Construction of Metal-Centered Chirality: Diastereoselective Addition of the Meerwein Reagent (Me_3OBF_4) to Rhodium Carbonyl Complexes Having the Cp′-P Ligand

Yasutaka Kataoka,*,† Yousuke Nakagawa,† Atsushi Shibahara,† Tsuneaki Yamagata,† Kazushi Mashima,† and Kazuhide Tani‡

Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan, and Higashiosaka University, Higashiosaka, Osaka 577-8567, Japan

Received December 15, 2003

Reaction of the rhodium(I) carbonyl complexes [η^5:η^1-{3-(R)Ind-P}$_{n=2}$]Rh(CO) (**1**; R = H (**a**), Et (**b**), Cy (**c**), (1′*S*,2′*S*,5′*R*)-neomenthyl (NM) (**d**), (1′*R*,2′*R*,5′*R*)-neoisomenthyl (NIM) (**e**)) with the Meerwein reagent (Me_3OBF_4) afforded the cationic rhodium(III) complexes [[η^5:η^1-{3-(R)Ind-P}$_{n=2}$]RhMe(CO)]BF_4, having metal-centered chirality, in good to excellent yields. When a bulkier substituent (R) was used, the corresponding cationic complex was obtained with higher diastereoselectivity. In the case of using an optically active substituent such as NM or NIM, complete stereodiscrimination around the rhodium center by the Meerwein reagent occurred to give the cationic complexes with 100% de.

Introduction

A three-legged piano-stool complex, Cp′$ML_1L_2L_3$ (Cp′ = cyclopentadienyl derivatives, M = metal, L_n = ligand), has a stereogenic center on the central metal, if all ligands are different. So far, several examples of asymmetric reactions catalyzed by such optically active Cp′$ML_1L_2L_3$-type complexes have been reported,[1] but it is too much to declare that their progress reaches the level of asymmetric reactions accomplished by organometallic catalysts having chiral ligands.[2] One reason is that easy and convenient methods for the preparation of the optically active complexes that are configurationally stable at the chiral center on the metal have not been established.[3]

Cp′-P denotes a "linked cyclopentadienyl and phosphine ligand" in which a cyclopentadienyl derivative and a tertiary phosphine group are connected by an appropriate spacer. The syntheses, reactivities, and catalytic activities of transition-metal complexes bearing the Cp′-P ligand recently have received much attention.[4−15] We also have been interested in such ligands and designed several types of Cp′-P ligands.[16] A Cp′-P ligand having an indenyl group as the cyclopentadienyl derivative part, which is called the Ind-P ligand here, generates planar chirality on the indenyl ring upon coordination to the metal. We demonstrated that the planar chirality was very effective for controlling the central chirality arising at the metal in the oxidative addition of alkyl halide to the Rh(I) carbonyl complex.[16c,d] Later, we also reported that the stereogenic center at the metal controlled by the Ind-P ligand was very stable through the stereospecific addition of alkynes to Rh(III) methyl complexes and the stereospecific migration of a methyl group between cationic Rh(III) methyl complexes and Rh(III) acyl complexes.[16e,f] These observations suggest

† Osaka University.

‡ Higashiosaka University.

(1) For a recent review, see: Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1195.

(2) *Asymmetric Catalysis in Organic Synthesis*; Noyori, R., Ed.; Wiley: New York, 1994. *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*; Jacqueline, S.-P., Ed.; Wiley: New York, 1995. *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfalts, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999. *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley: New York, 2000.

(3) (a) Brunner, H.; Zwack, T. *Organometallics* **2000**, *19*, 2423. (b) Pfeffer, M. *Organometallics* **2000**, *19*, 2427. (c) Brunner, H. *Eur. J. Inorg. Chem.* **2001**, 905.

(4) For a recent review on cyclopentadienylmetal complexes bearing tethered P-donor ligands, see: Butenschön, H. *Chem. Rev.* **2000**, *100*, 1527.

(5) (a) Foerstner, J. Kakoschke, A.; Wartchow, R.; Butenschön, H. *Organometallics* **2000**, *19*, 2108. (b) Foerstner, J. Kakoschke, A.; Goddard, R.; Rust, J.; Wartchow, R.; Butenschön, H. *J. Organomet. Chem.* **2001**, *617*, 412. (c) Yong, L.; Butenschön, H. *Chem. Commun*, **2002**, 2852. (d) Kakoschke, A.; Yong, L.; Wartchow, R.; Butenschön, H. *J. Organomet. Chem.* **2003**, *674*, 86.

(6) (a) Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Chem. Lett.* **2000**, 760. (b) Dodo, N.; Matsushima, Y.; Yno, M.; Onitsuka, K.; Takahashi, S. *J. Chem. Soc., Dalton Trans.* **2000**, 35. (c) Matsushima, Y.; Onitsuka, K.; Kondo, T.; Mitsudo, T.; Takahashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 10405. (d) Matsushima, Y.; Komatsuzaki, N.; Ajioka, Y.; Yamamoto, M.; Kikuchi, H.; Takata, Y.; Dodo, N.; Onitsuka, K.; Uno, M.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 527. (e) Onitsuka, K. Dodo, N.; Matsushima, Y.; Takahashi, S. *Chem. Commun.* **2001**, 521. (f) Onitsuka, K.; Ajioka, Y.; Matsushima, Y.; Takahashi, S. *Organometallics* **2001**, *20*, 3274. (g) Onitsuka, K.; Matsushima, Y.; Takahashi, S. *J. Synth. Org. Chem. Jpn.* **2002**, *60*, 752.

(7) (a) Klei, S. R.; Tilley, T. D.; Bergman, R. G. *Organometallics* **2002**, *21*, 4905. (b) Paisner, S. N.; Lavoie, G. G.; Bergman, R. G. *Inorg. Chim. Acta* **2002**, *334*, 253.

(8) (a) Ciruelos, S.; Englert, U.; Salzer, A.; Bolm, C.; Maischak, A. *Organometallics* **2000**, *19*, 2240. (b) Ciruelos, S.; Doppio, A.; Englert, U.; Salzer, A. *J. Organomet. Chem.* **2002**, *663*, 183. (c) Doppiu, A.; Englert, U.; Salzer, A. *Inorg. Chim. Acta* **2003**, *350*, 435.

(9) Kaulen, C.; Pala, C.; Hu, C.; Ganter, C. *Organometallics* **2001**, *20*, 1614.

(10) Brookings, D. C.; Harrison, S. A.; Whitby, R. J.; Crombie, B.; Jones, R. V. H. *Organometallics* **2001**, *20*. 4574.

(11) Ishiyama, T.; Nakazawa, H.; Miyoshi, K. *J. Organomet. Chem.* **2002**, *648*, 231.

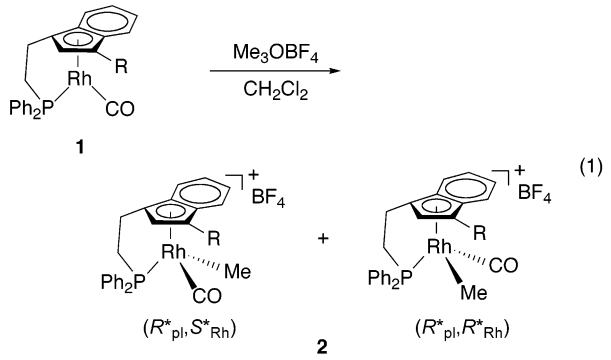
(12) Mayer, M. F.; Hossain, M. M. *J. Organomet. Chem.* **2002**, *654*, 202.

10.1021/om030688z CCC: $27.50
Publication on Web 03/26/2004

that optically active complexes having the Cp′-P ligand, in which configurational instability at the metal-centered chirality is prevented, might be useful for catalytic asymmetric reactions. Therefore, new convenient methodology for the preparation of complexes having metal-centered chirality is required.[17] Herein, we report another method for the generation of metal-centered chirality, in which diastereoselective addition of the Meerwein reagent (Me_3OBF_4) to rhodium carbonyl complexes having the Ind-P ligand provides cationic Rh(III) methyl complexes having a stereogenic center on the metal.

Results and Discussion

When the rhodium(I) carbonyl complex having the Ind-P ligand $\{\eta^5{:}\eta^1\text{-(Ind-P)}_{n=2}\}$Rh(CO) (**1a**) was treated with 1 equiv of the Meerwein reagent in CH_2Cl_2 at room temperature for 2 h, oxidative attack of the methyl group of the Meerwein reagent occurred to give the cationic rhodium(III) complex $[\{\eta^5{:}\eta^1\text{-(Ind-P)}_{n=2}\}$RhMe(CO)]$BF_4$ (**2a**) in 86% isolated yield (eq 1). We have



a: R = H; **b:** R = Et; **c:** R = Cy (C_6H_{11})

already prepared the same complex **2a** by the "$AgBF_4$ method", involving oxidative addition of MeI to **1a**, affording the acetyl rhodium(III) complex, $\{\eta^5{:}\eta^1$-(Ind-P)$_{n=2}\}$Rh(COMe)(I), followed by stereospecific migration of the methyl group by $AgBF_4$.[16c,f] The spectral and physical data of the complex obtained here were completely the same as those of **2a** prepared by the $AgBF_4$ method. The ^{31}P and ^{1}H NMR spectra of the reaction mixture before purification showed that **2a** was a mixture of two diastereomers (36% de, major:minor = 68:32), based on the difference in planar chirality on the indenyl ring and a stereogenic center on the metal. Each diastereomer of **2a** was configurationally very stable and did not epimerize at all after heating at 60 °C for 24 h in $CDCl_3$.[18] We reported that the relative configuration of the cationic complex **2a** was easily determined by the chemical shift of the methyl group attached directly to the rhodium.[16f] The methyl group located under the indene ring was shielded by the ring current of the benzene ring of the indenyl group, and the protons of the methyl group were shifted to upper field compared to that of the isomer. For example, the methyl signal of **2a**-major in the ^{1}H NMR spectrum appeared at δ −0.47 and that of **2a**-minor at δ 1.20, indicating that the relative configurations of **2a**-major and **2a**-minor were R^*_{pl},S^*_{Rh} and R^*_{pl},R^*_{Rh}, respectively.

Several substituents were easily introduced at the 3-position of the indenyl group of the Ind-P ligand. We named the ligand "the third generation of the Cp′-P ligand".[16d] We have prepared four kinds of the third generation of the Cp′-P ligand, $[\{3\text{-(R)Ind-P}\}_{n=2}]$H, with R = Et, Cy, 1′*S*,2′*S*,5′*R*-neomenthyl (NM), 1′*R*,2′*R*,5′*R*-neoisomenthyl (NIM).[19] Some representative results of the reaction of rhodium carbonyl complexes having the third generation of the Cp′-P ligand, $[\eta^5{:}\eta^1\text{-}\{3\text{-(R)Ind-P}\}_{n=2}]$Rh(CO), with the Meerwein reagent are shown in Table 1. When $[\eta^5{:}\eta^1\text{-}\{3\text{-(Et)Ind-P}\}_{n=2}]$Rh(CO) (**1b**), in which an ethyl group was attached to the indenyl ring, was used, the corresponding cationic complex **2b** was obtained quantitatively with 88% de (major:minor = 94:6) (entry 2).[18]

Recrystallization of a mixture of **2b**-major and **2b**-minor from ether and THF gave reddish orange single crystals of **2b**-major suitable for X-ray analysis. An ORTEP drawing and selected bond distances and angles are given in Figure 1, and relevant crystal and data parameters are presented in Table 2. The ORTEP drawing of **2b**-major showed that the relative configuration was R^*_{pl},S^*_{Rh} with the methyl group located under the indenyl ring, which was the same relative configuration as that of **2a**-major. The short length of the spacer (the ethylene group) causes distortion around the rhodium center. For example, the Cp−Rh−P angle (114.45°) was smaller than that (123.6°) in $[\{\eta^5{:}\eta^1\text{-(Ind-P)}_{n=3}\}$RhMe(CO)]$BF_4$ having a propylene group as a spacer.[16f,20] Similar distortion was also observed in other rhodium(I) and -(III) complexes having the Cp′-P ligand.[8a,10,21] Although the bond length of Rh−C(4) or Rh−C(5) was slightly longer than those of other bonds, the distortion of the indenyl ring toward η^3-coordination was not observed clearly, compared to that in rhodium complexes having the indenyl ligand.[10,22] The ^{1}H NMR data are consistent with the X-ray analysis. The ^{1}H NMR signal of the methyl group of **2b**-major appeared at δ −0.51, while that of **2b**-minor appeared at δ 1.11. From the fact that the methyl protons of **2b**-major were shifted to upper field compared to that of **2b**-minor, the major isomer was also assigned to R^*_{pl},S^*_{Rh} as the same

(13) McConnell, A. E. C.; Foster, D. F.; Pogorzelec, P.; Slawin, A. M. Z.; Law, D. J.; Cole-Hamilton, D. J. *Dalton* **2003**, 510.

(14) (a) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *Dalton* **2001**, 512. (b) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *Inorg. Chim. Acta* **2001**, *323*, 78. (c) Bellabarba, R. M.; Nieuwenhuyzen, M.; Saunders, G. C. *Organometallics* **2002**, *21*, 5726.

(15) Vogelgesang, J.; Frick, A.; Huttner, G.; Kircher, P. *Eur. J. Inorg. Chem.* **2001**, 949.

(16) (a) Kataoka, Y.; Saito, Y.; Nagata, K.; Kitamura, K.; Shibahara, A.; Tani, K. *Chem. Lett.* **1995**, 833. (b) Kataoka, Y.; Saito, Y.; Shibahara, A.; Tani, K. *Chem. Lett.* **1997**, 621. (c) Kataoka, Y.; Shibahara, A.; Saito, Y.; Yamagata, T.; Tani, K. *Organometallics* **1998**, *17*, 4338. (d) Kataoka, Y.; Iwato, Y.; Yamagata, T.; Tani, K. *Organometallics* **1999**, *18*, 5423. (e) Kataoka, Y.; Iwato, Y.; Shibahara, A.; Yamagata, T.; Tani, K. *Chem. Commun.* **2000**, 841. (f) Kataoka, Y.; Shibahara, A.; Yamagata, T.; Tani, K. *Organometallics* **2001**, *20*, 2431.

(17) For recent examples on the preparation of complexes having metal-centered chirality by using arene ligands bearing side chains, see: (a) Therrien, B.; Ward, T. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 405. (b) Therrien, B.; König, A.; Ward, T. R. *Organometallics* **1999**, *18*, 1565. (c) Faller, J. W.; D'Alliessi, D. G. *Organometallics* **2003**, *22*, 2749. (d) Marconi, G.; Baier, H.; Heinemann, F. W.; Pinto, P.; Pritzkow, H.; Zenneck, U. *Inorg. Chim. Acta* **2003**, *352*, 188. (e) Pinto, P.; Marconi, G.; Heinemann, F. W.; Zenneck, U. *Organometallics* **2004**, *23*, 374.

(18) The cationic complexes described in this paper are all configurationally rigid in solution. We did not observe any epimerization of the metal-centered chirality below 60 °C in $CDCl_3$.

(19) The third generation of the Cp′-P ligand could be prepared by a method similar to that described in our previous paper.[16d] A detailed procedure for the preparation of the ligand will be reported separately.

Table 1. Reaction of [η^5:η^1-{3-(R)Ind-P}$_{n=2}$]Rh(CO) (1) with Meerwein Reagent[a]

		cationic complex (**2**)					
					chemical shift of the Me group (δ_H, ppm)[e]		
entry	carbonyl complex (**1**)	yield (%)[b]	selectivity (% de)[c]	stereochemistry of the major isomer[d]	major	minor	selectivity by the "$AgBF_4$ method"[f] (% de)
1	**1a**	86	36	R^*_{pl},S^*_{Rh}	−0.47	1.20	36
2	**1b**	100	88	R^*_{pl},S^*_{Rh}	−0.51	1.11	66
3	**1c**	100	90	R^*_{pl},S^*_{Rh}	−0.51	1.14	76
4	**1d**-major (S_{pl})[g]	83[h]	100	S_{pl},R_{Rh}	−0.63		96
	1d-minor (R_{pl})[g]		100	R_{pl},S_{Rh}	−0.56		92
5	**1e**-major (R_{pl})[i]	87[j]	100	R_{pl},S_{Rh}	−0.48		92
	1e-minor (S_{pl})[i]		100	S_{pl},R_{Rh}	−0.68		74

[a] [η^5:η^1-{3-(R)Ind-P}$_{n=2}$]Rh(CO) (**1**) was treated with Meerwein reagent in CH_2Cl_2 at room temperature. [b] Isolated yield. [c] The ratio was determined by ^{31}P NMR of the reaction mixture. [d] The stereochemistry was determined by ^{1}H NMR and/or X-ray analyses. [e] Measured in $CDCl_3$ at 30 °C. [f] See the text; further details of this method will be reported separately. [g] A mixuure of (S_{pl})-**1d** and (R_{pl})-**1d** (66:34) was used. [h] Combined yield of the isolated acyl complex derived from **1d**-major and **1d**-minor. [i] A mixuure of (R_{pl})-**1e** and (S_{pl})-**1e** (85:15) was used. [j] Combined yield of the isolated acyl complex derived from **1e**-major and **1e**-minor.

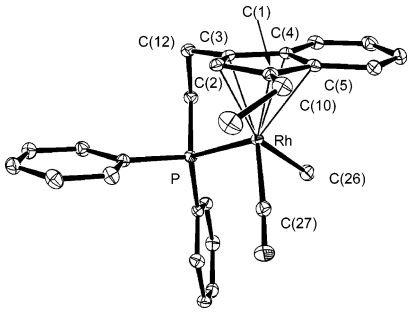


Figure 1. ORTEP drawing of the cationic part of (R^*_{pl},S^*_{Rh})-**2b** (**2b**-major). Selected bond lengths (Å): Rh−C1 = 2.2623(15), Rh−C2 = 2.2405(15), Rh−C3 = 2.1961(15), Rh−C4 = 2.3041(15), Rh−C5 = 2.3145(15), Rh−P = 2.2712(4), Rh−C26 = 2.1118(16), Rh−C27 = 1.8844(17). Selected bond angles (deg): C27−Rh−C26 = 86.14(7), C27−Rh−P = 101.31(5), C26−Rh−P = 86.44(5), Cp−Rh−P = 114.45, Cp−Rh−C26 = 121.80, Cp−Rh−C27 = 134.50. Cp is the gravimetric center of the cyclopentadienyl part of the indenyl group.

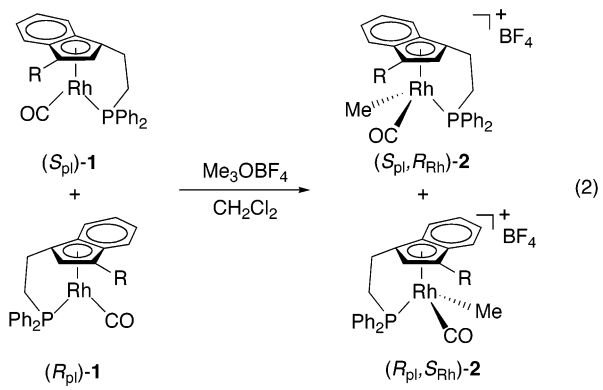
result as the X-ray analysis. Reaction of [η^5:η^1-{3-(Cy)-Ind-P}$_{n=2}$]Rh(CO) (**1c**) with the Meerwein reagent under the same conditions afforded [[η^5:η^1-{3-(Cy)Ind-P}$_{n=2}$]-RhMe(CO)]BF_4 (**2c**) quantitatively with 90% de (major:minor = 95:5) (entry 3).[18] Although we have not been able to succeed in obtaining an X-ray analysis of **2c** so far, the ^{1}H NMR spectrum, in which the chemical shift of the methyl group of the major isomer (δ −0.51) appeared at upper field compared to that of the minor isomer (δ 1.14), indicated that the relative configuration of the major isomer of **2c** was also R^*_{pl},S^*_{Rh}.

When an optically active substituent such as NM or NIM was introduced to the indenyl ring, the corresponding carbonyl complexes [η^5:η^1-{3-(NM)Ind-P}$_{n=2}$]-Rh(CO) (**1d**) and [η^5:η^1-{3-(NIM)Ind-P}$_{n=2}$]Rh(CO) (**1e**) formed as a mixture of two diastereomers due to a combination of the arising planar chirality and the stereogenic centers of the substituent. The absolute configuration of the major isomer of **1d** was determined to be S_{pl} by X-ray analysis.[16d] The absolute configuration of **1e**-major was determined to be R_{pl} by an X-ray analysis of the derivative complex of **1e** obtained by the stereospecific addition of 1-phenylpropyne to **2e**.[16e] In an analogous way, reaction of **1d** ((S_{pl})-**1d**:(R_{pl})-**1d** = 66:34) at room temperature afforded the cationic complex [[η^5:η^1-{3-(NM)Ind-P}$_{n=2}$]RhMe(CO)]BF_4 (**2d**) in 83% isolated yield. The ^{31}P NMR spectrum of the reaction mixture before purification showed only two doublet

Table 2. Crystal Data and Structure Refinement Details for (R^*_{pl},S^*_{Rh})-2b (2b-major)

empirical formula	$C_{27}H_{27}OBF_4PRh$
formula wt	588.18
temp, K	100(1)
wavelength, Å	0.710 69
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	
a, Å	15.14844(10)
b, Å	14.31749(13)
c, Å	15.22641(9)
β, deg	133.4424(2)
V, Å^3; Z	2397.78(3); 4
calcd density, Mg/m^3	1.629
abs coeff, mm^{-1}	0.830
F(000)	1192
cryst size, mm	0.23 × 0.13 × 0.11
θ range for data collecn, deg	2.76−31.50
limiting indices	$-22 \le h \le 22$, $-21 \le k \le 21$, $-22 \le l \le 22$
no. of rflns collected/unique	71 981/7988 (R_{int} = 0.0471)
completeness to θ = 31.50°, %	99.9
abs cor	numerical
max and min transmissn	0.9897 and 0.9672
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	7988/0/424
GOF on F^2	1.107
final R indices ($I > 2\sigma(I)$)	R1 = 0.0307, wR2 = 0.0550
R indices (all data)	R1 = 0.0404, wR2 = 0.0573
largest diff peak and hole, e Å^{-3}	0.478 and −0.695

signals at δ 71.9 (d, J = 148 Hz) and 72.1 (d, J = 147 Hz) in a 70:30 ratio,[18] indicating that **2d** consists of only two diastereomers though formation of four isomers (two isomers from each diastereomer of **1d**) is possible (eq 2). In the case of using **1d** with 90% de ((S_{pl})-**1d**:(R_{pl})-



(2)

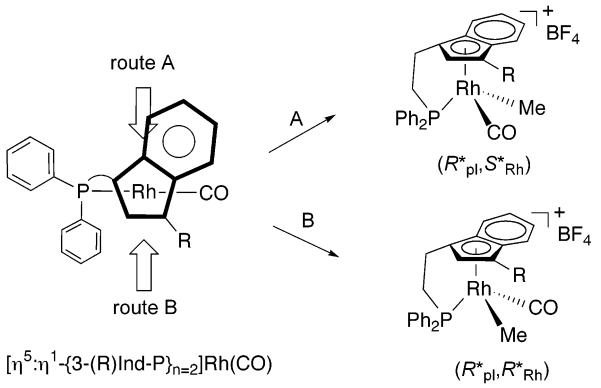


Figure 2.

1d = 5:95), **2d** was obtained as a mixture of two diastereomers in a 5:95 ratio. The diastereomer ratios of the carbonyl complex **1d** were almost the same as those of the cationic complex **2d**, indicating that both **1d**-major and **1d**-minor afford only a single isomer of the corresponding cationic complex. Although we have not determined the absolute configuration at the rhodium center in **2d** due to the lack of single crystals suitable for X-ray analysis, we can assume the absolute configuration from the chemical shift of the methyl group in the ^{1}H NMR spectrum. The methyl signal of the cationic complex in the ^{1}H NMR derived from (S_{pl})-**1d** appeared at δ −0.63 and that from (R_{pl})-**1d** at δ −0.56. The chemical shift of the methyl group which appeared around −0.5 ppm is characteristic of the methyl group affected by the phenyl ring current (see Table 1). Therefore, it is likely that the absolute configuration of the cationic complex derived from (S_{pl})-**1d** was S_{pl},R_{Rh} and that from (R_{pl})-**1d** was R_{pl},S_{Rh}, respectively (eq 2). A similar result was obtained in the case of using **1e** as the starting carbonyl complex. Reaction of **1e** with 70% de ((R_{pl})-**1e**:(S_{pl})-**1e** = 85:15) and **1e** with 92% de ((R_{pl})-**1e**:(S_{pl})-**1e** = 96:4) with the Meerwein reagent at room temperature in CH_2Cl_2 afforded the cationic complex **2e** in 72% de ((R_{pl},S_{Rh}):(S_{pl},R_{Rh}) = 86:14) and 92% de ((R_{pl},S_{Rh}):(S_{pl},R_{Rh}) = 96:4), respectively,[18] indicating that the methyl group added to the rhodium center in a completely stereodiscriminative manner. The relative relation between planar chirality and arising metal-centered chirality in **2d**,**e** was the same as that observed in **2a**−**c**.

Higher diastereoselectivity of the major isomer was obtained when bulkier substituents were introduced at the indenyl group in the Ind-P ligand, indicating that the methyl group of the Meerwein reagent approaches the rhodium center from a direction that avoids steric interaction between the substituent and the Meerwein reagent; that is, it adopts route A in Figure 2. Approach of the methyl group via route A results in the formation of the cationic complex with a R*$_{pl}$,S*$_{Rh}$ configuration, which is consistent with the relative configuration of all major isomers obtained in this procedure. In the case of using an optically active substituent such as NM and NIM, double stereodifferentiation occurs, due to induction by both the planar chirality and the stereogenic centers in the substituent.[23] By the $AgBF_4$ method, carbonyl complexes such as (S_{pl})-**1d** and (R_{pl})-**1e** were converted to the cationic complex with selectivities obviously higher than those from the complexes having opposite planar chirality, (R_{pl})-**1d** and (S_{pl})-**1e** (see Table 1). In particular, (S_{pl})-**1e** afforded the corresponding cationic complex with lower selectivity, indicating that two inductions by the planar chirality of *S* configuration and the stereogenic centers in NIM (1′*R*,2′*R*,5′*R*) counteract each other. On the other hand, the Meerwein method described here afforded the cationic complex under complete stereocontrol (entries 4 and 5 in Table 1). Steric hindrance arising from the bulkiness of the substituent in the Ind-P ligand would be effective to a great extent for stereodiscrimination of the Meerwein reagent around the rhodium center to prevent decrease of the selectivity by the competition between the two inductions.

In summary, we have developed a new method for the preparation of cationic rhodium(III) complexes having a stereogenic center on the metal by diastereoselective addition of the methyl group of the Meerwein reagent to rhodium(I) carbonyl complexes bearing the Ind-P ligand. Introduction of a bulkier substituent at the 3-position of the indenyl group in the Ind-P ligand was found to be crucial for the formation of cationic complexes with higher stereoselectivities.

Experimental Section

General Information. 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 instrument and are uncorrected. Infrared spectra were recorded on a JASCO FT/IR-230 instrument. Mass spectra were obtained on a JEOL JMS DX-303HF spectrometer. ^{1}H NMR spectra were recorded at either 270 MHz on a JEOL JNM-GSX270 or at 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 $CHCl_3$ resonance (δ 7.26). ^{31}P-{^{1}H} NMR spectra were recorded at either 109.25 MHz on a JEOL JNM-GSX270 or at 121.49 MHz on a Varian MERCURY 300 spectrometer, and the chemical shifts were referenced to external 85% H_3PO_4. Elemental analyses were recorded on a Perkin-Elmer 2400 instrument.

Dichloromethane was distilled from calcium hydride under argon prior to use, and other solvents for recrystallization were dried using standard procedures. The Ind-P ligands [{3-(R)-Ind-P}$_{n=2}$]H and their rhodium carbonyl complexes [η^5:η^1-{3-(R)Ind-P}$_{n=2}$]Rh(CO) (**1**) were prepared according to the published procedures.[16,19] The Meerwein reagent (Me_3OBF_4) was purchased from Tokyo Kasei Kogyo and used without further purification.

[{η^5:η^1-(Ind-P)$_{n=2}$}RhMe(CO)]BF$_4$ (2a).[16f] To a solution of {η^5:η^1-(Ind-P)$_{n=2}$Rh(CO) (**1a**; 42 mg, 0.092 mmol) in CH_2Cl_2 (5 mL) was added Me_3OBF_4 (14 mg, 0.095 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 2 h, and then the solvent was removed in vacuo to afford **2a** (36% de, (R*$_{pl}$,S*$_{Rh}$)-**2a**:(R*$_{pl}$,R*$_{Rh}$)-**2a**) = 68:32; the ratio

(20) Cp is the gravimetric center of the cyclopentadienyl part of the indenyl group in the Cp′-P ligand.

(21) (a) Lee, I.; Dahan, F.; Maisonnat, A.; Poilblanc, R. *Organometallics* **1994**, *13*, 2743. (b) Lee, I.; Dahan, F.; Maisonnat, A.; Poilblanc, R. *J. Organomet. Chem.* **1997**, *532*, 159. (c) Lefort, L.; Crane, T. W.; Farwell, M. D.; Baruch, D. M.; Kaeuper, J. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 3889.

(22) (a) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012. (b) Kakkar, A. K.; Taylor, N. J.; Calabrese, J. C.; Nugent, W. A.; Roe, D. C.; Connaway, E. A. Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 990.

(23) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.

was determined by ^{31}P NMR) as yellow powders. The residue was crystallized from THF and hexane to give **2a** as a yellow microcrystalline material (46 mg, 0.082 mmol, 86%, (R^*_{pl},S^*_{Rh})-**2a**:(R^*_{pl},R^*_{Rh})-**2a** = 68:32; the ratio was determined by ^{31}P NMR).

[{η^5:η^1-{3-(Et)Ind-P}$_{n=2}$RhMe(CO)}]BF$_4$ (2b). To a solution of [η^5:η^1-{3-(Et)Ind-P}$_{n=2}$]Rh(CO) (**1b**; 35 mg, 0.072 mmol) in CH_2Cl_2 (5 mL) was added Me_3OBF_4 (11 mg, 0.074 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 2 h, and then the solvent was removed in vacuo to afford **2b** (88% de, (R^*_{pl},S^*_{Rh})-**2b**:(R^*_{pl},R^*_{Rh})-**2b** = 89:11; the ratio was determined by ^{31}P NMR) as a brown powder. The residue was crystallized from THF and hexane to give **2b** as a yellow microcrystalline material (42 mg, 0.072 mmol, 100%, (R^*_{pl},S^*_{Rh})-**2b**:(R^*_{pl},R^*_{Rh})-**2b** = 94:6; the ratio was determined by ^{31}P NMR). Mp: 108−115 °C. ^{1}H NMR ($CDCl_3$): δ −0.51 (dd, J = 4.4, 1.6 Hz, 3H, RhCH_3, (R^*_{pl},S^*_{Rh})-**2b**), 1.11 (dd, J = 5.2, 2.2 Hz, 3H, RhCH_3, (R^*_{pl},R^*_{Rh})-**2b**), 1.42 (t, J = 7.4 Hz, 3H, −CH_2CH_3, (R^*_{pl},R^*_{Rh})-**2b**), 1.51 (t, J = 7.4 Hz, 3H, −CH_2CH_3, (R^*_{pl},S^*_{Rh})-**2b**), 2.42−2.62 (m, 1H, −CH_2−), 2.74−3.04 (m, 3H, −CH_2−), 3.66−3.82 (m, 1H, −CH_2−), 4.02−4.18 (m, 1H, −CH_2−), 5.96−6.00 (m, 1H, *Cp*, (R^*_{pl},S^*_{Rh})-**2b**), 6.18−6.20 (m, 1H, *Cp*, (R^*_{pl},R^*_{Rh})-**2b**), 7.20−7.40 (m, 3H), 7.36−7.54 (m, 5H), 7.52−7.68 (m, 4H), 7.69−7.83 (m, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 71.2 (d, J = 149 Hz, major), 68.8 (d, J = 141 Hz, minor). ^{13}C{^{1}H} NMR ($CDCl_3$, major): δ 184.4 (dd, J_{C-Rh} = 78 Hz, J_{C-P} = 12 Hz, *C*O), 1.70 (dd, J_{C-Rh} = 17 Hz, J_{C-P} = 4 Hz, Rh*C*H$_3$). IR (KBr, tablet, cm^{-1}): 2967, 2929, 2042 ($\nu_{C=O}$), 1675, 1646, 1436, 1084, 748, 694, 523. Anal. Calcd for $C_{27}H_{27}OPBF_4Rh$: C, 55.13; H, 4.63. Found: C, 54.58; H, 4.29.

[{η^5:η^1-{3-(Cy)Ind-P}$_{n=2}$RhMe(CO)}]BF$_4$ (2c). To a solution of [η^5:η^1-{3-(Cy)Ind-P}$_{n=2}$]Rh(CO) (**1c**; 53 mg, 0.098 mmol) in CH_2Cl_2 (5 mL) was added Me_3OBF_4 (16 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 2 h, and then the solvent was removed in vacuo to afford **2c** (90% de, (R^*_{pl},S^*_{Rh})-**2c**:(R^*_{pl},R^*_{Rh})-**2c** = 95:5; the ratio was determined by ^{31}P NMR) as an orange powder. The residue was crystallized from THF and hexane to give **2c** as an orange powder (63 mg, 0.098 mmol, 100%, (R^*_{pl},S^*_{Rh})-**2c**:(R^*_{pl},R^*_{Rh})-**2c** = 95:5; the ratio was determined by ^{31}P NMR). Mp: 132−138 °C. ^{1}H NMR ($CDCl_3$): δ −0.51 (dd, J = 4.4, 1.6 Hz, 3H, RhCH_3, (R^*_{pl},S^*_{Rh})-**2c**), 1.14 (dd, J = 5.8, 2.5 Hz, 3H, RhCH_3, (R^*_{pl},R^*_{Rh})-**2c**), 1.26−1.66 (m, 5H), 1.72−1.94 (m, 4H), 1.98−2.20 (m, 3H), 2.42−2.62 (m, 1H, −CH_2−), 2.78−2.90 (m, 1H), 2.92−3.22 (m, 1H, −CH_2−), 3.68−3.84 (m, 1H, −CH_2−), 4.08−4.24 (m, 1H, −CH_2−), 5.84−5.86 (m, 1H, *Cp*, (R^*_{pl},S^*_{Rh})-**2c**), 6.26−6.28 (m, 1H, *Cp*, (R^*_{pl},R^*_{Rh})-**2c**), 7.26−7.42 (m, 4H), 7.41−7.55 (m, 4H), 7.53−7.68 (m, 4H), 7.69−7.80 (m, 2H). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 71.1 (d, J = 149 Hz, (R^*_{pl},S^*_{Rh})-**2c**), 68.0 (d, J = 141 Hz, (R^*_{pl},R^*_{Rh})-**2c**). ^{13}C{^{1}H} NMR ($CDCl_3$, major): δ 184.8 (dd, J_{C-Rh} = 78 Hz, J_{C-P} = 12 Hz, Rh*C*O), 1.88 (dd, J_{C-Rh} = 17 Hz, J_{C-P} = 4 Hz, Rh*C*H$_3$). IR (KBr, tablet, cm^{-1}): 2927, 2852, 2038 ($\nu_{C=O}$), 1674, 1651, 1436, 1084, 753, 694, 523. MS (FAB): *m*/*z* 555 (M$^+$, cationic part) 527 (M$^+$ − CO), 512 (M$^+$ − CO − CH_3). Anal. Calcd for $C_{31}H_{33}OPBF_4Rh$: C, 57.97; H, 5.18. Found: C, 57.55; H, 5.08.

[{η^5:η^1-{3-(NM)Ind-P}$_{n=2}$RhMe(CO)}]BF$_4$ (2d). To a solution of [η^5:η^1-{3-(NM)Ind-P}$_{n=2}$]Rh(CO) (**1d**; 42 mg, 0.070 mmol, (S_{pl})-**1d**:(R_{pl})-**1d** = 66:34) in CH_2Cl_2 (5 mL) was added Me_3OBF_4 (12 mg, 0.081 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 2 h, and then the solvent was removed in vacuo to afford **2d** as a brown powder. The ^{31}P NMR spectrum of the reaction mixture showed two peaks at δ 71.9 (d, J = 148 Hz, $S_{pl,}R_{Rh}$) and 72.1 (d, J = 147 Hz, $R_{pl,}S_{Rh}$). The ratio of the two peaks was 70:30. The residue was crystallized from THF and hexane to give **2d** as a yellow powder (41 mg, 0.059 mmol, 83%, ($S_{pl,}R_{Rh}$)-**1d**:($R_{pl,}S_{Rh}$)-**1d** = 79:21; the ratio was determined by ^{31}P NMR). When the carbonyl complex **1d** in 90% de ((S_{pl})-**1d**:(R_{pl})-**1d** = 5:95) was used, the corresponding cationic complex **2d** was obtained in 86% de (($S_{pl,}R_{Rh}$)-**2d**:($R_{pl,}S_{Rh}$)-**2d** = 8:92). Mp (($S_{pl,}R_{Rh}$)-**2d**:($R_{pl,}S_{Rh}$)-**2d** = 8:92): 115−122 °C dec. ^{1}H NMR ($CDCl_3$): ($S_{pl,}R_{Rh}$)-**2d**, δ −0.63 (dd, J = 1.4, 4.1 Hz, 3H, RhCH_3), 0.48 (d, J = 6.6 Hz, 3H, CH_3), 0.68 (d, J = 6.6 Hz, 3H, CH_3), 0.74−1.32 (m, 2H), 1.09 (d, J = 5.8 Hz, 3H, CH_3), 1.38−2.16 (m, 2H), 1.62−1.82 (m, 4H), 2.34−2.58 (m, 2H), 2.94−3.26 (m, 1H), 3.38−3.46 (m, 1H), 3.68−3.86 (m, 1H), 4.10−4.28 (m, 1H), 5.74 (s, 1H), 7.18−7.30 (m, 4H), 7.32−7.46 (m, 2H), 7.46−7.64 (m, 5H), 7.62−7.84 (m, 3H); ($R_{pl,}S_{Rh}$)-**2d**, δ −0.56 (dd, J = 1.7, 4.1 Hz, 3H, RhCH_3), 0.67 (d, J = 6.3 Hz, 3H, CH_3), 0.84−1.04 (m, 1H), 1.08 (d, J = 6.5 Hz, 3H, CH_3), 1.12 (d, J = 6.3 Hz, 3H, CH_3), 1.34−1.50 (m, 3H), 1.68−2.00 (m, 4H), 2.20−2.34 (m, 1H), 2.34−2.58 (m, 1H), 2.94−3.24 (m, 1H), 3.70−3.84 (m, 1H), 3.68−3.86 (m, 1H), 4.10−4.28 (m, 1H), 5.59 (s, 1H), 7.18−7.26 (m, 4H), 7.24−7.46 (m, 2H), 7.40−7.66 (m, 5H), 7.64−7.82 (m, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 71.9 (d, J_{P-Rh} = 148 Hz, ($S_{pl,}R_{Rh}$)-**2d**), 72.1 (d, J_{P-Rh} = 149 Hz, ($R_{pl,}S_{Rh}$)-**2d**). IR (KBr, Nujol, cm^{-1}): 3050, 2038 ($\nu_{C=O}$), 1308, 1187, 1058, 755, 694, 523. MS (FAB): *m*/*z* 611 (M$^+$, cationic part), 596 (M$^+$ − CH_3). Anal. Calcd for $C_{35}H_{41}OPBF_4Rh$: C, 60.19; H, 5.92. Found: C, 59.88; H, 5.82.

[{η^5:η^1-{3-(NIM)Ind-P}$_{n=2}$RhMe(CO)}]BF$_4$ (2e). To a solution of [η^5:η^1-{3-(NIM)Ind-P}$_{n=2}$]Rh(CO) (**1e**; 49 mg, 0.082 mmol, (R_{pl})-**1e**:(S_{pl})-**1e** = 85:15) in CH_2Cl_2 (5 mL) was added Me_3OBF_4 (13 mg, 0.088 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 2 h and then the solvent was removed in vacuo to afford **2e** as a brown powder. The ^{31}P NMR spectrum of the reaction mixture showed two peaks at δ 70.4 (d, J = 148 Hz, ($S_{pl,}R_{Rh}$)-**2e**) and 71.0 (d, J = 147 Hz, ($R_{pl,}S_{Rh}$)-**2e**) along with small amounts of undefined peaks (less than 5%). The ratio of the two peaks was 14:86. The residue was crystallized from THF and hexane to give **2e** as a yellow powder (50 mg, 0.071 mmol, 87%, ($R_{pl,}S_{Rh}$)-**2e**:($S_{pl,}R_{Rh}$)-**2e** = 86:14; the ratio was determined by ^{31}P NMR). When the carbonyl complex **1e** in 92% de ((R_{pl})-**1e**:(S_{pl})-**1e** = 96:4) was used, the corresponding cationic complex **2e** was obtained in 92% de (($R_{pl,}S_{Rh}$)-**2e**:($S_{pl,}R_{Rh}$)-**2e** = 96:4). Mp: 110−112 °C dec. ^{1}H NMR ($CDCl_3$): δ −0.68 (m, 3H, RhCH_3, ($S_{pl,}R_{Rh}$)-**2e**), −0.48 (dd, J = 1.6, 4.7 Hz, 3H, RhCH_3, ($R_{pl,}S_{Rh}$)-**2e**), 0.36 (d, J = 6.6 Hz, 3H, CH_3), 0.87 (d, J = 5.8 Hz, 3H, CH_3), 1.14 (d, J = 6.0 Hz, 3H, CH_3), 1.22−1.34 (m, 2H), 1.46−1.97 (m, 5H), 1.92−2.14 (m, 2H), 2.41−2.63 (m, 1H), 2.99−3.30 (m, 1H), 3.31−3.44 (m, 1H), 3.70−3.92 (m, 1H), 4.10−4.32 (m, 1H), 5.73 (s, 1H, ($R_{pl,}S_{Rh}$)-**2e**), 6.12 (s, 1H, ($S_{pl,}R_{Rh}$)-**2e**), 7.24−7.51 (m, 7H), 7.54−7.70 (m, 5H), 7.76−7.88 (m, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 70.4 (d, J_{P-Rh} = 148 Hz, ($S_{pl,}R_{Rh}$)-**2e**), 71.0 (d, J_{P-Rh} = 148 Hz, ($R_{pl,}S_{Rh}$)-**2e**). ^{13}C{^{1}H} NMR ($CDCl_3$, ($R_{pl,}S_{Rh}$)-**2e**): δ 189.2 (dd, J_{C-Rh} = 79 Hz, J_{C-P} = 12 Hz, Rh*C*O). IR (KBr, Nujol, cm^{-1}): 3050, 2038, 1308, 1187, 1058, 755, 715, 694, 523. MS (FAB): *m*/*z* 611 (M$^+$, cationic part), 596 (M$^+$ − CH_3). Anal. Calcd for $C_{35}H_{41}OPBF_4Rh$: C, 60.19; H, 5.92. Found: C, 59.52; H, 5.88.

X-ray Structure Determination. Single crystals of **2b**-major, suitable for X-ray analysis, were obtained by recrystallization from ether and THF. Crystallographic data are collected in Table 2, and an ORTEP drawing is presented in Figure 1. Additional crystallographic data are available in the Supporting Information.

Acknowledgment. This work was supported in part by Grants-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

Supporting Information Available: Detailed crystallographic data, atomic positional parameters, and bond lengths and angles for **2b**-major. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030688Z