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Rhodium and iridium complexes bearing an alkyloxazoline-substituted indenyl ligand (Indox ligand) and their stereoselective construction of metal-centered chirality

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Abstract

The Indox ligands, [{(*S*)-(*i*Pr)Indox}$_n$]H (**1**) [$n = 2$ (**a**), 3 (**b**)] and [{(H)Indox}$_{n=3}$]H (**2**), in which an indenyl group and an oxazoline ring are connected by an ethylene or propylene spacer, have been prepared. Reaction of $[Ir(coe)_2Cl]_2$ or $[RhCl(C_2H_4)_2]_2$ with the potassium salt of **1** afforded η^5-[{(*S*)-(*i*Pr)Indox}$_n$]Ir(coe)$_2$ (**3**) or η^5-[{(*S*)-(*i*Pr)Indox}$_n$]Rh$(C_2H_4)_2$ (**6**) as a 1:1 mixture of two diastereomers. The oxazoline ring in **3** and **6** did not coordinate to the metal center. When the complexes **3** or **6** reacted with iodine in diethyl ether, oxidative addition proceeded and the oxazoline ring coordinated to the metal center to give diiodoiridium(III) or rhodium(III) complexes, η^5:η^1-[{(*S*)-(*i*Pr)Indox}$_n$]M$(I)_2$ [M = Ir (**4**), Rh (**7**)]. The corresponding diiodoiridium(III) complex bearing the Indox ligand **2**, η^5:η^1-[{(H)Indox}$_{n=2}$]Ir$(I)_2$ (**5**), was also prepared by a similar method. Reaction of **4** or **7** with PPh_3 in THF afforded diiodo-phosphine complexes, η^5-[{(*S*)-(*i*Pr)Indox}$_n$]M$(PPh_3)(I)_2$ [M = Ir (**8**), Rh (**9**)] as a 1:1 mixture of two diastereomers in which the oxazoline ring dissociated from the metal center. The related reaction of **8** or **9** with more than 2 equiv. of AgOTf afforded the cationic complexes, [η^5:η^1-[{(*S*)-(*i*Pr)Indox}$_n$]M(PPh_3)(OTf)]OTf [M = Ir (**10**), Rh (**11**)], having a stereogenic center at the metal center as a mixture of only two diastereomers. From ^{1}H and ^{31}P NMR analyses, each diastereomer of **8** or **9** afforded only a single isomer of **10** or **11**. The corresponding iridium(III) complex bearing the Indox ligand **2**, [η^5:η^1-[{(H)Indox}$_{n=3}$]Ir(PPh_3)(OTf)]OTf (**12**) was also prepared. The coordinated triflate ligand of **12** was slowly replaced by water in $CDCl_3$ to afford the dicationic aquo complex, (S^*_{pl}, R^*_{Ir})-[η^5:η^1-[{(H)Indox}$_{n=3}$]Ir$(PPh_3)(H_2O)$](OTf)$_2$ (**13**). The monocationic complex, [η^5:η^1-[{(*S*)-(*i*Pr)Indox}$_{n=2}$]Ir(PPh_3)(I)]OTf (**14a**), having metal-centered chirality, was observed as a mixture of only two diastereomers in the reaction of **10a** (a mixture of two diastereomers) with 1 equiv. of AgOTf. These observations indicated that the ligand exchange reaction of **8** or **9** with AgOTf contained the following three steps: (i) abstraction of one of the two prochiral iododes by AgOTf, (ii) recoordination of the oxazoline ring, and (iii) exchange of the remaining iodide for the triflate by AgOTf. The stereochemistry around the metal center was determined at the second step. All complexes have been characterized by usual spectroscopic methods as well as elemental analyses, and **4** and **13** have been characterized by X-ray analyses.

Keywords: Indox ligand; Oxazoline ring; Metal-centered chirality; Planar chirality; Ligand exchange reaction; Hemilabile

1. Introduction

Hybrid ligands, in which both a cyclopentadienyl derivative and a donor-ligand such as phosphine, amine, amide, sulfide and alcohol are connected by an appropriate spacer, have received much attention as heterofunctional ligands having the combined characters of their components, which could often induce some unexpected reactivities [1]. So far, we have concentrated on the chemistry of the linked cyclopentadienyl (or indenyl) and phosphine ligand (the Cp′–P ligand) and disclosed the unique characters of their rhodium, iridium and

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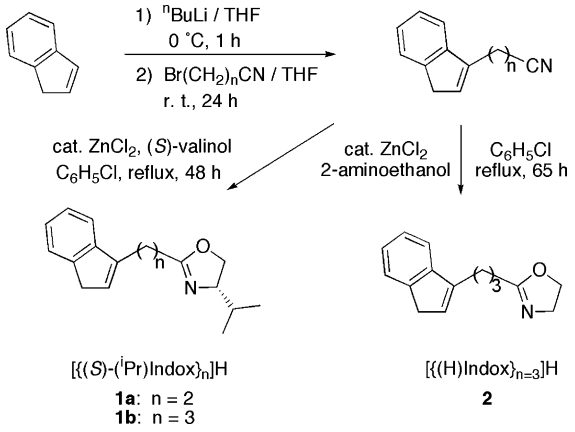
ruthenium complexes [2]. One significant character was the stereoselective construction of metal-centered chirality controlled by the planar chirality arising from the complexation of the Cp′–P ligand having an indenyl group [2c,2d,2e]. On the other hand, a wide variety of metal complexes having the Cp′–N ligand, in which an amino group was linked to a cyclopentadienyl derivative, have also been prepared and their reactivities were examined [1a,1b,1c]. Early transition metals and lanthanide complexes bearing the Cp′–N ligand are expected to be a post-metallocen catalyst [3]. Although late transition metals bearing the Cp′–N ligand have also provided many interesting properties including hemilability of the N-donor part, stabilization of unstable species, creation of bimetallic complexes and so on, several unexplored but fascinating fields still remain [4–10]. One is the utilization of an oxazoline ring as an N-donor ligand in the Cp′–N ligand. An optically active oxazoline ring is easily prepared from an amino alcohol and the complexes bearing the oxazoline-based chiral ligands are known as an effective asymmetric catalyst. The Cp′–N ligand having an optically active oxazoline ring could be effective in catalytic asymmetric reactions. Another is the preparation of the complexes having a stereogenic center on the metal by using the Cp′–N ligand. A three-legged piano stool complex, $Cp'ML_1L_2L_3$ (Cp' = cyclopentadienyl derivative, M = metal and L_n = ligand), has a stereogenic center on the metal if all ligands are different, but optically active complexes like that are usually troublesome to be prepared due to configurational instability of the chirality on the metal center. We already showed that a stable stereogenic center on the metal could be constructed by using the Cp′–P ligand. Although coordination of the N-donor is weaker than that of the P-donor, the Cp′–N ligand has possibility to create stable metal-centered chirality.

Herein, we report the preparation of a new series of the Cp′–N ligand, the Indox ligand, in which an optically active oxazoline ring as an N-donor and an indenyl group as a cyclopentadienyl derivative are connected by an alkylene spacer, and the synthesis and characterization of their iridium and rhodium complexes. Studies on the construction of metal-centered chirality by the stereoselective ligand exchange reaction of their iridium and rhodium complexes having two prochiral iodide ligands are also presented.

2. Results and discussion

2.1. Synthesis of the Indox ligand

The Indox ligands, [{(*S*)-(ⁱPr)Indox}$_n$]H (**1**) [$n = 2$ (**a**), 3 (**b**)] and [{(H)Indox}$_{n=3}$]H (**2**), in which an indenyl group and an oxazoline ring are connected by an ethylene or propylene spacer, were prepared from indene by



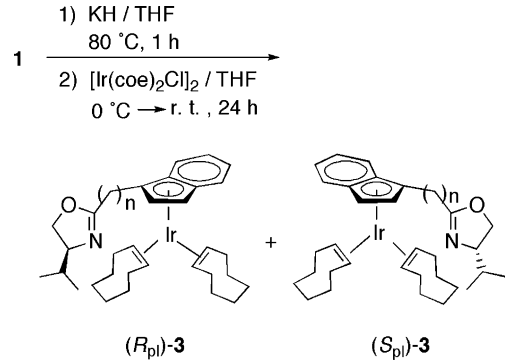
Scheme 1.

two steps as shown in Scheme 1. Treatment of the lithium salt of indene, prepared from indene and ⁿBuLi in THF at 0 °C, with 3-bromopropanenitrile or 4-bromobutanenitrile afforded 3-(3-indenyl)propanenitrile or 4-(3-indenyl)butanenitrile, respectively. Conversion of the nitrile group into an oxazoline ring by the $ZnCl_2$-catalyzed annulation with (*S*)-valinol or 2-aminoethanol gave the Indox ligands **1** or **2** in moderate to good yields [11]. This methodology can supply several Indox ligands having a different alkylene spacer, but unfortunately the Indox ligand having a methylene spacer could not be prepared because the reaction of bromoacetonitrile with the lithium salt of indene gave a complex mixture.

2.2. Synthesis and characterization of diiodo complexes bearing the Indox ligand

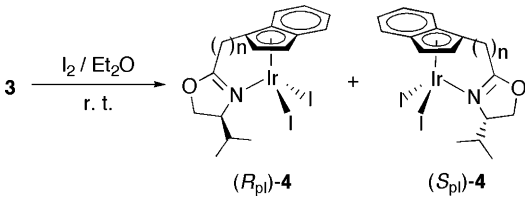
The Indox ligands **1** were treated with KH in THF at 80 °C for 1 h and the resulting brown suspension was added to a THF suspension of $[Ir(coe)_2Cl]_2$ at 0 °C. The reaction mixture was warmed to room temperature overnight and resulted in a dark red solution. After the solvent was removed in vacuo, the iridium complexes, η^5-[{(*S*)-(ⁱPr)Indox}$_n$]Ir(coe)$_2$ (**3**), were isolated by extraction with hexanes from the resulting residue (Eq. (1)). Purification of **3** by recrystallization failed due to the too rich solubility of **3** to various solvents, but the purity was satisfactory for the identification of **3** by spectroscopic methods and the utilization for the following reactions. Abstraction of the proton in the indenyl group by KH was indispensable for the preparation of the iridium complexes. A similar reaction using ⁿBuLi or ᵗBuLi instead of KH, which were usually used for the preparation of the rhodium or iridium complexes having the indenyl group, afforded many undefined impurities along with a small amount of **3** [12]. The molecular ion peak at *m/e* 667 (**3a**) and 682 (**3b**) in the mass spectra supported the proposed structure of **3**. The IR spectra showed the C=N stretching vibration

at 1669 cm^{-1} (**3a** and **3b**), which was hardly shifted from that of the free ligand (**1a**, 1672 cm^{-1}; **1b**, 1670 cm^{-1}), indicating that the oxazoline ring did not coordinate to the iridium center. The ^1H NMR analysis of the crude product showed that **3a** was obtained as a 1:1 mixture of two diastereomers due to combination of the arising planar chirality and the stereogenic center of the oxazoline ring. The terminal proton in the isopropyl group of **3a** was observed as two sets of two doublet signals with the same integral intensities (δ 0.81, 0.93 and 0.84, 0.89). Although the ratio of the diastereomers in **3b** could not be determined directly from the ^1H NMR spectrum because the signals were not unambiguously distinguished between the diastereomers, we estimated that **3b** also formed as a 1:1 mixture of the diastereomers from the following experiments (vide infra). In the complexation of the Indox ligand with the iridium metal, the stereogenic center in the oxazoline ring was ineffective for the induction of the arising planar chirality on the indenyl ring. Whitby and co-workers [13] reported that the coordination of the phosphino group to the metal center was essential for a high level of induction of planar chirality in the complexation of the Cp′–P type ligand. The stereogenic center of the oxazoline ring in the Indox ligand would locate remote to the metal center where the nucleophilic attack of the potassium salt of the indenyl group occurred. One reason is the weaker coordination ability of the oxazoline ring as an N-donor to the iridium(I) metal.



(R_{pl})-**3** (S_{pl})-**3** (1)

Reaction of **3** with 1 equiv. of elemental iodine in diethyl ether at room temperature according to the method of Jutzi afforded the diiodoiridium(III) complexes, η^5:η^1-[{(*S*)-(^{i}Pr)Indox}$_n$]Ir(I)$_2$ (**4**), in excellent yields (Eq. (2)) [7b]. The structure of **4** was confirmed by elemental analyses and spectroscopic methods. The IR spectra showed the C=N stretching vibration at 1632 cm^{-1} (**4a** and **4b**), which was shifted to a lower wave number by ca. 40 cm^{-1} compared to that of the free ligand, indicating that the Indox ligand coordinated to the iridium center in an η^5- and η^1-coordination manner. In the FAB mass spectra, the molecular ion peak at *m/e* 701 (**4a**) and 716 (**4b**) was observed. The ^1H NMR spectra showed that the signals of the cyclopentadienyl protons in the indenyl group appeared as two sets of two doublets with the same integral intensities (**4a**, δ 5.83, 5.93 and 5.86, 5.06; **4b**, δ 5.77, 6.17 and 5.82, 6.21), indicating that both **4a** and **4b** were also a 1:1 mixture of two diastereomers derived from the planar chirality and the stereogenic center in the oxazoline ring. It was reasonable that the ratio of the two diastereomers in **4** was the same as that of **3** because the oxidative iodination proceeded with no influence on the stereochemistry of the two chiralities. The ratio of the two diastereomers in **3b**, which was not confirmed by the ^1H NMR analysis of **3b**, could be determined to be 1:1 from these observations. Although we tried to isolate the diastereoisomerically pure form of **4** by repeated recrystallization, unfortunately our attempts have not been succeeded yet.



(R_{pl})-**4** (S_{pl})-**4** (2)

Single crystals of **4b** suitable for X-ray analysis were directly obtained from the reaction mixture under dilute conditions. An ORTEP drawing is given in Fig. 1, relevant crystal and data parameters are presented in Table 1, and selected bond lengths and angles are given in Table 2. The unit cell contained two diastereomers, (R_{pl})-**4b** which was the complex containing Ir1 and (S_{pl})-**4b** which was the complex containing Ir2. These crystals were in the monoclinic space group $P2_1$ with four molecules in the unit cell (two independent molecules are in the asymmetric unit). The dihedral angle between the least-square plane of the indenyl ring and the least-square plane of the oxazoline ring in (R_{pl})-**4b** was 30.24(47)°, while that in (S_{pl})-**4b** was 65.56(27)°. In order to avoid the steric repulsion between the isopropyl group in the oxazoline ring and the phenyl ring in the indenyl group, the isopropyl group in (S_{pl})-**4b** pointed away from the indenyl ring and the oxazoline ring coordinated to the iridium center with a slight leaning to the vertical direction compared to that in (R_{pl})-**4b**. The steric repulsion was also reflected in the N–Ir–Cpn angles [Cpn ($n = 1$ or 2) is the gravimetric center of the cyclopentadienyl part of the indenyl group]: The N2–Ir2–Cp2 bond angle (130.51°) in (S_{pl})-**4b** is larger than the N1–Ir1–Cp1 bond angle (124.92°). The distortion of the indenyl ring towards η^3-coordination was not observed clearly compared to that in the rhodium and iridium complexes having the Cp′–P type ligand, but it is undeniable. For example, the bond lengths of Ir1–C4 (2.253(10) Å) or Ir1–C5 (2.234(9) Å) in (R_{pl})-**4b** and Ir2–C22 (2.246(9) Å) or Ir2–C23 (2.292(8) Å) in (S_{pl})-**4b** were a little longer than those of other bonds in the ranges 2.135–2.182 Å. The two Ir–I bond lengths are different: The bond lengths of Ir1–I1 (2.7248(8) Å) and Ir2–I4

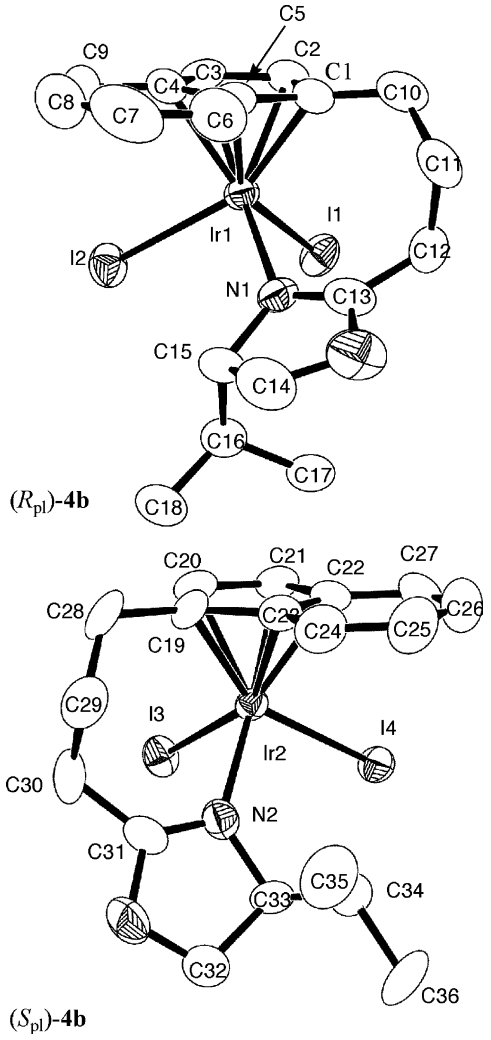
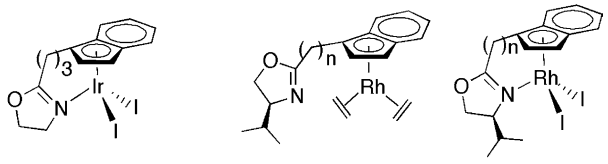


Fig. 1. ORTEP drawing of two diastereomers, (R_{pl})-**4b** and (S_{pl})-**4b**, in the asymmetric unit. Thermal ellipsoids are shown at the 50% probability level.

(2.7083(7) Å) are similar to those of the two Ir–I bonds in the diiodoiridium complexes having the Cp′–N type ligand prepared by Jutzi [7b], but the Ir1–I2 (2.6562(7) Å) and Ir2–I3 (2.6689(7) Å) bonds are a little but clearly shorter.

Reaction of the potassium salt of **2** with $[Ir(coe)_2Cl]_2$ in THF, followed by oxidation of iodine in diethyl ether afforded the diiodoiridium(III) complex, η^5:η^1-[{(H)Indox}$_{n=3}$]Ir(I)$_2$ (**5**) as a brown powder in 67% isolated yield. The IR spectrum at 1633 cm^{-1} for the C=N stretching vibration and mass spectrum at *m/e* 673 as a molecular ion peak suggested the formation of **5**. Since **5** was a 1:1 mixture of enantiomers based on the planar chirality on the indenyl ring, the ^{1}H NMR spectrum showed the two protons of the cyclopentadienyl part as one set of two doublets at δ 5.91 and 6.04. Similarly, the diiodorhodium(III) complexes, η^5:η^1-[{(*S*)-(^{i}Pr)Indox}$_n$]Rh(I)$_2$ (**7**) were prepared by the reaction of η^5-[{(*S*)-(^{i}Pr)Indox}$_n$]Rh(C_2H_4)$_2$ (**6**), obtained from the potassium salt of **1** with $[RhCl(C_2H_4)_2]_2$ in THF, with iodine in diethyl ether. The structure of these complexes was characterized by usual spectroscopic methods as well as elemental analyses, though an analytically pure form of **6** was not obtained due to its too rich solubility to various solvents. The ^{1}H NMR spectra showed that **7** was also an almost 1:1 mixture of two diastereomers, indicating that the stereogenic center in the oxazoline ring did not induce the planar chirality at all for the complexation with the rhodium in the same way as the iridium complexes.



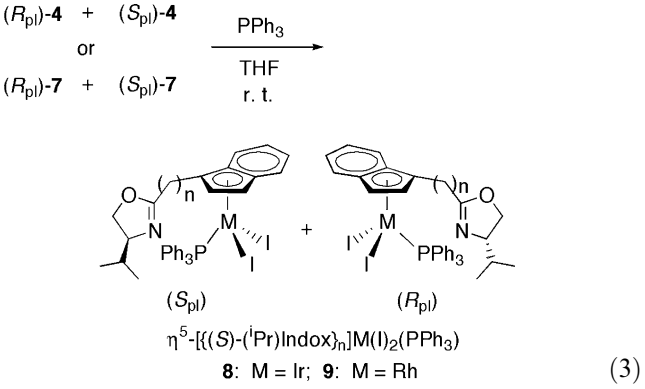
5 (only one enantiomer shown) **6** (only one diastereomer shown) **7**

2.3. Synthesis and characterization of diiodo-phosphine complexes bearing the η^1-coordinated Indox ligand

When the diiodoiridium(III) complexes **4** (1:1 mixture of two diastereomers) were treated with 1 equiv. of PPh_3 in THF at room temperature for 3 h, the oxazoline ring dissociated from the iridium center to afford the diiodophosphine complexes, η^5-[{(*S*)-(^{i}Pr)Indox}$_n$]Ir(PPh_3)(I)$_2$ (**8**) as a brown powder (Eq. (3)). In an analogous way, reaction of the rhodium(III) complexes **7** with 1 equiv. of PPh_3 in THF at room temperature for 24 h gave similar rhodium complexes, η^5-[{(*S*)-(^{i}Pr)Indox}$_n$]-Rh(PPh_3)-(I)$_2$ (**9**) as a brown powder (Eq. (3)). The structure of **8** and **9** was fully characterized by elemental analyses as well as spectral data. Dissociation of the oxazoline ring was confirmed by the IR spectra for the C=N stretching vibration (**8a**, 1669 cm^{-1}; **8b**, 1668 cm^{-1}; **9a**, 1669 cm^{-1}; **9b**, 1667 cm^{-1}), which were hardly shifted from that of the free ligand. The N-donor of the alkylamine-substituted cyclopentadienyl ligand in rhodium and iridium complexes easily dissociated from the central metals in the reaction with a phosphine, as reported by Jutzi [7b]. The ^{31}P NMR spectra displayed two singlet signals with the same integral intensities for **8** (**8a**, δ 1.57, 1.60; **8b**, δ 1.58, 1.60) and two doublet signals (J_{P-Rh} = 155 Hz) for **9** (**9a**, δ 48.1, 48.2; **9b**, δ 48.3, 48.4), respectively, indicating that both **8** and **9** were also a 1:1 mixture of two diastereomers. Repeated recrystallization from the mixtures did not afford the diastereoisomerically pure form, but the diastereomer mixtures containing a little excess amount of one diastereomer were obtained (**8a**, 55:45; **8b**, 51:49; **9a**, 57:43; **9b**, 51:49).

Table 1
Crystal data and structure refinement details for **4** and **13**

	4	**13**
Empirical formula	$C_{18}H_{22}I_2IrNO$	$C_{36}H_{34}Cl_3F_6IrNO_8PS_2$
Formula weight	714.34	1116.28
Temperature (K)	296(2)	173(1)
Wavelength (Å)	0.71069	0.71069
Crystal system	monoclinic	triclinic
Space group	$P2_1$ (#4)	$P\bar{1}$ (#2)
Unit cell dimensions		
a (Å)	15.7847(9)	13.2358(7)
b (Å)	9.8925(6)	13.3151(2)
c (Å)	13.5100(8)	12.5460(3)
α (°)	90	114.7063(6)
β (°)	110.0778(14)	94.932(2)
γ (°)	90	87.730(3)
Volume (Å^3)	1981.4(2)	2001.22(12)
Z	4	2
D_{calc} (Mg/m^3)	2.395	1.853
Absorption coefficient (mm^{-1})	9.858	3.761
$F(000)$	1312	1100
Crystal size (mm)	$0.35 \times 0.22 \times 0.22$	$0.20 \times 0.14 \times 0.13$
θ Range for data collection (°)	3.03–32.50	2.52–27.50
Limiting indices	$-23 \leqq h \leqq 23$, $-14 \leqq k \leqq 14$, $-20 \leqq l \leqq 20$	$-17 \leqq h \leqq 17$, $-17 \leqq k \leqq 17$, $-16 \leqq l \leqq 16$
Reflections collected	37 292	26 546
Unique reflections	13 896 [$R_{int} = 0.0841$]	9056 [$R_{int} = 0.1022$]
Maximum transmission	0.347875	0.728061
Minimum transmission	0.156259	0.602144
Goodness-of-fit on F^2	0.980	1.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0516$, $wR_2 = 0.1164$	$R_1 = 0.0659$, $wR_2 = 0.1430$
R indices [All data]	$R_1 = 0.0720$, $wR_2 = 0.1243$	$R_1 = 0.0878$, $wR_2 = 0.1565$
Largest difference peak and hole (e/Å^3)	3.04 and −2.001	4.116 and −1.719



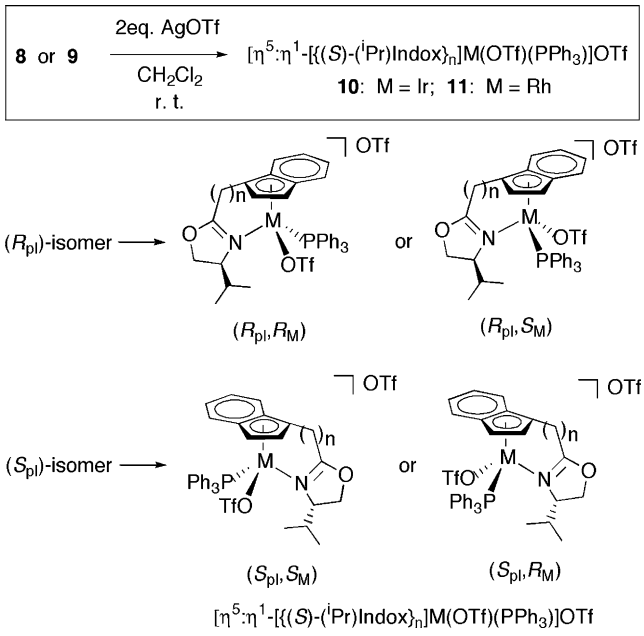
(3)

2.4. Construction of metal-centered chirality

Recoordination of the dissociated-oxazoline ring in **8** and **9** occurred by the ligand exchange reaction of two prochiral iodide ligands to give the cationic complex having a stereogenic center at the metal. For example, reaction of **8a** [(S_{pl})-**8a**:(R_{pl})-**8a** = 55:45 or vice versa] with more than 2 equiv. of AgOTf in dichloromethane at room temperature for 3 h afforded the cationic iridium complex, [η^5:η^1-[{(*S*)-(*i*Pr)Indox}$_{n=2}$]Ir(PPh$_3$)(OTf)]-OTf (**10a**), quantitatively as a yellow-brown powder (Scheme 2). The structure of **10a** was fully characterized by elemental analysis as well as spectral data. The IR

Table 2
Selected bond lengths (Å) and bond angles (°) for (R_{pl})-**4b** and (S_{pl})-**4b**

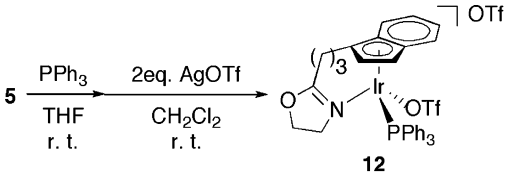
(R_{pl})-**4b**	
Bond lengths	
Ir1–C1	2.166(11)
Ir1–C2	2.135(9)
Ir1–C3	2.162(10)
Ir1–C4	2.253(10)
Ir1–C5	2.234(9)
Ir1–I1	2.7248(8)
Ir1–I2	2.6562(7)
Ir1–N1	2.112(8)
Bond angles	
I1–Ir1–Cp1	120.95
I2–Ir1–Cp1	127.32
N1–Ir1–Cp1	124.92
(S_{pl})-**4b**	
Bond lengths	
Ir2–C19	2.182(9)
Ir2–C20	2.146(9)
Ir2–C21	2.137(9)
Ir2–C22	2.246(9)
Ir2–C23	2.292(8)
Ir2–I3	2.6689(7)
Ir2–I4	2.7083(7)
Ir2–N2	2.140(8)
Bond angles	
I3–Ir2–Cp2	125.66
I4–Ir2–Cp2	120.27
N2–Ir2–Cp2	130.51



Scheme 2.

spectrum showed the C=N stretching at 1615 cm^{-1}, which was shifted to a lower wave number by ca. 60 cm^{-1} compared to that of the free ligand, indicating that the Indox ligand recoordinated to the iridium center in an η^5- and η^1-coordination manner. The FAB mass spectrum of **10a** showed three prominent and significant ions at *m/e* 859, 708 and 596 with mass and isotope distribution patterns corresponding to $[\{(S)\text{-}(^i\text{Pr})\text{Indox}\}_{n=2}]\text{Ir}(\text{PPh}_3)(\text{OTf})]^+ + 1$, $[[\{(S)\text{-}(^i\text{Pr})\text{Indox}\}_{n=2}]\text{Ir}(\text{PPh}_3)]^+ - 1$ and $[\{(S)\text{-}(^i\text{Pr})\text{Indox}\}_{n=2}]\text{Ir}(\text{OTf})]^+$, respectively. Since a new stereogenic center at the iridium is constructed in this reaction, **10a** has potentially four diastereomers [two isomers from each diastereomer (S_{pl})-**8** and (R_{pl})-**8**]. The ^{31}P NMR spectrum of the reaction mixture before purification showed only two singlet signals at δ 9.3 and 8.7 in a 56:44 ratio. The cationic complex **10a** consists of only two diastereomers and the diastereomer ratio of **10a** was almost the same as that of **8a**, indicating that both diastereomers (S_{pl})-**8a** and (R_{pl})-**8a** afford only a single isomer of **10a**. A similar discussion could be applied to the reaction of **8b** or the rhodium complexes **9** with more than 2 equiv. of AgOTf. Under similar conditions, each diastereomer of these complexes gave a single isomer of the corresponding cationic complexes **10b** and **11**.

Reaction of **5**, which has no chiral substituent in the oxazoline ring, with PPh_3 and more than 2 equiv. of AgOTf, successively afforded $[\eta^5:\eta^1\text{-}[\{(\text{H})\text{Indox}\}_{n=3}]\text{Ir}(\text{PPh}_3)(\text{OTf})]\text{OTf}$ (**12**) in 65% isolated yield as a yellow powder (Eq. (3)). All spectral data including the IR spectroscopy with the lower wave number shift of the C=N stretching to 1633 cm^{-1} from the free ligand and the FAB mass spectroscopy with the parent peak of the cationic part at *m/e* 830 in addition to the elemental analysis supported the structure of **12**. The ^{31}P NMR spectrum of the reaction mixture before purification with only one singlet signal at δ 10.6 indicated that **12** was a diastereoisomerically pure complex. The stereochemistry of the arising stereogenic center at the iridium was completely controlled by the Indox ligand regardless of having a chiral substituent or not in the oxazoline ring. That is, the planar chirality on the indenyl ring plays a determinant role in the induction of the stereogenic center on the metal.



(4)

Yellow single crystals suitable for X-ray analysis were obtained from a $CDCl_3$ solution of **12** in the NMR tube at room temperature for 4 days. An ORTEP drawing described in Fig. 2 showed that the crystals were a dicationic aquo complex, $[\eta^5:\eta^1\text{-}[\{(\text{H})\text{Indox}\}_{n=3}]\text{Ir}(\text{PPh}_3)(\text{H}_2\text{O})](\text{OTf})_2$ (**13**), as a three-legged piano stool type complex including one molecule of solvated $CDCl_3$. Relevant crystal and data parameters are given in Table 1, and selected bond lengths and angles are presented in Table 3. The most likely explanation of the formation of **13** is that the triflate ligand of **12** was slowly replaced by water in the solvent. The ORTEP drawing of **13** showed that the stereochemistry was S^*_{pl}, R^*_{Ir} with the aquo ligand locating under the benzene ring of the indenyl group and triphenylphosphine as a more stereodemanding ligand locating on the side opposite to the benzene ring. The stereochemistry around the iridium center in **13** is

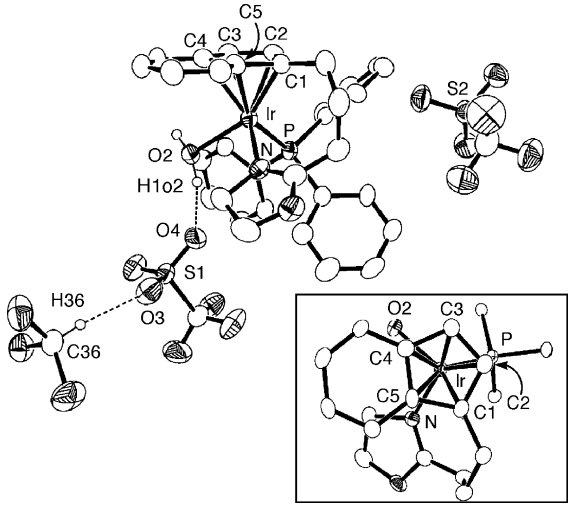


Fig. 2. ORTEP drawing of **13** showing the 50% probability thermal clipsoids. Hydrogen atoms are omitted for clarity except H-atoms of H_2O and $CHCl_3$. The inset is the top view of **13**. Some atoms are omitted for clarity.

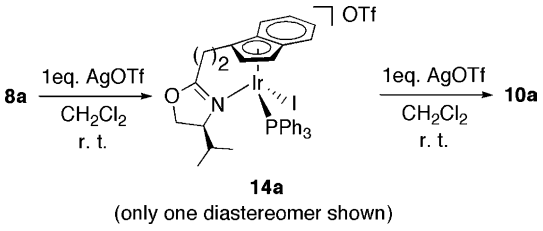
Table 3
Selected bond lengths (Å) and bond angles (°) for **13**

Bond lengths	
Ir–C1	2.161(9)
Ir–C2	2.146(9)
Ir–C3	2.172(9)
Ir–C4	2.346(9)
Ir–C5	2.332(9)
Ir–P	2.312(2)
Ir1–O2	2.276(6)
Ir1–N	2.071(8)
O3–H36	2.32
O3–C36	3.312(14)
O4–H1o2	1.86(14)
O4–O2	2.6931(10)
Bond angles	
P–Ir1–Cp	130.73
O2–Ir1–Cp	119.45
N–Ir1–Cp	121.34
O2–H1o2–O4	158.13
O3–H36–C36	171.4

Cp is the gravimetric center of the cyclopentadienyl part of the indenyl group.

probably controlled by the steric hindrance of the indenyl group. The shorter Ir–N distance [2.071(8) Å] and the narrower N–Ir–Cp angle (121.34°) compared to those in (R_{pl})-**4b** and (S_{pl})-**4b** are based on relief from the steric repulsion between the substituent in the oxazoline ring and the indenyl group. The bond lengths of Ir–C4 [2.346(9) Å] and Ir–C5 [2.332(9) Å] are longer than the corresponding value in (R_{pl})-**4b** and (S_{pl})-**4b**. The distortion of the indenyl ring towards η^3-coordination is evident compared to **4b**. One of the two triflate anions is quite close to the aquo ligand and the solvated $CDCl_3$. The distances between O4 and H1o2 [1.86(10) Å] and O3 and H36 [3.312(14) Å] are consistent with a weak interaction by hydrogen bonding.

We observed an interesting intermediate species of the ligand exchange reaction of **8a**. When the complex **8a** [(S_{pl})-**8a**:(R_{pl})-**8a** = 56:44 or vice versa] reacted with only 1 equiv. of AgOTf in dichloromethane at room temperature for 2 h, [η^5:η^1-[{(*S*)-(^{i}Pr)Indox}$_{n=2}$]Ir-(PPh_3)(I)]OTf (**14a**) was obtained as a brown powder along with **8a** and **10a** (Eq. (5)). Although an analytically pure form of **14a** was not obtained due to contamination of **10a**, spectroscopic data including the IR spectroscopy (1613 cm^{-1} for $\nu_{C=N}$) and the FAB mass spectroscopy [*m/e* 837 for [{(*S*)-(^{i}Pr)Indox}$_{n=2}$]Ir(PPh_3)-(I)]$^+$ + 1] supported the proposed structure of **14a**. Although the formation of four isomers is possible similarly to **10a**, the ^{31}P NMR spectrum displaying only two singlet signals at δ 4.4 and 0.4 in a 56:44 ratio, which was almost the same ratio as that of **8a**, suggested that both diastereomers (S_{pl})-**8a** and (R_{pl})-**8a** afforded only a single isomer of **14a**. Reaction of **14a** in a 56:44 ratio with 1 equiv. of AgOTf in dichloromethane at room temperature for 2 h afforded **10a** in a 56:44 ratio. From these observations, the stereoselectivity of the arising stereogenic center at the metal by the ligand exchange reaction of **8** or **9** with more than 2 equiv. of AgOTf would be explained as follows: In the first iodine abstraction step, one of the two prochiral iodides in each diastereomer is abstracted by 1 equiv. of AgOTf. The second step, in which the oxazoline ring recoordinated to the iridium center, proceeds stereoselectively and the stereogenic center on the metal is determined by the steric repulsion between the indenyl group and triphenylphosphine. The third step is the stereospecific ligand exchange reaction of the remaining iodine for the triflate to afford the single diastereomer of **10** or **11** from each diastereomer of **8** or **9**. The stereochemistry around the metal center in **10**, **11** and **14a** would be the configuration that triphenylphosphine locates on the side opposite to the benzene ring of the indenyl group due to the fact that **13** with S^*_{pl}, R^*_{Ir} configuration was obtained by the steric repulsion between the indenyl group and the triphenylphosphine ligand.



(5)

3. Conclusion

We have designed and prepared a series of new Indox ligands and synthesized iridium and rhodium complexes bearing these ligands. The oxazoline ring in the Indox ligand showed unique characters as a hemilabile ligand. The monocationic complexes having a stereogenic center at the metal have been prepared stereoselectively by the ligand exchange reaction of the neutral complexes bearing two prochiral iodido ligands with more than 2 equiv. of AgOTf. The stereochemistry around the metal-centered chirality would be controlled by the planar chirality arising from the complexation of the Indox ligand, though the absolute configuration of stereogenic centers in a series of the complexes was not determined by X-ray analysis. We are currently investigating the stereochemistry of these complexes and will show a more detailed reaction mechanism in due course.

4. Experimental

4.1. General

All reactions and manipulations were performed under argon by use of standard vacuum line and Schlenk

tube techniques. All melting points were recorded on a Yanaco MP-52982 and are uncorrected. Infrared spectra were recorded on a JASCO FT/IR-230. Mass spectra were obtained on a JEOL JMS DX-303HF spectrometer. ^{1}H NMR spectra were recorded on either 270 MHz on a JEOL JNM-GSX270 or 300 MHz on a Varian MERCURY 300 spectrometer. Chemical shifts are reported in ppm (δ) relative to tetramethylsilane and referenced to the chemical shift of the residual $CHCl_3$ (δ 7.26) or CH_2Cl_2 (δ 5.30) resonance. ^{31}P{1H} NMR spectra were recorded on either 109.25 MHz on a JEOL JNM-GSX270 or 121.49 MHz on a Varian MERCURY 300 spectrometer, and the chemical shifts are referenced to external 85% H_3PO_4. Elemental analyses were recorded on a Perkin–Elmer 2400.

Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Dichloromethane was distilled from calcium hydride under argon prior to use and other solvents for recrystallization were dried using standard procedures. Tetrahydrofuran, toluene, hexane and diethyl ether were distilled from sodium benzophenone ketyl under argon prior to use. Zinc chloride, which was purchased from Nacalai Tesque, was heated (ca. 250 °C) under high vacuum for 1 h and was cooled to room temperature under argon prior to use. Silver triflate (AgOTf) was purchased from Sigma–Aldrich Co. The starting materials, $[Ir(coe)_2Cl]_2$ and $[Rh(C_2H_4)_2Cl]_2$, were prepared according to literature methods [14,15]. Column chromatography was performed using silica gel (230–400 mesh ASTM, Merck Kieselgel 60).

4.2. Preparation of compounds

4.2.1. 3-(3-Indenyl)propanenitrile [16]

To a solution of indene (5.0 mL, 42.9 mmol) in THF (100 mL) at 0 °C was added a hexane solution of ^{n}BuLi (1.50 mol/L, 34.3 mL, 51.5 mmol). The resulting solution was stirred at 0 °C for 3 h and a solution of 3-bromopropanenitrile (3.6 mL, 43.4 mmol) in THF (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 12 h at room temperature and quenched with water, and extracted with diethyl ether (30 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The resulting oil was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 5/1) to afford 3-(3-indenyl)propanenitrile in 49% yield (3.58 g, 21.1 mmol) as a yellow oil. ^{1}H NMR ($CDCl_3$, δ): 2.70 (t, J = 7.2 Hz, 2H, –CH_2–), 2.85–2.98 (m, 2H, –CH_2–), 3.38 (s, 2H, alkane protons of the indene ring), 6.36 (bs, 1H, olefin proton of the indene ring), 7.20–7.49 (m, 4H, indene ring).

4.2.2. 4-(3-Indenyl)butanenitrile [16]

To a solution of indene (4.0 mL, 34.3 mmol) in THF (80 mL) at 0 °C was added a hexane solution of ^{n}BuLi (1.50 mol/L, 27.5 mL, 41.3 mmol). The resulting solution was stirred at 0 °C for 4 h and a solution of 4-bromobutanenitrile (3.4 mL, 34.4 mmol) in THF (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 12 h at room temperature and quenched with water, and extracted with diethyl ether (30 mL × 3). The combined organic layer was dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The resulting oil was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 5/1) to afford 4-(3-indenyl)butanenitrile in 83% yield (5.18 g, 28.3 mmol) as a yellow oil. ^{1}H NMR ($CDCl_3$, δ): 2.05 (quintet, J = 7.1 Hz, 2H, –CH_2–), 2.40 (t, J = 7.1 Hz, 2H, –CH_2–), 2.74 (t, J = 7.1 Hz, 2H, –CH_2–), 3.35 (s, 2H, alkane protons of the indene ring), 6.27 (bs, 1H, olefin proton of the indene ring), 7.18 (t, J = 7.4 Hz, 1H, indene ring), 7.28 (t, J = 7.1 Hz, 1H, indene ring), 7.36 (d, J = 7.1 Hz, 1H, indene ring), 7.44 (d, J = 6.9 Hz, 1H, indene ring).

4.2.3. (S)-2-{(2′-(1-Indenyl)ethyl)}-4-isopropyloxazoline, [{(S)-(^{i}Pr)Indox}$_{n=2}$]H (**1a**)

A solution of 3-(3-indenyl)propanenitrile (1.73 g, 10.3 mmol) in chlolobenzene (3.0 mL) and a solution of *L*-valinol (2.0 mL, 18.0 mmol) in chlolobenzene (7.0 mL) were successively added to zinc chloride (0.42 g, 3.1 mmol) in the Schlenk tube. The mixture was heated under reflux for 2 days. The solvent was removed in vacuo to give an oily residue. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 5/1) to give **1a** (1.32 g, 5.2 mmol, 50%) as an air-stable yellow oil. ^{1}H NMR ($CDCl_3$, δ): 0.87 (d, J = 6.9 Hz, 3H, –CH_3), 0.95 (d, J = 6.9 Hz, 3H, –CH_3), 1.67–1.82 (m, 1H, –CH(CH_3)$_2$), 2.63–2.72 (m, 2H, –CH_2–), 2.85–2.96 (m, 2H, –CH_2–), 3.32 (d, J = 1.6 Hz, 2H, alkane protons of the indene ring), 3.86–3.98 (m, 2H, oxazoline), 4.14–4.28 (m, 1H, oxazoline), 6.27 (t, J = 1.6 Hz, 1H, olefin proton of the indene ring), 7.19 (dt, J = 7.4, 1.1 Hz, 1H), 7.29 (dt, J = 7.4, 1.1 Hz, 1H), 7.38 (d, J = 7.4 Hz, 1H), 7.44 (d, J = 7.4 Hz, 1H). IR(KBr, neat, cm^{-1}): 770, 985, 1023, 1164, 1363, 1385, 1464, 1672 ($\nu_{C=N}$), 2899, 2958. HRMASS (EI): Calc. for $C_{17}H_{21}NO$: 255.1623. Found: *m*/*z* 255.1642. $[\alpha]_D^{25}$ −40.2° (*c* 0.737, EtOH).

4.2.4. (S)-2-{(3′-(1-Indenyl)propyl)}-4-isopropyloxazoline, [{(S)-(^{i}Pr)Indox}$_{n=3}$]H (**1b**)

A solution of 3-(3-indenyl)butanenitrile (0.49 g, 2.7 mmol) in chlolobenzene (5.0 mL) and a solution of *L*-valinol (0.38 mL, 3.4 mmol) in chlolobenzene (5.0 mL) were successively added to zinc chloride (0.065 g, 0.47 mmol) in the Schlenk tube. The mixture was heated under reflux for 2 days. The solvent was removed in vacuo to give an oily residue. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 3/1) to give **1b** (0.47 g, 1.8 mmol, 65%) as

an air stable yellow oil. ^{1}H NMR ($CDCl_3$, δ): 0.88 (d, $J = 6.9$ Hz, 3H, –CH_3), 0.96 (d, $J = 6.9$ Hz, 3H, –CH_3), 1.70–1.82 (m, 1H, –CH (CH_3)$_2$), 2.03 (dt, $J = 14.8$, 7.7 Hz, 2H, –CH_2–), 2.39 (t, $J = 7.7$ Hz, 2H, –CH_2–), 2.57–2.68 (m, 2H, –CH_2–), 3.32 (s, 2H, alkane protons of the indene ring), 3.84–3.98 (m, 2H, oxazoline), 4.13-4.26 (m, 1H, oxazoline), 6.23 (s, 1H, olefin proton of the indene ring), 7.18 (t, $J = 7.4$ Hz, 1H), 7.28 (t, $J = 7.1$ Hz, 1H), 7.36 (d, $J = 7.1$ Hz, 1H), 7.44 (d, $J = 6.9$ Hz, 1H). IR(KBr, neat, cm^{-1}): 770, 984, 1019, 1364, 1385, 1459, 1670 ($\nu_{C=N}$), 2894, 2957. HRMASS (EI): Calc. for $C_{18}H_{23}NO$: 269.1779. Found: *m*/*z* 269.1815. $[\alpha]_D^{25}$ −30.4° (*c* 0.507, EtOH).

*4.2.5. 2-{3′-(1-Indenyl)propyl}oxazoline, [{(H)Indox}$_{n=3}$]H (**2**)*

A solution of 3-(3-indenyl)butanenitrile (1.30 g, 7.1 mmol) in chlolobenzene (7 mL) and a solution of 2-aminoethanol (1.5 mL, 25 mmol) in chlolobenzene (7 mL) were successively added to zinc chloride (0.53 g, 3.9 mmol) in the Schlenk tube. The mixture was heated under reflux for 65 h. The solvent was removed in vacuo to give an oily residue. The residue was extracted with diethyl ether. The combined diethyl ether solution was dried over $MgSO_4$, filtered and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate = 3/1) to give **1c** (0.38 g, 1.7 mmol, 23%) as an air-stable yellow oil. ^{1}H NMR ($CDCl_3$, δ): 1.98–2.11 (m, 2H, –CH_2–), 2.34–2.42 (m, 2H, –CH_2–), 2.57–2.68 (m, 2H, –CH_2–), 3.29–3.35 (m, 2H, alkane protons of the indene ring), 3.77–3.88 (m, 2H, oxazoline), 4.21 (dt, $J = 9.1$, 0.8 Hz, 2H, oxazoline), 6.20–6.27 (m, 1H, olefin proton of the indene ring), 7.19 (td, $J = 7.4$, 1.1 Hz, 1H), 7.23–7.33 (m, 1H), 7.32–7.40 (m, 1H), 7.41–7.49 (m, 1H). IR(KBr, neat, cm^{-1}): 720, 771, 914, 953, 986, 1154, 1169, 1230, 1365, 1391, 1458, 1668 ($\nu_{C=N}$), 2881, 2901, 2938, 3016, 3064. HRMASS (EI): Calc. for $C_{15}H_{17}NO$: 227.1310. Found: *m*/*z* 227.1321.

*4.2.6. η^5-[{(S)-(^{i}Pr)Indox}$_{n=2}$]Ir(coe)$_2$ (**3a**)*

A solution of **1a** (0.33 g, 1.3 mmol) in THF (10 mL) was added to a brown suspension of KH (0.12 g, 3.1 mmol) in THF (10 mL) at 0 °C. The resulting suspension was stirred at 80 °C for 1 h and added dropwise to a suspension of $[IrCl(coe)_2]_2$ (0.58 g, 0.65 mmol) in THF (40 mL) at 0 °C and then warmed to room temperature. After the reaction mixture was stirred for 12 h, a dark red-brown solution was obtained and the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL × 3). The combined hexane extracts were concentrated in vacuo to afford **3a** (0.81 g, 1.2 mmol, 94%) as a brown oil with a mixture of two diastereomers A and B (A:B = 1:1 from ^{1}H NMR). Complete purification of **3a** was not successful due to high solubility to solvents, but its purity was satisfactory in the following reaction. ^{1}H NMR ($CDCl_3$, δ): 0.81 (d, $J = 6.6$ Hz, 3H, –CH_3, A or B), 0.84 (d, $J = 6.9$ Hz, 3H, –CH_3, B or A), 0.89 (d, $J = 6.9$ Hz, 3H, –CH_3, B or A), 0.93 (d, $J = 6.6$ Hz, 3H, –CH_3, A or B), 1.14–1.42 (m, 9H, A and B), 1.30–1.67 (m, 12H, A and B), 1.67–1.89 (m, 4H, A and B), 1.84–2.10 (m, 2H, A and B), 2.05–2.20 (m, 1H, A and B), 2.36–2.77 (m, 4H, A and B), 2.70–3.00 (m, 1H, A and B), 3.74–3.97 (m, 2H, oxazoline, A and B), 4.04–4.24 (m, 1H, oxazoline, A and B), 4.96 (t, $J = 2.5$ Hz, 1H, indene ring, A and B), 5.73 (bs, 1H, indene ring, A and B), 7.05–7.16 (m, 2H, indene ring, A and B), 7.17–7.26 (m, 1H, indene ring, A and B), 7.24–7.33 (m, 1H, indene ring, A and B). IR[KBr, Film (CH_2Cl_2), cm^{-1}]: 735, 807, 910, 1021, 1092, 1260, 1445, 1466, 1669 ($\nu_{C=N}$), 2850, 2922, 2960. MS (FAB): *m*/*z* 667 (M^+), 558 (M^+ − COE + 1), 447 (M^+ − 2COE).

*4.2.7. η^5-[{(S)-(^{i}Pr)Indox}$_{n=3}$]Ir(coe)$_2$ (**3b**)*

A solution of **1b** (0.42 g, 1.6 mmol) in THF (10 mL) was added to a suspension of KH (0.09 g, 2.3 mmol) in THF (10 mL) at 0 °C. The resulting suspension was stirred at 80 °C for 1 h and added dropwise to a suspension of $[IrCl(coe)_2]_2$ (0.70 g, 0.78 mmol) in THF (40 mL) at 0 °C and then warmed to room temperature. After the reaction mixture was stirred for 18 h, a dark red-brown solution was obtained and the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL × 3). The combined hexane extracts were concentrated in vacuo to afford **3b** (1.0 g, 1.5 mmol, 97%) as a brown oil with a mixture of two diastereomers A and B (A:B = 1:1 from ^{1}H NMR). Complete purification of **3b** was not successful due to high solubility to solvents, but its purity was satisfactory in the following reaction. ^{1}H NMR ($CDCl_3$, δ): 0.88 (d, $J = 6.9$ Hz, 3H, –CH_3, A and B), 0.96 (d, $J = 6.9$ Hz, 3H, –CH_3, A and B), 1.12–1.42 (m, 8H, A and B), 1.26–1.68 (m, 11H, A and B), 1.58–1.90 (m, 6H, A and B), 1.80–2.06 (m, 4H, A and B), 2.08–2.20 (m, 1H, A and B), 2.18–2.46 (m, 4H, A and B), 2.50–2.80 (m, 1H, A and B), 3.79–3.96 (m, 2H, oxazoline, A and B), 4.10–4.25 (m, 1H, oxazoline, A and B), 4.88–5.01 (m, 1H, indene ring, A and B), 5.64–5.84 (m, 1H, indene ring, A and B), 7.02–7.17 (m, 2H, A and B), 7.15–7.27 (m, 1H, A and B), 7.24–7.33 (m, 1H, A and B). IR[KBr, Film (CH_2Cl_2), cm^{-1}]: 739, 806, 1020, 1092, 1263, 1384, 1446, 1465, 1669 ($\nu_{C=N}$), 2851, 2921, 2956. MS (FAB): *m*/*z* 682 (M^+ + 1), 571 (M^+ − COE), 459 (M^+ − 2COE − 2).

*4.2.8. η^5:η^1-[{(S)-(^{i}Pr)Indox}$_{n=2}$]Ir(I)$_2$ (**4a**)*

A solution of I_2 (0.10 g, 0.40 mmol) in diethyl ether (10 mL) was added to a solution of **3a** (0.26 g, 0.39 mmol) in diethyl ether (20 mL) at room temperature and brown solids were precipitated immediately. After the reaction mixture was stirred for 14 h, the solution decanted and the resulting brown solids were washed with diethyl ether (10 mL × 3). The residue was dried in

vacuo to afford **4a** (0.24 g, 0.35 mmol, 88%) as a brown powder with a mixture of two diastereomers A and B (A:B = 1:1 from ^{1}H NMR). ^{1}H NMR ($CDCl_3$, δ): 0.69 (d, $J = 6.9$ Hz, 3H, –CH_3, A), 0.71(d, $J = 7.1$ Hz, 3H, –CH_3, B), 0.72 (d, $J = 6.9$ Hz, 3H, –CH_3, A and B), 1.88 (qqd, $J = 7.1$, 7.1, 2.2 Hz, 1H, B), 2.44 (qqd, $J = 6.9$, 6.9, 2.5 Hz, 1H, A), 2.43–2.88 (m, 2H, A and B), 3.04–3.46 (m, 2H, A and B), 4.05–4.14 (m, 1H, oxazoline, A), 4.16–4.24 (m, 1H, oxazoline, B), 4.27 (t, $J = 9.3$ Hz, 1H, oxazoline, B), 4.33 (t, $J = 9.1$ Hz, 1H, oxazoline, A), 4.40–4.49 (m, 1H, oxazoline, A and B), 5.83 (dd, $J = 2.2$, 0.6 Hz, 1H, indene ring, A or B), 5.86 (d, $J = 2.2$ Hz, 1H, indene ring, B or A), 5.93 (d, $J = 2.2$ Hz, 1H, indene ring, A or B), 6.01 (d, $J = 2.2$ Hz, 1H, indene ring, B or A), 7.15–7.47 (m, 3H, A and B), 7.49–7.59 (m, 1H, A and B). IR(KBr, tablet, cm^{-1}): 738, 751, 1013, 1196, 1253, 1387, 1398, 1430, 1458, 1478, 1632 ($\nu_{C=N}$), 2869, 2926, 2958. MS (FAB): *m/z* 701 (M^+), 574 ($M^+ - I$). *Anal.* Calc. for $C_{17}H_{20}I_2IrNO$: C, 29.15; H, 2.88; N, 2.00. Found: C, 28.73; H, 2.77; N, 1.83%.

4.2.9. η^5:η^1-[{(*S*)-(^{i}Pr)Indox}$_{n=3}$]Ir(I)$_2$ (**4b**)

A solution of I_2 (72 mg, 0.28 mmol) in diethyl ether (10 mL) was added to a solution of **3b** (0.17 g, 0.24 mmol) in diethyl ether (20 mL) at room temperature and brown solids were precipitated immediately. After the reaction mixture was stirred for 2 h, the solution decanted and the resulting brown solids were washed with diethyl ether (10 mL × 3). The residue was dried in vacuo to afford **4b** (0.18 g, 0.25 mmol, >99%) as a brown powder with a mixture of two diastereomers A and B (A:B = 1:1 from ^{1}H NMR). ^{1}H NMR ($CDCl_3$, δ): 0.54 (d, $J = 6.9$ Hz, 3H, –CH_3, A), 0.63 (d, $J = 6.9$ Hz, 3H, –CH_3, A), 0.75 (d, $J = 6.9$ Hz, 3H, –CH_3, B), 0.79 (d, $J = 7.1$ Hz, 3H, –CH_3, B), 0.86–1.03 [m, 1H, –C*H* (CH_3)$_2$, A], 2.00–2.36 [m, 1H (A or B) + 2H (B or A)], 2.29–2.53 [m 1H –C*H*(CH_3)$_2$ B + 1H (B or A)], 2.48–2.72 (m, 2H, A or B), 2.74–2.96 (m, 2H, B or A), 2.94–3.09 (m, 1H, A or B), 3.13–3.27 (m, 1H, A or B), 3.30–3.49 [m, 1H (A or B) + 1H (B or A)], 4.04–4.17 (m, 1H oxazoline A + 2H oxazoline B), 4.25 (dd, $J = 9.1$, 3.6 Hz, 1H, oxazoline, A), 4.35 (d, $J = 5.8$ Hz, 1H, oxazoline, B), 4.41–4.52 (m, 1H, oxazoline, A), 5.77 (d, $J = 2.5$ Hz, 1H, indene ring, B), 5.82 (d, $J = 2.5$ Hz, 1H, indene ring, A), 6.17 (d, $J = 2.5$ Hz, 1H, indene ring, B), 6.21 (d, $J = 2.2$ Hz, 1H, indene ring, A), 7.26–7.77 (m, 4H, A and B). IR(KBr, tablet, cm^{-1}): 459, 751, 802, 1038, 1084, 1123, 1261, 1385, 1457, 1632 ($\nu_{C=N}$), 2854, 2925, 2957. MS (FAB): *m/z* 716 ($M^+ + 1$), 588 ($M^+ - I$). *Anal.* Calc. for $C_{18}H_{22}I_2IrNO$: C, 30.26; H, 3.10; N, 1.96. Found: C, 30.44; H, 3.09; N, 1.89%.

4.2.10. η^5:η^1-[{(*H*)Indox}$_{n=3}$]Ir(I)$_2$ (**5**)

A solution of **2** (0.11 g, 0.48 mmol) in THF (5 mL) was added to a suspension of KH (37 mg, 0.92 mmol) in THF (5 mL) at 0 °C. The resulting suspension was stirred at 0 °C for 1 h and added dropwise to a suspension of $[IrCl(coe)_2]_2$ (0.22 g, 0.25 mmol) in THF (40 mL) at 0 °C and then warmed to room temperature. After the reaction mixture was stirred for 18 h, the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL × 3). The combined hexane extracts were concentrated in vacuo to afford a brown oil. A solution of I_2 (0.10 mg, 0.40 mmol) in diethyl ether (10 mL) was added to a solution of the brown oil in diethyl ether (20 mL) at room temperature and brown solids were precipitated immediately. After the reaction mixture was stirred for 3 h, the solution decanted and the resulting brown solids were washed with diethyl ether (10 mL × 3). The residue was dried in vacuo to afford **5** (0.22 g, 0.32 mmol, 67%) as a brown powder. ^{1}H NMR ($CDCl_3$, δ): 2.22–2.50 (m, 2H, –CH_2–), 2.63 (ddd, $J = 15.9$, 11.3, 4.4 Hz, 1H, –C*H*H–), 2.80–3.00 (m, 2H, –CH_2–), 3.11–3.29 (m, 1H, oxazoline), 3.41–3.57 (m, 1H, –C*H*H–), 4.10 (ddd, $J = 13.5$, 11.3, 8.2 Hz, 1H, oxazoline), 4.22–4.35 (m, 2H, oxazoline), 5.91 (d, $J = 2.5$ Hz, 1H, indene ring), 6.04 (d, $J = 2.5$ Hz, 1H, indene ring), 7.30–7.41 (m, 1H, indene ring), 7.42–7.51 (m, 1H, indene ring), 7.52–7.61 (m, 1H, indene ring), 7.67–7.78 (m, 1H, indene ring). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 22.8 (–*C*H_2–), 26.7 (–*C*H_2–), 27.2 (–*C*H_2–), 60.0 (oxazoline), 68.9 (oxazoline), 85.2 (indene), 100.4 (indene), 100.6 (indene), 121.6 (indene), 129.3 (indene), 130.2 (indene), 131.4 (indene), 177.3 (oxazoline). IR(KBr, tablet, cm^{-1}): 803, 1025, 1098, 1261, 1387, 1455, 1633 ($\nu_{C=N}$), 2853, 2925, 2960. MS (FAB): *m/z* 673 (M^+), 546 ($M^+ - I$). *Anal.* Calc. for $C_{15}H_{16}I_2IrNO$: C, 26.80; H, 2.40; N, 2.08. Found: C, 28.59; H, 2.55; N, 2.01%.

4.2.11. Preparation of η^5-[{(*S*)-(^{i}Pr)Indox}$_{n=2}$]Rh(C_2H_4)$_2$ (**6a**)

A solution of **1a** (0.20 g, 0.78 mmol) in THF (30 mL) was added to a suspension of KH (0.10 g, 2.6 mmol) in THF (10 mL) at 0 °C. The resulting suspension was stirred at 0 °C for 1 h and added dropwise to a suspension of $[RhCl(C_2H_4)_2]_2$ (0.16 mg, 0.40 mmol) in THF (30 mL) at 0 °C and then warmed to room temperature. After the reaction mixture was stirred for 13 h, a brown solution was obtained and the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL × 3). The combined hexane extracts were concentrated in vacuo to afford **6a** (0.26 g, 0.63 mmol, 79%) as a brown oil with a mixture of two diastereomers A and B (A:B = 1:1 from ^{1}H NMR). Complete purification of **6a** was not successful due to high solubility to solvents, but its purity was satisfactory in the following reaction. ^{1}H NMR ($CDCl_3$, δ): 0.84 (d, $J = 6.9$ Hz, 3H, –CH_3, A or B), 0.86 (d, $J = 6.9$ Hz, 3H, –CH_3, B or A), 0.91 (d, $J = 6.9$ Hz, 3H, –CH_3, B or A), 0.94 (d, $J = 6.9$ Hz, 3H, –CH_3, A or B), 1.58–1.82 (m, 1H, A and B), 1.77–2.02 (m, 4H, A and B), 1.89–2.09 (m, 4H, A and

B), 2.37–2.75 (m, 4H, A and B), 3.77–4.00 (m, 2H, oxazoline, A and B), 4.09–4.26 (m, 1H, oxazoline, A and B), 5.00 (d, $J = 2.7$ Hz, 1H, indene ring, A and B), 5.97–6.09 (m, 1H, indene ring, A and B), 7.07–7.24 (m, 2H, A and B), 7.19–7.36 (m, 2H, A and B). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 18.4 (–CH_3), 19.0 (–CH_3), 22.3 (–CH_2–), 28.4 (–CH_2–), 33.2 [–$CH(CH_3)_2$], 45.7 (d, $J_{Rh-C} = 12.7$ Hz, C_2H_4), 70.4 (oxazoline), 72.8 (oxazoline), 76.9–77.2 (m, indene ring), 92.1–92.4 (m, indene ring), 111.9–112.2 (m, indene ring), 117.7–117.9 (m, indene ring), 120.0 (indene ring), 123.66 (indene ring), 123.72 (indene ring), 166.3 (oxazoline). IR(KBr, neat, cm^{-1}): 742, 804, 914, 983, 1021, 1209, 1258, 1330, 1384, 1433, 1464, 1667 ($\nu_{C=N}$), 2926, 2957, 3059. MS (FAB): *m/z* 357 $[M^+ - (C_2H_4)_2]$.

4.2.12. η^5-[{(S)-(^{i}Pr)Indox}$_{n=3}$]Rh(C_2H_4)$_2$ (**6b**)

A solution of **1b** (0.14 g, 0.52 mmol) in THF (8 mL) was added to a suspension of KH (58 mg, 1.4 mmol) in THF (10 mL) at 0 °C. The resulting suspension was stirred at 80 °C for 1 h and added dropwise to a suspension of $[RhCl(C_2H_4)_2]_2$ (0.10 mg, 0.26 mmol) in THF (10 mL) at 0 °C and then warmed to room temperature. After the reaction mixture was stirred for 13 h, a brown solution was obtained and the solvent was removed in vacuo. The residue was extracted with hexanes (30 mL × 3). The combined hexane extracts were concentrated in vacuo to afford **6b** (0.19 mg, 0.44 mmol, 85%) as a brown oil. Complete purification of **6b** was not successful due to high solubility to solvents, but its purity was satisfactory in the following reaction. ^1H NMR (CD_2Cl_2, δ): 0.89 (d, $J = 6.6$ Hz, 3H, –CH_3, A and B), 0.96 (d, $J = 6.9$ Hz, 3H, –CH_3, A and B), 1.62–1.78 (m, 1H, A and B), 1.82–1.98 (m, 5H, A and B), 1.92–2.09 (m, 5H, A and B), 2.11–2.48 (m, 4H, A and B), 3.79–3.96 (m, 2H, oxazoline, A and B), 4.12–4.25 (m, 1H, oxazoline, A and B), 5.04 (d, $J = 2.7$ Hz, 1H, indene ring, A and B), 6.02–6.09 (m, 1H, indene ring, A and B), 7.10–7.22 (m, 2H, A and B), 7.29–7.39 (m, 2H, A and B). $^{13}C\{1H\}$ NMR (CD_2Cl_2, δ): 18.5 (–CH_3), 19.0 (–CH_3), 25.0 (–CH_2–), 26.3 (–CH_2–), 28.1 (–CH_2–), 33.2 [–$CH(CH_3)_2$], 45.6 (d, $J_{Rh-C} = 13.2$ Hz, C_2H_4), 70.3 (oxazoline), 72.8 (oxazoline), 76.9 (d, $J = 4.6$ Hz, indene ring), 92.2 (d, $J = 5.8$ Hz, indene ring), 92.3 (d, $J = 5.8$ Hz, indene ring), 93.99 (d, $J = 4.0$ Hz, indene ring), 94.02 (d, $J = 4.0$ Hz, indene ring), 112.0–112.2 (m, indene ring), 117.9–118.1 (m, indene ring), 120.0 (indene ring), 123.5 (indene ring), 123.7 (indene ring), 166.7 (oxazoline). IR(KBr, neat, cm^{-1}): 742, 986, 1199, 1209, 1431, 1459, 1670 ($\nu_{C=N}$), 2958, 3058. MS (FAB): *m/z* 371 $[M^+ - (C_2H_4)_2]$. *Anal.* Calc. for $C_{22}H_{30}NORh$: C, 61.83; H, 7.08; N, 3.28. Found: C, 62.56; H, 7.25; N, 3.22%.

4.2.13. η^5:η^1-[{(S)-(^{i}Pr)Indox}$_{n=2}$]Rh(I)$_2$ (**7a**)

A solution of I_2 (0.18 g, 0.70 mmol) in diethyl ether (15 mL) was added to a solution of **6a** (0.29 g, 0.70 mmol) in diethyl ether (10 mL) at room temperature and brown solids were precipitated immediately. After the reaction mixture was stirred for 1 h, the solution decanted and the resulting brown solids were washed with diethyl ether (10 mL × 3). The residue was dried in vacuo to afford **7a** (0.35 g, 0.57 mmol, 83%) as a brown powder with a mixture of two diastereomers A and B (A:B = 1:1 from ^1H NMR). ^1H NMR ($CDCl_3$, δ): 0.62 (d, $J = 6.9$ Hz, 3H, –CH_3, B), 0.67 (d, $J = 7.1$ Hz, 3H, –CH_3, A), 0.69 (d, $J = 7.1$ Hz, 3H, –CH_3, A), 0.70 (d, $J = 6.9$ Hz, 3H, –CH_3, B), 1.89 (qqd, $J = 7.1$, 7.1, 2.5 Hz, 1H, –$CH(CH_3)_2$, B), 2.28 (qqd, $J = 7.1$, 7.1, 2.5 Hz, 1H, –$CH(CH_3)_2$, A), 2.60–2.84 (m, 2H, A and B), 3.05–3.20 (m, 1H, A and B), 3.24–3.40 (m, 1H, B), 3.47–3.67 (m, 1H, A), 3.89–4.02 (m, 1H, oxazoline, A and B), 4.20 (t, $J = 9.1$ Hz, 1H, oxazoline, B), 4.29 (t, $J = 9.1$ Hz, 1H, oxazoline, A), 4.35–4.46 (m, 1H, oxazoline, A and B), 5.48 (t, $J = 2.7$ Hz, 1H, indene ring, A and B), 5.93 (d, $J = 2.5$ Hz, 1H, indene ring, B), 5.99 (d, $J = 2.2$ Hz, 1H, indene ring, A), 7.20–7.34 (m, 1H, indene ring, A and B), 7.39–7.66 (m, 3H, indene ring, A and B). IR(KBr, tablet, cm^{-1}): 454, 742, 754, 806, 952, 976, 1015, 1113, 1139, 1165, 1194, 1250, 1283, 1386, 1397, 1430, 1458, 1478, 1526, 1636 ($\nu_{C=N}$), 2869, 2958, 3074. MS (FAB): *m/z* 611 (M^+), 484 ($M^+ - I$). *Anal.* Calc. for $C_{17}H_{20}I_2NORh$: C, 33.41; H, 3.30; N, 2.29. Found: C, 32.98; H, 2.95; N, 2.12%.

4.2.14. η^5:η^1-[{(S)-(^{i}Pr)Indox}$_{n=3}$]Rh(I)$_2$ (**7b**)

A solution of I_2 (80 mg, 0.32 mmol) in diethyl ether (10 mL) was added to a solution of **6b** (0.13 g, 0.30 mmol) in diethyl ether (10 mL) at room temperature and brown solids were precipitated immediately. After the reaction mixture was stirred for 24 h, the solution decanted and the resulting brown solids were washed with diethyl ether (10 mL × 3). The residue was dried in vacuo to afford **7b** (0.15 g, 0.23 mmol, 77%) as a brown powder with a mixture of two diastereomers A and B (A:B = 1:1 from ^1H NMR). ^1H NMR ($CDCl_3$, δ): 0.52 (d, $J = 6.9$ Hz, 3H, –CH_3, A), 0.60 (d, $J = 6.9$ Hz, 3H, –CH_3, A), 0.63 (d, $J = 6.9$ Hz, 3H, –CH_3, B), 0.68 (d, $J = 6.9$ Hz, 3H, –CH_3, B), 0.93–1.07 (m, 1H, A), 2.20–2.55 (m, 2H A, 3H B), 2.58–3.05 (m, 3H, A and B), 3.38–3.47 (m, 1H, A and B), 3.69 (dt, $J = 9.1$, 2.8 Hz, 1H, oxazoline, B), 3.93 (t, $J = 8.8$ Hz, 1H, oxazoline, B), 3.99–4.10 (m, 1H, oxazoline, A), 4.14–4.25 (m, 2H, oxazoline, A), 4.29 (dd, $J = 8.8$, 3.0 Hz, 1H, oxazoline, B), 5.57 (d, $J = 2.7$ Hz, 1H, indene ring, A), 5.78 (d, $J = 2.7$ Hz, 1H, indene ring, B), 5.81 (d, $J = 2.5$ Hz, 1H, indene ring, B), 6.08 (d, $J = 2.5$ Hz, 1H, indene ring, A), 7.27–7.59 (m, 3H, indene ring, A and B), 7.76–7.86 (m, 1H, indene ring, A and B). IR(KBr, tablet, cm^{-1}): 523, 754, 1241, 1385, 1435, 1462, 1637 ($\nu_{C=N}$), 2957. MS (FAB): *m/z* 626 ($M^+ + 1$), 498 ($M^+ - I$), 371 ($M^+ - 2I$). *Anal.* Calc. for $C_{18}H_{22}I_2NORh$: C, 34.59; H, 3.55; N, 2.24. Found: C, 34.11; H, 3.87; N, 2.21%.

*4.2.15. η^5-[{(S)-(^{i}Pr)Indox}$_{n=2}$]Ir(PPh$_3$)(I)$_2$ (**8a**)*

Triphenylphosphine (22 mg, 0.085 mmol) was added to a solution of **4a** (49 mg, 0.070 mmol) as a 1:1 mixture of diastereomers in THF (10 mL). The reaction mixture was stirred for 3 h and the solvent was concentrated in vacuo. The ^{31}P NMR spectrum showed that **8a** was a 1:1 mixture of two diastereomers. Recrystallization from toluene and hexanes gave **8a** (55 mg, 0.057 mmol, 82%) as a brown powder with a mixture of two diastereomers A and B (A:B = 55:45 from ^{31}P NMR). ^{1}H NMR (CD_2Cl_2, δ): 0.76 (d, J = 6.9 Hz, 3H, –CH_3, A), 0.79 (d, J = 6.6 Hz, 3H, –CH_3, B), 0.81 (d, J = 6.6 Hz, 3H, –CH_3, A), 0.85 (d, J = 6.6 Hz, 3H, –CH_3, B), 1.39–1.63 (m, 1H, A and B), 2.12–2.28 (m, 1H, A and B), 2.27–2.41 (m, 1H, A and B), 2.43–2.59 (m, 1H, A and B), 3.12–3.27 (m, 1H, A and B), 3.60–3.84 (m, 2H, oxazoline, A and B), 4.02–4.15 (m, 1H, oxazoline, A and B), 4.84 (t, J = 2.2 Hz, 1H, indene ring, A), 4.87 (t, J = 2.2 Hz, 1H, indene ring, B), 5.45 (d, J = 2.2 Hz, 1H, indene ring, A), 5.47 (d, J = 2.2 Hz, 1H, indene ring, B), 7.11–7.29 (m, 1H, A and B), 7.35–7.53 (m, 9H, A and B), 7.47–7.60 (m, 3H, A and B), 7.63–7.79 (m, 6H, A and B). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 1.57 (s, B), 1.60 (s, A). IR(KBr, tablet, cm^{-1}): 502, 513, 536, 695, 748, 1093, 1435, 1482, 1669 ($\nu_{C=N}$), 2926, 2958, 3057. MS (FAB): *m/z* 964 ($M^+ + 1$), 836 ($M^+ - I$), 708 ($M^+ - 2I - 1$), 574 ($M^+ - PPh_3 - I$). *Anal.* Calc. for $C_{35}H_{35}I_2IrNOP$: C, 43.67; H, 3.66; N, 1.45. Found: C, 43.95; H, 3.48; N, 1.32%.

*4.2.16. η^5-[{(S)-(^{i}Pr)Indox}$_{n=3}$]Ir(PPh$_3$)(I)$_2$ (**8b**)*

Triphenylphosphine (26 mg, 0.098 mmol) was added to a solution of **4b** (57 mg, 0.080 mmol) as a 1:1 mixture of two diastereomers in THF (10 mL). The reaction mixture was stirred for 3 h and the solvent was concentrated in vacuo. The ^{31}P NMR spectrum showed that **8b** was a 1:1 mixture of two diastereomers. Recrystallization from toluene and hexanes gave **8b** (66 mg, 0.067 mmol, 85%) as a brown powder with a mixture of two diastereomers A and B (A:B = 51:49 from ^{31}P NMR). ^{1}H NMR (CD_2Cl_2, δ): 0.838 (d, J = 6.6 Hz, 3H, –CH_3, A), 0.843 (d, J = 6.6 Hz, 3H, –CH_3, B), 0.91 (d, J = 6.9 Hz, 3H, –CH_3, A), 0.92 (d, J = 6.6 Hz, 3H, –CH_3, B), 1.53–1.77 (m, 2H, A and B), 1.74–1.90 (m, 1H, A and B), 1.86–2.05 (m, 1H, A and B), 2.07–2.25 (m, 2H, A and B), 3.03–3.16 (m, 1H, A and B), 3.62–3.96 (m, 2H, oxazoline, A), 3.86 (t, J = 8.0 Hz, 2H, oxazoline, B), 4.12 (dd, J = 9.1, 8.0 Hz, 1H, oxazoline, A), 4.17 (dd, J = 9.3, 8.2 Hz, 1H, oxazoline, B), 4.74 (t, J = 2.5 Hz, 1H, indene ring, B), 4.80 (t, J = 2.5 Hz, 1H, indene ring, A), 5.40–5.47 (m, 1H, indene ring, A and B), 7.36–7.64 (m, 13H, A and B), 7.66–7.80 (m, 6H, A and B). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 1.58 (s, B or A), 1.60 (s, A or B). IR(KBr, Film (CH_2Cl_2), cm^{-1}): 502, 513, 536, 695, 748, 1093, 1264, 1435, 1481, 1668 ($\nu_{C=N}$), 2958, 3056. MS (FAB): *m/z* 978 ($M^+ + 1$), 850 ($M^+ - I$), 722 ($M^+ - 2I - 1$), 588 ($M^+ - PPh_3 - I$). *Anal.* Calc. for $C_{36}H_{37}I_2IrNOP$: C, 44.27; H, 3.82; N, 1.43. Found: C, 44.23; H, 3.65; N, 1.39%.

*4.2.17. Preparation of η^5-[{(S)-(^{i}Pr)Indox}$_{n=2}$]Rh(PPh$_3$)(I)$_2$ (**9a**)*

Triphenylphosphine (82 mg, 0.31 mmol) was added to a solution of **7a** (0.19 g, 0.31 mmol) as a 1:1 mixture of diastereomers in THF (10 mL). The reaction mixture was stirred for 2 h and the solvent was concentrated in vacuo. The ^{31}P NMR spectrum showed that **9a** was a 1:1 mixture of two diastereomers. Recrystallization from toluene and hexanes gave **9a** (0.17 g, 0.20 mmol, 64%) as a brown powder with a mixture of two diastereomers A and B (A:B = 55:45 from ^{31}P NMR). ^{1}H NMR ($CDCl_3$, δ): 0.74 (d, J = 6.6 Hz, 3H, –CH_3, A), 0.80 (d, J = 6.9 Hz, 3H, –CH_3, B), 0.81 (d, J = 6.6 Hz, 3H, –CH_3, A), 0.86 (d, J = 6.6 Hz, 3H, –CH_3, B), 1.48 (qqd, J = 6.6, 6.6, 6.6 Hz, 1H, –CH(CH$_3$)$_2$, A), 1.60 (qqd, J = 6.6, 6.6, 6.6 Hz, 1H, –CH(CH$_3$)$_2$, B), 2.20–2.56 (m, 3H, –CH_2–, A and B), 3.24–3.40 (m, 1H, –CH_2–, A and B), 3.64–3.81 [m, 2H (oxazoline, A) and 1H (oxazoline, B)], 3.81 (t, J = 8.0 Hz, 1H, oxazoline, B), 4.02–4.15 (m, 1H, oxazoline, A and B), 4.90–4.94 (m, 1H, indene ring, B), 4.93–4.98 (m, 1H, indene ring, A), 5.26–5.30 (m, 1H, indene ring, A and B), 7.28–7.53 (m, 11H, A and B), 7.52–7.60 (m, 1H, A and B), 7.66–7.85 (m, 7H, A and B). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 47.9 (d, J_{Rh-P} = 153 Hz, B), 48.0 (d, J_{Rh-P} = 155 Hz, A). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 48.1 (d, J_{Rh-P} = 155 Hz, B), 48.2 (d, J_{Rh-P} = 155 Hz, A). IR(KBr, tablet, cm^{-1}): 499, 512, 528, 695, 748, 1092, 1434, 1480, 1669 ($\nu_{C=N}$), 2958, 3057. MS (FAB): *m/z* 874 ($M^+ + 1$), 746 ($M^+ - I$), 619 ($M^+ - 2I$), 484 ($M^+ - PPh_3 - I$). *Anal.* Calc. for $C_{35}H_{35}I_2NOPRh$: C, 48.13; H, 4.04; N, 1.60. Found: C, 48.17; H, 3.94; N, 1.54%.

*4.2.18. Preparation of η^5-[{(S)-(^{i}Pr)Indox}$_{n=3}$]Rh(PPh$_3$)(I)$_2$ (**9b**)*

Triphenylphosphine (26 mg, 0.10 mmol) was added to a solution of **7b** (59 mg, 0.088 mmol) as a 1:1 mixture of two diastereomers in THF (10 mL). The reaction mixture was stirred for 2 h and the solvent was concentrated in vacuo. The ^{31}P NMR spectrum showed that **9b** was a 1:1 mixture of two diastereomers. Recrystallization from toluene and hexanes gave **9b** (46 mg, 0.052 mmol, 59%) as a brown powder with a mixture of two diastereomers A and B (A:B = 51:49 from ^{31}P NMR). ^{1}H NMR (CD_2Cl_2, δ): 0.85 (d, J = 6.9 Hz, 3H, –CH_3, A and B), 0.92 (d, J = 6.9 Hz, 3H, –CH_3, A and B), 1.53–1.84 (m, 2H, A and B), 1.74–2.04 (m, 2H, A and B), 2.07–2.32 (m, 2H, A and B), 3.10–3.23 (m, 1H, A and B), 3.70–3.88 (m, 1H, oxazoline, A and B), 3.84–3.94 (m, 1H, oxazoline, A and B), 4.17 (dt, J = 11.0, 8.5 Hz, 1H, oxazoline, A and B), 4.82–4.88 (m, 1H, indene ring, B), 4.86–4.93 (m, 1H, indene ring, A), 5.29–5.34 (m, 1H,

indene ring, A and B), 7.29–7.57 (m, 11H, A and B), 7.56–7.64 (m, 1H, A and B), 7.66–7.85 (m, 7H, A and B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 48.3 (d, $J_{Rh-P} = 155$ Hz, B), 48.4 (d, $J_{Rh-P} = 155$ Hz, A). IR(KBr, tablet, cm^{-1}): 499, 511, 528, 694, 748, 1092, 1434, 1480, 1667 ($\nu_{C=N}$), 2957, 3056. MS (FAB): *m/z* 888 ($M^+ + 1$), 760 ($M^+ - I$), 626 ($M^+ - PPh_3 + 1$), 498 ($M^+ - PPh_3 - I$), 371 ($M^+ - PPh_3 - 2I$). *Anal.* Calc. for $C_{36}H_{37}I_2NOPRh$: C, 48.73; H, 4.20; N, 1.58. Found: C, 48.44; H, 3.98; N, 1.56%.

4.2.19. $[\eta^5:\eta^1$-[{(S)-(^{i}Pr)Indox}$_{n=2}$]Ir(PPh$_3$)(OTf)]-OTf (**10a**)

AgOTf (17 mg, 0.066 mmol) was added to a solution of **8a** (28 mg, 0.029 mmol) as a 55:45 mixture of two diastereomers in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 3 h to afford a yellow suspension. After removal of a brown precipitate, the solution was concentrated in vacuo. The ^{31}P NMR spectrum showed that **10a** was a 56 : 44 mixture of two diastereomers. Recrystallization from CH_2Cl_2 and hexanes gave **10a** (24 mg, 0.024 mmol, 82%) as a yellow brown powder with a mixture of two diastereomers A and B (A:B = 56:44 from ^{31}P NMR). ^1H NMR ($CDCl_3$, δ): 0.42 (d, $J = 7.1$ Hz, 3H, –C*H*$_3$, A), 0.47 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, A), 0.63 (d, $J = 7.1$ Hz, 3H, –C*H*$_3$, B), 0.67 (d, $J = 6.6$ Hz, 3H, –C*H*$_3$, B), 1.13–1.33 (m, 1H, –C*H*(CH$_3$)$_2$, A), 1.68–1.90 (m, 2H, B), 1.88–2.09 (m, 2H, –C*H*H–, A), 2.52–2.69 [m, 1H (oxazoline, A) and 1H (–CHH–, B)], 2.70–2.91 (m, 2H, A), 3.20–3.40 (m, 2H, B), 3.59 (t, $J = 9.1$ Hz, 1H, oxazoline, A), 3.54–3.78 (m, 1H, –C*H*H–, B), 4.23 (dd, $J = 9.3$, 2.3 Hz, 1H, oxazoline, A), 4.24–4.43 (m, 1H, oxazoline, B), 4.46–4.59 (m, 1H, oxazoline, B), 4.95–5.03 (m, 1H, indene ring, A), 5.88–5.98 (m, 1H, indene ring, B), 6.18–6.28 (m, 1H, indene ring, B), 6.48 (d, $J = 2.2$ Hz, 1H, indene ring, A), 7.38–7.73 (m, 15H, A and B), 7.79–7.91 (m, 2H, A and B), 7.88–8.00 (m, 2H, A and B). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 8.7 (s, B), 9.3 (s, A). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 8.46 (s), 8.51 (s). IR(KBr, tablet, cm^{-1}): 463, 516, 535, 576, 638, 696, 755, 988, 1032, 1094, 1168, 1259, 1437, 1483, 1615 ($\nu_{C=N}$), 2930, 2966, 3061. MS (FAB): *m/z* 859 ($M^+ + 1$), 708 ($M^+ - OTf - 1$), 596 ($M^+ - PPh_3$). *Anal.* Calc. for $C_{37}H_{35}F_6IrNO_7PS_2$: C, 44.13; H, 3.50; N, 1.39. Found: C, 43.79; H, 3.75; N, 1.29%.

4.2.20. $[\eta^5:\eta^1$-[{(S)-(^{i}Pr)Indox}$_{n=3}$]Ir(PPh$_3$)(OTf)]-OTf (**10b**)

AgOTf (18 mg, 0.069 mmol) was added to a solution of **8b** (34 mg, 0.035 mmol) as a 51:49 mixture of diastereomers in CH_2Cl_2 (5.0 mL) at room temperature. The reaction mixture was stirred for 2 h to afford a pale yellow suspension. After removal of a brown precipitate, the solution was concentrated in vacuo. The ^{31}P NMR spectrum showed that **10b** was a 51 : 49 mixture of diastereomers. Recrystallization from CH_2Cl_2 and hexanes gave **9b** (20 mg, 0.020 mmol, 58%) as a yellow powder with a mixture of two diastereomers A and B (A:B = 53:47 from ^{31}P NMR). ^1H NMR (CD_2Cl_2, δ): 0.55 (d, $J = 6.6$ Hz, 3H, –C*H*$_3$, A), 0.59 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, B), 0.65 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, B), 0.86 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, A), 1.16–1.35 (m, 1H, –C*H*(CH$_3$)$_2$, A), 1.80–2.00 (m, 1H, –C*H*(CH$_3$)$_2$–, B), 2.00–2.53 [m, 5H (A) + 6H (B)], 2.57–2.75 (m, 1H, –C*H*H–, A), 2.94 (dt, $J = 8.8$, 3.3 Hz, 1H, oxazoline, B), 3.84 (dt, $J = 8.5$, 1.9 Hz, 1H, oxazoline, B), 3.93 (t, $J = 9.3$ Hz, 1H, oxazoline, B), 4.14 (t, $J = 9.3$ Hz, 1H, oxazoline, B), 4.37 (dd, $J = 9.3$, 3.0 Hz, 1H, oxazoline, A), 4.49 (dd, $J = 9.3$, 3.3 Hz, 1H, oxazoline, B), 5.88 (dd, $J = 3.3$, 2.7 Hz, 1H, indene ring, B), 5.95 (t, $J = 2.7$ Hz, 1H, indene ring, A), 6.34 (d, $J = 2.5$ Hz, 1H, indene ring, A), 6.60 (d, $J = 1.9$ Hz, 1H, indene ring, B), 7.04–7.98 (m, 17H, A and B), 7.70–8.10 [m, 2H (A) + 1H (B)], 8.19 (d, $J = 8.2$ Hz, 1H, B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 8.9 (s, B), 9.4 (s, A). IR(KBr, tablet, cm^{-1}): 516, 537, 638, 696, 754, 1033, 1094, 1169, 1230, 1261, 1436, 1626 ($\nu_{C=N}$), 2926, 2965, 3063. MS (FAB): *m/z* 873 ($M^+ + 1$), 723 ($M^+ - OTf$), 610 ($M^+ - PPh_3$). *Anal.* Calc. for $C_{38}H_{37}F_6IrNO_7PS_2$: C, 44.70; H, 3.65; N, 1.37. Found: C, 44.54; H, 3.89; N, 1.39%.

4.2.21. $[\eta^5:\eta^1$-[{(S)-(^{i}Pr)Indox}$_{n=2}$]Rh(PPh$_3$)(OTf)]-OTf (**11a**)

AgOTf (22 mg, 0.085 mmol) was added to a solution of **9a** (26 mg, 0.030 mmol) as a 57:43 mixture of diastereomers in CH_2Cl_2 (8.0 mL) at room temperature. The reaction mixture was stirred for 2 h to afford a dark red suspension. After removal of a brown precipitate, the solution was concentrated in vacuo. The ^{31}P NMR spectrum showed that **11a** was a 57 : 43 mixture of diastereomers. Recrystallization from CH_2Cl_2 and hexanes gave **11a** (17 mg, 0.018 mmol, 61%) as an orange powder with a mixture of two diastereomers A and B (A:B = 59:41 from ^{31}P NMR). ^1H NMR (CD_2Cl_2, δ): 0.43 (d, $J = 7.1$ Hz, 3H, –C*H*$_3$, A), 0.44 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, A), 0.64 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, B), 0.71 (d, $J = 6.6$ Hz, 3H, –C*H*$_3$, B), 1.13–1.30 (m, 1H, –C*H*H–, A), 1.36 (qqd, $J = 6.9$, 6.9, 2.2 Hz, 1H, –C*H*(CH$_3$)$_2$, A), 1.61–1.85 (m, 1H, –C*H*(CH$_3$)$_2$, B), 1.82-2.05 (m, 1H, –C*H*H–, B), 2.26 (ddd, $J = 16.5$, 7.2, 2.2 Hz, 1H, –C*H*H–, A), 2.44–2.74 [m, 1H (A) and 3H (B)], 3.10–3.28 (m, 1H, –C*H*H–, A), 3.34–3.50 (m, 1H, oxazoline, B), 3.57–3.74 (m, 1H, –C*H*H–, A), 3.73 (t, $J = 9.1$ Hz, 1H, oxazoline, A), 4.22–4.38 (m, 1H, oxazoline, A and B), 4.46–4.61 (m, 1H, oxazoline, B), 4.99–5.08 (m, 1H, indene ring, A), 5.83–5.92 (m, 1H, indene ring, B), 5.97–6.05 (m, 1H, indene ring, B), 6.57 (d, $J = 2.5$ Hz, 1H, indene ring, A), 7.42–7.80 (m, 16H, A and B), 7.78–7.92 (m, 1H, A and B), 7.95–8.10 (m, 2H, A and B). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 43.1 (d, $J_{Rh-P} = 146$ Hz, A), 44.6 (d, $J_{Rh-P} = 151$ Hz, B). IR(KBr, tablet, cm^{-1}): 528, 638,

696, 803, 1032, 1094, 1172, 1230, 1261, 1437, 1482, 1623 ($\nu_{C=N}$), 2964, 3061. MS (FAB): *m/z* 768 (M^+), 619 ($M^+ - OTf$), 506 ($M^+ - PPh_3$), 357 ($M^+ - OTf - PPh_3$). *Anal.* Calc. for $C_{37}H_{35}F_6NO7PRhS_2$: C, 48.43; H, 3.84; N, 1.53. Found: C, 48.22; H, 3.99; N, 1.58%.

4.2.22. [η^5:η^1-[{(*S*)-(^{i}Pr)Indox}$_{n=3}$]Rh(PPh$_3$)(OTf)]-OTf (**11b**)

AgOTf (17 mg, 0.066 mmol) was added to a solution of **9b** (26 mg, 0.030 mmol) as a 51:49 mixture of diastereomers in CH_2Cl_2 (8.0 mL) at room temperature. The reaction mixture was stirred for 2 h to afford an orange suspension. After removal of a brown precipitate and the solution was concentrated in vacuo. The ^{31}P NMR spectrum showed that **11b** was a 51:49 mixture of diastereomers. Recrystallization from CH_2Cl_2 and hexanes gave **11b** (30 mg, 0.033 mmol, >99%) as an orange powder with a mixture of two diastereomers A and B (A:B = 60:40 from ^{1}H and ^{31}P NMR). ^{1}H NMR (CD_2Cl_2, δ): 0.54 (d, $J = 6.3$ Hz, 3H, –C*H*$_3$, A), 0.59 (d, $J = 6.3$ Hz, 3H, –C*H*$_3$, A), 0.65 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, B), 0.87 (d, $J = 6.9$ Hz, 3H, –C*H*$_3$, B), 0.88–1.16 (m, 1H, A and B), 1.73–1.82 (m, 1H, B), 1.90–2.15 (m, 1H, A), 2.00–2.63 (m, 5H, A and B), 2.95–3.10 (m, 1H, oxazoline, B), 3.64–3.78 (m, 1H, oxazoline, A), 3.89 (t, $J = 9.3$ Hz, 1H, oxazoline, B), 4.18 (t, $J = 9.3$ Hz, 1H, oxazoline, A), 4.37 (dd, $J = 9.9$, 3.0 Hz, 1H, oxazoline, A), 4.47 (dd, $J = 9.3$, 4.1 Hz, 1H, oxazoline, B), 5.78–5.84 (m, 1H, indene ring, B), 5.95–5.99 (m, 1H, indene ring, A), 6.23 (d, $J = 2.7$ Hz, 1H, indene ring, A), 6.45 (d, $J = 2.5$ Hz, 1H, indene ring, B), 7.35–7.82 (m, 15H, A and B), 7.74–7.90 (m, 1H, A and B), 7.91–8.14 [m, 3H (A) and 2H (B)], 8.18–8.28 (m, 1H, B). ^{31}P{^{1}H} NMR (CD_2Cl_2, δ): 44.4 (d, $J_{Rh-P} = 149$ Hz, A), 45.3 (d, $J_{Rh-P} = 151$ Hz, B). IR(KBr, tablet, cm^{-1}): 516, 527, 638, 693, 759, 1033, 1094, 1171, 1260, 1437, 1627 ($\nu_{C=N}$), 2961. MS (FAB): *m/z* 782 (M^+), 633 ($M^+ - OTf$), 520 ($M^+ - PPh_3$), 371 ($M^+ - PPh_3 - OTf$). *Anal.* Calc. for $C_{38}H_{37}F_6NO_7PRhS_2$: C, 48.99; H, 4.00; N, 1.50. Found: C, 48.56; H, 4.22; N, 1.49%.

4.2.23. η^5-[{(H)Indox}$_{n=3}$]Ir(PPh$_3$)(I)$_2$

Triphenylphosphine (52 mg, 0.20 mmol) was added to a solution of **5** (132 mg, 0.20 mmol) in THF (10 mL). The reaction mixture was stirred for 3 h and the solvent was concentrated in vacuo. Recrystallization from toluene and hexanes gave η^5-[{P(H)Indox$_n = 3$]Ir(PPh$_3$)(I)$_2$ (46 mg, 0.050 mmol, 25%) as a brown powder. ^{1}H NMR ($CDCl_3$, δ): 1.57–1.81 (m, 2H, –C*H*$_2$–), 1.84–2.05 (m, 1H, –C*H*$_2$–), 2.07–2.22 (m, 2H, –C*H*$_2$–), 2.94–3.14 (m, 1H, –C*H*$_2$–), 3.70 (t, $J = 9.1$ Hz, 2H, oxazoline), 3.98–4.22 (m, 2H, oxazoline), 4.73 (t, $J = 2.2$ Hz, 1H, indene), 5.44 (d, $J = 2.2$ Hz, 1H, indene), 7.22–7.35 (m, 1H), 7.29–7.45 (m, 8H), 7.40–7.50 (m, 3H), 7.44–7.57 (m, 1H), 7.61–7.83 (m, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 1.6(s). IR[KBr, Film (CH_2Cl_2), cm^{-1}]: 501, 536, 667, 694, 752, 792, 999, 1093, 1161, 1187, 1260, 1435, 1481, 1666 ($\nu_{C=N}$), 2903, 2967, 3056. MS (FAB): *m/z* 936 (M^+), 808 ($M^+ - I$), 681 ($M^+ - 2I$), 546 ($M^+ - PPh_3 - I$). *Anal.* Calc. for $C_{33}H_{31}I_2IrNOP$: C, 42.41; H, 3.34; N, 1.50. Found: C, 38.20; H, 2.62; N, 1.31%.

4.2.24. [η^5:η^1-[{(H)Indox}$_{n=3}$]Ir(PPh$_3$)(OTf)]OTf (**12**)

AgOTf (39 mg, 0.15 mmol) was added to a solution of [{(H)Indox}$_{n=3}$]Ir(PPh$_3$)(I)$_2$ (45 mg, 0.048 mmol), which was not purified by recrystallization, in CH_2Cl_2 (5.0 mL) at room temperature. The reaction mixture was stirred for 3 h and the solution was concentrated in vacuo. The ^{1}H and ^{31}P NMR showed that **12** was a single diastereomer. Recrystallization from CH_2Cl_2 and hexanes gave **12** (30 mg, 0.031 mmol, 65%) as a yellow powder. ^{1}H NMR ($CDCl_3$, δ): 1.16–1.38 (m, 1H, –C*H*$_2$–), 2.10–2.52 (m, 5H, –C*H*$_2$–), 2.75 (ddd, $J = 12.9$, 10.2, 10.2 Hz, 1H, oxazoline), 3.50–3.70 (m, 1H, oxazoline), 4.27–4.57 (m, 2H, oxazoline), 5.83 (t, $J = 2.5$ Hz, 1H, indene), 6.39 (d, $J = 2.5$ Hz, 1H, indene), 7.33–7.52 (m, 6H), 7.48–7.69 (m, 9H), 7.66–7.77 (m, 1H), 7.82–7.96 (m, 2H), 7.98–8.09 (m, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 10.6 (s). IR(KBr, tablet, cm^{-1}): 502, 517, 536, 642, 696, 756, 1034, 1095, 1171, 1229, 1261, 1436, 1633 ($\nu_{C=N}$), 2927, 3055. MS (FAB): *m/z* 830 (M^+), 681 ($M^+ - OTf$), 568 ($M^+ - PPh_3$). *Anal.* Calc. for $C_{35}H_{31}F_6IrNO_7PS_2$: C, 42.94; H, 3.19; N, 1.43. Found: C, 38.05; H, 2.63; N, 1.33%.

4.3. Preparation of single crystals for X-ray analysis

4.3.1. Single crystals of **4b**

A solution of I_2 (27 mg, 0.10 mmol) in diethyl ether (35 mL) was added to a solution of **6b** (71 g, 0.11 mmol) in diethyl ether (70 mL) at room temperature. The reaction mixture was placed at room temperature for 20 days. Colorless single crystals were obtained along with a brown powder.

4.3.2. Single crystals of **13**

A solution of **12** (25 mg) in $CDCl_3$ (ca. 0.8 mL) was placed in the NMR tube at room temperature for 4 days to afford just a small amount of yellow single crystals of **13**. These crystals were not dissolved in various solvents. Unfortunately, spectral and physical data could not be obtained except for the melting point (>210 °C).

5. Supplementary material

The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers: CCDC 227510 for **4** and CCDC 227511 for **13**. Copies of this information may 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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