(bpy)Br]^+$ complexes (**6a–e**) have distinctive absorption bands around 400 and 305 nm in the UV/Vis spectra which may be attributed to a LMCT [$\pi(Cp') \rightarrow d(Rh^{III})$] and MLCT (metal to bipyridine), respectively.[49]

Table 3 Electrochemical properties[a] and UV/Vis absorption data of the rhodium complexes

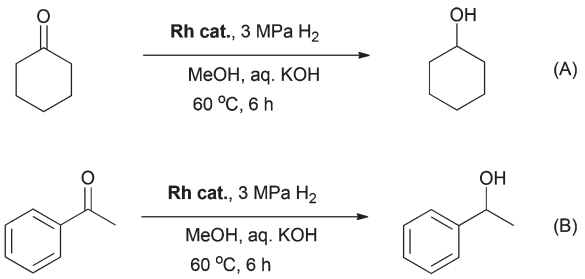
Complex	$Rh^{III/I}$		$bpy^{0/\cdot -}$		$bpy^{\cdot -/2-}$	UV/Vis
	$E_{1/2}$ [b]/V	ΔE_p/V	$E_{1/2}$ [b]/V	ΔE_p/V	E_{pc}/V	(λ_{max}/nm)
$[Cp^*Rh(bpy)Cl]^+$	−0.78	0.11	−2.23	0.18	—	380, 309, 301
6a	−0.51	0.08	−1.95	0.10	−2.40	399, 313, 305
6b	−0.45	0.07	−1.89	0.10	−2.39	409, 313, 305
6c	−0.56	0.08	−1.95	0.11	−2.39	393, 313, 305
6d	−0.52	0.09	−1.88	0.11	−2.35	410, 304
6e	−0.64	0.08	−1.97	0.10	−2.42	393, 313, 306

[a] The data were obtained from CV experiments in 0.1 M $TBAPF_6/CH_3CN$ at a scan rate of 100 mV s^{-1}. All potentials are reported *vs.* SCE. [b] $E_{1/2} = (E_{pa} + E_{pc})/2$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials, respectively.

4. Hydrogenation of ketones with complexes 6a–e

With these complexes in hand, we examined their catalytic activity in the hydrogenation of ketones with H_2 in MeOH in the presence of KOH. The yields were strongly affected by the amount of base. The best results were obtained using 0.2 equiv. of KOH. The results of the reaction under the optimized conditions are summarized in Table 4. Both of the reactions gave no product without catalyst (entry 1). $[Cp^*Rh(bpy)Cl]ClO_4$ showed high activity for both cyclohexanone and acetophenone (entry 2). It is noteworthy that chloro Rh complex **3** showed similar activity with the bromo analog **6a** for reaction A, but better performance than **6a** for reaction B (entry 3 *vs.* entry 4). These results suggest that the halogen ligand might play a role in its activity to different substrate. For the hydrogenation of cyclohexanone (reaction A), all the complexes **6** showed high yields (86–99%) except **6c** (64%). Interestingly, when acetophenone was used, **6c** gave a high yield of 89% under the same conditions. For the hydrogenation of acetophenone (reaction B), all the complexes **6** gave good to high yields (77–95%). The different activity of complexes **6a–e** for the different substrates may be due to the influence of the substituents on the Cp′ rings. In other words, the bulky substituents on the Cp ring may affect the accessibility of the aryl and alkyl ketones to the metal center and thus influence the catalytic process.

Table 4 Hydrogenation of cyclohexanone in MeOH catalyzed by [Cp*Rh(bpy)Cl]Cl, **3** and **6a–e**[a]



Entry	Complex	Yield of reaction A/%	Yield of reaction B/%
1	—	0	0
2	$[Cp^*Rh(bpy)Cl]^+$	99	97
3	**3**	90	95
4	**6a**	91	81
5	**6b**	93	95
6	**6c**	64	89
7	**6d**	86	77
8	**6e**	99	92

[a] The reaction was carried out with catalyst (2.5 μmol), cyclohexanone (0.25 mmol) and 1 M KOH (50 μl) in MeOH (2 ml) under 3 MPa of H_2 at 60 °C for 6 h.

Conclusions

The present work provides a method for convenient and efficient syntheses of multi-substituted cyclopentadienyl rhodium dibromides, $[Cp'RhBr_2]_2$, which can be used as useful starting materials for various functionalized half-sandwich rhodium complexes. Using the complexes $[Cp'RhBr_2]_2$, we synthesized a series of highly functionalized complexes $[Cp'Rh(bpy)X]^+$ which were fully characterized by NMR, ESI-MS and elemental analysis. These novel complexes can catalyze the hydrogenation of alkyl and aryl ketones with good to high yields. All the experimental data from spectroscopy (NMR, UV/Vis), electrochemistry, structure and catalytic activity demonstrated a significant substituent effect. Further studies on related catalytic reaction with these new complexes are now in progress.

Experimental section

General

All manipulations were carried out under an atmosphere of argon. All melting points were measured on a Mettler FP62 and are uncorrected. UV spectra were recorded on a JASCO V-550 spectrometer. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. ^1H NMR spectra were measured on a Varian Gemini 300BB spectrometer, using TMS as the internal standard. ^{13}C NMR were recorded on the spectrometer using solvent peak ($CDCl_3$: δ 77.0) as a reference. Mass spectra were collected on a Hitachi M-80B spectrometer. Fast atom bombardment mass spectra (FAB) were recorded on a JEOL JMS-DX303. Elemental analyses were carried out on an Eager 200 instrument. Preparative chromatography columns were

packed with aluminum oxide (activated, neutral, Brockmann I, *ca.* 150 mesh). CV was carried out on a BAS Inc., Electrochemical Analyzer, ALS Model 624D using a Ag/Ag^+ reference electrode (the electrolyte consists of 0.01 M $AgNO_3$, 0.1 M tetrabutylammonium perchlorate (TBAP) dissolved in acetonitrile), glassy carbon working electrode and platinum wire auxiliary electrode in anhydrous acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte, and the CH_3CN solutions were degassed with argon for approximately 10 min before data collection. All voltammograms were obtained with a scan rate of 100 mV s^{-1} at room temperature. Ferrocene was employed as an internal standard, and its $Fe^{(II/III)}$ half-wave potential ($E_{1/2}$) was taken to be +0.40 V *vs*. SCE. GC analysis was performed on a SHIMADZU gas chromatograph GC2014 using an external standard method. THF was distilled from sodium benzophenone ketyl. Aqueous solutions were degassed prior to use. $RhCl_3{\cdot}3H_2O$ and $[Rh(cod)Cl]_2$ were commercially available from Kanto Chemical Co. and were used without further purification.

Warning! All the perchlorate compounds used in this study are potentially explosive and must be handled with great care.

Preparation of [(η⁵-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)(2,2′-bipyridine)chlororhodium]-perchlorate (3)

A mixture of $RhCl_3{\cdot}3H_2O$ (186 mg, 0.71 mmol) and cyclopentadiene **1a** (130 mg, 0.78 mmol) in EtOH (10 ml) was refluxed under Ar for 5 h to give a precipitate as a dark red solid. After cooling, to the suspension was added 2,2′-bipyridine (110 mg, 0.71 mg) to give a clear yellow solution. After stirring at room temperature for 3 h, the solution was filtered to remove the insoluble materials. Addition of excess $LiClO_4$ (85 mg, 80 mmol) to the filtrate gave a yellow solid. The resultant solid was recrystallized by dissolving in acetonitrile (3 ml) and then adding diethyl ether to give complex **3** (233 mg, 60%) as a yellow solid. mp >200 °C (dec.); IR (KBr) 1724, 1606, 1448 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 9.23 (dt, J = 5.8, 0.7 Hz, 1H, 6-H of bpy), 9.09 (dt, J = 5.8, 0.7 Hz, 1H, 6′-H of bpy), 8.40 (bd, J = 8.2 Hz, 2H, 3,3′-H of bpy), 8.26 (dt, J = 1.1, 8.0 Hz, 2H, 4,4′-H of bpy), 7.80 (dt, J = 1.3, 5.8 Hz, 1H, 5′-H of bpy), 7.78 (dt, J = 1.3, 5.8 Hz, 1H, 5-H of bpy), 6.13 (d, J = 1.3 Hz, 1H, 5-H of Cp′), 5.61 (d, J = 1.3 Hz, 1H, 3-H of Cp′), 4.25 (q, J = 7.1 Hz, 2H, CH_2CH_3), 2.14 (s, 3H, 2-Me of Cp′), 1.86 (s, 3H, 4-Me of Cp′), 1.23 (t, J = 7.1 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, CD_3CN) δ 163.05 (C═O), 154.13 (6-C of bpy), 153.96 (2′-C of bpy), 153.56 (2-C of bpy), 152.72 (6′-C of bpy), 139.95, 139.92 (4,4′-C of bpy), 127.58, 127.55 (5,5′-C of bpy), 123.47, 123.40 (3,3′-C of bpy), 115.73 (d, J_{Rh-C} = 6.1 Hz, 2-C of Cp′), 107.97 (d, J_{Rh-C} = 6.9 Hz, 4-C of Cp′), 87.44 (d, J_{Rh-C} = 7.6 Hz, 5-C of Cp′), 82.27 (d, J_{Rh-C} = 6.8 Hz, 3-C of Cp′), 76.45 (d, J_{Rh-C} = 9.1 Hz, 1-C of Cp′), 61.60 (CH_2CH_3), 12.44 (CH_2CH_3), 11.26 (2-Me of Cp′), 10.64 (4-Me of Cp′); FAB-MS: m/z 459 $[M - ClO_4]^+$; Anal. Calcd for $C_{20}H_{21}Cl_2N_2O_6Rh$: H, 3.79; C, 42.96; N, 5.01. Found: H, 3.63; C, 43.34; N, 4.99.

Preparation of complexes 4a–e

(1,5-Cyclooctadiene)(η⁵-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)rhodium (**4a**): to a solution of **1a** (138 mg, 0.84 mmol) in MeOH (15 ml) was added $[Rh(cod)Cl]_2$ (187 mg, 0.38 mmol) and Na_2CO_3 (190 mg). After the mixture was stirred at room temperature for 5 h, the solvent was removed under reduced pressure. Diethyl ether (10 ml) was added to the residue. After filtration, the solvent of the filtrate was removed *in vacuo*. The residue was purified by short column chromatography on alumina using diethyl ether as an eluent to give **4a** (262 mg, 92%) as a yellow oil. IR (neat) 1701, 1412 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.31 (s, 1H, H of Cp′), 5.25 (d, J = 2.2 Hz, 1H, H of Cp′), 4.35–4.18 (m, 2H, OCH_2CH_3), 3.92–3.78 (m, 2H, HC═C of cod), 3.41–3.32 (m, 2H, HC═C of cod), 2.23–2.15 (m, 4H, CH_2 of cod), 1.98–1.88 (m, 4H, CH_2 of cod), 1.87 (s, 3H, Me of Cp′), 1.86 (s, 3H, Me of Cp′), 1.34 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.10 (C═O), 103.06 (d, J_{Rh-C} = 3.4 Hz, C of Cp′), 100.89 (d, J_{Rh-C} = 3.4 Hz, C of Cp′), 94.42 (d, J_{Rh-C} = 4.0 Hz, C of Cp′), 89.62 (C of Cp′), 88.56 (d, J_{Rh-C} = 4.0 Hz, C of Cp′), 72.40 (d, J_{Rh-C} = 13.7 Hz, CH of cod), 67.27 (d, J_{Rh-C} = 13.7 Hz, CH of cod), 59.26 (CH_2CH_3), 32.23, 32.12 (CH_2 of COD), 14.52, 12.76, 11.94; HRMS Calcd for $C_{18}H_{25}O_2Rh$ (M^+) 376.0908, found 376.0996; Anal. Calcd for $C_{18}H_{25}O_2Rh$: H, 6.70; C, 57.45. Found: H, 6.74; C, 57.60.

(1,5-Cyclooctadiene)(η⁵-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)rhodium (**4b**): in the same manner as described for the preparation of complex **4a**, **1b** (139 mg, 0.57 mmol) was reacted with $[Rh(cod)Cl]_2$ (130 mg, 0.26 mmol) and Na_2CO_3 (130 mg) in MeOH (15 ml) to give **4b** (226 mg, 98%) as a yellow needle crystal; mp 98.8–99.4 °C (recrystallization from petroleum ether); IR (KBr) 1686, 1601, 1410 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (tt, J = 7.3, 1.4 Hz, 2H, Ph), 7.30 (dt, J = 7.3, 1.4 Hz, 2H, Ph), 7.19 (tt, J = 7.3, 1.4 Hz, 1H, Ph), 5.77 (d, J = 2.1 Hz, 1H, 3-H of Cp′), 5.76 (d, J = 2.1 Hz, 1H, 5-H of Cp′), 4.40–4.24 (m, 2H, OCH_2CH_3), 3.98–3.90 (m, 2H, HC═C of cod), 3.29–3.20 (m, 2H, HC═C of cod), 2.22–2.03 (m, 4H, CH_2 of cod), 2.00 (s, 3H, Me of Cp′), 1.98–1.82 (m, 4H, CH_2 of cod), 1.38 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.87 (C═O), 134.00, 128.56, 126.63, 125.39 (C of Ph), 106.28 (d, J_{Rh-C} = 3.0 Hz, C of Cp′), 102.49 (d, J_{Rh-C} = 3.8 Hz, C of Cp′), 91.61 (d, J_{Rh-C} = 4.6 Hz, C of Cp′), 91.00 (d, J_{Rh-C} = 3.8 Hz, C of Cp′), 84.79 (d, J_{Rh-C} = 3.8 Hz, C of Cp′), 74.16 (d, J_{Rh-C} = 13.7 Hz, CH of cod), 68.12 (d, J_{Rh-C} = 13.7 Hz, CH of cod), 59.58 (CH_2CH_3), 32.16, 31.94 (CH_2 of cod), 14.68 (CH_2CH_3), 12.43 (2-Me of Cp′); HRMS Calcd for $C_{23}H_{27}O_2Rh$ (M^+) 438.1065, found 438.1057; Anal. Calcd for $C_{23}H_{27}O_2Rh$: H, 6.21; C, 63.02. Found: H, 6.20; C, 63.06.

(1,5-Cyclooctadiene)(η⁵-2-ethoxy-1-ethoxycarbonyl-4-methylcyclopentadienyl)rhodium (**4c**): to a solution of **1c** (150 mg, 0.76 mmol) in 10 ml of THF at −78 °C was added *n*-BuLi (0.48 ml, 1.6 M in hexane, 0.76 mmol) dropwise *via* a syringe. After stirring for 20 min, a solution of $[Rh(cod)Cl]_2$ (172 mg, 0.35 mmol) in THF (10 ml) was added to the reaction mixture. After 24 h of stirring at room temperature, the solvent was

removed under reduced pressure and the residue was purified by short column chromatography on alumina using diethyl ether as an eluent to give **4c** (268 mg, 87%) as a yellow oil: IR (neat) 1707, 1449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.27 (d, J = 2.0 Hz, 1H, H of Cp′), 5.06 (d, J = 2.0 Hz, 1H, H of Cp′), 4.38–4.18 (m, 2H, $CO_2CH_2CH_3$), 4.00–3.92 (m, 2H, HC═C of cod), 3.92–3.82 (m, 1H, OCH_2CH_3), 3.70–3.58 (m, 1H, OCH_2CH_3), 3.56–3.46 (m, 2H, HC═C of cod), 2.30–2.12 (m, 4H, CH_2 of cod), 2.08–1.84 (m, 4H, CH_2 of cod), 1.84 (s, 3H, 4-Me), 1.33 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.32 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.78 (C═O), 135.61, 96.75 (d, J_{Rh-C} = 4.0 Hz, C of Cp′), 81.97 (d, J_{Rh-C} = 4.6 Hz, C of Cp′), 79.27 (d, J_{Rh-C} = 4.5 Hz, C of Cp′), 77.28 (d, J_{Rh-C} = 2.9 Hz, C of Cp′), 72.02 (d, J_{Rh-C} = 14.2 Hz, CH of cod), 67.32 (d, J_{Rh-C} = 13.7 Hz, CH of cod), 66.345 (OCH_2CH_3), 59.32 ($CO_2CH_2CH_3$), 32.44, 31.93 (CH_2 of cod), 14.68 (OCH_2CH_3), 14.54 ($CO_2CH_2CH_3$), 13.06 (4-Me of Cp′); HRMS Calcd for $C_{19}H_{27}O_3Rh$ (M^+) 406.1014, found 406.1001.

(1,5-Cyclooctadiene)(η^5-2-ethoxy-1-ethoxycarbonyl-4-ethylthiocyclopentadienyl)rhodium (**4d**): in the same manner as described for the preparation of complex **4c**, **1d** (125 mg, 0.52 mmol) was reacted with $[Rh(cod)Cl]_2$ (116 mg, 0.23 mmol) and n-BuLi (0.32 ml, 1.6 M in hexane, 0.52 mmol) to give **4d** (195 mg, 92%) as a yellow oil; IR (neat) 1711, 1446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.30 (d, J = 2.0 Hz, 1H, H of Cp′), 5.17 (d, J = 2.0 Hz, 1H, H of Cp′), 4.41–4.19 (m, 2H, $CO_2CH_2CH_3$), 4.16–4.07 (m, 2H, HC═C of cod), 3.94–3.83 (m, 1H, OCH_2CH_3), 3.75–3.66 (m, 2H, HC═C of cod), 3.66–3.56 (m, 1H, OCH_2CH_3), 2.73 (q, J = 7.4 Hz, 2H, SCH_2CH_3), 2.30–2.12 (m, 4H, CH_2 of cod), 2.06–1.85 (m, 4H, CH_2 of cod), 1.34 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.33 (t, J = 7.1 Hz, 3H, OCH_2CH_3), 1.28 (t, J = 7.4 Hz, 3H, SCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.00 (C═O), 136.70 (C of Cp′), 92.50 (d, J_{Rh-C} = 4.6 Hz, C of Cp′), 85.51 (d, J_{Rh-C} = 4.6 Hz, C of Cp′), 81.48 (C of Cp′), 80.17 (d, J_{Rh-C} = 2.9 Hz, C of Cp′), 72.64 (d, J_{Rh-C} = 14.2 Hz, CH of cod), 68.75 (d, J_{Rh-C} = 13.5 Hz, CH of cod), 66.63 (OCH_2CH_3), 59.54 ($CO_2CH_2CH_3$), 32.11, 32.01 (CH_2 of cod), 31.50, 31.37 (SCH_2CH_3), 14.83 (OCH_2CH_3), 14.61 ($CO_2CH_2CH_3$), 14.50 (SCH_2CH_3); HRMS Calcd for $C_{20}H_{29}O_3RhS$ (M^+) 452.0891, found 452.0821; Anal. Calcd for $C_{20}H_{29}O_3RhS$: H, 6.46; C, 53.10. Found: H, 6.50; C, 53.09.

(1,5-Cyclooctadiene)(η^5-2-ethoxy-1-ethoxycarbonyltetrahydroindenyl)rhodium (**4e**): in the same manner as described for the preparation of complex **4c**, **1e** (150 mg, 0.64 mmol) was reacted with $[Rh(cod)Cl]_2$ (157 mg, 0.32 mmol) and n-BuLi (0.45 ml, 1.6 M in hexane, 0.72 mmol) to give **4e** (197 mg, 70%) as a yellow oil; IR (neat) 1690, 1439 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.22 (bs, 1H, H of Cp′), 4.31 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 3.86–3.74 (m, 1H, OCH_2CH_3), 3.70–3.62 (m, 2H, HC═C of cod), 3.64–3.52 (m, 1H, OCH_2CH_3), 3.52–3.42 (m, 2H, HC═C of cod), 2.68–0.80 (m, 16H), 1.35 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.28 (t, J = 7.1 Hz, 3H, OCH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.58 (C═O), 133.58 (d, J_{Rh-C} = 3.4 Hz, C of Cp′), 128.06 (C of Cp′), 99.11 (d, J_{Rh-C} = 4.6 Hz, C of Cp′), 98.43 (d, J_{Rh-C} = 4.6 Hz, C of Cp′), 73.37 (d, J_{Rh-C} = 13.7 Hz, CH of cod), 73.67 (d, J_{Rh-C} = 3.4 Hz, C of Cp′), 70.26 (d, J_{Rh-C} = 13.7 Hz, CH of cod), 66.14 (OCH_2CH_3), 59.04 ($CO_2CH_2CH_3$), 32.89, 31.53 (CH_2 of cod), 23.25, 23.10, 22.97, 22.79, 22.65 (CH_2), 14.70, 14.57, 13.89; HRMS Calcd for $C_{22}H_{31}O_3Rh$ (M^+) 446.1327, found 446.1283.

Typical procedure for preparation of complexes 5a–e

A solution of complex **4** (0.50 mmol) in diethyl ether (10 ml) was cooled in an ice bath. After addition of bromine (0.5 ml), the ice bath was removed and the mixture was stirred at room temperature for 10 min. The solvent was then removed under reduced pressure. The residue was washed with hexane and dried *in vacuo* to give the rhodium dimer **5** as a dark red powder. An analytical sample was recrystallized by dissolving in acetonitrile (3 ml) and then adding diethyl ether.

Dibromo(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)-rhodium dimer (**5a**): IR (KBr) 1730, 1425 cm^{-1}; ^1H NMR (300 MHz, CD_3CN) δ 5.81 (s, 1H, H of Cp′), 5.31 (s, 1H, H of Cp′), 4.40–4.21 (m, 2H, OCH_2CH_3), 2.18 (s, 3H, Me of Cp′), 1.99 (s, 3H, Me of Cp′), 1.34 (t, J = 7.1 Hz, 3H, OCH_2CH_3); FAB-MS: m/z 775 $[M - Br]^+$; Anal. Calcd for $C_{20}H_{26}Br_4O_4Rh_2$: H, 3.06; C, 28.07; Br, 37.34. Found: H, 2.99; C, 28.10; Br, 37.44.

Dibromo(η^5-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)rhodium dimer (**5b**): IR (neat) 1725, 1468 cm^{-1}; ^1H NMR (300 MHz, CD_3CN) δ 7.81–7.74 (bd, J = 6.8 Hz, 2H, Ph), 7.58–7.45 (m, 3H, Ph), 6.56 (bs, 1H, H of Cp′), 6.05 (bs, 1H, H of Cp′), 4.41–4.28 (m, 2H, OCH_2CH_3), 2.30 (s, 3H, Me of Cp′), 1.37 (t, J = 7.1 Hz, 3H, OCH_2CH_3); FAB-MS: m/z 900 $[M - Br]^+$; Anal. Calcd for $C_{30}H_{30}Br_4O_4Rh_2$: H, 3.09; C, 36.77. Found: H, 3.01; C, 36.85.

Dibromo(η^5-2-ethoxy-1-ethoxycarbonyl-4-methylcyclopentadienyl)rhodium dimer (**5c**): IR (neat) 1718, 1514 cm^{-1}; ^1H NMR (300 MHz, CD_3CN) δ 5.70 (bd, J = 1.6 Hz, 1H, H of Cp′), 5.18 (bs, 1H, H of Cp′), 4.36–4.16 (m, 4H, OCH_2CH_3), 1.99 (s, 3H, Me of Cp′), 1.41 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.32 (t, J = 7.1 Hz, 3H, OCH_2CH_3); FAB-MS: m/z 834 $[M - Br]^+$; Anal. Calcd for $C_{22}H_{30}Br_2O_6Rh_2$: H, 3.30; C, 28.85. Found: H, 3.27; C, 29.09.

Dibromo(η^5-2-ethoxy-1-ethoxycarbonyl-4-ethylthiocyclopentadienyl)rhodium dimer (**5d**): IR (neat) 1726, 1512 cm^{-1}; ^1H NMR (300 MHz, CD_3CN) δ 5.70 (bs, 1H, H of Cp′), 5.50 (bs, 1H, H of Cp′), 4.46–4.10 (m, 4H, OCH_2CH_3), 3.18–2.97 (m, 2H, SCH_2CH_3), 1.42 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.39 (t, J = 7.4 Hz, 3H, SCH_2CH_3), 1.32 (t, J = 7.1 Hz, 3H, OCH_2CH_3); FAB-MS: m/z 1006 $[M]^+$, 928 $[M - Br]^+$; Anal. Calcd for $C_{24}H_{34}Br_4O_6Rh_2S_2$: H, 3.40; C, 28.59; Br, 31.70. Found: H, 3.30; C, 28.41; Br. 31.87.

Dibromo(η^5-2-ethoxy-1-ethoxycarbonyltetrahydroindenyl)-rhodium dimer (**5e**): IR (neat) 1723, 1512 cm^{-1}; ^1H NMR (300 MHz, CD_3CN) δ 5.11 (bs, 1H, H of Cp′), 4.27 (q, J = 7.1 Hz, 2H, $CO_2CH_2CH_3$), 4.30–4.18 (m, 1H, OCH_2CH_3), 4.16–4.05 (m, 1H, OCH_2CH_3), 2.85–1.60 (m, 8H), 1.40 (t, J = 7.1 Hz, 3H, $CO_2CH_2CH_3$), 1.31 (t, J = 7.1 Hz, 3H, OCH_2CH_3); FAB-MS: m/z 915 $[M - Br]^+$; Anal. Calcd for $C_{28}H_{38}Br_4O_6Rh_2$: H, 3.85; C, 33.76. Found: H, 3.78; C, 33.47.

Typical procedure for preparation of complexes 6a–e

To a suspension of complex **5** (0.2 mmol) in MeOH (10 ml) was added 2,2′-bipyridine (0.42 mmol). After stirring at room

temperature for 3 h, a solution of lithium perchlorate (0.42 mmol) in MeOH (10 ml) was added to the reaction mixture. Precipitated solid was collected by filtration and dried under vacuum to give the rhodium complexes **6** as a yellow solid. An analytical sample was recrystallized by dissolving in acetonitrile (3 ml) and then adding diethyl ether.

[(η^5-1-Ethoxycarbonyl-2,4-dimethylcyclopentadienyl)(2,2′-bipyridine)bromorhodium]perchlorate (**6a**): IR (neat) 1725, 1448 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 9.20 (td, J = 0.7, 5.6 Hz, 1H, 6-H of bpy), 9.06 (td, J = 0.7, 5.6 Hz, 1H, 6′-H of bpy), 8.40 (bd, J = 7.7 Hz, 2H, 3,3′-H of bpy), 8.25 (dt, J = 1.3, 7.7 Hz, 2H, 4,4′-H of bpy), 7.78 (dt, J = 1.3, 5.6 Hz, 1H, 5′-H of bpy), 7.77 (dt, J = 1.3, 5.6 Hz, 1H, 5-H of bpy), 6.13 (d, J = 1.3 Hz, 1H, 5-H of Cp′), 5.58 (d, J = 1.3 Hz, 1H, 3-H of Cp′), 4.26 (dq, J = 1.5, 7.1 Hz, 2H, CH_2CH$_3$), 2.23 (s, 3H, 2-Me of Cp′), 1.94 (s, 3H, 4-Me of Cp′), 1.24 (t, J = 7.1 Hz, 3H, CH$_2$CH_3); ^{13}C NMR (100 MHz, CD_3CN) δ 163.00 (C═O), 154.52 (6-C of bpy), 153.94 (2′-C of bpy), 153.53 (2-C of bpy), 153.17 (6′-C of bpy), 139.90 (4,4′-C of bpy), 127.52, 127.47 (5,5′-C of bpy), 123.52, 123.50 (3,3′-C of bpy), 115.47 (d, J_{Rh-C} = 6.1 Hz, 2-C of Cp′), 107.44 (d, J_{Rh-C} = 6.9 Hz, 4-C of Cp′), 88.30 (d, J_{Rh-C} = 6.9 Hz, 5-C of Cp′), 83.13 (d, J_{Rh-C} = 6.9 Hz, 3-C of Cp′), 76.80 (d, J_{Rh-C} = 9.0 Hz, 1-C of Cp′), 61.53 (CH_2CH$_3$), 12.52 (CH$_2$CH_3), 11.79 (2-Me of Cp′), 11.09 (4-Me of Cp′); ES-MS: m/z 503.74 [M − ClO_4]$^+$; UV λ_{max} (MeCN) 399 (2 300), 313 (18 300), 305 nm (sh); Anal. Calcd for $C_{20}H_{21}BrClN_2O_6Rh$: H, 3.51; C, 39.79; N, 4.64. Found: H, 3.40; C, 39.92; N, 4.50.

[(η^5-1-Ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)-(2,2′-bipyridine)bromorhodium]perchlorate (**6b**): IR (neat) 1719, 1449 cm^{-1}; ^1H NMR (300 MHz, CD_3CN) δ 9.05 (bd, J = 5.5 Hz, 1H, 6-H of bpy), 8.53 (bd, J = 5.7 Hz, 1H, 6′-H of bpy), 8.34 (bd, J = 7.6 Hz, 1H, 3-H of bpy), 8.28 (bd, J = 7.5 Hz, 1H, 3′-H of bpy), 8.23–8.12 (m, 2H, 4,4′-H of bpy), 7.70–7.35 (m, 7H, 5,5′-H of bpy, Ph), 6.87 (d, J = 1.9 Hz, 1H, H of Cp′), 6.27 (d, J = 1.9 Hz, 1H, H of Cp′), 4.45 (q, J = 7.1 Hz, 2H, OCH_2CH$_3$), 2.36 (s, 3H, Me of Cp′), 1.41 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, CD_3CN) δ 163.39 (C═O), 154.08 (2′-C of bpy), 153.72 (6-C of bpy), 153.31 (2-C of bpy), 152.40 (6-C of bpy), 140.10 (4,4′-C of bpy), 130.86, 128.94 (C of Ph), 127.68 (5′-C of bpy), 127.42 (C of Ph), 127.11 (5-C of bpy), 125.07, 123.62 (C of Ph), 123.17 (3,3′-C of bpy), 115.86 (d, J_{Rh-C} = 5.6 Hz, 2-C of Cp′), 103.82, (4-C of Cp′) 86.31 (d, J_{Rh-C} = 6.8 Hz, 5-C of Cp′), 81.57 (d, J_{Rh-C} = 6.8 Hz, 3-C of Cp′), 76.15 (1-C of Cp′) 61.81 (OCH_2CH$_3$), 12.74 (OCH$_2$CH_3), 11.96 (2-Me of Cp′); UV λ_{max} (MeCN) 409 (3300), 313 (18 000), 305 nm (16 400); FAB-MS: m/z 567 [M − ClO_4]$^+$; Anal. Calcd for $C_{25}H_{23}BrClN_2O_6Rh$: H, 3.48; C, 45.11; N, 4.21. Found: H, 3.54; C, 45.40; N, 4.04.

[(η^5-2-Ethoxy-1-ethoxycarbonyl-4-methylcyclopentadienyl)-(2,2′-bipyridine)bromorhodium]perchlorate (**6c**): IR (neat) 1713, 1451 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 9.20 (bd, J = 5.5 Hz, 1H, 6-H of bpy), 8.96 (bd, J = 5.5 Hz, 1H, 6′-H of bpy), 8.42 (bd, J = 8.2 Hz, 2H, 3,3′-H of bpy), 8.31–8.21 (m, 2H, 4,4′-H of bpy), 7.84 (ddd, J = 7.7, 5.5, 1.3 Hz, 1H, 5-H of bpy), 7.76 (ddd, J = 7.7, 5.5, 1.3 Hz, 1H, 5′-H of bpy), 6.04 (d, J = 1.6 Hz, 1H, 3-H of Cp′), 5.52 (d, J = 1.6 Hz, 1H, 5-H of Cp′), 4.38 (q, J = 7.1 Hz, 2H, CO$_2$CH_2CH$_3$), 4.18–4.07 (m, 1H, OCH_2CH$_3$), 3.93–3.80 (m, 1H, OCH_2CH$_3$), 1.88 (s, 3H, 4-Me of Cp′), 1.35 (t, J = 7.1 Hz, 3H, CO$_2$CH$_2$CH_3), 1.33 (t, J = 6.9 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (100 MHz, CD_3CN) δ 162.52 (C═O), 154.11 (2′-C of bpy), 153.62 (2-C of bpy), 152.35 (6-C of bpy), 152.21 (6′-C of bpy), 147.04 (d, J_{Rh-C} = 3.8 Hz, 2-C of Cp′), 139.77, 139.71 (4,4′-C of bpy), 127.43 (5-C of bpy), 127.01 (5′-C of bpy), 123.38 (3′-C of bpy), 122.96 (3-C of bpy), 101.78 (d, J_{Rh-C} = 7.6 Hz, 4-C of Cp′), 83.53 (d, J_{Rh-C} = 7.6 Hz, 3-C of Cp′), 70.22 (OCH_2CH$_3$), 64.08 (d, J_{Rh-C} = 6.9 Hz, 5-C of Cp′), 61.45 (d, J_{Rh-C} = 8.4 Hz, 1-C of Cp′), 61.33 (CO$_2$CH_2CH$_3$), 12.77 (CO$_2$CH$_2$CH_3), 12.38 (OCH$_2$CH_3), 10.77 (4-Me of Cp′); UV λ_{max} (MeCN) 393 (2400), 313 (20 200), 304 nm (sh); ES-MS: m/z 533.75 [M − ClO_4]$^+$; Anal. Calcd for $C_{21}H_{23}BrClN_2O_7Rh$: H, 3.66; C, 39.80; N, 4.42. Found: H, 3.61; C, 39.93; N, 4.37.

[(η^5-2-Ethoxy-1-ethoxycarbonyl-4-ethylthiocyclopentadienyl)-(2,2′-bipyridine)bromorhodium]perchlorate (**6d**): IR (neat) 1726, 1451 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 9.15 (dd, J = 0.7, 5.5 Hz, 1H, 6-H of bpy), 9.06 (bd, J = 5.0 Hz, 1H, 6′-H of bpy), 8.43 (dd, J = 4.0, 8.0 Hz, 2H, 3,3′-H of bpy), 8.27 (tt, J = 0.7, 7.7 Hz, 1H, 4,4′-H of bpy), 7.92–7.82 (dd, J = 5.5, 7.1 Hz, 2H, 5,5′-H of bpy), 6.03 (d, J = 2.0 Hz, 1H, 3-H of Cp′), 5.63 (d, J = 2.0 Hz, 1H, 5-H of Cp′), 4.39 (q, J = 7.1 Hz, 2H, CO$_2$CH_2CH$_3$), 4.14–3.98 (m, 1H, OCH_2CH$_3$), 3.68–3.56 (m, 1H, OCH_2CH$_3$), 2.90–2.72 (m, 2H, SCH_2CH$_3$), 1.37 (t, J = 7.1 Hz, 3H, CO$_2$CH$_2$CH_3), 1.28 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3), 1.27 (t, J = 7.4 Hz, 3H, SCH$_2$CH_3); ^{13}C NMR (100 MHz, CD_3CN) δ 162.43 (C═O), 154.26, 153.23 (2,2′-C of bpy), 151.27, 149.37 (6,6′-C of bpy), 144.73 (d, J_{Rh-C} = 5.0 Hz, 2-C of Cp′), 139.97, 139.83 (4,4′-C of bpy), 127.42, 126.87 (5,5′-C of bpy), 123.21, 122.65 (3,3′-C of bpy), 114.25 (d, J_{Rh-C} = 6.8 Hz, 4-C of Cp′), 74.73(d, J_{Rh-C} = 8.3 Hz, 3-C of Cp′), 70.15 (OCH_2CH$_3$), 61.77 (d, J_{Rh-C} = 7.6 Hz, 5-C of Cp′), 61.37 (CO$_2$CH_2CH$_3$), 60.36 (d, J_{Rh-C} = 9.1 Hz, 1-C of Cp′), 25.37 (SCH_2CH$_3$), 12.84 (CO$_2$CH$_2$CH_3), 12.27, 11.89 (CH$_2$CH_3); UV λ_{max} (MeCN) 410 (sh), 304 nm (19 000); ES-MS: m/z 579.63 [M − ClO_4]$^+$; Anal. Calcd for $C_{22}H_{25}BrClN_2O_7RhS$: H, 3.71; C, 38.87; N, 4.12; S, 4.72. Found: H, 3.65; C, 38.59; N, 4.19; S, 4.51.

[(η^5-2-Ethoxy-1-ethoxycarbonyltetrahydroindenyl)(2,2′-bipyridine)bromorhodium]perchlorate (**6e**): IR (neat) 1723, 1451 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 9.26 (bd, J = 5.5 Hz, 1H, 6-H of bpy), 8.96 (bd, J = 5.5 Hz, 1H, 6′-H of bpy), 8.40 (bd, J = 8.2 Hz, 2H, 3,3′-H of bpy), 8.30–8.23 (m, 2H, 4,4′-H of bpy), 7.83 (bt, J = 6.7 Hz, 2H, 5,5′-H of bpy), 5.43 (s, 1H, 3-H of Cp′), 4.41 (q, J = 7.1 Hz, 2H, CO$_2$CH_2CH$_3$), 4.20–4.06 (m, 1H, OCH_2CH$_3$), 3.98–3.82 (m, 1H, OCH_2CH$_3$), 2.61–2.35 (m, 2H), 2.22–1.90 (m, 2H), 1.72–1.60 (m, 2H), 1.52–1.30 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H, CO$_2$CH$_2$CH_3), 1.32 (t, J = 7.1 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (100 MHz, CD_3CN) δ 163.42 (C═O), 153.91, 153.43 (2,2′-C of bpy), 152.56 (2-C of Cp′), 151.32 (6,6′-C of bpy), 139.57 (4,4′-C of bpy), 127.72, 127.62 (5,5′-C of bpy), 123.10, 122.88 (3,3′-C of bpy), 103.88 (d, J_{Rh-C} = 7.7 Hz, 4-C of Cp′), 99.22 (d, J_{Rh-C} = 8.1 Hz, 5-C of Cp′), 69.88 (OCH_2CH$_3$), 61.23 (CO$_2$CH_2CH$_3$), 59.54 (d, J_{Rh-C} = 7.7 Hz, 3-C of Cp′), 59.49 (d, J_{Rh-C} = 8.1 Hz, 1-C of Cp′), 20.76, 19.76, 19.50, 19.48 (CH$_2$), 12.69 (CO$_2$CH$_2$CH_3), 12.36 (OCH$_2$CH_3); UV λ_{max} (MeCN) 393 (2000), 313 (17 000), 306 nm (sh); ES-MS: m/z 574.9 [M –

$ClO_4]^+$; Anal. Calcd for $C_{24}H_{27}BrClN_2O_7Rh$: H, 4.04; C, 42.78; N, 4.16. Found: H, 3.98; C, 42.76; N, 4.17.

Typical procedure for the hydrogenation of ketones by rhodium complexes

A degassed MeOH solution (2 ml) of the complex (2.5 μmol), ketone (0.25 mmol), and 50 μl of 1 M KOH solution (50 μmol) was added into a glass reactor and stirred vigorously under 3 MPa of H_2 at 60 °C for 6 h. The reaction solution was analyzed by GC after the reaction to determine the yield.

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