Synthesis and catalytic activity of rhodium diene complexes bearing indenyl-type fullerene η^5-ligand

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Abstract

Rhodium η^5-complexes bearing an indenyl-type fullerene ligand, Rh[C$_{60}$(PhCH$_2$)$_2$Ph](cod) (**2**), Rh[C$_{60}$(PhCH$_2$)$_2$Ph](nbd) (**3**) and Rh(C$_{70}$Ph$_3$)(cod) (**4**), have been synthesized from the corresponding fullerene tri-adducts in 93–96% yields. X-ray crystallographic analysis of **4** indicated that the structure of **4** is similar to that of Rh(Ind)(cod). The rhodium complex **2** catalyzes alkyne trimerization reactions and hydroboration reactions.
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Keywords: Fullerene; Rh complex; Indenyl ligand; Catalysis

1. Introduction

We previously reported a regioselective synthesis of fullerene tri-adducts, C$_{60}$R$_3$H and C$_{70}$R$_3$H [1,2]. Thus, treatment of 1,7-diorgano[60]fullerene [3] with a Grignard reagent affords, after hydrolysis and HPLC purification, the [60]fullerene tri-adduct C$_{60}$R$_3$H in good yield, and treatment of [70]fullerene with an organo-copper reagent gives, after aqueous work up, the [70]fullerene tri-adduct C$_{70}$R$_3$H in quantitative yield. Both compounds were easily converted to the corresponding potassium complexes, K(C$_{60}$R$_3$) and K(C$_{70}$R$_3$), by treatment with *t*-BuOK in THF at ambient temperature. Theoretical studies on the model compounds K(C$_{60}$H$_3$) and K(C$_{70}$H$_3$) revealed that the structural as well as electronic properties of the indenyl moiety embedded in the extensive π-electron conjugation of the fullerene sphere is similar to those of a simple indenyl ligand. One can therefore expect to synthesize their transition metal complexes. We wish to report here the synthesis of rhodium diene complexes bearing the indenyl-type fullerene ligands. Catalytic activity of such a complex will also be briefly discussed.
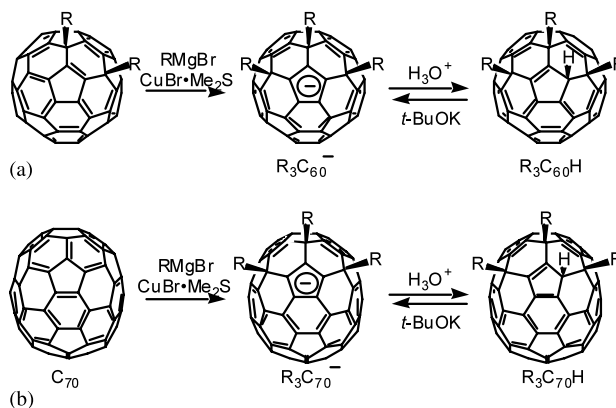
2. Results and discussion

In the C$_{60}$R$_5$ metal η^5-cyclopentadienyl complexes that we reported previously [4,5], the five R groups surround the metal center, leaving little free space between them and the metal atom. Likely owing to this effect, we could not synthesize rhodium diene complexes such as Rh(C$_{60}$Me$_5$)(cod) (cod = 1,5-cyclooc-tadiene), which we expected to be useful for catalysis [6–

8]. We therefore considered that the less sterically encumbered $C_{60}R_3$ and $C_{70}R_3$ ligands would give us more flexibility in the synthesis of η^5-transition metal complexes of fullerenes.

Unlike the $C_{60}R_5$ ligand (note that we could only synthesize a Rh dicarbonyl complex) [5], the $C_{60}R_3$ ligand readily formed the desired rhodium complexes by simple transmetallation strategy. Thus, treatment of $C_{60}(PhCH_2)_2PhH$ (**1**, a near 3:2 mixture of regioisomers as shown) with t-BuOK (1.2 equivalent) in THF at 25 °C caused an immediate color change from brown to dark green, suggesting generation of the corresponding potassium complex $K[C_{60}(PhCH_2)_2Ph]$ [1]. ^{1}H-NMR analysis in THF-d_8 showed that the isomeric mixture of **1** gave a single product, $K[C_{60}(PhCH_2)_2Ph]$. $[RhCl(cod)]_2$ (2.0 equivalent) was then added to this green solution in one portion. HPLC analysis on the reaction mixture indicated that the reaction was rapid, completing within 45 min. The crude product was isolated as dark green powder by precipitation with hexane. After washing and air-drying overnight, $Rh[C_{60}(PhCH_2)_2Ph](cod)$ (**2**) was obtained in 93% yield (Scheme 1) as a single product. The rhodium complex **2** is stable and easy to handle: it remains stable for a few months in air under ambient light. Support for the assigned C_1 symmetric structure of **2** came from the HRMS, ^{1}H-NMR, and ^{13}C-NMR data. The ^{1}H-NMR spectrum shows four distinct doublet peaks at δ 4.05, 4.19, 4.74, 4.84 ppm due to the methylene groups of the benzyl addends, multiplet peaks between δ 2.22 and 2.32 ppm and between δ 2.50 and 2.72 ppm due to the methylene groups of the 1,4-cyclooctadiene ligand, and multiplet peaks between δ 4.65 and 4.73 ppm and between δ 5.40 and 5.48 ppm due to the protons attached to the sp^2 carbon atoms of the 1,4-cycloocta-
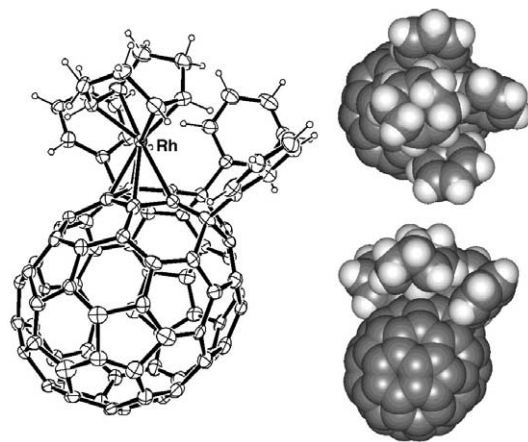

Fig. 1. Molecular structure of **4**.

diene ligand. The ^{13}C-NMR spectrum shows two doublet peaks due to the sp^2 carbon atoms of the 1,4-cyclooctadiene ligand at δ 74.73 and 74.92 ppm, which are coupled with the rhodium atom with coupling constants of $^1J_{Rh-C} = 12.5$ and 13.3 Hz, respectively. A similar reaction with $[RhCl(nbd)]_2$ (nbd = norbonadiene) afforded $Rh[C_{60}(PhCH_2)_2Ph](nbd)$ (**3**) in 96% yield as a single product.

We also synthesized a rhodium η^5-complex from the indenyl-type [70]fullerene ligand. The metathesis reaction of $K(C_{70}Ph_3)$ [2] with $[RhCl(cod)]_2$ gave the desired dark-brown rhodium complex $Rh(C_{70}Ph_3)(cod)$ (**4**) in 94% yield as single product (Eq. (1)). The HRMS and ^{1}H-NMR spectra are fully consisted with the assigned C_s symmetry structure. X-ray crystallographic analysis proved the molecular structure that we propose for **4**. Slow diffusion of hexane into a CS_2 solution of **4** gave black thin plates, one of which was analyzed by X-ray diffraction. The ORTEP drawing and space-filling models are shown in Fig. 1. One can see in the top view some free space around the metal center, which may allow fast ligand exchange required in catalysis. The structure around the rhodium metal shares some feature with that of Rh(Ind)(cod) (**5**) [9]. For example, lengths of the Rh–cod bonds (avg. **4**: 2.149 Å, **5**: 2.127 Å) and the lengths of the Rh–indenyl bonds (avg. **4**: 2.317 Å, **5**: 2.282 Å) are similar to each other.
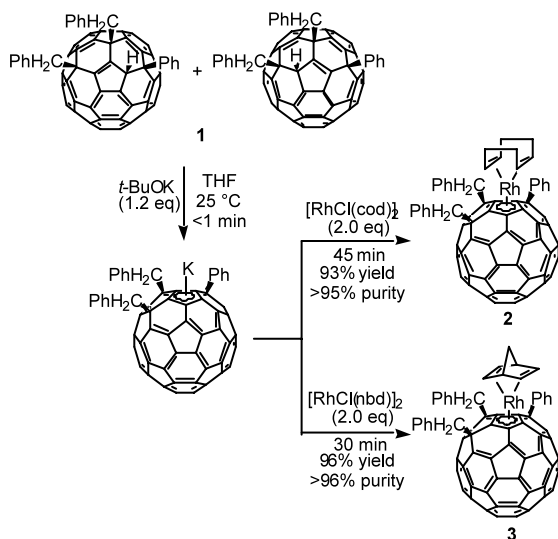
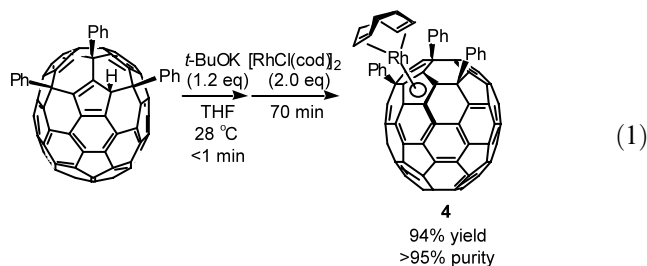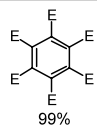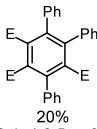Scheme 1. Synthesis of rhodium complexes bearing the $(PhCH_2)_2PhC_{60}$ ligand.

(1)

Table 1
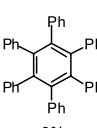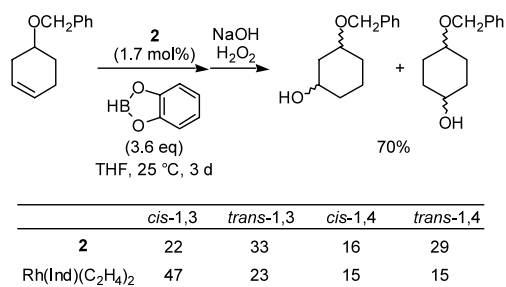Alkyne trimerization reaction catalyzed by **2**

Acetylene	Catalyst	Conditions	Product yield	Recovery of alkyne
E≡E	1 mol%	60 °C, 1 d	hexa(methoxycarbonyl)benzene 99%	0%
Ph≡E	0.5 mol%	100 °C, 3 d	20% (1,2,4-:1,3,5- = 91 : 9)	76%
Ph≡Ph	0.5 mol%	60 °C, 2 d	9%	82%

E = COOMe

The rhodium complexes thus obtained show considerable catalytic activity in an alkyne trimerization reaction [10]. The complex **2** was examined, since it shows the highest solubility among the rhodium complexes synthesized in the present studies (Table 1). When dimethyl acetylenedicarboxylate was treated with **2** (1.0 mol.%) in 1,2-dichlorobenzene at 60 °C for 1 d, hexa(methoxycarbonyl)benzene was obtained in 99% isolated yield. Tri(methoxycarbonyl)triphenylbenzene and hexaphenylbenzene were also obtained albeit in low yields. The catalytic activity and regioselectivity of **2** in alkyne trimerization reactions is comparable to that of **5** [7].

The rhodium complex **2** also catalyzes hydroboration reaction (Scheme 2) [11]. When 4-(benzyloxy)cyclohexene was treated with catecholborane (3.6 equivalent) in the presence of a catalytic amount of **2** (1.7 mol.%) in THF for 3 d at 25 °C, hydroboration products were obtained in 70% yield as a mixture of four isomers as shown. It is notable that the fullerene complex exhibits a product selectivity different from that of a Rh(Ind)(C_2H_4)$_2$ catalyst [8], favoring the formation of the 1,4-isomers and of the trans isomers as shown in Scheme 2. It seems likely that the steric effect of the

fullerene ligand is responsible for the change of the selectivity, and this issue will be subject of further studies.

Starting with the indenyl-type fullerene η^5-ligands, we have synthesized a new class of rhodium diene complexes, which have not so far been obtainable from the more hindered $C_{60}R_5$ ligand. The rhodium complex exhibited a considerable catalytic activity in the alkyne trimerization and the hydroboration reactions, where we obtained a sign of favorable effects of the use of the fullerene ligand system. Given the various new possibilities of the fullerene cyclopentadienyl ligand systems [12], we expect that the indenyl ligands and their transition metal complexes will offer exciting new opportunities for chemists in the field of organic synthesis, catalysis, and nano-science.

3. Experimental

3.1. General procedures

All reactions were carried out in an oven-dried reaction vessel under argon or nitrogen and were analyzed by HPLC (column: Buckyprep, 4.6×250 mm, Nacalai tesque; flow rate: 1.0 ml min^{-1}; eluent: toluene/2-propanol = 7/3; detector: SPD-M10Avp, Shimadzu). All ^{1}H-NMR spectra were taken at 400 MHz (JEOL EX-400 and AL400), and ^{13}C-NMR spectra at 100 MHz. Spectra are reported in part per million from internal tetramethylsilane or the residual protons of the deutrated solvent for the ^{1}H-NMR spectra, and from the deutrated solvent for the ^{13}C-NMR spectra. IR spectra were recorded on an Applied Systems Inc., REACT IR 1000 instrument as powders on a diamond probe; absorptions are reported in cm^{-1}. Mass spectra were measured with a Shimadzu LCMS-QP8000 instrument (APCI mode) equipped with a Buckyprep column. High resolution mass spectra were recorded on a JEOL JMS-T100LC machine.

3.2. Solvents and materials

All commercially available reagents were distilled or recrystallized before use unless otherwise noted. THF was purchased from KANTO KAGAKU and stored over MS4A under nitrogen. 1,2-Dichlorobenzene was distilled from CaH_2 and dried over MS4A. The water content of the solvents was determined each time with a Karl-Fischer moisture titrator (MK-210, Kyoto Electronics Company) to be less than 20 ppm. $C_{60}(PhCH_2)_2PhH$ and $C_{70}Ph_3H$ were prepared in a reported manner [1,2]. A solution of t-BuOK in THF (1 M) was purchased from Sigma Aldrich Japan K.K. and used as received.

	cis-1,3	trans-1,3	cis-1,4	trans-1,4
2	22	33	16	29
Rh(Ind)(C_2H_4)$_2$	47	23	15	15

Scheme 2. Hydroboration reaction catalyzed by **2**.

3.3. Synthesis of [(1,2,3,4,5-η)-6,9-dibenzyl-12-phenyl-9,12-dihydro(C_{60}-I_h)[5,6]fulleren-1(6H)-yl](η^2,η^2-1,4-cyclooctadiene)rhodium(I) ⟨Rh[C_{60}(PhCH$_2$)$_2$Ph](cod) (2)⟩

To a solution of C_{60}(PhCH$_2$)$_2$PhH (**1**, 50.5 mg, 51.5 µmol) in 5.00 ml of THF was added a solution of *t*-BuOK in THF (1.0 M, 60.0 µl) at 25 °C, giving a dark green solution. [RhCl(cod)]$_2$ (25.0 mg, 101 µmol) was then added to the solution in one portion at 25 °C. After stirring for 45 min at this temperature, 30 ml of hexane (degassed by bubbling a dry nitrogen gas over 30 min) was added to give greenish precipitates. The precipitates were collected by filtration and washed thoroughly with ether, hexane, and water, then dried in the air over night to afford 57.0 mg (47.9 µmol, 93% yield) of the rhodium complex **2** as a dark green solid (>95% purity in HPLC and ^{1}H-NMR analysis). IR (powder) 3025 (w), 2873 (w), 2829 (w), 1600 (w), 1493 (w), 1455 (w), 1430 (w), 1189 (w), 1152 (w), 1100 (w), 1084 (w), 1075 (w), 1063 (w), 1030 (w), 851 (m), 759 (m), 741 (s), 724 (m), 699 (s); ^{1}H-NMR (CS$_2$, 400 MHz) δ 2.22–2.32 (m, 2H, CH=CHCH$_2$), 2.50–2.72 (m, 6H, CH=CHCH$_2$), 4.05 (d, *J* = 12.4 Hz, 1H, PhCH*H*), 4.19 (d, *J* = 12.4 Hz, 1H, PhCH*H*), 4.65–4.73 (m, 2H, CH=C*H*), 4.74 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 4.84 (d, *J* = 13.2 Hz, 1H, PhCH*H*), 5.40–5.48 (m, 2H, CH=C*H*), 7.37–7.57 (m, 4H, Ph), 7.67–7.75 (m, 5H, Ph), 7.85 (t, *J* = 7.8 Hz, 2H, Ph), 7.94 (d, *J* = 7.2 Hz, 2H, Ph), 8.35 (d, *J* = 7.2 Hz, 2H, Ph); ^{13}C-NMR (CS$_2$, 100 MHz) δ 31.10, 33.63, 47.99, 53.94, 57.24, 58.75, 59.83, 74.73, 74.92, 127.43, 127.88, 127.99, 128.24, 128.39, 128.59, 128.93, 129.23, 129.25, 129.29, 130.08, 131.03, 131.20, 135.15, 135.47, 135.49, 135.57, 135.89, 139.54, 140.50, 142.37, 142.49, 142.50, 142.70, 142.79, 143.01, 143.12, 143.23, 143.28, 143.39, 143.75, 143.94, 144.00, 144.14, 144.36, 144.62, 144.75, 145.39, 145.43, 145.49, 145.51, 145.62, 146.45, 146.55, 146.72, 146.84, 147.01, 147.03, 147.08, 147.14, 147.20, 147.22, 148.26, 148.41, 148.43, 148.88, 149.12, 149.26, 150.14, 150.18, 156.63, 157.60; UV λ_{max} 696, 379, 311 nm; HRMS (APCI-) Found: 1190.14575; Calc. for C$_{88}$H$_{31}$^{103}Rh: 1190.14808%.

3.4. Synthesis of [(1,2,3,4,5-η)-6,9-dibenzyl-12-phenyl-9,12-dihydro(C_{60}-I_h)[5,6]fulleren-1(6H)-yl](η^2,η^2-norbonadiene)rhodium(I) ⟨Rh[C_{60}(PhCH$_2$)$_2$Ph](nbd) (3)⟩

This compound was synthesized in the same manner as **2**. Starting from 21.0 mg of **1** (21.4 µmol), 24.2 mg of **3** (20.6 µmol, 96% yield) was obtained as a dark green solid (>96% purity in HPLC and ^{1}H-NMR analysis). IR (powder) 3060 (w), 3027 (w), 2917 (w), 1600 (m), 1493 (m), 1453 (w), 1030 (m), 739 (m), 697 (s); ^{1}H-NMR (CS$_2$, 400 MHz) δ 1.63–1.67 (m, 2H), 3.86–3.98 (m, 4H), 4.02–4.10 (m, 2H), 4.73–4.78 (m, 2H) 4.65 (d, *J* =

13.2 Hz, 1H), 4.86 (d, *J* = 13.2 Hz, 1H), 7.38–7.52 (m, 5H), 7.61–7.77 (m, 4H), 7.81–7.87 (m, 2H), 7.93–8.00 (m, 2H), 8.25–8.31 (m, 2H); ^{13}C-NMR (toluene-d_8, 100 MHz) δ 47.71, 48.58, 49.60, 50.04, 50.80, 50.91, 53.94, 55.89, 57.11, 58.06, 60.22, 61.06, 82.87, 102.08, 127.28, 127.45, 127.81, 128.05, 128.48, 128.95, 129.19, 130.86, 131.31, 136.00, 136.23, 137.04, 139.47, 140.35, 142.34, 142.48, 142.78, 142.75, 142.98, 143.12, 143.24, 143.47, 143.71, 143.93, 144.13, 144.18, 144.42, 144.51, 144.66, 144.72, 145.30, 145.37, 145.55, 145.65, 145.78, 145.92, 146.50, 146.59, 146.68, 146.91, 146.97, 147.21, 147.28, 147.34, 147.77, 147.95, 148.27, 148.43, 148.91, 149.03, 149.20, 149.38, 150.18, 150.23, 150.33, 150.44, 150.61, 150.87, 151.04, 156.58, 158.56; UV λ_{max} 684, 375, 309 nm; HRMS (APCI-) Found: 1174.11690; Calc. for C$_{87}$H$_{27}$^{103}Rh: 1174.11678%.

3.5. Synthesis of (η^2,η^2-1,4-cyclooctadiene)-[(1,6,7,8,9-η)-10,22,25-triphenyl-22,25-dihydro(C_{70}-$D_{5h(6)}$)[5,6]fulleren-7(10H)-yl]rhodium(I) ⟨Rh(C_{70}Ph$_3$)(cod) (4)⟩

This compound was synthesized in the same manner as **2**. Starting from 49.8 mg of C_{70}Ph$_3$H (46.4 µmol), 56.1 mg of **4** (43.8 µmol, 94% yield) was obtained as a dark green solid (>95% purity in HPLC and ^{1}H-NMR analysis). IR (powder) 3059 (w), 3027 (w), 2914 (w), 2872 (w), 2837 (w), 1492 (m), 1456 (s), 1446 (m), 1126 (m), 1074 (w), 1034 (s), 943 (w), 863 (m), 792 (m), 748 (s), 694 (s); ^{1}H-NMR (400 MHz, C$_6$D$_6$) δ 1.34–1.39 (m, 4H, CH$_2$), 1.64–1.74 (m, 4H, CH$_2$), 3.43 (br s, 4H, CH=CH), 6.85–6.97 (m, 6H, Ph), 7.32–7.38 (m, 3H, Ph), 7.40–7.46 (m, 4H, Ph), 8.92–8.89 (m, 2H, Ph); ^{13}C-NMR (CS$_2$/toluene-d_8, 100 MHz) δ 30.94, 56.90, 57.71, 71.76, 92.14, 100.23, 109.84, 129.25, 129.63, 129.89, 131.77, 131.87, 132.45, 132.88, 138.25, 139.89, 140.74, 142.80, 144.25, 144.43, 144.56, 144.65, 145.26, 145.78, 145.92, 146.22, 146.35, 146.59, 147.14, 147.34, 147.42, 147.54, 147.71, 147.85, 148.61, 148.97, 149.05, 149.54, 149.97, 150.97, 154.84, 157.75; HRMS (APCI-) Found: 1282.11576; Calc. for C$_{96}$H$_{27}$^{103}Rh: 1282.11678%.

3.6. General procedure of alkyne trimerization reaction catalyzed by 2

To a degassed solution of **2** (4–8 µmol) in 1,2-dichlorobenzene was added an alkyne substrate (0.8 mmol) in one portion at ambient temperature and the resulting mixture was heated at 60–100 °C. The reactions were monitored with TLC as well as HPLC (Buckyprep column), indicating the reactions were stopped after 1–3 days. After cooling, the reaction mixture was diluted with toluene and purified by flash column chromatography to give a trimerization product together with the recovered starting material (if any).

Table 2
Crystal data and data collection parameters of **4**·CS$_2$

Complex	Rh(C$_{70}$Ph$_3$)(cod)·CS$_2$
Formula	C$_{97}$H$_{27}$RhS$_2$
Formula weight	1359.32
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.257(3)
b (Å)	17.780(4)
c (Å)	29.447(5)
α (°)	90
β (°)	94.110(14)
γ (°)	90
V (Å^3)	5356(2)
Z	4
D_{calc} (g cm^{-3})	1.667
$F(0\,0\,0)$	2660
Temperature (K)	153(2)
Crystal size (mm)	$0.30 \times 0.10 \times 0.02$
$2\theta_{min}$, $2\theta_{max}$ (°)	4.8, 51.2
Number of reflection measured (Total)	9791
Number of reflection measured [$I > 2.0\sigma(I)$]	5501
Number of variables	1021
R_1, wR_2 (all data)	0.2126, 0.4106
R, R_w [$I > 2.0\sigma(I)$]	0.1447, 0.3668
Goodness-of-fit on F^2	1.34

3.7. Hydroboration reaction catalyzed by 2

A solution of 4-(benzyloxy)cyclohexene (49 mg, 0.26 mmol) and **2** (5.3 mg, 4.4 μmol, 1.7 mol.%) in 2.5 ml of THF was degassed with freeze–thaw cycles 3 times. To this solution was added catecholborane (100 μl, 0.94 mmol, 3.6 equivalent) at 25 °C and the resulting mixture was stirred at this temperature for 3 d. The reaction mixture was treated with MeOH (1 ml), aq. NaOH (2 N, 1 ml) and H$_2$O$_2$ (35%, 1 ml), and extracted with ether. The extracts were washed with aq. NaOH and brine, dried over anhydrous MgSO$_4$, filtered and evaporated to give a crude product. Purification was achieved by flash column chromatography to give hydroboration products as a mixture of four isomers. The isomeric ratio was determined by ^{1}H-NMR analysis [8].

3.8. Crystallographic data collections and structure determination of 4

A single crystal of **4** suitable for the X-ray diffraction study was mounted on a MacScience DIP2030 Imaging Plate diffractometer with Mo–K$_\alpha$ (graphite monochromated, $\lambda = 0.71069$) radiation. Crystal data and data statistics are summarized in Table 2. The structure was solved by the direct method (SHELXS-97) [13] and expanded using Fourier techniques (DIRDIF-94) [14]. The non-hydrogen atoms were refined anisotropically by the full-matrix least-square method (SHELXL-97) [13].

Hydrogen atoms were placed at calculated positions (C–H = 0.95 Å) and kept fixed. In the subsequent refinement, the function $\Sigma\omega(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $wR_2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma(\omega F_o^4)]^{1/2}$. Since Rh[C$_{70}Ph_3$(cod)] molecule was positionally disordered, R indices of this analysis were not ideal, but the structural data were judged to be reliable enough for confirmation of the structure assigned by the spectroscopic methods.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 209668 for complex **4**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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