# Synthesis and structure of $Cr(CO)_3$ complexes of biphenyl compounds with axial chirality

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(Received January 10, 1994)

**Abstract**

Chromium complexation of a 2,6,2′-trisubstituted biphenyl compound gave four mono-$Cr(CO)_3$ and one di-$Cr(CO)_3$ complexation products in a variable ratio depending on the reaction conditions. However, cross-coupling of (2,6-disubstituted-1-bromobenzene)$Cr(CO)_3$ with 2-substituted phenylboronic acid catalyzed by palladium(0) produced a stereoselectively coupled product without the formation of the axial isomer. The crystal structures of these chromium complexes were determined by X-ray crystallography.

*Key words:* Crystal structures; Chromium complexes; Carbonyl complexes; Biphenyl complexes

## Introduction

Biphenyl or binaphthyl compounds with an axial chirality are attractive compounds not only as chiral ligands in asymmetric reactions but also for the synthesis of biologically active natural products. There is a considerable current interest in the development of efficient methodologies for the stereoselective synthesis of *ortho* substituted biphenyl or binaphthyl compounds without any detectable form of the other atropisomer [1]. $\eta^6$-Polysubstituted (arene)chromium complexes can exist in two enantiomeric forms based on a planar chirality when the arene ring is substituted with different substituents at the *ortho* or *meta* position. The mono-$Cr(CO)_3$ complexes of *ortho* substituted biphenyl compounds with a hindered rotation about the central bond have both the axial and planar chiralities. (Arene)chromium complexes have some characteristic properties due to the strong electron-withdrawing ability and steric bulkiness of the tricarbonylchromium group, and significant applications have been developed in organic synthesis [2]. Thus, the $Cr(CO)_3$ complexed arene ring of the biphenyl compounds would be regioselectively susceptible to organic transformations such as a nucleophilic addition to the arene ring and a nuclear lithiation [2, 3] to afford further functionalized products. The preparation of mono-$Cr(CO)_3$ complexed biphenyl compounds was carried out by the following two methods: tricarbonylchromium complexation of the biphenyl compounds and cross-coupling of the (arene)chromium complex with the other arene compound. In this article, we report the synthesis and structure of tricarbonylchromium complexes of biphenyl derivatives.

## Results and discussion

### *Synthesis of mono-$Cr(CO)_3$ complexes of biphenyl compounds with axial chirality*

For the preparation of mono-$Cr(CO)_3$ complexed biphenyl compounds, we first turned our attention to the chromium complexation method with $Cr(CO)_6$ or (naphthalene)chromium(tricarbonyl) [4]. 2-Methoxy-6-hydroxymethyl-2′-methylbiphenyl (**1**)† was reacted with (naphthalene)chromium in a mixture of ether and 1 equiv. of THF at 75 °C in a sealed tube to give four mono-$Cr(CO)_3$ complexes **2–5** and one di-$Cr(CO)_3$ com-

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**Fellowship of the Japan Society for the Promotion of Science for Japanese Junior Scientists.

†Compound **1** was prepared by palladium(0) catalyzed cross-coupling of 2-methoxy-6-hydroxymethyl-1-bromobenzene with 2-methylphenylboronic acid in 80% yield.

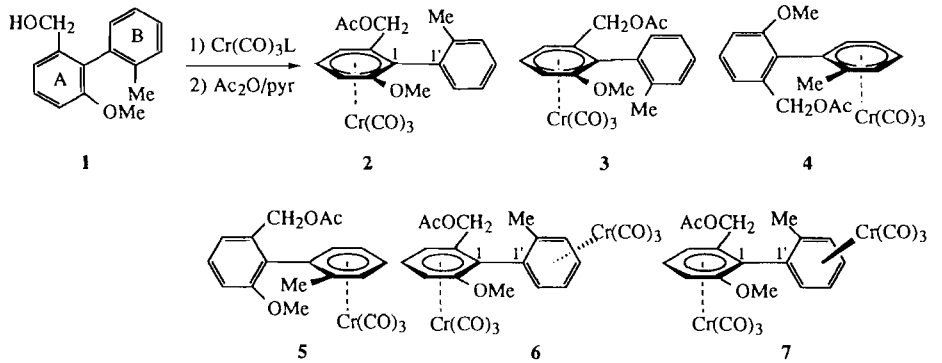

*SSDI* 0020-1693(94)03894-T

plex **6** of the biphenyl compound (Scheme 1, Table 1). Purification was carried out by flash chromatography after conversion of the hydroxymethyl group into the corresponding acetoxymethyl complexes. The major product **2** is formed by mono-chromium complexation of the arene ring with 1,2,3-trisubstituents (A-ring), and the stereochemistry of **2** was found to be the (*S**,*R**)-configuration* by X-ray crystallography. The corresponding (*S**,*S**)-configuration **3** with the axial isomer was obtained in less than 1.2% yield. The complexation of the arene A-ring takes place to avoid a severe steric interaction between the methyl and $Cr(CO)_3$ groups giving complex **2** as the major product. The (*R**,*S**)-complex **4** formed by mono-$Cr(CO)_3$ complexation of the other arene ring (B-ring) was preferentially obtained. The B-ring chromium complexed compounds **4** and **6** are formed in the same way with the hydroxymethyl group via the chromium benzyloxide bond [5]. The stereochemistry of the di-$Cr(CO)_3$ complexed biphenyl compound **6** showed the (*S**,*S**,*R**)-configuration** by X-ray crystallography. Since the ligand transfer reaction with (naphthalene)chromium seems to afford kinetically controlled products, the thermodynamic chromium complexation reaction with hexacarbonylchromium was investigated next. The biphenyl **1** was reacted with $Cr(CO)_6$ at 120 °C for 24 h in a mixture of butylether, heptane and THF (10/1/1) under nitrogen to give the (*S**,*R**)-complex **2** as the major product along with a mixture of the (*R**,*R**)-complex **5** and one bis-$Cr(CO)_3$ complex **7**. During mono-$Cr(CO)_3$ complexation on the B-ring, the (*R**,*S**)-configuration product **4** was not isolated under thermodynamic reaction conditions. It is noteworthy that the reversal of the selectivity of the B-ring complexation was observed between (naphthalene)-$Cr(CO)_3$ and $Cr(CO)_6$ reagents. Further, it is interesting to note that the configuration of the bis-$Cr(CO)_3$ complexed biphenyl **7** (*S**,*R**,*R**) obtained under thermal conditions with $Cr(CO)_6$ was different from that of complex **6** obtained by the ligand transfer reaction with (naphthalene)$Cr(CO)_3$. The chromium complexation products **5** and **7** under thermodynamic conditions are formed via the complexation of one face of the B-ring to avoid the steric interaction between the hydroxymethyl and $Cr(CO)_3$ groups. Although the mono-$Cr(CO)_3$ complexation products of the biphenyl compounds were prepared as the major product by the chromium complexation method with $Cr(CO)_6$ or (naphthalene)$Cr(CO)_3$, this procedure has the following disadvantages: (i) stereo- and regioselectivities for the formation of $Cr(CO)_3$ complexes were not observed: (ii) preparation as an optically active form is difficult. Therefore, another efficient method should be developed for the synthesis of mono-chromium complexed biphenyl compounds to overcome the above disadvantages.

Cross-coupling reactions of arylhalides or aryltriflates with various arylmetals such as areneboronic acids, arylzinc chloride and aryltributylstannane catalyzed by a palladium(0) catalyst provide useful methods for the synthesis of biphenyl compounds [6]. For an efficient preparation of mono-$Cr(CO)_3$ complexed biphenyl compounds via cross-coupling reactions, the following two connecting methods were devised: (A) coupling of (arylmetal)$Cr(CO)_3$ with arylhalide, (B) coupling of (arylhalide)$Cr(CO)_3$ with arylmetal. However, the coupling of (arylmetal)$Cr(CO)_3$ with arylhalide (method A) gave unsatisfactory yields for the preparation of *ortho* substituted biphenyl derivatives [7]. It has been reported that an oxidative addition of the carbon–halogen bond of the arylhalide to the palladium(0)

*The first symbol indicates a configuration of planar chirality of the chromium complexed arene at C-1 position of the compounds **2**, **3**; at C-1′ position of the compounds **4**, **5**, and the second symbol shows the configuration of the axial chirality. The symbol (*S**,*R**) represents a racemic mixture of (*S*,*R*)- and (*R*,*S*)-configurations, and the (*S*,*R*)-isomer is only shown for clarity.

**The first symbol indicates a planar configuration at C-1, the second one shows the configuration at C-1′ position, and the last one represents the axial chirality.

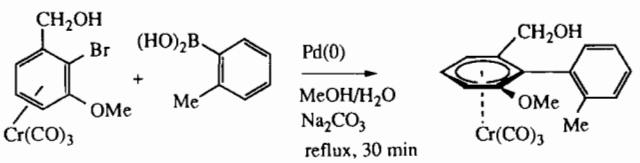



Scheme 1.

TABLE 1. Chromium complexation of 2-methoxy-2'-methyl-6-hydroxymethylbiphenyl (**1**)

| Complexation reagent | Conditions | Ratio (**2**:**3**:**4**:**5**:**6**:**7**) | Yield (%) |
|---|---|---|---|
| (Naphthalene)$Cr(CO)_3$ | ether, 1 equiv. THF; 70 °C, 4 h | 45:2:27:10:16:0 | 62 |
| $Cr(CO)_6$ | butylether/THF (10/1); 120 °C, 24 h | 73:1:0:10:0:16 | 83 |

is accelerated by coordination of the electron-withdrawing tricarbonylchromium group to the arene ring [8]. Even chlorobenzene can be easily susceptible to the oxidative addition by utilizing the corresponding tricarbonylchromium complex. Thus, the reaction of tricarbonyl(2-methoxy-6-hydroxymethyl-1-bromobenzene)chromium (**8**)* with *ortho* tolylboronic acid (**9**) in the presence of 10 mol% of $Pd(PPh_3)_4$ gave 76% yield of the coupling product **10** (Scheme 2) whose configuration was confirmed as the (*S**, *S**)-configuration by conversion of the hydroxymethyl into the corresponding acetoxymethyl group (**3**). The diastereomeric (*S**, *R**)-chromium complex **2**, the major product of the chromium complexation reaction with (naphthalene)$Cr(CO)_3$ or $Cr(CO)_6$ reagent, was not formed by the cross-coupling reaction. It is interesting to note that the methyl group of complex **3** is directed toward the tricarbonylchromium group in spite of a severe steric interaction between the methyl and $Cr(CO)_3$ groups. The (*S**, *S**)-complex **10** would be stereoselectively formed by a reductive elimination of the *cis* di-organo palladium(II) intermediate complex. Since the (arene)chromium complex **8** can be easily obtained as an optically active form**, the cross-coupling product and its photo-oxidized chromium free biphenyl derivative can be prepared as enantiomerically pure compounds.




**8** **9** **10**

Scheme 2.

*Complex **8** was prepared from tricarbonyl(*m*-methoxybenzaldehyde ethyleneacetal)chromium by lithiation (n-BuLi/ether, −78 °C) followed by treatment with 1,2-dibromo-tetrafluoroethane. The obtained 2-bromo chromium complex was treated with dilute aqueous HCl followed by reduction with sodium borohydride to give complex **8** in good overall yield.

**Racemic tricarbonyl(2-methoxy-6-formyl-1-bromobenzene)-chromium was resolved into the optically active complex by column chromatographical separation of diastereomers derived from L-valinol [9]. The optically resolved complex was converted to the corresponding optically active complex **8** by $LiAlH_4$ reduction of the formyl group.

*Structure of $Cr(CO)_3$ complexes of biphenyl*

X-ray crystallography of complexes **2**, **3**, **4**, **6** and **7** was performed, and the relative stereochemistry of complex **5** was determined by X-ray after conversion of the acetoxymethyl to the corresponding methoxymethyl group **11**. Crystal data of these chromium complexes are presented in Table 2, the molecular structures are given in Figs. 1–6. All measurements were made on a Rigaku AFC5R diffractometer. Cell constants were refined by a least-squares refinement using the $2\theta$ angles of 20 carefully centered reflections in the $45 \leqslant 2\theta \leqslant 55°$ range. Intensities collected by the $\omega$–$2\theta$ scan technique were corrected for Lorentz and polarization effects. The space groups were determined based on the systematic absences and the successful solution and refinement. The structures were solved by heavy-atom Patterson methods and expanded using the Fourier technique. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods, the hydrogen atoms being fixed at their calculated positions. Absorption corrections were applied after isotropic refinement using the program DIFABS. All calculations were made using the teXsan [10] crystallographic software package of the Molecular Structure Cooperation.

It is well known [11] that the *syn* eclipsed conformation **12** (Scheme 3) of the $Cr(CO)_3$ tripod to electron-donating substituents such as MeO or the alkyl group of (mono-substituted arene)$Cr(CO)_3$ complexes is normally found in the solid state. The $Cr(CO)_3$ tripod of the (*S**, *R**)-complex **2** is rotated about 7.8° from the *syn* eclipsed conformation of appropriate Cr–CO and C2–O, C4–H or C6–C14 bonds. For the stereoisomeric (*S**, *S**)-complex **3**, the rotated deviation from the eclipsed conformation is largely shifted to 23.7°. This large deviation is attributed to the severe steric interaction between $Cr(CO)_3$ and C17 methyl groups. The same behavior is also observed between the B-ring chromium complexes **4** and **11**. The deviation of the $Cr(CO)_3$ tripod from the eclipsed conformation is 4.5° for complex **11**, while the deviation is 16.5° for complex **4** due to the steric interaction with the sterically bulky acetoxymethyl group. The dihedral angles (C2–C1···C7–C8) formed by the mean planes of the aromatic ring are 82.7(6), 67.8(9), 64.4(5) and 100.4(7)° for complexes **2**, **3**, **4** and **11**, respectively. Larger deviations from the perpendicular of the biphenyl ring for complexes **3** and **4** can be attributed to the severe

TABLE 2. Crystallographic data, collection data and refinement procedures

| | **2** | **3** | **4** | **11** | **6** | **7** |
|---|---|---|---|---|---|---|
| Formula | $C_{20}H_{18}O_6Cr$ | $C_{20}H_{18}O_6Cr$ | $C_{20}H_{18}O_6Cr$ | $C_{19}H_{18}O_5Cr$ | $C_{23}H_{18}O_9Cr_2$ | $C_{23}H_{18}O_9Cr_2$ |
| Molecular weight | 406.35 | 406.35 | 406.35 | 378.34 | 542.38 | 542.38 |
| Crystal size (mm) | $0.40\times0.20\times0.05$ | $0.30\times0.30\times0.10$ | $0.30\times0.20\times0.10$ | $0.40\times0.10\times0.10$ | $0.32\times0.16\times0.08$ | $0.30\times0.30\times0.30$ |
| Crystal color, habit | yellow, plate | yellow, prismatic | yellow, plate | yellow, prismatic | yellow, plane | yellow, prismatic |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ |
| $a$ (Å) | 8.007(6) | 9.718(4) | 9.876(5) | 7.562(2) | 9.854(2) | 8.456(2) |
| $b$ (Å) | 18.654(4) | 13.189(5) | 19.453(6) | 14.883(2) | 14.016(3) | 19.265(2) |
| $c$ (Å) | 13.028(9) | 15.450(5) | 10.787(5) | 15.753(3) | 16.937(4) | 14.171(2) |
| $\beta$ (°) | 99.23(5) | 91.57(7) | 114.45(3) | 91.41(2) | 96.75(2) | 91.48(2) |
| $V$ (Å$^3$) | 1920(1) | 1979(1) | 1886(1) | 1773(7) | 2323(8) | 2308(7) |
| $Z$ | 4 | 4 | 4 | 4 | 4 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.405 | 1.363 | 1.430 | 1.418 | 1.551 | 1.561 |
| $\mu$(Cu K$\alpha$) (cm$^{-1}$) | 52.00 | 50.45 | 53.50 | 55.45 | 82.90 | 82.30 |
| $F$(000) | 840.00 | 840.00 | 840.00 | 784.00 | 1104.00 | 1104 |
| $2\theta_{max}$ (°) | 110.4 | 120.8 | 120.2 | 110.3 | 120.2 | 110.1 |
| No. reflection measured | 2445 | 3233 | 3084 | 2554 | 3756 | 3153 |
| No. unique reflections | 2334 | 3105 | 2917 | 2345 | 3623 | 3016 |
| No. observations ($I>3.00\sigma(I)$) | 1521 | 1826 | 1871 | 1522 | 2219 | 1922 |
| Parameters refined | 244 | 245 | 299 | 227 | 362 | 308 |
| Max. height in final $\Delta F$ map (e/Å$^3$) | 0.18 | 0.37 | 0.17 | 0.28 | 0.27 | 0.23 |
| $R$, $R_w$ | 0.048, 0.060 | 0.063, 0.083 | 0.039, 0.042 | 0.049, 0.063 | 0.041, 0.044 | 0.042, 0.050 |

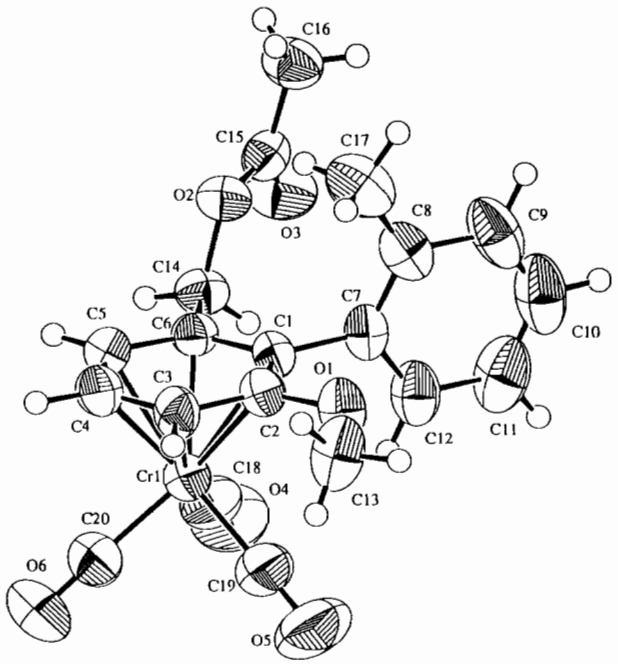



Fig. 1. Molecular structure of compound **2**.

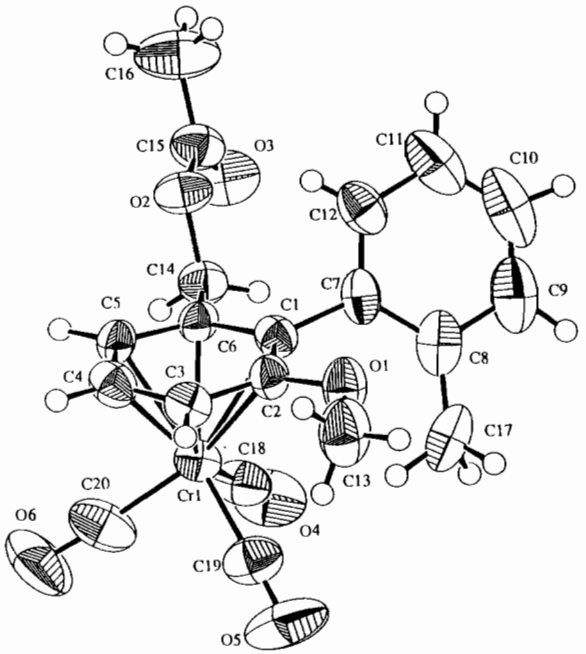



Fig. 2. Molecular structure of compound **3**.

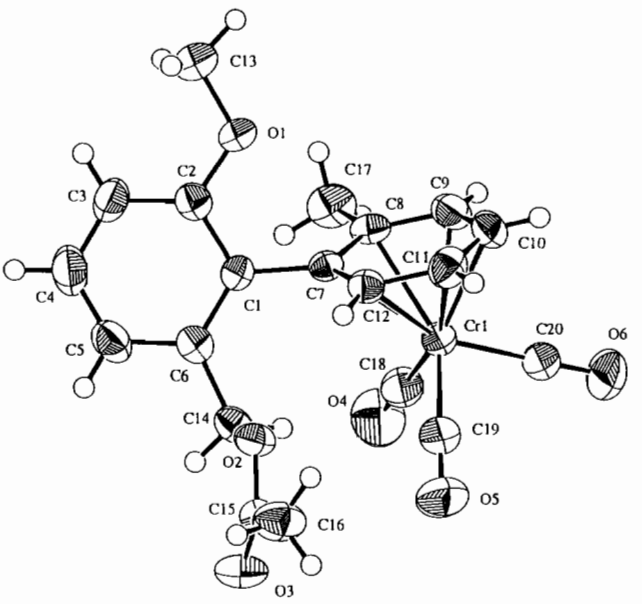



Fig. 3. Molecular structure of compound **4**.

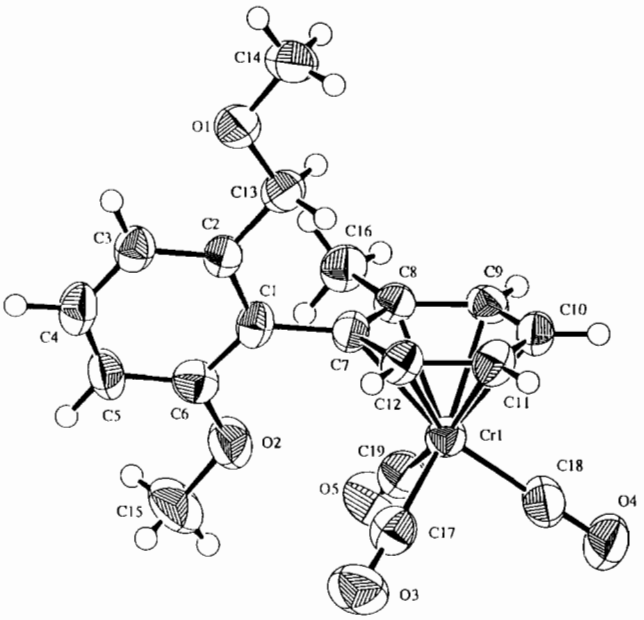



Fig. 4. Molecular structure of compound **11**.

between $Cr(CO)_3$ and the methyl for complex **3**, or the acetoxymethyl for complex **4**.

The representative proton NMR spectra of the chromium complexes are summarized in Table 3. The chemical shifts characteristic for the chromium complexed biphenyl compounds dependent on the axial chirality are as follows. The methyl signal of the uncomplexed B-ring for chromium complexes **2** and **3** appeared at 2.10 and 2.64 ppm, respectively. The lower field signal of the methyl proton is assigned to the (*S**,*S**)-complex **3**, in which the methyl group and $Cr(CO)_3$ are located on the same side of the chromium complexed arene ring. Similarly, among the B-ring complexed compounds **4** and **5**, the signals of the $CH_2$ bonded C/14 position showed a double of doublets at 5.62 and 5.78 ppm for the (*R**,*S**)-complex **4**, in which the methylene protons gave lower signals than those of the corresponding (*R**,*R**)-complex **5** (4.78 and 4.98 ppm). The signal of the methoxy group of complex **4** is shifted upfield compared to that of the corresponding axially isomeric

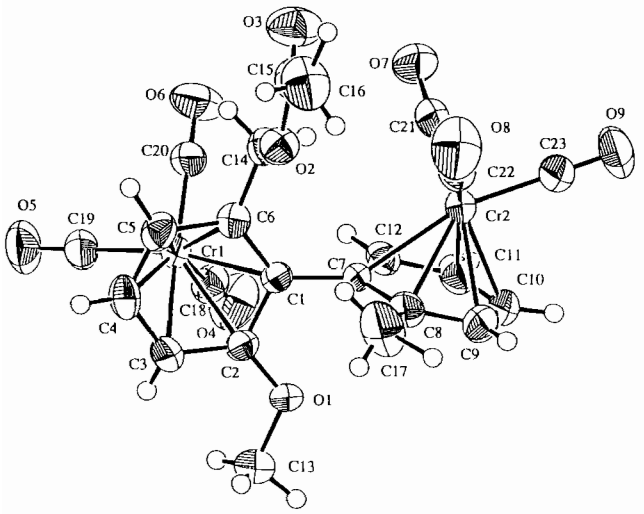



Fig. 5. Molecular structure of compound **6**.

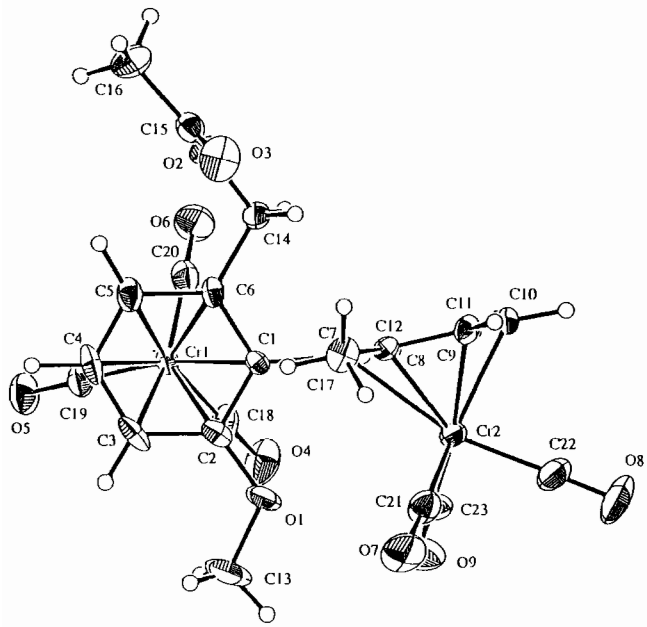
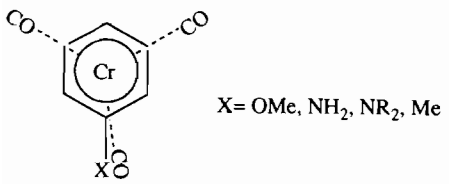



Fig. 6. Molecular structure of compound **7**.




**12**

Scheme 3.

complex **5**. This is consistent with the chemical shift of the aromatic methyl proton of the cross-coupling product **10** (2.64 ppm). These results show that the chemical shifts of the protons in the same direction to the $Cr(CO)_3$ group of the other ring are shifted to lower field than those of the protons in opposite directions. Such an interpretation of the chemical shifts agrees with that for other chromium complexes of biphenyl derivatives [12]. These observations are also consistent with configurations of the bis-$Cr(CO)_3$ complexed biphenyl compounds **6** and **7**. Thus, it is demonstrated that the $Cr(CO)_3$ is complexed to the A-ring in the opposite direction to the B-ring Me group, based on the chemical shifts of the $CH_3$ proton (2.02 ppm for **6**, 1.99 for **7**). Meanwhile, the B-ring $Cr(CO)_3$ group is oriented in the same direction as the A-ring $CH_2OAc$ group (5.37 ppm; $CH_2$ proton) for complex **6**, but the B-ring $Cr(CO)_3$ group is oriented in the opposite direction to the acetoxymethyl for complex **7** (4.45 ppm).

TABLE 3. Chemical shifts (ppm) for the complexes **2**, **3**, **4**, **5**, **6** and **7**

| Complex | OMe | $CH_2OAc$ | Ar-*Me* | OAc |
|---|---|---|---|---|
| **2** | 3.65 | 4.52, 4.53 | 2.10 | 1.99 |
| **3** | 3.70 | 4.60, 4.65 | 2.64 | 2.04 |
| **4** | 3.71 | 5.62, 5.78 | 1.94 | 2.11 |
| **5** | 3.94 | 4.78, 4.98 | 1.94 | 2.00 |
| **6** | 3.62 | 5.37 | 2.02 | 2.15 |
| **7** | 3.86 | 4.45 | 1.99 | 2.01 |

## Experimental

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon with an inert gas/vacuum double-manifold technique. All melting points were determined on a Yanagimoto MPJ-2 micromelting point apparatus and were uncorrected. $^1H$ NMR spectra were measured on an Hitachi R-90 or a JEOL GX-400 instrument. All NMR spectra were recorded in $CDCl_3$ solvent with tetramethylsilane as an internal reference. IR spectra were determined on a JASCO A-100 spectrometer.

*Chromium complexation of* ***1*** *with (naphthalene)$Cr(CO)_3$*

A mixture of tricarbonyl(naphthalene)chromium (1.21 g, 4.59 mmol) and (2-methoxy-2'-methyl-6-hydroxymethyl biphenyl (**1**) (700 mg, 3.06 mmol) in ether (35 ml) and THF (661 mg) in a sealed tube was degassed by three cycles of freeze/pump/thaw, and stirred at 75 °C for 4 h under argon. After cooling to room temperature, a precipitate was filtered off and the organic layer was evaporated *in vacuo*. The residue was acetylated by reaction with acetic anhydride (1 ml), pyridine (2 ml) and a catalytic amount of 4-dimethylaminopyridine at room temperature under argon. The reaction mixture was quenched with water and extracted with ether. The extract was washed with dilute aqueous

hydrochloric acid and brine, dried over $MgSO_4$ and evaporated *in vacuo*. The residue was purified by silica gel chromatography (50 g, ether/hexane = 1/20) to give the mono-$Cr(CO)_3$ complexed biphenyls, **2** (344 mg), **3** (15 mg), **4** (211 mg), **5** (75 mg), and the di-$Cr(CO)_3$ biphenyl complex **6** (55 mg). Physical data of these chromium complexes are as follows.

*(S*, R*)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-acetoxymethyl-2'-methylbiphenyl]chromium (2)*

M.p. 166 °C. IR ($CHCl_3$): 1965, 1890, 1740, 1200 $cm^{-1}$. $^1H$ NMR (400 MHz) δ: 1.99 (s, 3H), 2.10 (s, 3H), 3.65 (s, 3H), 4.52 (d, $J$ = 12.8 Hz, 1H), 4.53 (d, $J$ = 12.8 Hz, 1H), 4.95 (d, $J$ = 6.1 Hz, 1H), 5.01 (d, $J$ = 6.7 Hz, 1H), 5.55 (dd, $J$ = 6.1, 6.7 Hz, 1H), 7.22–7.34 (m, 3H), 7.43 (dd, $J$ = 6.1, 6.7 Hz, 1H). $^{13}C$ NMR (100 MHz) δ: 19.63, 20.53, 55.98, 62.99, 71.27, 83.34, 94.52, 104.51, 108.59, 126.57, 128.99, 129.72, 130.30, 134.16, 137.64, 142.42, 169.93, 232.69. *Anal.* Calc. for $C_{20}H_{18}O_6Cr$: C, 59.12; H, 4.46. Found: C, 59.00; H, 4.45%.

*(S*, S*)-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-acetoxymethyl-2'-methylbiphenyl]chromium (3)*

M.p. 131 °C. IR ($CHCl_3$): 1980, 1905, 1745, 1210 $cm^{-1}$. $^1H$ NMR (400 MHz) δ: 2.04 (s, 3H), 2.64 (s, 3H), 3.70 (s, 3H), 4.60 (d, $J$ = 12.8 Hz, 1H), 4.65 (d, $J$ = 12.8 Hz, 1H), 5.02 (d, $J$ = 6.1 Hz, 1H), 5.13 (d, $J$ = 6.7 Hz, 1H), 5.72 (dd, $J$ = 6.1, 6.7 Hz, 1H), 7.05 (d, $J$ = 7.3 Hz, 1H), 7.16 (ddd, $J$ = 7.0, 6.5, 2.0 Hz, 1H), 7.26–7.32 (m, 2H). *Anal.* Calc. for $C_{20}H_{18}O_6Cr$: C, 59.12; H, 4.46. Found: C, 59.06; H, 4.44%.

*(R*, S*)-Tricarbonyl[(1',2',3',4',5',6'-η)-2-methoxy-6-acetoxymethyl-2'-methylbiphenyl]chromium (4)*

M.p. 113 °C. IR ($CHCl_3$): 1970, 1895, 1740, 1210 $cm^{-1}$. $^1H$ NMR (400 MHz) δ: 1.94 (s, 3H), 2.11 (s, 3H), 3.71 (s, 3H), 5.13 (d, $J$ = 6.1 Hz, 1H), 5.17 (dd, $J$ = 6.1, 6.7 Hz, 1H), 5.57 (d, $J$ = 6.7 Hz, 1H), 5.62 (d, $J$ = 12.2 Hz, 1H), 5.64 (dd, $J$ = 6.1, 6.7 Hz, 1H), 5.78 (d, $J$ = 12.2 Hz, 1H), 6.90 (d, $J$ = 8.5 Hz, 1H), 7.13 (d, $J$ = 7.9 Hz, 1H), 7.38 (dd, $J$ = 7.9, 8.5 Hz, 1H). $^{13}C$ NMR (100 MHz) δ: 19.55, 21.07, 55.81, 63.18, 87.38, 90.14, 96.14, 99.48, 106.50, 110.35, 111.58, 122.51, 123.87, 129.75, 135.05, 158.15, 170.61, 233.08. *Anal.* Calc. for $C_{20}H_{18}O_6Cr$: C, 59.12; H, 4.46. Found: C, 58.96; H, 4.49%.

*(R*, R*)-Tricarbonyl[(1',2',3',4',5',6'-η)-2-methoxy-6-acetoxymethyl-2'-methylbiphenyl]chromium (5)*

M.p. 121 °C. IR ($CHCl_3$): 1970, 1895, 1740, 1210 $cm^{-1}$. $^1H$ NMR (400 MHz) δ: 1.94 (s, 3H), 2.00 (s, 3H), 3.94 (s, 3H), 4.78 (d, $J$ = 12.2 Hz, 1H), 4.98 (d, $J$ = 12.2 Hz, 1H), 5.01 (t, $J$ = 6.1 Hz, 1H), 5.13 (d, $J$ = 6.1 Hz, 1H), 5.46 (d, $J$ = 6.1 Hz, 1H), 5.56 (t, $J$ = 6.1 Hz, 1H), 7.02 (d, $J$ = 8.4 Hz, 1H), 7.05 (d, $J$ = 7.7 Hz, 1H), 7.39 (dd, $J$ = 8.4, 7.7 Hz, 1H). $^{13}C$ NMR (100 MHz) δ: 18.93, 20.81, 55.23, 64.32, 85.85, 90.24, 95.87, 98.21, 103.10, 111.39, 112.09, 121.55, 123.57, 129.84, 136.84, 136.99, 155.23, 170.29, 233.52. *Anal.* Calc. for $C_{20}H_{18}O_6Cr$: C, 59.12; H, 4.46. Found: C, 59.09; H, 4.52%.

*(S*, S*, R*)-Di-tricarbonyl[(1,2,3,4,5,6-η)-(1',2',3',4',5',6'-η)-2-methoxy-6-acetoxymethyl-2'-methylbiphenyl]chromium (6)*

M.p. 172 °C. IR ($CHCl_3$): 1985, 1970, 1905, 1750, 1210 $cm^{-1}$. $^1H$ NMR (400 MHz) δ: 2.02 (s, 3H), 2.15 (s, 3H), 3.62 (s, 3H), 4.99 (d, $J$ = 6.3 Hz, 1H), 5.02 (d, $J$ = 6.6 Hz, 1H), 5.05 (d, $J$ = 7.2 Hz, 1H), 5.08 (t, $J$ = 6.6 Hz, 1H), 5.37 (d, $J$ = 12.5 Hz, 2H), 5.70–5.79 (m, 3H). $^{13}C$ NMR (100 MHz) δ: 19.51, 20.77, 56.23, 62.25, 71.32, 83.58, 85.64, 88.55, 94.81, 97.11, 98.19, 100.40, 103.45, 107.52, 112.44, 142.56, 170.22, 231.59, 232.09. *Anal.* Calc. for $C_{23}H_{18}O_9Cr_2$: C, 50.93; H, 3.34. Found: C, 50.85; H, 3.37%.

*(S*, R*, R*)-Di-tricarbonyl[(1,2,3,4,5,6-η)-(1',2',3',4',5',6'-η)-2-methoxy-6-acetoxymethyl-2'-methylbiphenyl]chromium (7)*

M.p. 170 °C. IR ($CHCl_3$): 1980, 1960, 1890, 1740, 1280, 1210 $cm^{-1}$. $^1H$ NMR (400 MHz) δ: 1.99 (s, 3H), 2.01 (s, 3H), 3.86 (s, 3H), 4.45 (d, $J$ = 12.8 Hz, 2H), 4.89 (d, $J$ = 7.2 Hz, 1H), 4.97 (d, $J$ = 7.2 Hz, 1H), 5.04 (t, $J$ = 7.2 Hz, 2H), 5.63 (t, $J$ = 7.2 Hz, 1H), 5.75 (t, $J$ = 7.2 Hz, 1H), 5.84 (t, $J$ = 7.2 Hz, 1H). $^{13}C$ NMR (100 MHz) δ: 19.29, 20.56, 55.82, 63.22, 70.52, 83.80, 85.22, 87.89, 94.71, 96.97, 97.30, 97.90, 101.46, 108.45, 111.78, 140.97, 169.62, 231.48, 232.29. *Anal.* Calc. for $C_{23}H_{18}O_9Cr_2$: C, 50.93; H, 3.34. Found: C, 50.87; H, 3.33%.

*Cross-coupling of 8 with 2-methylphenylboronic acid*

A mixture of tricarbonyl(2-bromo-3-methoxybenzyl-alcohol)chromium (**8**) (150 mg, 0.45 mmol), *o*-methylphenylboronic acid (150 mg, 0.89 mmol) and $Pd(PPh_3)_4$ (25.8 mg, 0.022 mmol) in aqueous sodium carbonate (2 M, 0.5 ml) and MeOH (5 ml) was degassed by three cycles of freezer/pump/thaw, and refluxed at 75 °C for 30 min under nitrogen. The reaction mixture was extracted with ether, and the extract was washed with aqueous 10% sodium hydroxide and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was purified by silica gel flash chromatography to give the (*S**, *S**)-chromium complex **10** (140 mg, 76.5%) without any detectable formation of the other atropisomer. M.p. 156 °C. IR ($CHCl_3$): 3325, 1960, 1885, 1670 $cm^{-1}$. $^1H$ NMR (400 MHz) δ: 1.71 (m, 1H), 2.64 (s, 3H), 3.71 (s, 3H), 4.09 (dd, $J$ = 15.0, 6.0 Hz, 1H), 4.34 (dd, $J$ = 15.0, 8.0 Hz, 1H), 5.16 (d, $J$ = 6.1 Hz, 1H),

5.21 (d, $J=6.1$ Hz, 1H), 5.77 (t, $J=6.1$ Hz, 1H), 7.02 (d, $J=7.9$ Hz, 1H), 7.16 (dd, $J=7.8$, 6.7 Hz, 1H), 7.28–7.33 (m, 2H). *Anal.* Calc. for $C_{18}H_{16}O_6Cr$: C, 59.34; H, 4.39. Found: C, 59.24; H, 4.47%.

## Supplementary material

Lists of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, torsion angles for complexes **2**, **3**, **4**, **6**, **7** and **11** are available from author M.U.

## Acknowledgements

Partial financial support for this work was provided by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan, and by a Ciba-GEIGY Foundation (Japan) for the promotion of Science. We thank Miss Junko Shinya for a measurement of NMR spectra.

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