

Highly Diastereoselective Oxidative Addition of Alkyl Halides to Rhodium and Iridium Carbonyl Complexes Having an $\eta^5:\eta^1$ -(Ind-P) $_n$ Ligand ((Ind-P) $_n$ H = C $_9$ H $_7$ (CH $_2$) $_n$ PR $_2$; R = Ph, Cy; n = 2–4)

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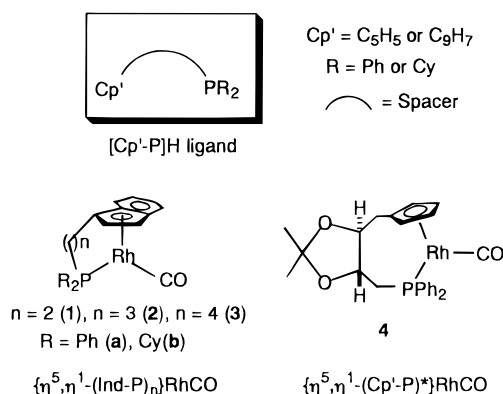
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Summary: Highly diastereoselective oxidative addition of alkyl halides to $\{\eta^5:\eta^1$ -(Ind-P) $_n\}$ RhCO ((Ind-P) $_n$ = C $_9$ H $_6$ (CH $_2$) $_n$ PR $_2$; n = 2 (**1**), 3 (**2**), 4 (**3**); R = Ph (**a**), Cy (**b**), Cy = cyclohexyl) has been achieved and the stereoselectivity was governed by the length of spacer of the (Ind-P) $_n$ ligand and the kind of alkyl halide; reaction of $\{\eta^5:\eta^1$ -(Ind-P) $_{n=2}$ RhCO (**1a**) with EtI in CH $_2$ Cl $_2$ gave (R*,R*)- $\{\eta^5:\eta^1$ -(Ind-P) $_{n=2}$ RhI(COEt) (**7a**) in 98% yield with 92% de, whereas $\{\eta^5:\eta^1$ -(Ind-P) $_{n=4}$ RhCO (**3a**) gave the other diastereomer, (R*,S*)- $\{\eta^5:\eta^1$ -(Ind-P) $_{n=4}$ RhI(COEt), in 97% yield with 96% de. Reaction of $\{\eta^5:\eta^1$ -(Ind-P) $_{n=4}$ Ir(CO) (**8a**) with MeI gave a diastereomer mixture of $\{\eta^5:\eta^1$ -(Ind-P) $_{n=4}$ Ir(Me)(CO)I (**9a**) in a 92:8 ratio, which did not afford the corresponding acetyl complex upon heating under reflux in CH $_2$ Cl $_2$.

The hybrid ligands (Cp'-P) $_n$ H, which contain both a cyclopentadienyl or an indenyl group and a tertiary phosphine connected by an appropriate spacer, should have the combined characteristics of their components (Chart 1).^{1–3} Therefore, their transition-metal complexes would have a great possibility of inducing some unexpected stoichiometric or catalytic reactions. Moreover, although optically active transition-metal complexes bearing a Cp'-P ligand are expected to exhibit potential activity for asymmetric catalysis,^{3a,b} synthetic procedures for obtaining such optically active complexes remain relatively undeveloped. Some chiral transition-metal complexes having a stereogenic center on the metal have been prepared and applied to asymmetric synthesis,^{4–7} but the controlled generation or the reso-

Chart 1



lution of the chiral metal center is still one of the challenging projects. Thus, if the method of controlling generation of a chiral metal center is available, a new way to obtain optically active complexes having a chiral metal center would be opened. On the basis of these concepts we have performed oxidative addition of alkyl halides to rhodium and iridium complexes having an $\eta^5:\eta^1$ -(Ind-P) $_n$ ligand ((Ind-P) $_n$ = C $_9$ H $_6$ (CH $_2$) $_n$ PR $_2$; C $_9$ H $_6$ = 1-indenyl; n = 2 (**1**), 3 (**2**), 4 (**3**); R = Ph (**a**), Cy (**b**); Cy = cyclohexyl) in order to examine the ability of the "planar chirality" (indenyl-based chirality) controlling the stereochemistry of the "central chirality" (metal-centered chirality) arising at the metal.

We have recently disclosed the preparation of several types of achiral or chiral (Cp'-P) $_n$ H ligands and the synthesis of rhodium(I) and ruthenium(II) complexes with their anions, such as $\{\eta^5:\eta^1$ -(Ind-P) $_n\}$ RhCO or $\{\eta^5:\eta^1$ -(Ind-P) $_n\}$ Ru(PPh $_3$)Cl.³ It is well-known that the oxidative addition of an alkyl or an aryl halide R'X to $(\eta^5$ -C $_5$ H $_5$)Rh(CO)PPh $_3$ affords the rhodium(III) acyl complexes $(\eta^5$ -C $_5$ H $_5$)RhX(COR)PPh $_3$.⁸ If this oxidative addition is applied to $\{\eta^5:\eta^1$ -(Ind-P) $_n\}$ RhCO (**1-3**), the resulting acyl complexes exhibit both planar chirality and central chirality. We have found that the oxidative

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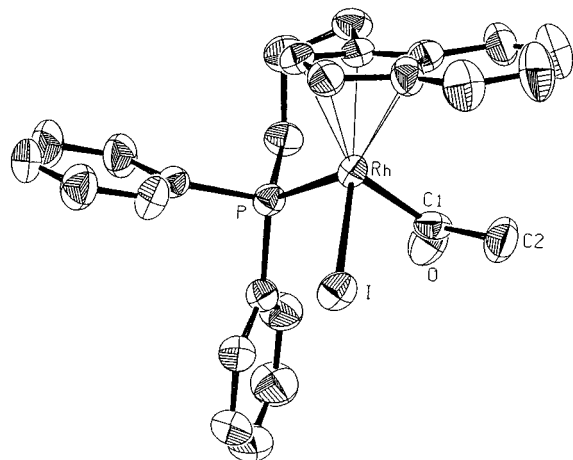
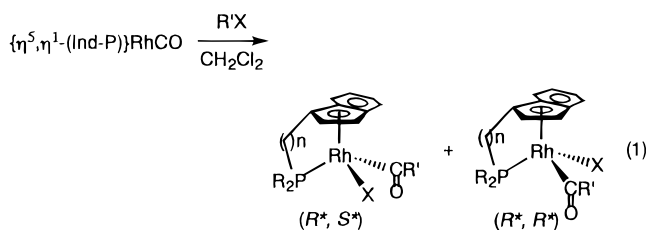


Figure 1. Crystal structure of $(R^*,S^*)\text{-}\{\eta^5:\eta^1\text{-C}_9\text{H}_6(\text{CH}_2)_3\text{-PPh}_2\}\text{RhI}(\text{COMe})$ ($(R^*,S^*)\text{-5a}$; 50% probability ellipsoids).

addition of an alkyl halide to $\{\eta^5:\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ occurs with high stereoselectivity induced by the encumbrance of the benzene ring of the indenyl moiety; i.e., the planar chirality can control the formation of the central chirality (eq 1).



The $\{\eta^5:\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ complexes were readily prepared from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and a lithium salt of $(\text{Ind-P})_n\text{H}$ in THF.³ Reaction of $\{\eta^5:\eta^1\text{-(Ind-P)}_{n=3}\}\text{RhCO}$ (**2a**) with excess MeI in CH_2Cl_2 at 20 °C for 1 h gave a red solution, from which the acetyl rhodium(III) complex $\{\eta^5:\eta^1\text{-(Ind-P)}_{n=3}\}\text{RhI}(\text{COMe})$ (**5a**) was obtained in 97% yield as orange powders which were purified by silica gel column chromatography (hexane:AcOEt = 5:1). The acetyl complex was fully characterized by the usual spectroscopic methods as well as elemental analyses.⁹ ^1H and ^{31}P NMR spectra showed that the acetyl complex **5a** was a mixture of two diastereomers (major:minor = 89:11, 78% de). The ^1H NMR (C_6D_6) spectrum of **5a** displayed an acetyl methyl proton of the major isomer at δ 2.21 and that of the minor one at δ 2.85. The structure of the major isomer has been finally confirmed to be the R^*,S^* isomer¹⁰ by X-ray crystallography. Crystals of the major isomer suitable for X-ray analysis were obtained by recrystallization of the diastereomer mixture from a toluene-hexanes solution. The ORTEP drawing of $(R^*,S^*)\text{-5a}$ is presented in Figure 1.¹¹ The acetyl complex has a monomeric three-legged piano-stool structure. The iodide resides at the less hindered site,

(9) **5a**: The ratio of the diastereomer mixtures was determined by ^1H NMR and ^{31}P NMR (R^*,R^* : R^*,S^* = 11:89). Mp: 147.0–150.0 °C dec. The analytical and spectral data are provided in the Supporting Information.

(10) The first chirality symbol shows the planar chirality, and the second one indicates the central chirality around the rhodium. The priorities of substituents around the metal were determined according to the rules reported by Tirouflet et al.; see: Lecomte, C.; Dusaosoy, Y.; Protas, J.; Tirouflet, J.; Dormond, A. *J. Organomet. Chem.* **1974**, 73, 67.

and the acetyl moiety is situated just below the benzene ring of the indenyl group. Therefore, the higher field shift of the acetyl methyl proton of the major isomer may be ascribed to the shielding effect of the aromatic ring current of the indenyl group. In contrast, the ^{31}P NMR signal of the major isomer appears at lower field than that of the minor isomer.

Some representative results on the reaction of $\{\eta^5:\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ with alkyl halides are shown in Table 1. The reaction of $\{\eta^5:\eta^1\text{-(Ind-P)}_{n=2}\}\text{RhCO}$ (**1a**), which has a shorter alkylene spacer, with MeI in CH_2Cl_2 at 20 °C for 1 h also afforded the rhodium acetyl complex $\{\eta^5:\eta^1\text{-(Ind-P)}_{n=2}\}\text{RhI}(\text{COMe})$ (**6a**)¹¹ but with greatly inferior stereoselectivity, a diastereomer mixture of 33:67 (run 1). The major isomer was found to be the other diastereomer, R^*,R^* , different from the case of **5a** by X-ray analysis.¹¹ Consistently, ^1H NMR spectra of **6a** showed a tendency in the chemical shift values opposite to that of the acyl complex **5a**. The acetyl methyl proton of the major isomer of **6a** was observed at a lower field (δ 3.10) than that of the minor isomer (δ 2.39). The ^1H NMR and the ^{31}P NMR spectra of the acetyl complexes obtained from **3a**, which has a longer alkylene spacer of $n = 4$, showed a tendency similar to that of **5a**; thus, the major isomer was assigned to be R^*,S^* (run 6). The diastereoselectivity was also on a level similar to that found for $n = 3$ but much higher than that of $n = 2$ (run 1 vs runs 5 and 6).

Small differences in the bulkiness of R' in the alkyl halide influence the stereoselectivity of the oxidative addition considerably. For example, the oxidative addition of EtI toward **1a** proceeded slowly compared to that of MeI but with much higher diastereoselectivity, 92% de, for the production of the acyl complex $\{\eta^5:\eta^1\text{-(Ind-P)}_{n=2}\}\text{RhI}(\text{COEt})$ (**7a**)¹¹ (run 3). The highest selectivity, $R^*,R^*:R^*,S^*$ = 98:2 (96% de), has been accomplished for the reaction of **3a** with EtI. The structure of the major isomer has also been confirmed to be R^*,R^* by X-ray crystallography.^{11,12} The reactivity for the oxidative addition was also influenced by the length of the spacer; **1a** showed a higher reactivity than **3a** (run 2 vs run 7). The angle $\text{Ind}(\text{centroid})\text{-Rh-P}$ in **1a** should become smaller compared to that of **3a** due to the shorter spacer. There is more reaction space around the rhodium in **1a** compared to that in **3a**. The easier access of EtI to the rhodium center should enhance the reaction rates, but at the same time the diastereoselectivity decreases due to less influence of the steric hindrance not only of the bulky indenyl group but also of the phosphorus substituents.

When a bulkier alkyl halide such as *i*-PrI or *t*-BuI was employed, the $\{\eta^5:\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ was consumed very

(11) The reflection data for X-ray analyses were collected on a Rigaku AFC-7R diffractometer equipped with a Rotaflex rotating anode X-ray generator (50 kV, 200 mA) with graphite-monochromated Mo $\text{K}\alpha$ radiation (0.710 69 Å). Crystal data for $(R^*,S^*)\text{-5a}$: red prismatic crystal, $0.3 \times 0.2 \times 0.2$ mm; $P1$ (No. 2), $a = 10.946(8)$ Å, $b = 12.800(6)$ Å, $c = 9.184(5)$ Å, $\alpha = 101.84(4)^\circ$, $\beta = 112.44(4)^\circ$, $\gamma = 91.29(5)^\circ$, $V = 1157(1)$ Å³, $Z = 2$, $D_{\text{calcd}} = 1.764$ g/cm³, $\mu = 21.30$ cm⁻¹, 23 °C, ω - 2θ scan, 5594 measured reflections with $3.0^\circ < 2\theta < 55.0^\circ$ collected, 5315 unique reflections, $R_{\text{int}} = 0.022$, direct method (SHELXS-86), $T_{\text{min}} = 0.570$, $T_{\text{max}} = 0.652$, 4320 reflections with $F_o > 3.0\sigma(F_o)$ used refinements (Imoto, H., ANYBLK program for Least-Squares refinement. Department of Chemistry, School of Science, The University of Tokyo, Hongo, Tokyo, 113, Japan), $R = 0.0342$, $R_w = 0.0303$, $w = 1/\sigma^2(F_o)$, $\Delta/\sigma_{\text{max}} = 0.000$, GOF = 3.173, $\Delta\rho_{\text{min, max}} = -0.85, 0.97$ e/Å³. Crystal data for $(R^*,R^*)\text{-6a}$ and $(R^*,R^*)\text{-7a}$ are provided in the Supporting Information.

Table 1. Reaction of $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ with $\text{R}'\text{X}^a$

run no.	$\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$	$\text{R}'\text{I}$	$\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{RhX(COR')}$		$R^*, S^*: R^*, R^{*c}$
			time (h)	yield (%) ^b	
1	1a	MeI	1	90 (6a)	33:67 ^d
2	1a	EtI	13	83 (convn) ^e	4:96 ^d
3	1a	EtI	51	98 (7a)	4:96 ^d
4	1a	EtBr	72	40	1:>99 ^f
5	2a	MeI	1	97 (5a)	89:11 ^d
6	3a	MeI	1	92	85:15
7	3a	EtI	13	77 (convn) ^e	98:2
8	3a	EtI	66	97	98:2
9	1b	MeI	1	97 (6b)	34:66
10	1b	EtI	13	53 (convn) ^e	6:94

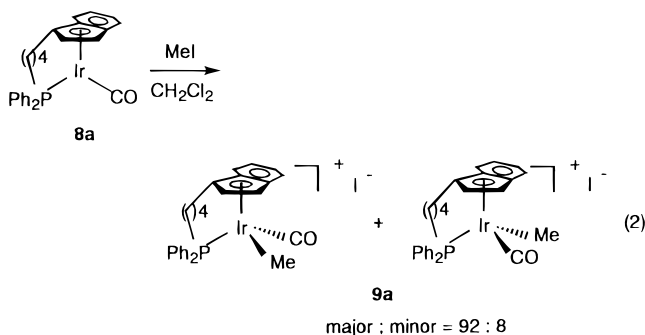
^a $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ was treated with excess $\text{R}'\text{X}$ in CH_2Cl_2 at 20 °C. ^b Isolated yield. ^c The structures of diastereomers and their ratio were estimated by ^1H and ^{31}P NMR except as otherwise noted. ^d The structures of the major isomers were determined by X-ray analysis. ^e Conversion was determined by ^1H and ^{31}P NMR. ^f After purification, the ratio changed to 33:67.

slowly and the acyl complex was scarcely obtained. In contrast, the reactivity of benzyl bromide or allyl bromide toward $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$ was so high that several side reactions occurred concomitantly. In the case of the reaction of **1a** with EtBr, though the reaction did not go to completion even after 72 h under reflux conditions, the acyl complex $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_{n=2}\}\text{RhBr}(\text{COEt})$ obtained in the reaction was only the R^*, R^* -isomer, but it easily epimerized to give a diastereomer mixture ($R^*, R^*: R^*, S^* = 67:33$) during the purification by silica gel column chromatography (run 4). The other rhodium acyl complexes examined did not show such epimerization during similar purification by column chromatography as monitored with NMR spectra. The reason only the complex $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_{n=2}\}\text{RhBr}(\text{COEt})$ undergoes epimerization during the purification is not clear at the moment. When the diphenylphosphino group was changed to a dicyclohexylphosphino group in the $(\text{Ind-P})_n$ ligands, the diastereoselectivity of the oxidative addition was not affected (runs 1 and 2 vs runs 9 and 10) but the reactivity diminished apparently (run 2 vs run 10).

Reaction of the optically active complex $\{\eta^5\text{-}\eta^1\text{-(Cp}'\text{-P)}^*\}\text{RhCO}$ (**4**), which has stereogenic centers in the spacer of a $\text{Cp}'\text{-P}$ ligand, with MeI in CH_2Cl_2 at 20 °C for 1 h afforded the corresponding acetyl complex in 99% isolated yield as a diastereomer mixture (major:minor = 64:36). Compared to the reaction of **3a**, which has the same length of the spacer, the diastereoselectivity was low. In the oxidative addition of alkyl halides to the $\text{Cp}'\text{-P}$ rhodium complex, the planar chirality can better control the chiral center arising at rhodium than the chiral center in the backbone. This is probably due to the fact that the planar chirality is situated much closer to the reaction center compared to the chiral center in the spacer.

As an intermediate in the oxidative addition of an alkyl halide, $\text{R}'\text{X}$, to $(\eta^5\text{-C}_5\text{H}_5)\text{RhCO}(\text{PPh}_3)$, a cationic rhodium(III) complex, $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{CO})\text{R}'(\text{PPh}_3)]\text{X}$, has been postulated.⁸ Despite our research, we could not observe any evidence for the formation of the intermediate $[\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{Rh}(\text{CO})\text{R}']\text{X}$. In contrast, when an iridium-carbonyl complex was employed, the corresponding cationic complex could be isolated.^{8b} Reaction of $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_{n=4}\}\text{IrCO}$ (**8a**) with MeI in CH_2Cl_2 gave the cationic iridium(III) complex $[\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_{n=4}\}\text{Ir}(\text{CO})(\text{Me})\text{I}]$ (**9a**) as a pale yellow powder in 94% yield

(major:minor = 92:8) (eq 2). However, the iridium



cationic complex was too inert to be transformed to the corresponding acetyl complex even under a prolonged reaction time or under reflux conditions.¹²

To clarify why the diastereoselectivity was changed by the different length of the spacer in $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{RhCO}$, we are now investigating the preparation of the cationic rhodium(III) complexes by changing the counteranion from iodide to a more weakly coordinating anion such as PF_6 or BF_4 and their reactivity, including the stereoselectivity.

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Supporting Information Available: Text giving synthetic experimental details and tables giving full crystallographic data, positional parameters, bond lengths, and bond angles and ORTEP drawings for (R^*, S^*) -**5a**, (R^*, R^*) -**6a**, and (R^*, R^*) -**7a** (44 pages). Ordering information is given on any current masthead page.

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(12) The present stereoselective reaction may involve a mechanism similar to that proposed for the oxidative addition of $(\eta^5\text{-C}_5\text{H}_5)\text{RhCO}(\text{PPh}_3)$ with methyl iodide:^{8b} (1) nucleophilic attack by the metal on the alkyl halide opposite the indenyl group, (2) methyl migration to the CO under the benzene ring, and (3) coordination of the halide to the vacant site on the metal, which could explain the stereochemical results. However, because of lack of an X-ray structure for the starting carbonyl complexes as well as of a kinetic study, the exact mechanism is not clear at present. Moreover, from the preliminary studies on the stereochemistry for the reaction of $[\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{Rh}(\text{CO})\text{R}']^+$ with a halide X, giving the complex $\{\eta^5\text{-}\eta^1\text{-(Ind-P)}_n\}\text{RhX}(\text{COR}')$, we suspect that the reaction mechanism may not be explained simply.