Stereoselective Synthesis of Both Enantiomers of Axially Chiral Biaryls Utilizing Planar Chiral Tricarbonyl(arene)chromium Complexes

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Tricarbonyl(2,6-disubstituted 1-bromobenzene)chromium complexes were treated with *ortho*-substituted arylboronic acids in the presence of Pd(0) catalyst to give mono $Cr(CO)_3$ complexes of biphenyl compounds with complementary axial chirality, with extremely high stereoselectively depending upon the steric bulkiness of the *ortho* substituents. Cross-coupling of *o*-alkyl- or hydroxymethyl-substituted phenylboronic acids with (arene)chromium complexes diastereoselectively gave $Cr(CO)_3$-complexed biaryls in which the *ortho* substituents are in a *syn*-orientation to the tricarbonylchromium fragment. With *o*-formyl phenylboronic acids, diastereoisomeric *anti*-coupling products were stereoselectively obtained. The kinetically controlled coupling products were easily isomerized to thermodynamically more stable mono-$Cr(CO)_3$-complexed biaryls by modification of the *o*-substituents to less hindered ones, or the thermal conditions assisted the axial isomerization. The overall process can be considered to be an enantioselective preparation of both axially chiral biaryls starting from a single planar chiral (arene)chromium complex.

Introduction

Biaryl compounds with axial chirality are of potential importance not only as chiral ligands for asymmetric reactions but also as intermediates for the synthesis of biologically active natural products, e.g., steganacin, vancomycin, and the naphthyltetrahydroisoquinoline alkaloids. There is considerable current interest in the development of efficient methodologies for the synthesis of biaryls as their various atropisomers in enantiomerically pure form.[1] The nucleophilic displacement of an *o*-methoxy group from a chiral aryloxazoline by an aryl Grignard reagent has been widely employed in asymmetric biaryl syntheses.[2] Very high atropisomeric excess is generally obtained with aromatic compounds in which the substituents adjacent to the coupling position are of very different size. A decisive influence by metal cation on stereoselection in this nucleophilic substitution is suggested. A copper-mediated Ullmann homocoupling reaction has recently been observed to effect the biaryl coupling of the chiral *o*-bromophenyloxazolines giving diastereomerically pure bis-oxazolines.[3] Nucleophilic aromatic substitution on the arene ring activated with other functional groups, e.g., ester, imine, has also been accomplished in the preparation of chiral biaryl compounds.[4] For an intramolecular aryl coupling reaction[5] giving lignans and related compounds, the bridge, which contains the chiral fragment, is not only a constituent of the target molecule but also determines the steric course of the coupling reaction. Cyanocuprate-mediated biaryl intramolecular coupling of a tethered nonracemic chiral compound has also been reported.[6] Atropenantioselective biaryl synthesis has been even more uniquely achieved by the stereocontrolled torsion of completely flat, achiral lactone precursors by means of optically active ring-opening nucleophiles.[7] Other interesting methods, including catalytic asymmetric coupling,[8] have been reported to provide biaryls in optically active form.

(η^6-Disubstituted arene)chromium complexes exist in two enantiomeric forms, based on planar chirality, when the arene ring is substituted at the *ortho*- or *meta*-positions with different substituents. This fact, in concert with the ability of the tricarbonylchromium function to effectively block one face of the arene ring, has led to a rapid increase in the use of (arene)chromium complexes as synthetic intermediates and as catalysts for asymmetric reactions.[9] The mono-$Cr(CO)_3$ complexes of biphenyl compounds with hindered rotation about the central bond have both axial and planar chiralities. We wish to report our results of palladium(0)-catalyzed

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intermolecular cross-coupling reactions that give the mono-$Cr(CO)_3$-complexed biaryls, whose axial stereochemistry is dependent upon the steric bulkiness of the *ortho* substituents of the (arene)chromium complexes and phenylboronic acids.

Results and Discussion

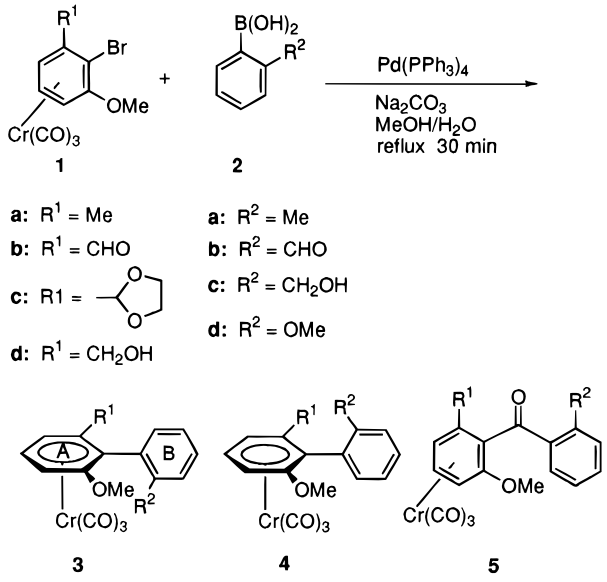
Diastereoselective Suzuki−Miyaura Cross-Coupling of (Arene)$Cr(CO)_3$ with Arylboronic Acids. Cross-coupling reactions of aryl halides or aryl triflates with arylmetals catalyzed by palladium(0) are commonly used for the preparation of biphenyl compounds.[10] For the efficient preparation of mono-$Cr(CO)_3$-complexed biaryls, we have devised[11] two connecting cross-coupling methods for (arene)chromium complexes and other aryl compounds: (A) the coupling of an (*arylmetal*)$Cr(CO)_3$ with an aryl halide and (B) the coupling of an (*aryl halide*)$Cr(CO)_3$ with an arylmetal. An oxidative addition of the carbon−halogen bond of the aryl halide to the palladium(0) is accelerated by coordination of an electron-withdrawing tricarbonylchromium group to the arene.[12] Even chlorobenzene can be made susceptible to oxidative addition by utilizing the corresponding tricarbonylchromium complex to give cross-coupling products. In particular, method B was found to give mono-$Cr(CO)_3$ complexes of *ortho*-substituted biphenyls in good yields.[11] Thus, the cross-coupling of tricarbonylchromium complexes of *o*-substituted halobenzene with phenylmetals such as phenylboronic acid, Grignard reagent, and phenylzinc chloride, in the presence of palladium(0) catalyst, afforded the hetero-cross-coupling products in good yields. However, method A proved unsatisfactory. Thus, (*arylmetal*)$Cr(CO)_3$ complexes (metal; MgBr, ZnCl, $B(OH)_2$, $SnBu_3$) were treated with bromobenzene in the presence of palladium(0) catalyst and gave (demetalated arene)-$Cr(CO)_3$ as the major product along with a small amount of coupling products.

Table 1. Palladium(0)-Catalyzed Cross-Coupling of (Arene)chromium Complexes 1 with Phenylboronic Acids 2

entry	complex	phenylboronic acid	R^1	R^2	ratio **3**:**4**:**5**	yield (%)
1	**1a**	**2a**	Me	Me	100:0:0	96
2	**1b**	**2a**	CHO	Me	92:0:8	89
3	**1c**	**2a**	$CHO(CH_2)_2O$	Me	100:0:0	81
4	**1d**	**2a**	CH_2OH	Me	100:0:0	77
5	**1a**	**2b**	Me	CHO	0:100:0	95
6	**1b**	**2b**	CHO	CHO	0:100:0	43
7	**1c**	**2b**	$CHO(CH_2)_2O$	CHO	0:100:0	52
8	**1a**	**2c**	Me	CH_2OH	81:0:19	68
9[a]	**1c**	**2c**	$CHO(CH_2)_2O$	CH_2OH	0:0:100	40
10	**1a**	**2d**	Me	OMe	97:3:0	94
11	**1b**	**2d**	CHO	OMe	4:96:0	85
12	**1d**	**2d**	CH_2OH	OMe	94:6:0	90

[a] De-tricarbonylchromium product derived from **3** was obtained in 29% yield.

Scheme 1



We examined the axial stereochemistry in the cross-coupling reaction of tricarbonyl(*aryl halide*)chromium complexes with arylboronic acids in the presence of Pd(0) catalyst. Tricarbonyl(2-methoxy-6-methyl-1-bromobenzene)chromium (**1a**) was allowed to react with *o*-methylphenylboronic acid (**2a**) catalyzed by 5 mol % of $Pd(PPh_3)_4$ in the presence of sodium carbonate in aqueous methanol at 75 °C to give cross-coupling product **3** ($R^1 = R^2 = Me$) in 96% yield with no formation of the corresponding atropisomer (Scheme 1, Table 1).[13] The stereochemistry of the coupling product **3** ($R^1 = R^2 = Me$) was determined to be the (*S**,*S**)-configuration[14] by comparison with an authentic sample derived from a stereodefined complex **3** ($R^1 = CH_2OAc$, $R^2 = Me$), whose configuration was determined by X-ray crystallography.[15] The methyl group on the *B*-ring of complex **3** is directed

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(14) The first symbol indicates a configuration of planar chirality of the chromium complexed arene ring (at C-1 position), and the second one represents the axial chirality. The symbol * shows racemate, and only one enantiomer is shown for clarity.

toward the tricarbonylchromium fragment of the chromium-complexed *A*-ring in spite of a severe steric interaction between the methyl and $Cr(CO)_3$ groups. Similarly, the cross-coupling reaction of *o*-methylphenylboronic acid (**2a**) with other chromium complexes **1b**, **1c**, and **1d** (R = CHO, $\overline{CHO(CH_2)_2O}$, CH_2OH) gave the products **3** with the same axial chirality (Table 1, entries 2−4). With *o*-methoxyphenylboronic acid (**2d**), the axial stereochemistry of the coupling products was dependent upon the steric bulkiness of the *ortho* substituents of the (arene)chromium complex **1**. Thus, the coupling of chromium complexes **1a** and **1d**, possessing methyl or hydroxymethyl as the R^1 substituent, with **2d** produced the (*S**,*S**)-complexes **3** as the major product along with a small amount of the diastereomeric compounds **4** (Table 1, entries 10 and 12). However, the complex **1b**, bearing a formyl group, reacted with **2d** to give the diastereoisomeric (*S**,*R**)-complex **4** (R^1 = CHO, R^2 = OMe) as the major product (Table 1, entry 11). On the other hand, the cross-coupling of *o*-formylphenylboronic acid (**2b**) with chromium complexes **1a**−**c** gave the diastereoisomeric (*S**,*R**)-chromium complexes **4** (R^2 = CHO) as the only isolated coupling products regardless of the *ortho* substituents on the (arene)chromium complexes **1** (Table 1, entries 5−7). The formation of (*S**,*R**)-products can be attributed to a thermodynamically controlled reaction *via* an axial isomerization of the initially formed (*S**,*S**)-products (*vide infra*). The coupling of *o*-(hydroxymethyl)-phenylboronic acid (**2c**)[16] with (arene)chromium complexes **1** gave the (*S**,*S**)-biphenylchromium complex **3** and CO-inserted product **5** in various ratios depending upon the *ortho* substituents of the chromium complexes (Table 1, entries 8 and 9). Thus, reaction of (2-methoxy-6-methyl-1-bromobenzene)$Cr(CO)_3$ (**1a**) with **2c** produced the (*S**,*S**)-coupling product **3** as the major product, whereas the coupling with 1,3-dioxolane complex **1c** afforded CO-inserted compound **5** without formation of mono-$Cr(CO)_3$-complexed biphenyl (Table 1, entry 9). The formation of CO inserted products **5** was suppressed by the use of other palladium catalysts or higher reaction temperature.[17] It is obvious from the above results that the axial stereochemistry of the coupling products is strictly controlled by the steric bulkiness of the *ortho* substituents adjacent to the coupling positions.

Next, the axial stereochemistry of mono-$Cr(CO)_3$-complexed biphenyls derived from the cross-coupling of tricarbonyl(*ortho*-substituted bromobenzene)chromium complexes with 2,6-disubstituted phenylboronic acid was examined (Scheme 2). The cross-coupling of tricarbonyl-(2-methyl-1-bromobenzene)chromium (**6**, R = Me) with 2-methoxy-6-[(methoxymethoxy)methyl]phenylboronic acid (**7**) under the same conditions gave the (*S**,*R**)[14]-complex **8** (R = Me) and diastereomeric (*S**,*S**)-complex **9** (R = Me) in a ratio of 94:6, in 77% yield (Table 2). With (*o*-methoxybromobenzene)$Cr(CO)_3$ (**6**) (R = OMe), the reaction was performed in DME with aqueous barium hydroxide giving coupling products **8**, **9**, and CO inserted complex **10** in a ratio of 55:22:23. However, the coupling of 2-bromobenzaldehyde chromium complex (**6**) (R = CHO) with **7** gave the corresponding benzophenone chromium complex **10** in 40% yield and debrominated product tricarbonyl(benzaldehyde)chromium in 52% yield without formation of the biphenyl coupling products. The axial configuration of the major coupling products shows that the sterically hindered *ortho* substituent of the chromium uncomplexed arene ring of the biphenyl is *syn* to the $Cr(CO)_3$ group. Also, it was found that the cross-coupling of (2,6-disubstituted aryl halide)$Cr(CO)_3$ with *o*-monosubstituted phenylboronic acids gives the coupling products in good yields (Scheme 1), while the reaction of (*o*-monosubstituted aryl halide)$Cr(CO)_3$ with 2,6-disubstituted arylboronic acids results in a lower yield of the coupling products (Scheme 2). The lower yield in the latter coupling would be attributed to lower propensity for displacement of the *o*-disubstituted arylboronic acids, in a transmetalation step on the palladium(II) intermediates, due to steric effects.

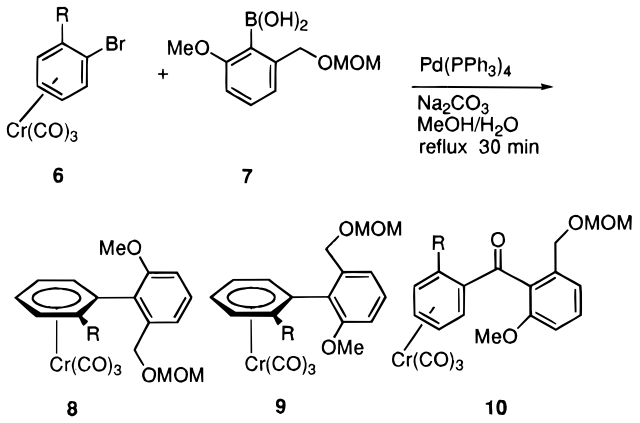
We further studied the cross-coupling of (arene)$Cr(CO)_3$ complexes with naphthylboronic acids, as directed toward the total synthesis of naphthyltetrahydroisoquinoline alkaloids.[18] The (2-methoxy-6-methyl-1-bromobenzene)-$Cr(CO)_3$ (**11**) (R^1 = OMe, R^2 = Me) reacted with 1-naphthylboronic acid (**12**) (R^3 = H) to give the (*S**,*S**)-coupling product **13** (R^1 = OMe, R^2 = Me, R^3 = H) in 88% yield without formation of the diastereomeric product **14** under the same conditions (Scheme 3, Table 3). The NMR

Table 2. Cross-Coupling of Complex 6 with Arylboronic Acid 7

entry	R	conditions	ratio of **8**:**9**:**10**	yield (%)
1	Me	Na_2CO_3/MeOH/H_2O	94:6:0	77
2	OMe	$Ba(OH)_2$/DME/H_2O	55:22:23	86
3[a]	CHO	Na_2CO_3/MeOH/H_2O	0:0:100	40

[a] Tricarbonyl(benzaldehyde)chromium was obtained in 52% yield.

Scheme 2



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(16) Compound **2c** adopted a dehydrated structure, 1,3-dihydro-2,1-benzoxaborol-1-ol: Brown, A. G.; Crimmin, M. J.; Edwards, P. D. *J. Chem. Soc., Perkin Trans. 1* **1992**, 123.

(17) (a) Cross-coupling of **1b** with **2a** at rt gave a 1:1 mixture of CO-inserted product and the coupling product in 28% yield, together with 46% of the starting arenechromium complex, but at higher reaction temperature (75 °C) gave the coupling product **3** as the major product (see Table 1, entry 2). Reaction of complex **1c** with phenylboronic acid **2c** catalyzed by $Pd_2(dba)_3{\cdot}CHCl_3$ produced the de-$Cr(CO)_3$ product of **3** (52%) without formation of CO-insertion product **5**. (b) A recent paper reports that Stille-type palladium-catalyzed reaction of (trialkylstannylbenzene)$Cr(CO)_3$ complexes with iodobenzene gave carbonyl-insertion products. Caldirola, P.; Chowdhury, R.; Johansson, A. M.; Hacksell, U. *Organometallics* **1995**, *14*, 3897.

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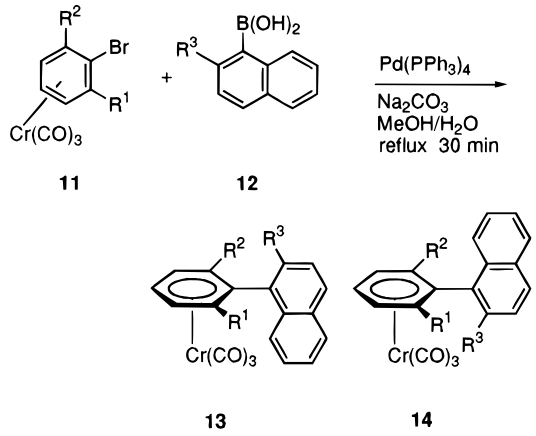
Table 3. Cross-Coupling of Complex 11 with Naphthylboronic Acid 12

entry	complex **11**	naphthylboronic acid **12**	ratio **13**:**14**	yield (%)
1	R^1 = OMe, R^2 = Me	R^3 = H	100:0	88
2	R^1 = OMe, R^2 = CHO	R^3 = H	100:0	89
3	R^1 = OMe, R^2 = CH_2OH	R^3 = H	100:0	86
4	R^1 = OMe, R^2 = $\overline{CHO(CH_2)_2O}$	R^3 = H	100:0	85
5	R^1 = Me, R^2 = H	R^3 = Me	95:5	25[a]
6	R^1 = OMe, R^2 = H	R^3 = Me	71:29	71
7	R^1 = $\overline{CHO(CH_2)_2O}$, R^2 = H	R^3 = Me	100:0	57
8	R^1 = Me, R^2 = H	R^3 = OMe	97:3	78

[a] Yield increased to 70% (ratio of **13**:**14** = 85:15) by using the following conditions: $Pd(dba)_2$ (5 mol %), PPh_3 (20 mol %), TlOH (2 equiv) in DME/H_2O. Reflux for 30 min.

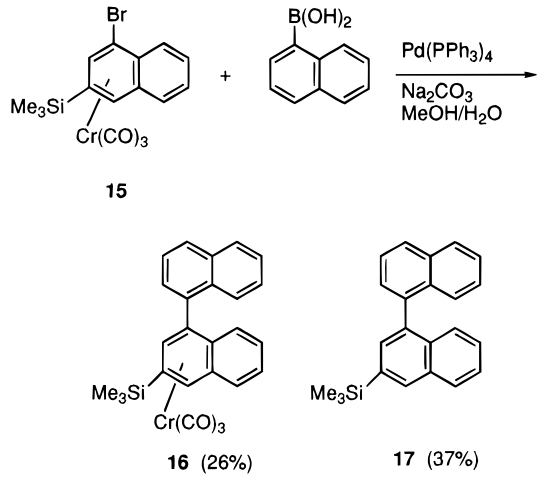
Scheme 3



signal of the proton *peri*- to the linkage position of the naphthalene appeared characteristically at lower field (9.30 ppm). The axial structure was confirmed by X-ray crystallography of **13** (R^1 = OMe, R^2 = CH_2OAc, R^3 = H).[19] Similarly, the other chromium complexes of 2,6-disubstituted 1-bromobenzene with 1-naphthylboronic acid gave stereoselectively the (*S**,*S**)-coupling products **13**.[20] The coupling products of (2-substituted bromobenzene)chromium complexes with 2-substituted 1-naphthylboronic acids were obtained as a diastereomeric mixture (Table 3, entries 5, 6, and 8). The formation of axially diastereomeric mono-$Cr(CO)_3$-complexed biaryls **14** might be attributed to a thermodynamically-controlled reaction *via* an axial isomerization (*vide infra*). In any case, the major coupling products have the axial configuration where the larger substituent next to the biaryl axis is in a *syn* orientation to the $Cr(CO)_3$ fragment.

Finally, we examined the coupling reaction of (naphthalene)$Cr(CO)_3$ with naphthylboronic acid for the preparation of axially chiral binaphthyls. Tricarbonyl[(1,2,3,4,5,6-η)-1-bromo-3-(trimethylsilyl)naphthalene]chromium (**15**) was prepared by repeated regioselective lithiation of (naphthalene)$Cr(CO)_3$ according to the literature procedure.[21] The cross-coupling of **15** with

Scheme 4



1-naphthylboronic acid under the same conditions gave a mono-$Cr(CO)_3$-complex of binapthyl **16** and detricarbonylchromium binaphthyl compound **17** in 26% and 37% yields, respectively (Scheme 4). Formation of **17** as the major coupling product presents a serious problem with respect to the axial chirality of binaphthyl compounds. (Naphthlane)$Cr(CO)_3$ is labile to thermal conditions and used for ligand transfer[22] of a $Cr(CO)_3$ fragment to other arene compounds due to the ready departure of $Cr(CO)_3$ upon interaction of another coordination ligand. If decomplexed free arene is formed prior to the coupling with naphthylboronic acid, the binapthyl coupling compounds could be obtained in racemic form since the planar chirality of (arene)chromium complexes is lost. In consideration of this result, we have been actively investigating a new method for the preparation of optically active binaphthyls utilizing planarly chiral (arene)-chromium complexes.

Axial Isomerization of Mono-$Cr(CO)_3$-Complexed Biaryls. In many biaryls, bulky *ortho* substituents adjacent to the central bond hinder free rotation around the biaryl axis. But axial isomerization takes place in some biphenyls with three *ortho* substituents, giving racemic compounds.[23] Since the mono $Cr(CO)_3$ complexes of biaryls have both axial and planar chiralities, the chromium-complexed biaryls can exist in an enantiomeric form based on the planar chirality even when the central bond rotates. Therefore, both enantiomerically pure biaryls with axial chirality could be obtainable by the cross-coupling and subsequent central bond rotation, starting from a single planarly chiral (arene)chromium complex. We investigated the axial isomerization of the chromium complexed biaryls by the following two procedures: (1) modification of both the *ortho* substituent to one less hindering and (2) the thermal conditions to assist the central bond isomerization. (*S**,*S**)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′-(hydroxymethyl)-6-methylbiphenyl]chromium (**18**) (R = Me), obtained by the palladium(0)-catalyzed cross-coupling, was oxidized[24] with DMSO/Ac_2O at room temperature to give the (*S**,*R**)-tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′-formyl-6-methylbiphenyl]chromium (**19**) (R = Me) in 53% yield by

(19) Crystal structure data: formula = $C_{23}H_{18}O_6Cr$, FW = 442.39, monoclinic, space group $P2_{1/c}$, a = 15.504(2) Å, b = 9.228(2) Å, c = 15.746(2) Å, β = 115.219(9)°, V = 2038.0(7) Å^3, Z = 4, D_{calc} = 1.442 g cm^{-3}. The authors have deposited atomic coordinates for the structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(20) A preliminary report: Watanabe, T.; Kamikawa, K.; Uemura, M. *Tetrahedron Lett.* **1995**, *36*, 6695.

(21) Kündig, E. P.; Desobry, V.; Grivet, C.; Rudolph, B.; Spichiger, S. *Organometallics* **1987**, *6*, 1173.

(22) (a) Kündig, E. P.; Perret, C.; Spichinger, S. J. *J. Organomet. Chem.* **1985**, *286*, 183. (b) Uemura, M.; Kobayashi, T.; Isobe, K.; Minami, T.; Hayashi, Y. *J. Org. Chem.* **1986**, *51*, 2859.

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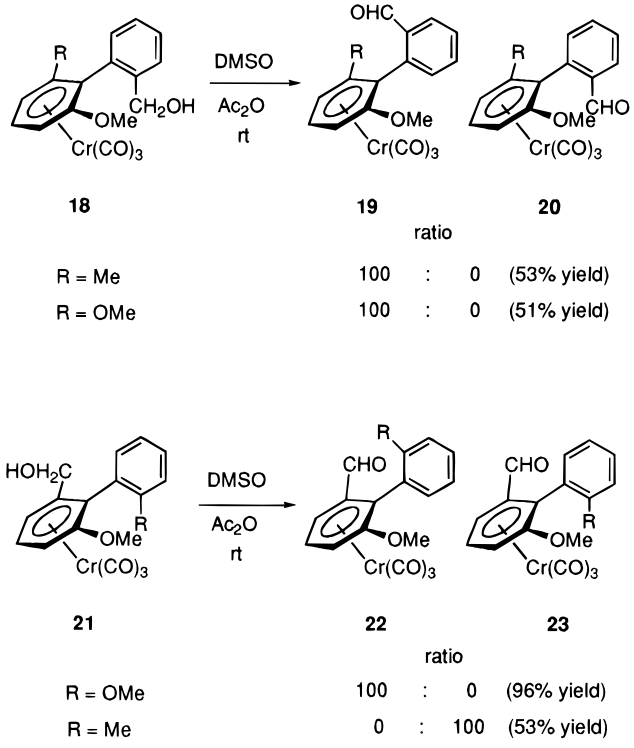
(24) Levine, S. G.; Gopalakrishnan, B. *Tetrahedron Lett.* **1982**, *23*, 1239.

Scheme 5. Axial Isomerization by Oxidation of Alcohol



the complete axial bond rotation of the initially produced (*S**,*S**)-product **20** (Scheme 5). The axial stereochemistry of the $Cr(CO)_3$-complexed biphenyls can be easily identified by ^1H NMR analysis, as follows. The proton NMR signal for CH_2OH of the (*S**,*S**)-complex **18** (R = Me) appeared at 5.13 and 5.21 ppm as a double doublet, while those of the (*S**,*R**)-isomer derived from reduction of **19** (R = Me) appeared at 4.41−4.42 ppm as multiplets. Generally, NMR signals of the protons *syn* to the $Cr(CO)_3$ fragment are shifted to far lower field than are those of the *anti* protons.[25] (*S**,*S**)-Dimethoxy compound **18** (R = OMe) was also isomerized to the corresponding (*S**,*R**)-complex **19** (R = OMe) by oxidation at room temperature. Similarly, the axial isomerization of another (*S**,*S**)-complex **21** (R = OMe) by oxidation of the alcohol under the same conditions gave the thermodynamically stable (*S**,*R**)-complex **22** (R = OMe). However, when the analogous methyl-substituted complex **21** (R = Me) was oxidized at room temperature, the (*S**,*S**)-complex **23** (R = Me) was obtained selectively probably due to steric hindrance preventing the axial bond rotation. But, the (*S**,*S**)-complex **23** (R = Me) was easily isomerized to the thermodynamically more stable (*S**,*R**)-isomer under thermal conditions (*vide infra*). Thus, some $Cr(CO)_3$ complexes of biphenyls are easily isomerized to the corresponding thermodynamically-stable, axially diastereisomeric complexes, as a result of having unbulky *o*-substituents. Also, these results indicate that the formation of (*S**,*R**)-biaryls in the cross-coupling reaction between *o*-formylphenylboronic acid and (*o*-substituted arene)chromium complexes is due to the isomerization of the initially formed (*S**,*S**)-biphenyls.

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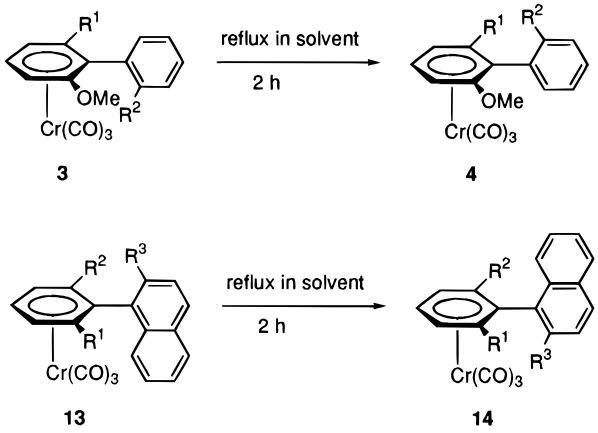
Scheme 6. Axial Isomerization under Thermal Conditions



Several $Cr(CO)_3$-complexed (*S**,*S**)-biaryls obtained by the palladium(0)-catalyzed cross-coupling reaction would be expected to isomerize to the thermodynamically more stable (*S**,*R**)-complexes upon refluxing in high boiling solvent (Scheme 6, Table 4).[26] When complex **3** (R^1 = CHO, R^2 = Me) in toluene was refluxed for 2 h, the axially isomerized biphenyl **4** (R^1 = CHO, R^2 = Me) was obtained along with a small amount of the starting material (ratio of 98:2). The ratio was easily determined by ^1H NMR analysis of the crude product. The methyl signal of the (*S**,*R**)-isomer **4** (R^1 = CHO, R^2 = Me) appeared at 2.09 ppm, while that of the corresponding (*S**,*S**)-isomer **3** was shifted to 2.62 ppm as mentioned above. No migration of the $Cr(CO)_3$ group to another arene ring or to solvent was observed during the isomerization. Refluxing of hindered complex **3** (R^1 = Me, R^2 = OMe) in toluene for 2 h gave a 58:42 mixture of the axially isomerized product and the starting material. Although this isomerization was incomplete under conditions of refluxing toluene, the rotation of the axial bond increased upon refluxing in xylene (Table 4, entries 3 and 4). With the more hindered complex **3** (R^1 = R^2 = Me), the axially isomerized product **4** was obtained as the major product by refluxing in mesitylene (Table 4, entry 6). Similarly, naphthyl(η^6-phenyl)$Cr(CO)_3$ complexes **13** gave the coresponding axially isomerized products **14** (Table 4, entries 7−12).

Synthesis of Both Enantiomers of Axial Biphenyls Using Single Chiral (Arene)chromium Complex. The diastereoselective cross-coupling reaction provides a promising approach to the synthesis of both optically pure atropisomers starting from a single chiral arene chromium complex (Scheme 7). Enantiomerically pure (+)-chromium complex **24**[27] was coupled with *o*-methylphenylboronic acid to give (+)-(*R*,*R*)-complex **25**, which was converted into (−)-(*R*)-2-methoxy-2′-methyl-6-(1,3-dioxolanyl)biphenyl (**26**) upon exposure to sunlight. On the other hand, diastereomeric (+)-(*R*,*S*)-chromium complex **27** was stereoselectively obtained by the cross-coupling of the complex **24** with *o*-formylphenylboronic acid (**2b**). The (+)-(*R*,*S*)-biphenyl complex **27** was converted to an antipode (+)-(*S*)-2-methoxy-2′-methyl-6-(1,3-dioxolanyl)biphenyl (**28**) by reduction of the formyl group to a methyl group, followed by demetalation.

Combination of the axial isomerization described above and the diastereoselective cross-coupling reaction can also be utilized for the preparation of both enantiomers

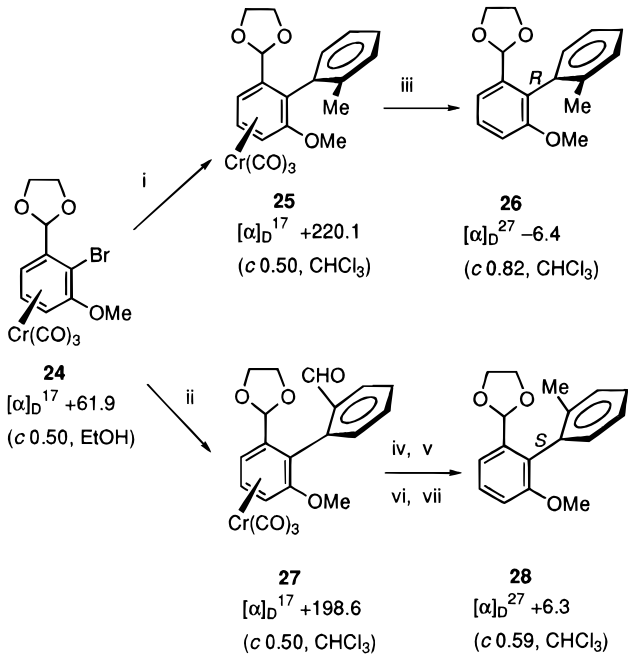
(26) Kamikawa, K.; Watanabe, T.; Uemura, M. *Synlett* **1995**, 1041.

Table 4. Axial Isomerization of Mono-Cr(CO)$_3$ Complexes of Biaryls under Thermal Conditions

entry	complex **3** (or **13**)	solvent	ratio[a] of **3**:**4** (or **13**:**14**)	yield[b] (%)
1	**3** (R^1 = CHO, R^2 = Me)	toluene	2:98	98
2	**3** (R^1 = CHO, R^2 = Me)	xylene	1:>99	98
3	**3** (R^1 = CHO, R^2 = OMe)	toluene	42:58	98
4	**3** (R^1 = CHO, R^2 = OMe)	xylene	9:91	98
5	**3** (R^1 = R^2 = Me)	xylene	80:20	98
6	**3** (R^1 = R^2 = Me)	mesitylene	2:98	79
7	**13** (R^1 = CHO, R^2 = OMe, R^3 = H)	toluene	13:87	98
8	**13** (R^1 = CHO, R^2 = OMe, R^3 = H)	xylene	1:99	98
9	**13** (R^1 = Me, R^2 = OMe, R^3 = H)	xylene	93:7	85
10	**13** (R^1 = Me, R^2 = OMe, R^3 = H)	mesitylene	15:85	82
11	**13** (R^1 = H, R^2 = Me, R^3 = OMe)	xylene	26:74	88
12	**13** (R^1 = H, R^2 = Me, R^3 = OMe)	mesitylene	18:82	60

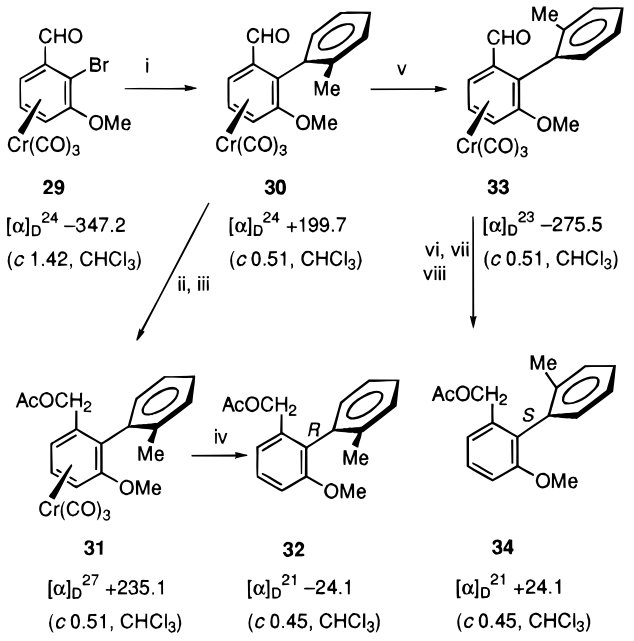
[a] Ratio was determined by 400 MHz ^{1}H NMR. [b] Isolated yield.

Scheme 7. Synthesis of Both Atopisomers of Axial Biphenyl[a]



[a] Reagents and conditions: (i) *o*-methylphenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, MeOH, H_2O, 75 °C, 30 min, 81%; (ii) *o*-formylphenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, MeOH, H_2O, 70 °C, 30 min, 52%; (iii) $h\nu-O_2$, 90%; (iv) LAH, 62%; (v) MsCl, py, 38%; (vi) LAH, 51%; (vii) $h\nu-O_2$, 90%.

Scheme 8. Synthesis of Both Atopisomers of Axial Biphenyl by Cross-Coupling and Subsequent Axial Isomerization[a]



[a] Reagents and conditions: (i) *o*-methylphenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3, MeOH, H_2O, 75 °C, 30 min, 80%; (ii) $NaBH_4$, MeOH, 98%; (iii) Ac_2O, py, 91%; (iv) $h\nu-O_2$, 60%; (v) reflux in xylene, 98%; (vi) $NaBH_4$, MeOH, 96%; (vii) Ac_2O, py, 90%; (viii) $h\nu-O_2$, 52%.

of axial biphenyls (Scheme 8). Enantiomerically pure (−)-(2-bromo-3-methoxybenzaldehyde)chromium complex (**29**)[27] was reacted with 2-methylphenylboronic acid in the presence of palladium(0) catalyst to give (+)-(*R*,*R*)-tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′-methyl-6-formylbiphenyl]chromium (**30**), which was successively reduced with $NaBH_4$ acetylated to give (+)-(*R*,*R*)-complex **31** in 71% overall yield. Photooxidative demetalation of **31** gave (−)-(*R*)-2-methoxy-2′-methyl-6-(acetoxymethyl)biphenyl (**32**). On the other hand, the axial isomerization of **30**, upon refluxing in xylene for 2 h, gave the diastereomer, (*R*,*S*)-tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′-methyl-6-formylbiphenyl]chromium (**33**), in 98% yield. The axially isomerized product **33** was converted into the corresponding antipode (+)-(*S*)-2-methoxy-2′-methyl-6-(acetoxymethyl)biphenyl (**34**) by a similar reaction sequence.

Stereochemical Considerations of Diastereoselective Cross-Coupling. Although the precise mechanism of the cross-coupling reaction has not been revealed adequately to say that the stereochemistry of the axial chirality depends on the *ortho* substituents of the phenylboronic acids and (arene)chromium complexes, the observed stereoselectivity can be rationalized by examining the transition states of the palladium intermediates (Figure 1). Two *cis* diorganopalladium(II) intermediates **35** and **36**, having a square configuration, would be the transient species prior to the biaryl carbon−carbon bond formation.[28] Complex **35** depicts a crowded system in

(27) Optically pure (+)-complex **24** ($[\alpha]^{17}_D$ +61.9 (*c* 0.5, EtOH) was prepared from optically resolved (−)-tricarbonyl(2-bromo-3-methoxybenzaldehyde)chromium ($[\alpha]^{24}_D$ −347.2 (*c* 1.415, $CHCl_3$)) by reaction with ethylene glycol and a catalytic amount of *p*-TsOH in acetonitrile at rt. Resolution of racemic tricarbonyl(2-bromo-3-methoxybenzaldehyde)chromium was achieved by the Davies method.[33] Optical purity of the resolved compounds was determined by HPLC with Chiralpak AS eluted with hexane/2-propanol (9/1): flow rate 0.5 mL/min, column temperature 40 °C; retention times: 27.48 min for (+)-isomer, 38.71 min for (−)-isomer.

(28) Tamao, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 3, p 435.

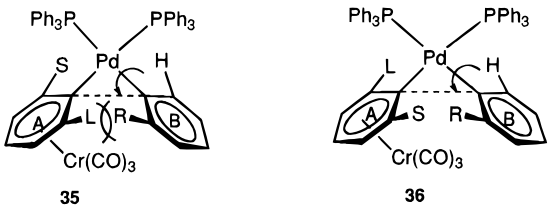


Figure 1. Proposed transition states for cross-coupling.

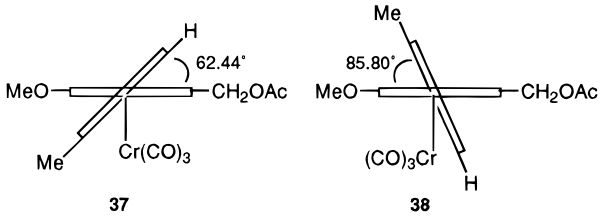


Figure 2. Dihedral angles of biphenyl $Cr(CO)_3$ complexes.

which the substituent R on the *B*-ring and the sterically bulky L substituent are face-to-face. The alternative complex **36** appears to be free of any severe nonbonded interactions.[29] The R substituent of **36** is oriented *syn* to the less bulky S group, and the tricarbonylchromium group is farther away from the bulky triphenylphosphine. A transmetalation between Ar(Cr)Pd−Br and arylboronic acid to form both intermediates **35** and **36** is an equilibrium step, and the subsequent reductive elimination step would be rate determining in this cross-coupling reaction. Moreover, both arene rings are coupled *via* an overlapping[30] of p-orbitals, avoiding severe nonbonding interactions between the R and triphenylphosphine groups in the intermediates **35** and **36**, and the R substituent rotates toward the $Cr(CO)_3$ moiety. In the newly formed biaryl system, prior to dissociation, the $Pd-(PPh_3)_2$ unit binds transiently to the least hindered face of the arene B ring of **36**, giving the (*S*,S**)-configuration products **3**. The formation of the (*S*,R**)-complexes **4** by the coupling with *o*-formylphenylboronic acid can be attributed to an axial isomerization of the kinetically-controlled (*S*,S**)-complexes **3**, as mentioned above. This speculated intermediacy of **36** is supported by the dihedral angles of the coupling products (Figure 2). The dihedral angle of **37** derived from **3** ($R^1 = CH_2OH$, R^2 = Me) is 62.44° and that of the corresponding diastereomeric (*S*,R**)-complex **38** derived from the coupling product **4** ($R^1 = \overline{CHO(CH_2)_2O}$, $R^2 = CHO$) is 85.80°, with an opposite incline. In all cases, the bulky *ortho* substituent, CH_2OAc, on the chromium-complexed arene ring is found to be *syn* to the *ortho* hydrogen and *anti* to the methyl substituent on the other arene ring. Further investigation to clarify the precise structures of the Pd(II) complexes and the reaction mechanism is under way.

Experimental Section

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using inert gas/vacuum double manifold techniques. All melting points are uncorrected. ^1H NMR spectra were measured in $CDCl_3$ solvent with TMS as an internal reference. IR spectra were determined in $CHCl_3$ solution. Mass spectra were determined in the EI mode (70 eV). Optical rotations were obtained at 589 nm (sodium D line) using a 1.0-dm cell with a total volume of 3 mL. Ether and THF were distilled from sodium/benzophenone ketyl immediately before use. Arylboronic acids **2a**−**d** were prepared according to reported methods.[31]

Tricarbonyl(2-bromo-3-methoxybenzaldehyde ethylene acetal)chromium (1c). Tricarbonyl(3-methoxybenzaldehyde ethylene acetal)chromium was prepared by the usual thermal conditions[32] from 3-methoxybenzaldehyde ethylene acetal with $Cr(CO)_6$ in 76% yield. To a solution of tricarbonyl(3-methoxybenzaldehyde ethylene acetal)chromium (2.50 g, 7.9 mmol) and TMEDA (1.38 g, 11.9 mmol) in THF (50 mL) and ether (150 mL) was added *n*-BuLi (8.1 mL, 1.6 M in hexane, 13.0 mmol) at −78 °C under nitrogen. The reaction mixture was stirred for 1 h at −78 °C followed by addition of 1,2-dibromo-1,1,2,2-tetrafluoroethane (4.16 g, 16.0 mmol). After the addition, the reaction mixture was warmed to 0 °C over 2 h, quenched with saturated aqueous NH_4Cl, and extracted with ether. The extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give **1c** as yellow crystals. Recrystallization from hexane/ether gave 2.16 g (72%) of **1c**: mp 118 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.84 (3H, s), 4.08−4.22 (4H, m), 5.15 (1H, d, J = 6.1 Hz), 5.27 (1H, d, J = 6.1 Hz), 5.39 (1H, t, J = 6.1 Hz), 6.02 (1H, s); IR ($CHCl_3$) 1980, 1900, 1280, 1060 cm^{-1}. Anal. Calcd for $C_{13}H_{11}O_6BrCr$: C, 39.52; H, 2.81. Found: C, 39.48; H, 2.77.

Chromium complexes **1a**, **1b**, and **1d** were prepared from **1c** by standard reaction sequences. Physical data are as follows. **1a**: 77 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.47 (3H, s), 3.84 (3H, s), 4.92 (1H, d, J = 6.1 Hz), 5.04 (1H, d, J = 6.7 Hz), 5.39 (1H, dd, J = 6.1, 6.7 Hz); IR ($CHCl_3$) 1965, 1880, 1505, 1460 cm^{-1}. Anal. Calcd for $C_{11}H_9O_4BrCr$: C, 39.19; H, 2.69. Found: C, 39.32; H, 2.69.

1b: mp 88 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.82 (3H, s), 5.33 (1H, t, J = 6.1 Hz), 5.46 (1H, d, J = 6.1 Hz), 5.74 (1H, d, J = 6.1 Hz), 10.10 (1H, s); IR ($CHCl_3$) 1990, 1920, 1790, 1500 cm^{-1}. Anal. Calcd for $C_{11}H_7O_5BrCr$: C, 37.63; H, 2.01. Found: C, 37.71; H, 1.96.

1d: mp 131 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (1H, brs), 3.86 (3H, s), 4.70 (1H, d, J = 14.0 Hz), 4.82 (1H, d, J = 14.0 Hz), 5.13 (1H, d, J = 6.1 Hz), 5.26 (1H, d, J = 6.7 Hz), 5.48 (1H, dd, J = 6.1, 6.7 Hz); IR ($CHCl_3$) 3000, 1960, 1890, 1500, 1410 cm^{-1}. Anal. Calcd for $C_{11}H_9O_5BrCr$: C, 37.42; H, 2.57. Found: C, 37.53; H, 2.55.

Preparation of 2-Methoxy-6-[(methoxymethoxy)methyl]phenylboronic Acid (7). To a solution of 2-methoxy-6-[(methoxymethoxy)methyl]-1-bromobenzene (4.70 g, 19.0 mmol) in ether (150 mL) was added *n*-BuLi (17.8 mL, 1.6 M in hexane, 28.5 mmol) at −78 °C under nitrogen. After 1 h, trimethyl borate (3.95 g, 38.0 mmol) was added to the mixture and the reaction mixture was warmed to 25 °C and quenched with water. The mixture was extracted with ether, and the extract was washed with 10% aqueous NaOH (100 mL). The aqueous solution was acidified with concd HCl at 0 °C and extracted with ether (100 mL × 2). The ether solution was washed with brine, dried over $MgSO_4$ and evaporated under reduced pressure to leave colorless crystals. Recrystallization from hexane/ether gave 1.36 g (32%) of **7**: mp 97−99 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.40 (3H, s), 3.89 (3H, s), 4.69 (2H, s), 4.71 (2H, s), 6.69 (2H, brs), 6.93 (1H, d, J = 7.9 Hz), 7.02 (1H, d, J = 7.9 Hz), 7.38 (1H, t, J = 7.9 Hz); IR ($CHCl_3$) 3000, 1570, 1470, 1330, 1020 cm^{-1}. Anal. Calcd for $C_{10}H_{15}BO_5$: C, 53.14; H, 6.69. Found: C, 53.16; H, 6.65.

(29) Molecular modeling of **35** and **36** (L = CH_2OH, S = OMe, R = Me) was performed using a Tectronix CAChe work system (MM2 parameters, Ver. 3). Type method: Exhaustive search, optimized Map. The conformation **36** was found by MM2 calculations to be more stable than **35**.

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(33) (a) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans. 1* **1989**, 192; **1990**, 393. (b) Bromley, L. A.; Bromley, Davies, S. G.; Goodfellow, C. L. *Tetrahedron Asymmetry* **1991**, *2*, 139. (c) Davies, S. G.; Goodfellow, C. L. *Synlett* **1989**, 59.

Typical Procedure for Cross-Coupling of (Arene)chromium Complexes and Phenylboronic Acids. A mixture of (arene)chromium complex **1a** (R^1 = Me) (218.4 mg, 0.60 mmol), phenylboronic acid **2a** (R^2 = Me) (139.6 mg, 1.20 mmol), and $Pd(PPh_3)_4$ (34 mg, 0.03 mmol) in aqueous 2 M Na_2CO_3 (0.8 mL) and MeOH (8 mL) was degassed by three freeze/vacuum/thaw cycles and heated at 75 °C for 30 min under argon. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with aqueous 10% NaOH and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography (8 g, eluted with 10% ether in hexane) to give 184 mg (96%) of coupling product **3** (R^1 = R^2 = Me): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (3H, s), 2.66 (3H, s), 3.68 (3H, s), 4.85 (1H, d, J = 6.1 Hz), 5.06 (1H, d, J = 6.1 Hz), 5.67 (1H, t, J = 6.1 Hz), 6.98 (1H, d, J = 7.3 Hz), 7.17 (1H, t, J = 7.3 Hz), 7.26−7.32 (2H, m); IR ($CHCl_3$) 1960, 1880, 1500, 1460 cm^{-1}; MS (relative intensity) m/z 348 (M^+ 17), 292 (7), 264 (75), 249 (100); HRMS calcd for $C_{18}H_{16}O_4Cr$ 348.0458, found 348.0463. Other coupling products were obtained by using the same procedure, and the physical data are as follows.

3 (R^1 = CHO, R^2 = Me): mp 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.62 (3H, s), 3.80 (3H, s), 5.39 (1H, d, J = 6.7 Hz), 5.53 (1H, d, J = 6.1 Hz), 5.79 (1H, dd, J = 6.1, 6.7 Hz), 7.06 (1H, d, J = 7.3 Hz), 7.17−7.23 (1H, m), 7.36 (2H, d, J = 7.3 Hz), 9.48 (1H, s); IR ($CHCl_3$) 1980, 1910, 1700, 1520 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_5Cr$: C, 59.67; H, 3.89. Found: C, 59.61; H, 3.85.

3 (R^1 = 1,3-dioxolane, R^2 = Me): mp 154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (3H, s), 3.70 (3H, s), 3.82−4.08 (4H, m), 5.14 (1H, d, J = 7.3 Hz), 5.17 (1H, d, J = 7.3 Hz), 5.19 (1H, s), 5.74 (1H, t, J = 7.3 Hz), 7.18−7.29 (4H, m); IR ($CHCl_3$) 1980, 1900, 1460, 1430, 1278 cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_6Cr$: C, 59.12; H, 4.46. Found: C, 59.08; H, 4.48.

3 (R^1 = CH_2OH, R^2 = Me): mp 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (1H, m), 2.64 (3H, s), 3.71 (3H, s), 4.09 (1H, dd, J = 6.0, 15.0 Hz), 4.34 (1H, dd, J = 8.0, 15.0 Hz), 5.16 (1H, d, J = 6.1 Hz), 5.21 (1H, d, J = 6.1 Hz), 5.77 (1H, t, J = 6.1 Hz), 7.02 (1H, d, J = 7.3 Hz), 7.16 (1H, t, J = 7.3 Hz), 7.28−7.33 (2H, m); IR ($CHCl_3$) 3325, 1960, 1885, 1270 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_6Cr$: C, 59.34; H, 4.39. Found: C, 59.24; H, 4.47.

3 (R^1 = Me, R^2 = CH_2OH): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96 (3H, s), 2.10 (1H, m), 3.67 (3H, s), 4.89 (1H, d, J = 6.1 Hz), 5.10 (1H, d, J = 6.7 Hz), 5.13 (1H, dd, J = 5.5, 13.1 Hz), 5.21 (1H, dd, J = 5.5, 13.1 Hz), 5.69 (1H, dd, J = 6.1, 6.7 Hz), 7.00 (1H, d, J = 7.3 Hz), 7.28 (1H, dd, J = 7.3, 7.9 Hz), 7.44 (1H, dd, J = 7.3, 7.9 Hz), 7.72 (1H, d, J = 7.3 Hz); IR ($CHCl_3$) 3350, 1970, 1900, 1460, 1420; MS (relative intensity) m/z 364 (M^+ 8), 336 (10), 308 (9), 280 (100), 265 (20); HRMS calcd for $C_{18}H_{16}O_5Cr$ 364.0403, found 364.0393.

3 (R^1 = Me, R^2 = OMe): mp 177 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00 (3H, s), 3.64 (3H, s), 3.94 (3H, s), 4.83 (1H, d, J = 6.1 Hz), 4.98 (1H, d, J = 6.7 Hz), 5.57 (1H, dd, J = 6.1, 6.7 Hz), 6.94 (1H, dd, J = 7.3, 7.9 Hz), 7.01 (1H, d, J = 7.9 Hz), 7.09 (1H, d, J = 7.3 Hz), 7.37 (1H, dd, J = 7.3, 7.9 Hz); IR ($CHCl_3$) 1960, 1885, 1460, 1260 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_5Cr$: C, 59.34; H, 4.43. Found: C, 59.02; H, 4.36.

3 (R^1 = CH_2OH, R^2 = OMe): mp 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.77 (1H, t, J = 6.7 Hz), 3.66 (3H, s), 3.94 (3H, s), 4.29 (2H, m), 5.07 (1H, d, J = 6.7 Hz), 5.19 (1H, d, J = 6.1 Hz), 5.67 (1H, dd, J = 6.1, 6.7 Hz), 6.95 (1H, dd, J = 7.3, 7.9 Hz), 7.02 (1H, d, J = 7.9 Hz), 7.12 (1H, d, J = 6.7 Hz), 7.39 (1H, dd, J = 6.7, 7.9 Hz); IR ($CHCl_3$) 3300, 1960, 1890, 1500 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_6Cr$: C, 56.85; H, 4.24. Found: C, 56.63; H, 4.25.

4 (R^1 = Me, R^2 = CHO): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (3H, s), 4.83 (1H, d, J = 6.1 Hz), 5.00 (1H, d, J = 6.7 Hz), 5.74 (1H, dd, J = 6.1, 6.7 Hz), 7.60 (1H, t, J = 7.3 Hz), 7.66 (1H, d, J = 7.3 Hz), 7.72 (1H, t, J = 7.3 Hz), 7.93 (1H, d, J = 7.3 Hz), 9.93 (1H, s); IR ($CHCl_3$) 1960, 1890, 1700, 1460, 1270 cm^{-1}; MS (relative intensity) m/z 362 (21), 278 (100), 263 (26); HRMS calcd for $C_{18}H_{14}O_5Cr$ 362.0249, found 362.0251.

4 (R^1 = CHO, R^2 = CHO): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (3H, s), 5.26 (1H, d, J = 6.7 Hz), 5.46 (1H, d, J = 6.1 Hz), 5.87 (1H, dd, J = 6.1, 6.7 Hz), 7.66−7.76 (3H, m), 7.94 (1H, d, J = 7.3 Hz), 9.49 (1H, s), 9.95 (1H, s); IR ($CHCl_3$) 1960, 1890, 1680, 1260 cm^{-1}; MS (relative intensity) m/z 376 (M^+ 7), 292 (22), 240 (20), 211 (100); HRMS calcd for $C_{18}H_{12}O_6Cr$ 376.0041, found 376.0043.

4 (R^1 = 1,3-dioxolane, R^2 = CHO): mp 126 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (3H, s), 3.69−4.02 (4H, m), 5.07 (1H, d, J = 7.3 Hz), 5.12 (1H, d, J = 6.1 Hz), 5.29 (1H, s), 5.80 (1H, dd, J = 6.1, 7.3 Hz), 7.58−7.69 (3H, m), 7.95 (1H, d, J = 7.3 Hz), 9.88 (1H, s); IR ($CHCl_3$) 1960, 1880, 1682, 1480, 1300 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_7Cr$: C, 57.15; H, 3.84. Found: C, 57.25; H, 4.06.

4 (R^1 = CHO, R^2 = OMe): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (3H, s), 3.73 (3H, s), 5.33 (1H, d, J = 6.7 Hz), 5.50 (1H, d, J = 6.7 Hz), 5.73 (1H, t, J = 6.7 Hz), 6.94 (1H, d, J = 7.9 Hz), 7.09 (1H, t, J = 7.3 Hz), 7.43 (1H, dd, J = 7.3, 7.9 Hz), 7.59 (1H, d, J = 7.3 Hz), 9.41 (1H, s); IR ($CHCl_3$) 1980, 1910, 1700, 1500, 1270 cm^{-1}; MS (relative intensity) m/z 378 (M^+ 20), 322 (3), 294 (100), 242 (14); HRMS calcd for $C_{18}H_{14}O_6Cr$ 378.0212, Found: 378.0204.

5 (R^1 = CHO, R^2 = Me): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.71 (3H, s), 3.69 (3H, s), 5.31 (1H, d, J = 6.1 Hz), 5.43 (1H, d, J = 6.7 Hz), 5.60 (1H, dd, J = 6.1, 6.7 Hz), 7.17 (1H, t, J = 7.3 Hz), 7.32 (1H, d, J = 7.3 Hz), 7.41 (1H, t, J = 7.3 Hz), 7.46 (1H, d, J = 7.3 Hz), 9.58 (1H, s); IR ($CHCl_3$) 1990, 1930, 1690, 1510, 1270 cm^{-1}; MS (relative intensity) m/z 390 (M^+ 5), 362 (1), 334 (28), 306 (100), 278 (68), 263 (52); HRMS calcd for $C_{19}H_{14}O_6Cr$ 390.0196, found 390.0171.

5 (R^1 = Me, R^2 = CH_2OH): mp 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (3H, s), 3.62 (3H, s), 3.65 (1H, brs), 4.72 (1H, d, J = 6.1 Hz), 4.76 (1H, dd, J = 6.7, 13.1 Hz), 4.85 (1H, dd,, J = 6.7, 13.1 Hz), 4.94 (1H, d, J = 6.7 Hz), 5.61 (1H, dd, J = 6.1, 6.7 Hz), 7.33−7.37 (1H, m), 7.56−7.58 (2H, m), 7.64 (1H, d, J = 7.9 Hz); IR ($CHCl_3$) 3380, 1970, 1890, 1665, 1460, 1425, 1200 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_6Cr$: C, 58.01; H, 4.12. Found: C, 58.17; H, 4.11.

5 (R^1 = 1,3-dioxolane, R^2 = CH_2OAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (3H, s) 3.60 (3H, s), 3.81−3.93 (4H, m), 4.99 (1H, d, J = 6.1 Hz), 5.07 (1H, d, J = 6.1 Hz), 5.57 (2H, s), 5.61 (1H, t, J = 6.1 Hz), 5.77 (1H, s), 7.30−7.33 (1H, m), 7.50−7.52 (2H, m), 7.67 (1H, d, J = 7.9 Hz); IR ($CHCl_3$) 1980, 1910, 1730, 1680, 1210 cm^{-1}; MS (relative intensity) m/z 492 (M^+ 2), 408 (33), 380 (26), 307 (47), 209 (100); HRMS calcd for $C_{23}H_{20}O_9Cr$ 492.0487, found 492.0461.

8 (R = Me): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (3H, s), 3.43 (3H, s), 3.70 (3H, s), 4.80 (2H, dd, J = 6.7, 11.0 Hz), 5.06 (1H, d, J = 12.8 Hz), 5.14−5.16 (2H, m), 5.20 (1H, d, J = 12.8 Hz), 5.54 (1H, d, J = 6.1 Hz), 5.61 (1H, dd, J = 6.1, 6.7 Hz), 6.87 (1H, d, J = 7.9 Hz), 7.26 (1H, d, J = 7.9 Hz), 7.38 (1H, t, J = 7.9 Hz); IR ($CHCl_3$) 1960, 1880, 1580, 1460 cm^{-1}; MS (relative intensity) m/z 408 (M^+ 18), 380 (5), 324 (83), 264 (100), 249 (93); HRMS calcd for $C_{20}H_{20}O_6Cr$ 408.0665, found 408.0658.

13 (R^1 = OMe, R^2 = Me, R^3 = H): mp 175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (3H, s), 3.59 (3H, s), 4.93 (1H, d, J = 6.1 Hz), 5.11 (1H, d, J = 6.7 Hz), 5.69 (1H, dd, J = 6.1, 6.7 Hz), 7.25 (1H, d, J = 7.3 Hz), 7.45 (1H, t, J = 7.9 Hz), 7.53 (1H, dd, J = 7.3, 7.9 Hz), 7.66 (1H, dd, J = 7.9, 8.5 Hz), 7.89 (2H, d, J = 7.9 Hz), 9.30 (1H, d, J = 8.5 Hz); IR ($CHCl_3$) 1960, 1875, 1500, 1460, 1425 cm^{-1}. Anal. Calcd for $C_{21}H_{16}O_4Cr$: C, 65.63; H, 4.20. Found: C, 65.52; H, 4.19.

13 (R^1 = OMe, R^2 = CHO, R^3 = H): mp 152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.72 (3H, s), 5.51 (1H, d, J = 6.7 Hz), 5.69 (1H, d, J = 6.1 Hz), 5.77 (1H, t, J = 6.1 Hz), 7.33 (1H, d, J = 6.7 Hz), 7.46 (1H, t, J = 7.3 Hz), 7.58 (1H, t, J = 7.3 Hz), 7.68 (1H, t, J = 7.3 Hz), 7.93 (1H, d, J = 7.9 Hz), 7.97 (1H, d, J = 7.9 Hz), 8.79 (1H, d, J = 8.6 Hz), 9.43 (1H, s); IR ($CHCl_3$) 1975, 1900, 1700, 1510, 1460 cm^{-1}. Anal. Calcd for $C_{21}H_{14}O_5Cr$: C, 63.32; H, 3.54. Found: C, 63.20; H, 3.55.

13 (R^1 = OMe, R^2 = H, R^3 = OMe): mp 153 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (3H, s), 3.84 (3H, s), 5.04 (1H, t, J = 6.1 Hz), 5.27 (1H, d, J = 6.7 Hz), 5.69 (1H, t, J = 6.1 Hz), 5.71 (1H, d, J = 6.1 Hz), 7.29 (1H, d, J = 9.1 Hz), 7.39 (1H, dd, J = 6.7, 7.9 Hz), 7.61 (1H, t, J = 6.7 Hz), 7.80 (1H, d, J = 7.9 Hz), 7.91 (1H, d, J = 9.1 Hz), 9.02 (1H, d, J = 9.1 Hz); IR ($CHCl_3$) 1960, 1880, 1600, 1510, 1465 cm^{-1}. Anal. Calcd for $C_{21}H_{16}O_5Cr$: C, 63.00; H, 4.03. Found: C, 62.89; H, 4.03.

13 (R^1 = Me, R^2 = H, R^3 = Me): mp 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.87 (3H, s), 2.14 (3H, s), 5.19 (1H, t, J = 6.1 Hz), 5.25 (1H, d, J = 6.1 Hz), 5.52 (1H, d, J = 6.1Hz), 5.71 (1H, t, J = 6.1 Hz), 7.35 (1H, d, J = 8.6 Hz), 7.49 (1H, dd, J = 6.7, 7.3 Hz), 7.64 (1H, dd, J = 6.7, 7.9 Hz), 7.81 (1H, d, J = 8.6 Hz), 7.84 (1H, d, J = 8.6 Hz), 9.32 (1H, d, J = 8.6 Hz); IR ($CHCl_3$) 1960, 1880, 1510, 1450, 1035 cm^{-1}. Anal. Calcd for $C_{21}H_{16}O_3Cr$: C, 68.47; H, 4.42. Found: C, 68.20; H, 4.38.

Axial Isomerization of (*S*,S)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methyl-2′-(hydroxymethyl)-6-methylbiphenyl]chromium (18) (R = Me) to (*S*,S**)-Isomer 19 by Oxidation of the Alcohol.** A solution of **18** (R = Me) (60 mg, 0.17 mmol) in acetic anhydride (2.0 mL) and DMSO (2.5 mL) was stirred at rt for 2 h under nitrogen. The mixture was extracted with ether, and the extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by silica gel chromatography eluted with hexane/ether (3/1) to give **19** (R = Me) (32 mg, 53%) as a red liquid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.93 (3H, s), 3.61 (3H, s), 4.83 (1H, d, J = 6.1 Hz), 5.00 (1H, d, J = 6.7 Hz), 5.74 (1H, dd, J = 6.1, 6.7 Hz), 7.60 (1H, t, J = 7.3 Hz), 7.66 (1H, d, J = 7.3 Hz), 7.72 (1H, t, J = 7.3 Hz), 7.93 (1H, d, J = 7.3 Hz), 9.93 (1H, s); IR ($CHCl_3$) 1960, 1890, 1700 cm^{-1}; MS (relative intensity) m/z 360 (M^+ 21), 278 (100), 263 (26); HRMS calcd for $C_{18}H_{14}O_5Cr$ 362.0249, found 362.0251.

Tricarbonyl[(1,2,3,4,5,6-η)-2,2′-dimethoxy-6-formylbiphenyl]chromium (22) (R = OMe): ^{1}H NMR (400 MHz) δ 3.70 (3H, s), 3.73 (3H, s), 5.33 (1H, d, J = 6.7 Hz), 5.50 (1H, d, J = 6.7 Hz), 5.73 (1H, t, J = 6.7 Hz), 6.94 (1H, d, J = 7.9 Hz), 7.09 (1H, t, J = 7.3 Hz), 7.43 (1H, dd, J = 7.3, 7.9 Hz), 7.59 (1H, d, J = 7.3 Hz), 9.41 (1H, s); IR ($CHCl_3$) 1980, 1910, 1700 cm^{-1}; MS (relative intensity) m/e 378 (20), 322 (3), 294 (100), 242 (14); HRMS calcd for $C_{18}H_{14}O_6Cr$ 378.0212, found 378.0204.

Axial Isomerization under Thermal Conditions. A typical procedure is as follows: A solution of *(S*,S*)*-tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′,6-dimethylbiphenyl]chromium (**3**) (R^1 = Me, R^2 = OMe) (20 mg, 0.055 mmol) in xylene (3 mL) was degassed by three cycles of freeze/pump/thaw and refluxed for 2 h under nitrogen. The reaction mixture was evaporated *in vacuo*, the residue was dissolved in ether (5 mL), and the precipitate was filtered. The filtrate was evaporated under reduced pressure, and the residue was purified by silica gel chromatography eluted with hexane/ether (5/1) to give 19.6 mg of the crude product. The ratio (91:9) of the crude product was determined by the proton area of OMe in 400 MHz ^{1}H NMR analysis: 3.63 and 3.74 ppm for methoxyl protons of **4** (R^1 = Me, R^2 = OMe), 3.64 and 3.94 ppm for the corresponding protons **3** (R^1 = Me, R^2 = OMe). Recrystallization from ether/hexane gave pure central bond rotation product **4**: mp 130 °C; ^{1}H NMR ($CDCl_3$) δ 1.95 (3H, s), 3.63 (3H, s), 3.74 (3H, s), 4.81 (1H, d, J = 6.7 Hz), 4.98 (1H, d, J = 6.7 Hz), 5.67 (1H, t, J = 6.7 Hz), 6.93 (1H, d, J = 7.9 Hz), 7.05 (1H, t, J = 7.9 Hz), 7.38 (1H, dd, J = 7.3, 7.9 Hz), 7.45 (1H, d, J = 7.3 Hz); IR ($CHCl_3$) 1960, 1885, 1460, 1260 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_5Cr$: C, 59.34; H, 4.43. Found: C, 59.00; H, 4.42. Physical data of the axial isomerization products are as follows.

(*S*,R)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′,6-dimethylbiphenyl]chromium (4) (R^1 = R^2 = Me):** mp 153 °C; ^{1}H NMR ($CDCl_3$) δ 1.90 (3H, s), 2.06 (3H, s), 3.63 (3H, s), 4.80 (1H, d, J = 6.7 Hz), 4.98 (1H, d, J = 6.7 Hz), 5.68 (1H, t, J = 6.7 Hz), 7.24−7.30 (3H, m), 7.45−7.47 (1H, m); IR ($CHCl_3$) 1960, 1880, 1500, 1265 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_4Cr$: C, 62.07; H, 4.63. Found: C, 61.80; H, 4.65.

(*S*,R)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-formyl-1,1′-naphthylbenzene]chromium (14) (R^1 = CHO, R^2 = OMe, R^3 = H):** ^{1}H NMR ($CDCl_3$) δ 3.61 (3H, s), 5.34 (1H, d, J = 6.7 Hz), 5.52 (1H, d, J = 6.7 Hz), 5.89 (1H, t, J = 6.7 Hz), 7.42−7.46 (2H, m), 7.49−7.53 (1H, m), 7.61 (1H, t, J = 7.9 Hz), 7.83 (1H, d, J = 7.9 Hz), 7.93 (1H, d, J = 7.9 Hz), 7.97 (1H, d, J = 7.9 Hz); IR ($CHCl_3$) 1975, 1900, 1700, 1510, 1460 cm^{-1}; MS (relative intensity) m/z 398 (M^+, 95), 342 (23), 316 (100), 299 (92), 281 (95); HRMS calcd for $C_{21}H_{14}O_5Cr$ 398.0247, found 398.0182.

Optical Resolution of Tricarbonyl(2-bromo-3-methoxybenzaldehyde)chromium. A mixture of racemic tricarbonyl(2-bromo-3-methoxybenzaldehyde)chromium (2.0 g, 6.6 mmol), L-valinol (1.4 g, 13.2 mmol), MS 4A (200 mg), and a catalytic amount of *p*-TsOH in dry ether (50 mL) was stirred at room temperature for 1 h under nitrogen, and the reaction mixture was filtered. The filtrate was reduced *in vacuo*, and the residue was separated to two fractions by silica gel chromatography (35 g) and eluted with hexane/ether/triethylamine (30/10/1). The first fraction was evaporated under reduced pressure, and the residue was dissolved in THF (25 mL) and hydrolyzed with aqueous 2 M HCl (15 mL) at room temperature for 1 h under nitrogen. The color of the solution immediately turned to deep red upon addition of HCl, and the reaction mixture was extracted with ether. The extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and reduced *in vacuo* to give 800 mg (40%) of (−)-isomer: mp 107 °C; $[\alpha]^{24}_D$ −347.2 (*c* 1.42, $CHCl_3$). The optical purity (>99.9% ee) was determined by HPLC with Chiralpak AS eluted with 10% 2-propanol in hexane; flow rate 0.5 mL/min; column temperature 40 °C; UV detector 254 nm. Retention time: 26.9 min for (+)-isomer, 36.4 min for (−)-isomer. The second fraction on column chromatography gave 630 mg (36.5%) of antipode (+)-isomer by the same procedure. Recrystallization of the crude complex (98.7% ee) with hexane/ether produced the optically pure complex: $[\alpha]^{24}_D$ +347.4 (*c* 1.23, $CHCl_3$); >99% ee.

Preparation of Complex 24. A mixture of (−)-(2-bromo-3-methoxybenzaldehyde)$Cr(CO)_3$ (500 mg, 1.49 mmol), ethylene glycol (185 mg, 2.9 mmol), and a catalytic amount of *p*-TsOH in acetonitrile (25 mL) was stirred at room temperature for 2 h under nitrogen. The reaction mixture was extracted with ether (20 mL x 2), and the extract was washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel chromatography to produce 491 mg (87%) of **24**: mp 118 °C; $[\alpha]^{20}_D$ +61.85 (*c* 0.50, EtOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (3H, s), 4.09−4.22 (4H, m), 5.15 (1H, d, J = 6.1 Hz), 5.27 (1H, d, J = 6.1 Hz), 5.39 (1H, dd, J = 6.7, 6.1 Hz), 6.02 (1H, s); IR ($CHCl_3$) 1980, 1905, 1420, 1280 cm^{-1}. Anal. Calcd for $C_{13}H_{11}O_6BrCr$: C, 39.52; H, 2.81. Found: C, 39.48; H, 2.77.

Preparation of (*R*)-Biphenyl 26. A solution of (*R,R*)-biphenyl complex **25** (30.0 mg, 0.074 mmol) in methylene chloride (20 mL) was exposed to sunlight for 3 h until the yellow solution became colorless. The precipitate was filtrated, and the filtrate was evaporated under reduced pressure. Purification by silica gel chromatography gave (*R*)-biphenyl **26** (18.0 mg): mp 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (3H, s), 3.71 (3H, s), 3.80−3.82 (2H, m), 4.02−4.05 (2H, m), 5.32 (1H, s), 6.97 (1H, d, J = 7.9 Hz), 7.13 (1H, d, J = 7.9 Hz), 7.22−7.30 (4H, m), 7.40 (1H, t, J = 7.9 Hz); IR ($CHCl_3$) 1465, 1260, 1060 cm^{-1}; $[\alpha]^{27}_D$ −6.4 (*c* 0.82, $CHCl_3$). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.30; H, 6.57. The optical purity of the biphenyl compounds **26** and **28** was determined by HPLC with chiralcel OJ (eluted with hexane/ethanol 75/25; column temperature 25 °C; flow rate 0.5 mL/min); retention times: 12.72 min for (−)-**26**; 15.44 min for (+)-**28**.

(+)-(*R,R*)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′-methyl-6-formylbiphenyl]chromium (30). A mixture of **29** (400 mg, 1.20 mmol), *o*-methylphenylboronic acid (325 mg, 2.40 mmol), and $Pd(PPh_3)_4$ (69 mg, 0.06 mmol) in aqueous 2 M Na_2CO_3 (1 mL) and MeOH (10 mL) was degassed by three freeze/vacuum/thaw cycles and heated at 75 °C for 30 min under argon. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with aqueous NaOH and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by silica gel chromatography (20 g, eluted with 10% ether in hexane) to give 348 mg (80%) of **30**: mp 118 °C; ^{1}H NMR ($CDCl_3$) δ 2.62 (3H, s), 3.80 (3H, s), 5.39 (1H, d, J = 6.7 Hz), 5.53 (1H, d, J = 6.1 Hz), 5.79 (1H, dd, J = 6.1, 6.7 Hz), 7.06 (1H, d, J = 7.3 Hz), 7.17−7.23 (1H, m), 7.36 (2H, d, J = 7.3 Hz), 9.48 (1H, s); IR ($CHCl_3$) 1980, 1910, 1690, 1520 cm^{-1}; $[\alpha]^{23}_D$ +199.7° (*c* 0.51, $CHCl_3$). Anal. Calcd for $C_{18}H_{14}O_5Cr$: C, 59.67; H, 3.89. Found: C, 59.61; H, 3.85. The purity (>99.9%) was determined by HPLC with Chiralcel OJ eluted with hexane/ethanol

(3/1); flow rate 0.5 mL/min; column temperature 25 °C; UV detector 254 nm. Retention time: 28.55 min for the (+)-isomer.

Preparation of (+)-(*R,R*)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-2′-methyl-6-(acetoxymethyl)biphenyl]chromium (31). A solution of $NaBH_4$ (13.6 mg, 0.36 mmol) in MeOH (5 mL) was slowly added to a solution of **30** (65.0 mg, 0.18 mmol) in MeOH (4 mL) at 0 °C, and the reaction mixture was stirred under nitrogen for 30 min at 0 °C. The mixture was quenched with water and extracted with ether, and the extract was washed with brine, dried over $MgSO_4$, and evaporated *in vacuo* to give yellow crystals. The crude product was used immediately without further purification for the next step. A solution of the crude reduction product, a catalytic amount of DMAP, and acetic anhydride (2 mL) in pyridine (2 mL) was stirred at rt for 3 h under nitrogen. The mixture was extracted with ether, and the extract was washed with aqueous 1 N HCl, saturated aqueous $NaHCO_3$, and brine, and dried over $MgSO_4$. The extract was evaporated *in vacuo*, and the residue was purified by silica gel chromatography (eluted with hexane/ether) to give yellow crystals. Recrystallization from hexane/ether gave 65.0 mg (89% from **30**) of **31**: mp 104 °C; ^{1}H NMR ($CDCl_3$) δ 2.04 (3H, s), 2.64 (3H, s), 3.70 (3H, s), 4.60 (1H, d, J = 12.8 Hz), 4.65 (1H, d, J = 12.8 Hz), 5.02 (1H, d, J = 6.1 Hz), 5.13 (1H, d, J = 6.7 Hz), 5.72 (1H, dd, J = 6.1, 6.7 Hz), 7.05 (1H, d, J = 7.3 Hz), 7.16 (1H, t, J = 7.3 Hz)., 7.26−7.32 (2H, m); IR ($CHCl_3$) 1980, 1905, 1745, 1210 cm^{-1}; $[\alpha]^{27}_D$ +235.1 (*c* 0.51, $CHCl_3$). Anal. Calcd for $C_{20}H_{18}O_6Cr$: C, 59.12; H, 4.46. Found: C, 59.06; H, 4.44. The purity (>99.9%) was determined by HPLC with Chiralcel OF eluted with hexane/2-propanol (50/1); flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm. Retention time: 43.13 min for **31**; 37.33 and 43.13 min for the racemate.

Preparation of (−)-(*R*)-2-Methoxy-2′-methyl-6-(acetoxymethyl)biphenyl (32). A solution of **31** (45.0 mg, 0.11 mmol) in ether (20 mL) was exposed to sunlight until the yellow solution became colorless at 0 °C for 30 min. The precipitate was filtered off, and the solution was evaporated *in vacuo* and purified by silica gel chromatography to give **32** (20 mg, 60%): ^{1}H NMR ($CDCl_3$) δ 1.98 (3H, s), 2.02 (3H, s), 3.72 (3H, s), 4.71 (1H, d, J = 7.9 Hz), 4.78 (1H, d, J = 12.8 Hz), 6.95 (1H, d, J = 7.9 Hz), 7.07 (2H, t, J = 6.7 Hz), 7.21−7.27 (3H, m), 7.35 (1H, t, J = 7.9 Hz); IR ($CHCl_3$) 1720, 1460, 1030, 750 cm^{-1}; $[\alpha]^{21}_D$ −24.1° (*c* 0.45, $CHCl_3$); MS (relative intensity) *m/z* 270 (M^+, 35), 228 (10), 210 (100), 195 (57); HRMS calcd for $C_{17}H_{18}O_3$ 270.1256, found 270.1283. The optical purity (>99.9% ee) was determined by HPLC with Ceramospher RU-1 (Shiseido Ltd.) eluted with methanol; flow rate 0.5 mL/min; column temperature 40 °C; UV detector 254 nm. Retention time: 18.98 min for (−)-**32**, 16.76 min for (+)-**34**.

Axial Isomerization of 30 to 33 under Thermal Conditions. A solution of **30** (80 mg, 0.22 mmol) in xylene (3 mL) was refluxed for 2 h under argon. The mixture was evaporated *in vacuo*, and the residue was purified by silica gel chromatography to give 78.4 mg of the isomerized product. Recrystallization of the crude product from ether/hexane gave axially pure compound **33**: mp 130 °C; ^{1}H NMR ($CDCl_3$) δ 2.09 (3H, s), 3.67 (3H, s), 5.27 (1H, d, J = 6.7 Hz), 5.43 (1H, d, J = 6.7 Hz), 5.80 (1H, t, J = 6.7 Hz), 7.26 (1H, d, J = 7.3 Hz), 7.31−7.38 (2H, m), 7.57 (1H, d, J = 7.3 Hz); IR ($CHCl_3$) 1980, 1910, 1700 cm^{-1}; $[\alpha]^{23}_D$ −275.5° (*c* 0.51, $CHCl_3$). Anal. Calcd for $C_{18}H_{14}O_5Cr$: C, 59.67; H, 3.89. Found: C, 59.61; H, 3.85. The purity (>99%) was determined by HPLC with Chiralcel OJ eluted with hexane/ethanol (3/1); flow rate 0.5 mL/min; column temperature 25 °C; UV detector 254 nm. Retention time: 17.11 min.

Preparation of (+)-(*R,S*)-Tricarbonyl[(1,2,3,4,5,6-η)2-methoxy-2′-methyl-6-(acetoxymethyl)biphenyl]chromium from Complex 33. The axially isomerized product **33** (55 mg, 0.15 mmol) was reduced with $NaBH_4$ followed by acetylation under the same conditions with **30** to give 52 mg (86%): mp 127 °C; ^{1}H NMR ($CDCl_3$) δ 1.99 (3H, s), 2.10 (3H, s), 3.65 (3H, s), 4.52 (1H, d, J = 12.8 Hz), 4.53 (1H, d, J = 12.8 Hz), 4.95 (1H, d, J = 6.1 Hz), 5.01 (1H, d, J = 6.7 Hz), 5.55 (1H, dd, J = 6.1, 6.7 Hz), 7.22−7.34 (3H, m), 7.43 (1H, dd, J = 6.1, 6.7 Hz), 9.41(1H, s); IR ($CHCl_3$) 1965, 1890, 1740, 1200 cm^{-1}; $[\alpha]^{23}_D$ +117.8° (*c* 0.50, $CHCl_3$). Anal. Calcd for $C_{20}H_{18}O_6Cr$: C, 59.12; H, 4.46. Found: C, 59.00; H, 4.45. The optical purity was determined by HPLC with Chiralcel OF eluted with hexane/2-propanol (50/1); flow rate 1.0 mL/min; column temperature 40 °C; UV detector 254 nm. Retention time: 48.07 min for the title compound; 43.05 and 48.07 min for the racemate.

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