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Stereoselective tricarbonylchromium migration reactions in axially chiral biaryl chromium complexes

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Abstract

The tricarbonylchromium group in thermodynamically unstable biaryl chromium complexes with a coordinating heteroatom at the side chain stereoselectively migrated to the other arene face to release the steric repulsion.

Keywords: Arene–chromium complex; Planar chirality; Stereoselective migration; Mobile chiral auxiliary

1. Introduction

Metal migration from one site of a coordinated organometallic ligand to another is a well-known process occurring in oligocyclic fused π-arene complexes due to the haptotropic ring slippage from η^6 to η^4 coordination mode [1]. This kind of migration has been actively studied in naphthalene tricarbonylchromium complexes and widely utilized for useful organometallic reagents [2]. On the other hand, the migration of a tricarbonylchromium group between two different and nonadjacent six-membered rings, such as in biphenyl tricarbonylchromium complexes, was reported by several groups [3]. One attractive yet troublesome feature of these tricarbonylchromium migrations to the arene ring having different substituents at *ortho* or *meta* positions is the stereoselectivity based on planar chirality, which may lead to the formation of an enantiomer or a diastereomer via the migration reaction. Although the tricarbonylchromium slippage in oligocyclic fused π-arene complexes was proven to be an equilibrium process with retention of planar chirality, the migration between two different and nonadjacent six-membered rings has never been examined so far.

We reported previously the inversion of planar chirality in thermodynamically unstable *syn*-biaryl chromium complexes having a coordinating heteroatom at the side chain of arene–chromium complexes under thermal conditions (Scheme 1) [4].

The tricarbonylchromium migration to another arene B ring in *syn*-biaryl chromium complexes, which is attractive in terms of transfer of planar chirality as a mobile chiral auxiliary, is expected [5]. Thus, asymmetric reactions leading to regio- and stereoselective tricarbonylchromium migrations between two different and nonadjacent six-membered rings have much room for further development, utilizing planar chiral arene–chromium complexes.

Herein, we report in detail stereoselective tricarbonylchromium migration to another arene ring and its application to the stereoselective synthesis of axially chiral biaryl tricarbonylchromium complexes.

2. Results and discussion

We previously examined the inversion of planar chirality in thermodynamically unstable *syn*-biaryl chromium

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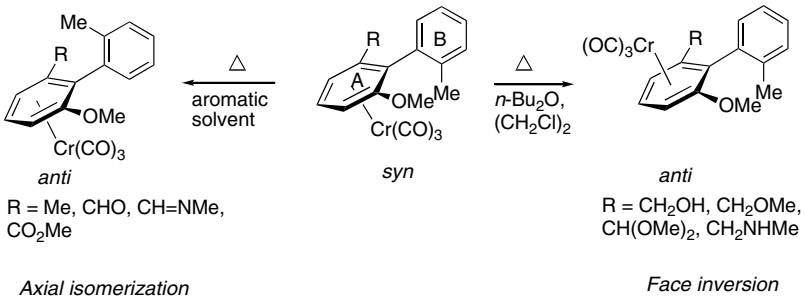


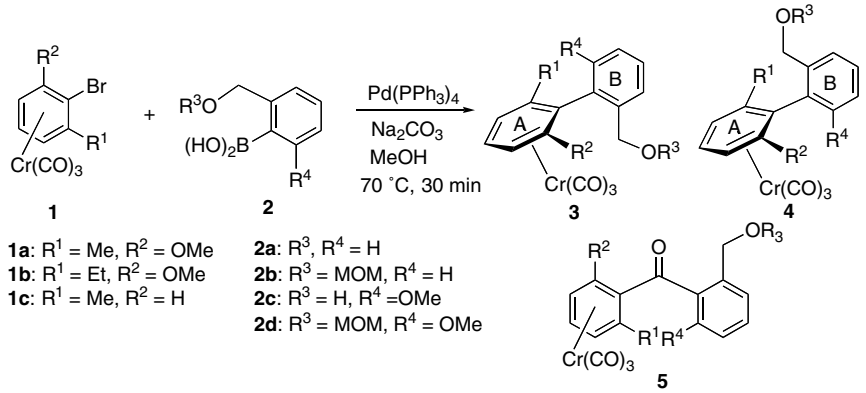
Scheme 1. Axial isomerization vs. planar chirality inversion.

complexes under thermal conditions, and found that the coordinating heteroatom at the sp^3-benzylic position plays an important role in lowering the arene–chromium bond cleavage of the complexes [4]. Thus, we examined the stereochemical behavior under thermal conditions of *syn*-biaryl chromium complexes having a coordinating heteroatom at the sp^3-benzylic position of the chromium-uncomplexed arene ring.

Initially, starting thermodynamically unstable *syn*-biaryl chromium complexes were prepared by stereoselective Suzuki–Miyaura cross-coupling reactions utilizing the planar chirality of arene–chromium complexes developed by our group. The results are summarized in Table 1. In most cases, desired biaryl chromium complexes **3** were obtained in moderate to good yields with high diastereoselectivities.

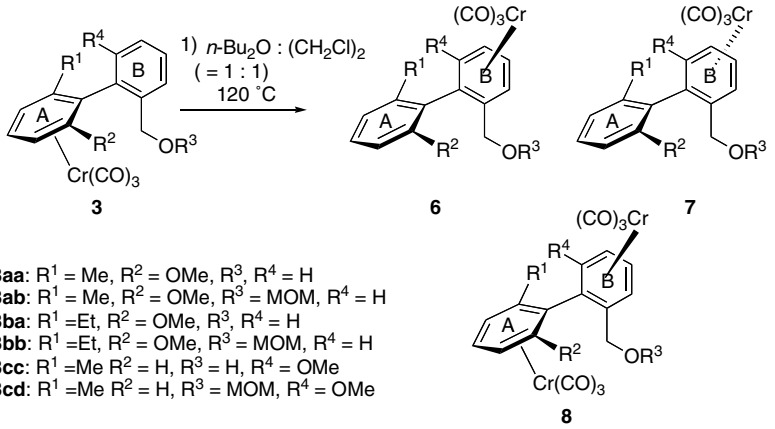
With the starting *syn*-biaryl chromium complexes in hand, we next examined the stereoselective migration reactions under thermal conditions (Table 2). *syn*-(η-1,2,3,4,5,6)-Tricarbonyl(2-methoxy-6-methyl-2′-hydroxymethylbiphenyl)chromium complex (**3aa**) was refluxed in a mixture of di-*n*-butyl ether and dichloroethane to give tricarbonylchromium migration products **6aa** (36%) and **7aa** (8%) as an 82:18 diastereomeric mixture along with 37% yield of a de-chromium product (entry 1). The relative stereochemistry of these complexes was determined from the chemical shifts in the ^{1}H NMR spectra [6]. Neither central bond rotation nor chromium migration to the reversed arene A ring was observed under the conditions employed. Thus, the $Cr(CO)_3$ fragment migrated exclusively to the arene ring that was substituted with a hydroxymethyl group regardless of the electron density of the arene ring. In addition, complex **6aa** was formed as a major diastereomer to avoid the steric repulsion between the $Cr(CO)_3$ fragment and the methyl group, which is a larger substituent than a methoxy group. We next examined the migration reactions utilizing complex **3ab** that hydroxymethyl group on the B ring was protected with a methoxymethyl group (entry 2), and found that the reaction, although time-consuming, gave migration product **6ab**, presumably due to the lowering of the coordinating ability by protection of

Table 1
Stereoselective synthesis of axially chiral biaryls by Suzuki–Miyaura cross-coupling reactions



Entry	Complex	Boronic acid	Product (yield, (%))			Ratio (**3**:**4**)
			3	**4**	**5**	
1	**1a**	**2a**	**3aa** (54)		**5aa** (14)	>98:<2
2	**1a**	**2b**	**3ab** (81)			>98:<2
3	**1b**	**2a**	**3ba** (40)		**5ba** (20)	>98:<2
4	**1b**	**2b**	**3bb** (85)			>98:<2
5	**1c**	**2c**	**3cc** (28)		**5cc** (14)	>98:<2
6	**1c**	**2d**	**3cd** (72)	**4cd** (5)		94:6

Table 2
Stereoselective tricarbonylchromium migration reactions under thermal conditions



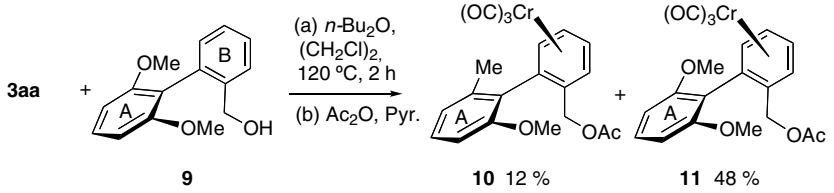
Entry	Complex	Time (h)	Products (yield, (%))		
			6	**7**	**8**
1	**3aa**	1.5	**6aa** (36)	**7aa** (8)	
2	**3ab**	4.0	**6ab** (23)	**7ab** (2)	**8ab** (15)
3	**3ba**	1.5	**6ba** (45)		
4	**3bb**	4.0	**6bb** (17)		**8bb** (8)
5	**3cc**	2.0	**6cc** (47)		**8cc** (3)
6	**3cd**	4.0			**8cd** (1)

the hydroxyl group. Furthermore, bis-tricarbonylchromium coordinated product **8ab** was obtained, which was not isolated in the migration reaction utilizing complex **3aa** having a hydroxyl group. With the intent of improving the diastereoselectivity, we next examined the migration reaction using complexes **3ba** and **3bb**, both of which have an ethyl group on the A ring (entries 3 and 4). As expected, the diastereoselectivity was improved by increasing the steric demand to discriminate the arene faces. Furthermore, when the *ortho*-three-substituted biaryl complex **3cc** having one methoxy group and one hydroxymethyl group on the B ring was used, the migration reaction proceed smoothly to give **6cc** in moderate yield with high diastereoselectivity (entry 5). In contrast, the migration reaction utilizing complex **3cd** having a methoxymethyl ether group was unsuccessful, and 60% of the starting material was recovered (entry 6).

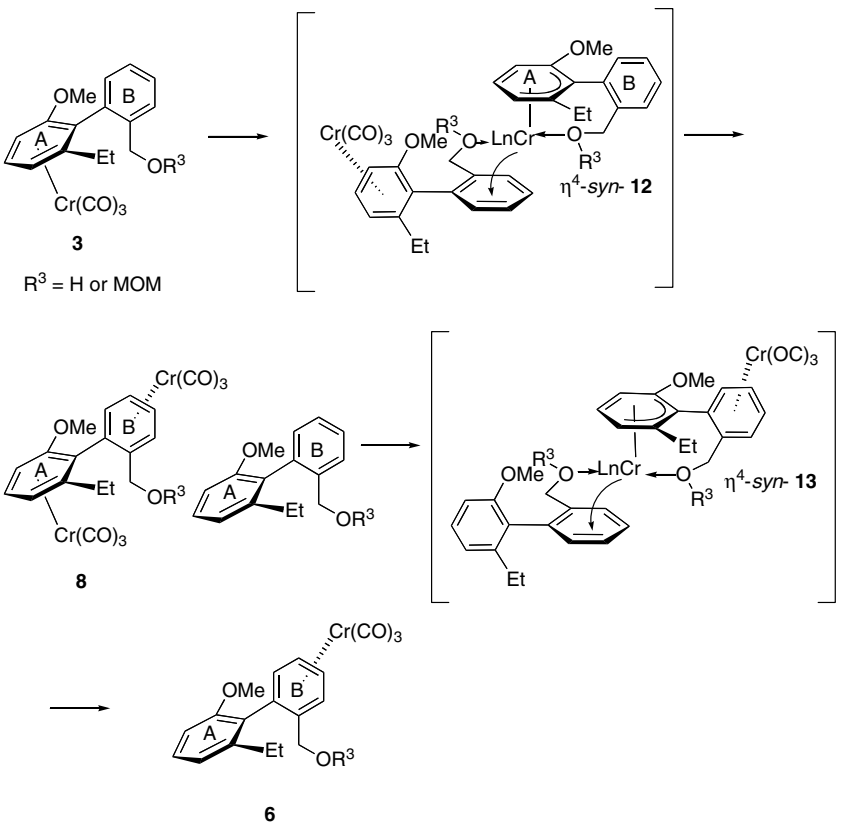
To clarify the reaction mechanism, we next studied the crossover reaction between a *syn*-biaryl chromium complex and a chromium-free biaryl compound under thermal conditions. A 1:1 mixture of *syn*-biaryl chromium complex **3aa** and 2,6-dimethoxy-2′-hydroxymethyl biphenyl (**9**) in di-*n*-butyl ether and dichloroethane was heated at 120 °C for 2 h, and the reaction products were analyzed after acetylation (Scheme 2). The $Cr(CO)_3$ fragment of complex **3aa** migrated to the B ring of biaryl compound **9** to give biaryl complex **11** as the major chromium complex. These results indicate that the migration of chromium in **3aa** having benzylic heteroatom substituents under thermal conditions proceeds in an *intermolecular* fashion.

In addition, from the finding that the direct chromium complexation of chromium-free biaryl compound gave a variety of regio- and stereoisomers, the hypothesis that tricarbonylchromium migration is attributed to the recomplexation of the $Cr(CO)_3L_3$ (L = solvent) species generated by de-chromium complexation can be ruled out [4,6].

On the basis of these experiments, a plausible mechanism for the stereoselective chromium migration is proposed in Scheme 3. Intramolecular coordination of chromium with the benzylic heteroatom on the B ring occurs and a coordinating solvent assists slippage for a η^4-*syn*-**12** intermediate of *syn*-biphenyl complex **3**. Subsequently, another benzylic heteroatom of the *syn*-biaryl



Scheme 2. Crossover reaction.

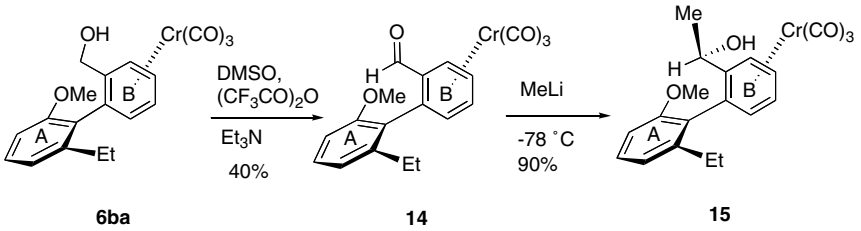


Scheme 3. Proposed mechanism.

chromium complex coordinates with the chromium of the η^4-*syn*-**12** intermediate for dual activation. Then, chromium migration proceeds from the less hindered side of the B ring regardless of electron density. As a result, bis-tricarbonylchromium coordinated biaryl **8** and uncomplexed biaryl are generated. Next, the second migration reaction proceeds between **8** and uncomplexed biaryl via the η^4-*syn*-**13** intermediate in a similar manner. In this way, a tricarbonylchromium group stereoselectively migrates to the less hindered side of the B ring.

As the planar chirality of biaryl chromium complex was transferred to another arene ring by the stereoselective tricarbonylchromium migration reactions, we next studied the stereoselective functionalization at the side chain utilizing the newly generated planar chirality of the complexes (Scheme 4). The stereoselective addition to the *ortho* formyl group of biaryl chromium complexes was examined, because planar chiral *o*-substituted benzaldehyde chromium complexes are versatile compounds in asymmetric synthesis [7]. The hydroxymethyl group of complex **6ba** was oxidized with dimethylsulfoxide and trifluoroacetic anhydride to form the formyl group. The resulting benzaldehyde chromium complex **14** was treated with MeLi to give predominantly biaryl secondary alcohol **15** in a ratio of >98:<2. The high diastereoselectivity of the addition of MeLi to the chromium-complexed benzaldehyde is due to an *exo* attack of nucleophile at the *anti*-oriented carbonyl group with an *ortho*-substituent due to stereoelectronic effect [8].

Therefore, we succeeded in controlling not only the axial chirality but also the chirality at the side chain from a single mobile chiral auxiliary.



Scheme 4. Stereoselective nucleophilic reaction utilizing a mobile chiral auxiliary.

3. Conclusion

In conclusion, we demonstrated the stereoselective tricarbonylchromium migration reactions of thermodynamically unstable biaryl chromium complexes. The incorporation of a directing group such as a hydroxyl group plays an important role in the migration of the tricarbonylchromium group.

Together, these results indicate that we could control both the axial chirality and the chirality at the side chain from a single chiral source.

4. Experimental

4.1. Preparation for syn-biaryl mono tricarbonylchromium complexes

Complexes **3aa**–**3cd** were prepared by reported stereoselective cross-coupling reaction of corresponding arene–chromium complexes with aryl boronic acids, in addition, complexes **3aa**, **5aa**, **3cd**, **4cd** were known compounds [9].

4.1.1. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-methyl-2′-methoxymethoxy methylbiphenyl]chromium complex *3ab*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (3H, s), 3.47 (3H, s), 3.68 (3H, s), 4.83–4.90 (4H, m), 5.06 (1H, d, $J = 6.6$ Hz), 5.35 (1H, d, $J = 13.4$ Hz), 5.67 (1H, d, $J = 6.6$ Hz), 7.01 (1H, d, $J = 7.6$ Hz), 7.26 (1H, t, $J = 7.6$ Hz), 7.43 (1H, t, $J = 7.6$ Hz), 7.73 (1H, d, $J = 7.6$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 55.4, 55.8, 66.4, 72.1, 86.0, 94.5, 96.3, 101.6, 111.5, 126.6, 127.5, 128.5, 129.8, 132.2, 133.4, 137.7, 140.8; IR ($CHCl_3$) 2947, 1974, 1900, 1668, 1601, 1573, 1269 cm^{-1}; MS (relative intensity) *m*/*z*; 408 (M, +2), 380 (1), 352 (5), 324 (52), 264 (90), 249 (100); HRMS calcd for $C_{20}H_{20}O_6Cr$: 408.0665, found 408.0663.

4.1.2. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-ethyl-2′-hydroxymethyl biphenyl]chromium complex *3ba*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (3H, t, $J = 7.3$ Hz), 2.01 (1H, br), 2.17–2.29 (2H, m), 3.66 (3H, s), 4.90 (1H, d, $J = 6.4$ Hz), 5.09 (1H, d, $J = 6.4$ Hz), 5.19–5.21 (2H, m), 5.73 (1H, t, $J = 6.4$ Hz), 7.00 (1H, d, $J = 7.7$ Hz), 7.27 (1H, t, $J = 7.7$ Hz), 7.44 (1H, t, $J = 7.7$ Hz), 7.72 (1H, d, $J = 7.7$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 26.5, 55.8, 56.0, 62.0, 72.4, 83.9, 94.9, 117.5, 126.8, 128.7, 128.8, 129.6, 132.6, 139.4, 140.8, 233.4; IR ($CHCl_3$) 3690, 2925, 2853, 1963, 1886, 1601, 1571 cm^{-1}; MS (relative intensity) *m*/*z* 378 (M, +3), 350 (8), 322 (11), 294 (100), 276 (28), 261 (53); HRMS calcd for $C_{19}H_{18}O_5Cr$: 378.0559, found 378.0559.

4.1.3. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-ethyl-2′-methoxymethoxymethylbiphenyl]chromium complex *3bb*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (3H, t, $J = 7.5$ Hz), 2.17–2.35 (2H, m), 3.47 (3H, s), 3.66 (3H, s), 4.83–4.89 (3H, m), 4.99 (1H, d, $J = 13.0$ Hz), 5.06 (1H, d, $J = 6.7$ Hz), 5.33 (1H, d, $J = 13.0$ Hz), 5.71 (1H, t, $J = 6.7$ Hz), 7.01 (1H, d, $J = 7.2$ Hz), 7.25 (1H, t, $J = 7.2$ Hz), 7.43 (1H, t, $J = 7.2$ Hz), 7.72 (1H, d, $J = 7.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.7, 26.4, 55.5, 55.9, 66.4, 72.0, 83.7, 94.7, 96.4, 101.7, 117.4, 126.5, 127.7, 128.5, 129.6, 132.6, 137.4, 140.9, 233.4; IR ($CHCl_3$) 3689, 2931, 2851, 1963, 1889, 1601, 1576, 1506 cm^{-1}; MS (relative intensity) *m*/*z* 422 (M, +3), 394 (2), 366 (5), 338 (63), 278 (100); HRMS calcd for $C_{21}H_{22}O_6Cr$: 422.0821, found 422.0823.

4.1.4. (S^*_{ax}, R^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-methyl-2′-methoxy-6′-hydroxymethylbiphenyl]chromium complex *3cc*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.93 (3H, s), 1.98 (1H, br), 3.71 (3H, s), 5.03 (1H, d, $J = 12.2$ Hz), 5.16–5.20 (2H, m), 5.35 (1H, d, $J = 12.2$ Hz), 5.60 (1H, d, $J = 6.2$ Hz), 5.65 (1H, t, $J = 6.2$ Hz), 6.88 (1H, d, $J = 8.0$ Hz), 7.28 (1H, d, $J = 8.0$ Hz), 7.41 (1H, t, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5, 55.7, 62.0, 87.7, 90.6, 96.4, 100.1, 107.1, 110.0, 112.1, 121.9, 122.6, 129.8, 139.3, 157.9, 233.6; IR ($CHCl_3$) 3358, 2994, 1970, 1890, 1563 cm^{-1}; MS (relative intensity) *m*/*z* 364 (M, +8), 336 (13), 308 (11), 280 (100), 247 (61), 232 (40), 228 (32); HRMS calcd for $C_{18}H_{16}O_5Cr$: 364.0405, found 364.0404.

4.1.5. Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-ethyl-2′-hydroxymethylbenzophenone]chromium complex *5ba*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (3H, t, $J = 7.6$ Hz), 2.44–2.55 (2H, m), 2.61 (3H, s), 3.67 (1H, br s), 4.72–4.77 (3H, m), 4.85 (1H, dd, $J = 5.6$, 12.9 Hz), 4.96 (1H, d, $J = 6.7$ Hz), 5.64 (1H, t, $J = 6.7$ Hz), 7.33–7.37 (1H, m), 7.56–7.57 (1H, m), 7.67 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 25.2, 56.1, 64.4, 70.0, 82.6, 94.1, 103.6, 115.4, 127.6, 130.5, 132.2, 133.6, 136.0, 140.6, 142.4, 194.4, 232.0; IR ($CHCl_3$) 2989, 1973, 1896, 1572, 1456 cm^{-1}; MS (relative intensity) *m*/*z* 406 (M, +3), 388 (2), 364 (5), 350 (10), 322 (50), 293 (66), 278 (100); HRMS calcd for $C_{20}H_{18}O_6Cr$: 406.0509, found 406.0512.

4.1.6. Tricarbonyl[(1,2,3,4,5,6-η)-2-methyl-2′-methoxy-6′-hydroxymethyl benzophenone]chromium complex *5cc*

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (1H, s), 2.51 (3H, s), 3.75 (3H, s), 4.54-4.68 (2H, m), 4.98 (1H, t, $J = 6.3$ Hz), 5.07 (1H, d, $J = 6.3$ Hz), 5.65–5.70 (2H, m), 6.91 (1H, d, $J = 8.0$ Hz), 7.15 (1H, d, $J = 8.0$ Hz), 7.45 (1H, t, $J = 8.0$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.8, 55.7, 63.3, 86.4, 91.8, 96.0, 98.1, 110.5, 112.7, 121.9, 127.5, 131.9, 140.9, 154.7, 156.6, 197.0, 231.1; IR ($CHCl_3$) 3360, 3006, 1977, 1900, 1600 cm^{-1}; MS (relative intensity) *m*/*z* 392 (M, +7), 374 (24), 336 (43), 308 (93), 275 (100); HRMS calcd for $C_{19}H_{16}O_5Cr$: 392.0352, found 392.0355.

4.2. General procedure for stereoselective tricarbonylchromium migration reaction

A solution of *syn* biaryl complex **3** (0.25 mmol) in mixture of *n*-dibutylether (2 mL) and dichroloethane (2 mL)

was stirred at 120 °C for 2 h. The solvent was removed under reduced pressure, and the residue was purified by silica gel chromatography to give tricarbonylchromium migrated biaryl complex.

Complexes **6aa**, **6ba**, **6cc** and **8cc** were characterized after transformed to acetylated complexes **10**, **6ba′**, **6cc′** and **8cc′** respectively. Complex **10** was known compound [4a].

4.2.1. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxymethoxymethyl-2′-methoxy-6′-methylbiphenyl]chromium complex **6ab**

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (3H, s), 3.21 (3H, s), 3.89 (3H, s), 4.00 (1H, d, $J = 12.5$ Hz), 4.21 (1H, d, $J = 12.5$ Hz), 4.47 (1H, d, $J = 6.6$ Hz), 4.57 (1H, d, $J = 6.6$ Hz), 5.09 (1H, t, $J = 6.8$ Hz), 5.41 (1H, d, $J = 6.8$ Hz), 5.51 (1H, d, $J = 6.8$ Hz), 5.62 (1H, t, $J = 6.8$ Hz), 6.81–6.88 (2H, m), 7.26 (1H, t, $J = 7.9$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 30.5, 55.1, 55.2, 66.1, 85.3, 86.8, 95.1, 96.4, 98.3, 108.7, 110.5, 122.6, 129.5, 135.6, 139.4, 155.1, 233.3; IR ($CHCl_3$) 2991, 1966, 1891 cm^{-1}; MS (relative intensity) *m/z* 408 (M, +1), 324 (50), 264 (83), 249 (100); HRMS calcd for $C_{20}H_{20}O_6Cr$: 408.0656, found 408.0666.

4.2.2. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-acetoxymethyl-2′-methoxy-6′-ethylbiphenyl]chromium complex **6ba′**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (3H, t, $J = 7.5$ Hz), 1.99 (3H, s), 2.39–2.57 (2H, m), 3.90 (3H, s), 4.58 (1H, d, $J = 13.2$ Hz), 4.75 (1H, d, $J = 13.2$ Hz), 5.10 (1H, t, $J = 6.1$ Hz), 5.38 (1H, d, $J = 6.1$ Hz), 5.44 (1H, d, $J = 6.1$ Hz), 5.59 (1H, t, $J = 6.1$ Hz), 6.82 (1H, d, $J = 8.0$ Hz), 6.92 (1H, d, $J = 8.0$ Hz), 7.33 (1H, t, $J = 8.0$ Hz); IR ($CHCl_3$) 2972, 2361, 1338, 1969, 1898, 1727, 1599, 1577 cm^{-1}; MS (relative intensity) *m/z* 420 (M, +3), 364 (6), 336 (79), 321 (82), 305 (41); HRMS calcd for $C_{21}H_{20}O_6Cr$: 420.0665, found 420.0660.

4.2.3. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxymethoxymethyl-2′-methoxy-6′-ethylbiphenyl]chromium complex **6bb**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (3H, t, $J = 7.5$ Hz), 2.42–2.53 (2H, m), 3.21 (3H, s), 3.89 (3H, s), 4.00 (1H, d, $J = 12.7$ Hz), 4.21 (1H, d, $J = 12.7$ Hz), 4.49 (1H, d, $J = 6.6$ Hz), 4.59 (1H, d, $J = 6.6$ Hz), 5.08 (1H, t, $J = 6.1$ Hz), 5.44 (1H, d, $J = 6.1$ Hz), 5.53 (1H, d, $J = 6.1$ Hz), 5.62 (1H, t, $J = 6.1$ Hz), 6.82 (1H, d, $J = 8.2$ Hz), 6.90 (1H, d, $J = 8.2$ Hz), 7.32 (1H, t, $J = 8.2$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.0, 26.7, 55.0, 55.2, 66.0, 86.6, 88.3, 95.2, 96.4, 98.3, 103.3, 108.6, 110.9, 120.9, 127.3, 129.8, 145.5, 154.9, 233.4; IR ($CHCl_3$) 3694, 2967, 2923, 1966, 1891, 1605, 1576, 1464 cm^{-1}; MS (relative intensity) *m/z* 422 (M, +3), 394 (2), 366 (5), 338 (63), 278 (100); HRMS calcd for $C_{21}H_{22}O_6Cr$: 422.0821, found 422.0823.

4.2.4. (S^*_{ax}, R^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-methoxy-6-acetoxymethyl-2′-methylbiphenyl]chromium complex **6cc′**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (3H, s), 2.09 (3H, s), 3.65 (3H, s), 4.59 (1H, d, $J = 12.8$ Hz), 4.65 (1H, d, $J = 12.8$ Hz), 4.98 (1H, d, $J = 6.2$ Hz), 5.04 (1H, d, $J = 6.2$ Hz), 5.73 (1H, t, $J = 6.2$ Hz), 7.22–7.32 (3H, m), 7.42 (1H, d, $J = 6.1$ Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.6, 20.5, 56.0, 62.9, 71.2, 83.3, 94.5, 104.4, 108.5, 126.5, 129.0, 129.7, 130.2, 134.1, 137.6, 142.4, 169.9, 232.7; IR ($CHCl_3$) 3000, 1968, 1893, 1738, 1562 cm^{-1}; MS (relative intensity) *m/z* 406 (M, +6), 350 (4), 322 (20), 307 (15), 270 (100); HRMS calcd for $C_{20}H_{18}O_6Cr$: 406.0509, found 406.0505.

4.2.5. ($S^*_{ax}, R^*_{pl}, S^*_{pl}$)-Di-tricarbonyl[(1,2,3,4,5,6-η)-(1′,2′,3′,4′,5′,6′-η)-2-methoxy-6-methyl-2′-methoxymethoxymethylbiphenyl]chromium complex **8ab**

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.16 (3H, s), 3.46 (3H, s), 3.90 (3H, s), 4.34 (1H, d, $J = 13.7$ Hz), 4.83–4.87 (3H, m), 4.93 (1H, d, $J = 13.7$ Hz), 5.06 (1H, t, $J = 6.6$ Hz), 5.18 (1H, d, $J = 6.6$ Hz), 5.35 (1H, t, $J = 6.6$ Hz), 5.65–5.72 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 55.7, 55.8, 65.8, 72.1, 86.1, 92.9, 94.4, 96.4, 112.2, 126.6, 127.5, 128.0, 128.6, 132.3, 158.3, 170.7, 232.5, 232.6; IR ($CHCl_3$) 3006, 2949, 1963, 1892 cm^{-1}; MS (relative intensity) *m/z* 544 (M, +3), 459 (20), 345 (100), 248 (65); HRMS calcd for $C_{23}H_{20}O_9Cr_2$: 543.9918, found 543.9906.

4.2.6. ($S^*_{ax}, R^*_{pl}, S^*_{pl}$)-Di-tricarbonyl[(1,2,3,4,5,6-η)-(1′,2′,3′,4′,5′,6′-η)-2-methoxy-6-ethyl-2′-methoxymethoxymethylbiphenyl]chromium complex **8bb**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (3H, t, $J = 7.4$ Hz), 2.25–2.33 (1H, m), 2.57–2.66 (1H, m), 3.46 (3H, s), 3.90 (3H, s), 4.38 (1H, d, $J = 13.4$ Hz), 4.81 (1H, d, $J = 6.3$ Hz), 4.85 (1H, d, $J = 6.3$ Hz), 4.92 (1H, d, $J = 6.4$ Hz), 4.95, (1H, d, $J = 13.4$ Hz), 5.03 (1H, t, $J = 6.4$ Hz), 5.20 (1H, d, $J = 6.4$ Hz), 5.38 (1H, d, $J = 6.4$ Hz), 5.64–5.76 (3H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 29.7, 55.9, 65.7, 73.5, 83.5, 85.6, 87.9, 94.7, 95.4, 96.8. 99.1, 116.3, 126.5, 127.6, 128.5, 132.6, 138.3, 232.5, 233.4; IR ($CHCl_3$) 3694, 2971, 2930, 2253, 1963, 1892, 1601, 1567, 1456 cm^{-1}; MS (relative intensity) *m/z* 558 (M, +4), 530 (3), 474 (11), 446 (9), 360 (69), 338 (20), 278 (42), 263 (46), 224 (82), 209 (100); HRMS calcd for $C_{24}H_{22}O_9Cr_2$: 558.0074, found 558.0070.

4.2.7. ($S^*_{ax}, S^*_{pl}, S^*_{pl}$)-Di-tricarbonyl[(1,2,3,4,5,6-η)-(1′,2′,3′,4′,5′,6′-η)-2-methoxy-6-acetoxymethyl-2′-methylbiphenyl]chromium complex **8cc′**

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02 (3H, s), 2.14 (3H, s), 3.65 (3H, s), 4.95–5.10 (5H, m), 5.70–5.80 (4H, m); IR ($CHCl_3$) 2977, 2254, 1980, 1966, 1898, 1602 cm^{-1}; MS (relative intensity) *m/z* 542 (M, +4), 486 (6), 458 (34), 420 (3), 406 (7), 374 (100), 346 (16), 322 (52); HRMS calcd for $C_{23}H_{18}O_9Cr_2$: 541.9761, found 541.9759.

4.3. Oxidation reaction of the planar chiral biaryl chromium complex **6ba**

Oxidation reaction of biaryl chromium complex **14** was carried out according to the reported procedure [10].

4.3.1. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-formyl-2′-methoxy-6′-ethylbiphenyl]chromium complex **14**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (3H, t, $J = 7.6$ Hz), 2.53–2.65 (2H, m), 3.88 (3H, s), 5.41 (1H, d, $J = 6.4$ Hz), 5.47 (1H, t, $J = 6.4$ Hz), 5.55 (1H, t, $J = 6.4$ Hz), 5.91 (1H, d, $J = 6.4$ Hz), 6.87 (1H, d, $J = 8.0$ Hz), 6.98 (1H, d, $J = 8.0$ Hz), 7.38 (1H, t, $J = 8.0$ Hz), 9.40 (1H, s); ^{13}C NMR (125 MHz, C_6D_6) δ 27.0, 30.2, 54.9, 87.9, 90.0, 92.4, 109.0, 121.5, 127.3, 127.9, 128.1, 128.6, 130.6, 176.3, 232.4; IR ($CHCl_3$) 3160, 2257, 1980, 1913, 1802, 1599 cm^{-1}; MS (relative intensity) *m/z* 376 (M, +6), 292 (78), 193 (32), 58 (100); HRMS calcd for $C_{19}H_{16}O_5Cr$: 376.0402, found 376.0400.

4.4. Stereoselective nucleophilic addition reaction

The stereoselective nucleophilic addition reaction to the complex **15** was carried out according to the reported procedure [4a].

4.4.1. (S^*_{ax}, S^*_{pl})-Tricarbonyl[(1,2,3,4,5,6-η)-2-hydroxyethyl-2′-methoxy-6′-ethylbiphenyl]chromium complex **15**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (3H, d, $J = 6.4$ Hz), 1.15 (3H, t, $J = 7.7$ Hz), 2.25 (1H, br), 2.41 (2H, dq, $J = 3.2$, 7.7 Hz), 3.93 (3H, s), 4.39–4.44 (1H, m), 5.10 (1H, t, $J = 6.5$ Hz), 5.37 (1H, d, $J = 6.5$ Hz), 5.63 (1H, d, $J = 6.5$ Hz), 5.67 (1H, t, $J = 6.5$ Hz), 6.83 (1H, d, $J = 8.2$ Hz), 6.95 (1H, d, $J = 8.2$ Hz), 7.34 (1H, t, $J = 8.2$ Hz); IR ($CHCl_3$) 3360, 3000, 1964, 1887, 1561 cm^{-1}; MS (relative intensity) *m/z* 392 (M, +3), 336 (16), 308 (43), 290 (75), 275 (40), 256 (12), 238 (50), 223 (100); HRMS calcd for $C_{20}H_{20}O_5Cr$: 392.0716, found 392.0717.

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