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Third Generation of the Cp′−P Ligand: Highly Stereoselective Control of Central Chirality Arising at a Metal Center

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*Summary: A new type of Cp′−P ligand (the third generation of the Cp′−P ligand), [{3-(NM)Ind−P}$_{n=2}$]H (**3a**), in which an indenyl group, having a neomenthyl group, and a diphenylphosphino group are connected by an ethylene group, was designed and prepared. The presence of the two kinds of chiralities, indenyl-based planar chirality and stereogenic centers of the neomenthyl group, was an indispensable factor for inducing high stereoselectivity around the metal center.*

Hybrid ligands [Cp′−P]H, containing both a cyclopentadienyl derivative and a tertiary phosphine group connected by an appropriate spacer (Scheme 1), have attracted much attention due to the combined characters of their components, which could induce some unexpected reactivity and phenomena.[1−10] So far, we have designed and prepared several types of [Cp′−P]H ligands and disclosed unique characters of their Rh, Ru, and Ir complexes.[2] The first one is the optically active [Cp′−P]H ligand **1**, in which stereogenic centers are in the spacer. The second one is the [(Ind−P)$_n$]H ligand **2**, in which indenyl-based planar chirality will arise on coordinating to a metal center. Recently, we have found that the indenyl-based planar chirality (the latter ligand) can better control the chiral center arising at Rh by the oxidative addition of alkyl halides to its

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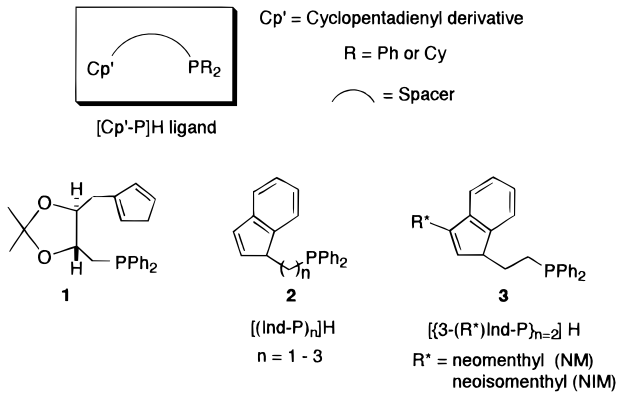
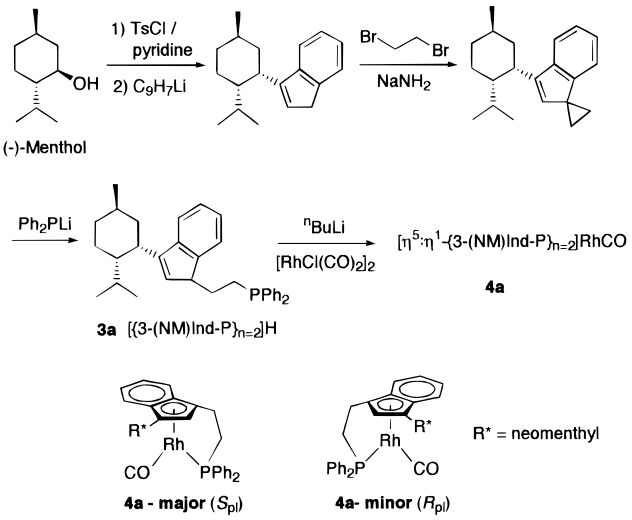
Scheme 1



Scheme 2



carbonyl complex, (Cp′−P)RhCO,[11] than the chiral center in the spacer (the former ligand).[2d] Herein we report that the third generation of [Cp′−P]H ligand, [{3-(NM)Ind−P}$_{n=2}$]H (**3a**) or [{3-(NIM)Ind−P}$_{n=2}$]H (**3c**), in which an optically active substituent (a neomenthyl or a neoisomenthyl group) is attached to the indenyl ring of **2**, can control more efficiently the stereochemistry of the reaction of its metal complexes.

The general method for the preparation of **3a** and its rhodium complex [η^5:η^1-{3-(NM)Ind−P}$_{n=2}$]RhCO (**4a**) is shown in Scheme 2. Experimental details are provided as Supporting Information. The rhodium complex **4a** was obtained as orange powders in 89% isolated yield from **3a**. ^{1}H and ^{31}P NMR showed that **4a** is a mixture of two diastereomers (major:minor = 62:38, 24% de). Recrystallization from hexanes at 4 °C gave only the major isomer of **4a** as yellow powders. The planar chirality of **4a**-major was found to be *S* configuration from the X-ray analysis (Figure 1a).[12] The cyclopentadienyl analogue [η^5:η^1-{3-(NM)C$_5$H$_3$−P}$_{n=2}$]RhCO (**4b**) was also prepared by a similar method using cyclopentadiene instead of indene, but its de was much lower (8% de). A combination of two kinds of substituents (a neomenthyl group and a benzene ring) is more effective

(11) (Cp′−P) shows the anion of the [Cp′−P]H ligand.

(12) Crystallographic data for **4a**-major: $C_{34}H_{38}OPRh$, (M_r = 596.52), orthorhombic, $P2_12_12_1$ (No. 19), a = 16.308(6) Å, b = 26.862(5) Å, c = 6.661(5) Å, V = 2917.8(23) Å^3, Z = 4, D_{calcd} = 1.358 Mg/m^3, μ = 0.664 mm^{-1}, R_{int} = 0.0133, R1(all) = 0.0327, R1(obsd) = 0.0256 (>2σ(I)), wR2(all) = 0.0747, wR2(obsd) = 0.0705 (>2σ(I)).

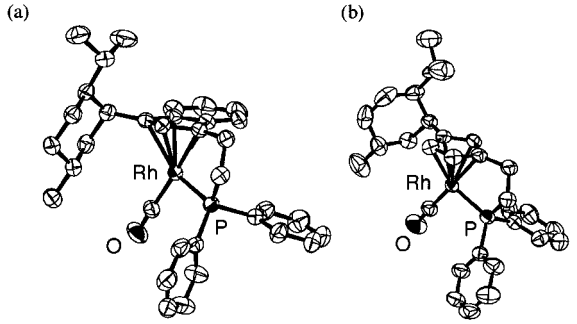


Figure 1. ORTEP drawing of the X-ray crystal structure: (a) (S_{pl})-[η^5:η^1-{3-(NIM)Ind−P}$_{n=2}$]RhCO (**4a**-major). (b) (S_{pl})-[η^5:η^1-{3-(NIM)C$_5$H$_3$−P}$_{n=2}$]RhCO (**4b**-major).

for controlling the planar chirality arising on complexation to the metal. The major isomer of **4b** could be isolated by recrystallization from hexanes at 5 °C. The X-ray analysis of **4b**-major (Figure 1b)[13] showed that the relative location of the neomenthyl group and the pendant group (diphenylphosphinoethyl group) was different from that in **4a**-major, but the planar chirality was also *S* configuration according to a general system for designating an absolute configuration. When (+)-isomenthol was used as the starting alcohol, [η^5:η^1-{3-(NIM)Ind−P}$_{n=2}$]RhCO (**4c**) was obtained with 74% de. The neoisomenthyl group caused much higher asymmetric induction with regard to the arising planar chirality than the neomenthyl group.

Some representative results on the reaction of the Rh carbonyl complexes **4** with alkyl halides are shown in Table 1. The complex **4a**-major reacted with MeI in CH_2Cl_2 at room temperature for 2 h to afford the rhodium(III) acyl complex [η^5:η^1-{(3-NM)Ind−P}$_{n=2}$]RhI(COMe) (**5a**) in 93% yield.[14] ^{1}H and ^{31}P NMR spectra of the reaction mixture showed that the acyl complex **5a** was a mixture of two diastereomers (R_{pl},R_{Rh} and R_{pl},S_{Rh})[15] in 96% de (run 1). The complex **4a**-major also reacted with EtI or PhCH$_2$Br to afford the corresponding acyl complex with high diastereoselectivity in good yield (runs 2 and 3). A combination of the planar chirality (indenyl-based chirality) and the stereogenic centers of the neoisomenthyl group was highly effective for controlling the evolving central chirality (metal-centered chirality) in the oxidative addition. For example, when the cyclopentadienyl derivative **4b**-major, which has a cyclopentadienyl-based planar chirality and an optically active substituent on the cyclopentadienyl ring, reacted with MeI under the same conditions, **4b**-major was consumed within 1 h and the corresponding acyl complex **5b** was obtained in 79% yield, but its de was only 56%. The oxidative addition of MeI toward the Rh

(13) Crystallographic data for **4b**-major: $C_{30}H_{36}OPRh$, (M_r = 546.47), hexagonal, $P6_1$ (No. 169), a = 18.8504(13) Å, b = 18.8504(13) Å, c = 13.7819(14) Å, α = 90.0°, β = 90.0°, γ = 120.0°, V = 42141.1(6) Å^3, Z = 6, D_{calcd} = 1.284 Mg/m^3, μ = 0.679 mm^{-1}, R_{int} = 0.0175, R1(all) = 0.0598, R1(obsd) = 0.0360 (>2σ(I)), wR2(all) = 0.1291, wR2(obsd) = 0.1119 (>2σ(I)).

(14) Excess amount of methyl iodide (0.27 mL, 4.3 mmol) was added to a solution of **4a**-major (26 mg, 0.044 mmol) in CH_2Cl_2 (5 mL) at 25 °C. The reaction mixture was stirred for 2 h, and then the solvent was removed in vacuo to afford **5a** (major:minor = 98:2, 96% de; the ratio was determined by ^{31}P NMR). The resulting solid was purified by column chromatography on silica gel (eluent:hexane/AcOEt = 5:1) to give **5a** (30 mg, 0.041 mmol, 93%, 96% de) as deep red powders. Mp: 108−112 °C (dec). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 55.5 (d, J_{P-Rh} = 171 Hz, major), 57.6 (d, J_{P-Rh} = 173 Hz, minor). Anal. Found: C, 56.56; H, 5.82. Calcd for $C_{35}H_{41}IOPRh$: C, 56.92; H, 5.60%.

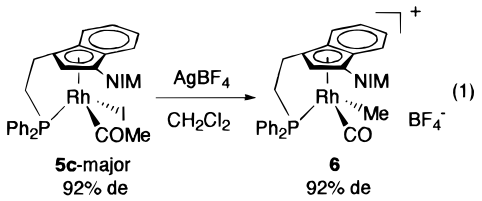
Table 1. Reaction of [η^5:η^1-(Cp′−P)]RhCO with RX[a]

entry	[η^5:η^1-(Cp′P)]-RhCO	RX	time (h)	[η^5:η^1-(Cp′P)]Rh(X)COR yield (%)[b]	major: minor[c]
1	**4a**-major	MeI	2	93	98:2
2	**4a**-major	EtI	72	91	96:4
3	**4a**-major	$PhCH_2Br$	12	92	95:5
4	**4b**-major	MeI	1	79	78:22
5	**4c**[d]	MeI	2	95	96:4[e]

[a] [η^5:η^1-(Cp′−P)]RhCO was treated with excess RX in CH_2Cl_2 at room temperature. [b] Isolated yield. [c] The ratio was determined by ^{1}H NMR and/or ^{31}P NMR of the reaction mixture. [d] 86% de. [e] The ratio of the product obtained from **4c**-major.

carbonyl complex having the Cp′−P ligand of the second generation, [η^5:η^1-(Ind−P)$_{n=2}$]RhCO, gave the corresponding acyl complex with lower diastereoselectivity (34% de).[2d] Both indenyl-based chiralirty and stereogenic centers of a substituent of the indenyl group are essential factors for inducing the high stereoselectivity around the metal in the oxidative addition.

Reaction of **4c** with 86% de (**4c**-major:**4c**-minor = 93:7) with MeI under the same conditions gave the acyl complex [η^5:η^1-{3-(NM)Ind−P}$_{n=2}$]RhI(COMe) (**5c**) in 95% yield (run 5). From the ^{31}P NMR of the reaction mixture, **5c** was found to contain four diastereomers (two sets of the diastereomers were produced from **4c**-major and **4c**-minor, respectively). The ratio of the diastereomers derived from **4c**-major (**5c**-major) was 96:4, and that from **4c**-minor (**5c**-minor) was ca. 82:18.[16] After purification by silica gel column chromatography, **5c**-major with 92% de was isolated in 75% yield. Reaction of the complex **5c**-major (92% de) with $AgPF_6$ in CH_2Cl_2 at room temperature for 2 h gave the cationic complex **6** in 87% yield with 92% de (eq 1). The ratio of



5c-major 92% de **6** 92% de

the diastereomers was much the same before and after the reaction, indicating that the stereospecific retromigratory insertion of CO proceeded.[17] Now we are investigating the application of the optically active complex shown in this paper to new stereospecific or asymmetric catalytic reactions.

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Supporting Information Available: Text giving synthetic procedures and spectroscopic and analytical data for all new compounds and text and tables giving X-ray structural information on **4a**-major and **4b**-minor. The material is available free of charge via the Internet at http://pubs.acs.org.

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(15) The chirality symbol with subscript "pl" indicates planar chirality, and that with subscript "Rh" means the chirality around the metal center.

(16) The integral value of the minor product derived from **5c**-minor contained errors to some extent.

(17) From the separate experiments using (R^*_{pl},R^*_{Rh})-[η^5:η^1-(Ind−P)$_{n=2}$]RhI(COMe), we have elucidated that the methyl group migrated from the acyl group to the Rh.[18] Thus, the structure of the major isomer of **6** will be shown as in eq 1.

(18) Unpublished results.