Stereoselective Pinacol Coupling of Planar Chiral (Benzaldehyde)Cr(CO)3, (Benzaldimine)Cr(CO)3, Ferrocenecarboxaldehyde and (Dienal)Fe(CO)3 Complexes with Samarium Diiodide

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Abstract: An intermolecular pinacol coupling of the planar chiral tricarbonylchromium complexes of o-substituted benzaldehydes or benzaldimines with samarium(II) diiodide in THF produces exclusively *threo* 1,2-diols or 1,2-diamines in an optically pure form, while the corresponding *racemic* o-substituted benzaldehyde or benzaldimine chromium complexes give a mixture of *threo* and *erythro* pinacol coupling products in a various ratio depending upon the nature of o-substituent. Similarly, planar chiral 2-substituted ferrocenecarboxaldehydes and (dienal)Fe(CO)3 produce the corresponding 1,2-diols with high stereoselectivity. The generated transition metal-complexed ketyl radical intermediates are configurationally stable with restriction to a rotation about C_α-C_{ipso} bond.
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Keywords: planar chirality; pinacol coupling; (arene)chromium complex; 1,2-diol; 1,2-diamine

Introduction

Enantiomerically pure 1,2-diols or diamines and the related compounds have found widespread use as chiral ligands in asymmetric reactions.[1] While the optically active 1,2-diols have been conveniently synthesized by a catalytic asymmetric dihydroxylation of the olefins in good yields with high enantiopurity,[2] the generally accepted method for the preparation of chiral 1,2-diamines involves an optically resolution of racemic compounds with certain chiral carboxylic acids.[3] The reductive coupling of carbonyl compounds, pinacol coupling, is the most direct way to synthesize 1,2-diols. Although this reaction can be achieved in high yield by lanthanoid metals or low valent transition metals,[4] highly diastereoselective formation of 1,2-diols is problematic under conventional reductive coupling methods; e.g., benzaldehyde gave ca. a 1 : 1 mixture of *threo-* (*dl*) and *erythro* (*meso*) pinacols by reductive coupling of benzaldehyde with samarium diiodide(II).[5] The utilization of some modified reducing agents in the catalytic or stoichiometric reaction have been developed recently for the achievement of high stereoselectivity for the pinacol coupling.[6] However, the *threo* 1,2-diols can not be obtained in an enantiomerically enriched form by this type of coupling of aldehydes or ketones.

(η6-Arene)tricarbonylchromium complexes have some characteristic properties due to the strong electron-withdrawing ability and steric bulkiness of tricarbonylchromium fragment, and significant applications in organic synthesis have been developed.[7-9] The tricarbonylchromium group is well known to stabilize both the benzylic carbanion[8] and carbocation[9] intermediates. However, the reactivity, stability and stereochemical
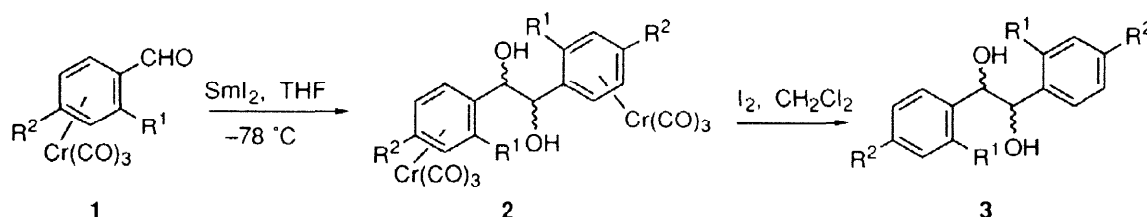
behavior of the chromium-complexed benzyl radical intermediates are little investigated.[10] In this paper, we wish to report that the ketyl radicals derived from tricarbonylchromium-complexed benzaldehydes, benzaldimines and the related metal-complexed substrates with samarium diiodide are stereoselectively coupled to give the corresponding pinacol adducts with *threo*-configuration.

Results and Discussion
Pinacol Coupling of Tricarbonyl(benzaldehyde)chromium Complexes

The reaction of tricarbonyl(benzaldehyde)chromium (1) ($R^1 = R^2 = H$) with 2.5 eq of samarium diiodide(II), generated *in situ* from Sm metal and 1,2-diiodoethane,[11] in THF at -78 °C gave the corresponding pinacol 3 as a diastereomeric mixture in a ratio of 91 : 9 after an oxidative demetalation of the coupling product 2 with I_2. The major product was assigned as the *threo* (*dl*) configuration by a comparison with authentic sample.[12] Thus, the tricarbonylchromium complexation of benzaldehyde resulted in extremely high *threo* selectivity by Sm(II)-mediated reductive coupling. Other results of the pinacol coupling of the tricarbonylchromium complexes of *o*- or *p*- substituted benzaldehydes are summarized in Table 1, and several facts are worthy of comment.[13] In addition to the unsubstituted benzaldehyde chromium complex, *ortho* or *para* substituted benzaldehyde chromium complexes afforded predominantly the corresponding *threo* pinacols. Slightly reduced *threo* selectivities were observed in a case of the hetero-atom substituted benzaldehyde chromium complexes at the *ortho* position (entries 7-10). In a striking contrast to the *threo* selectivity for these chromium complexes, *o*-bromobenzaldehyde chromium complex gave the corresponding *erythro* pinacol as a major product (entries 11,12), while the corresponding *p*-bromobenzaldehyde chromium complex produced the *threo* isomer as the major product (entry 16). The tricarbonylchromium complexation of bromobenzaldehyde is

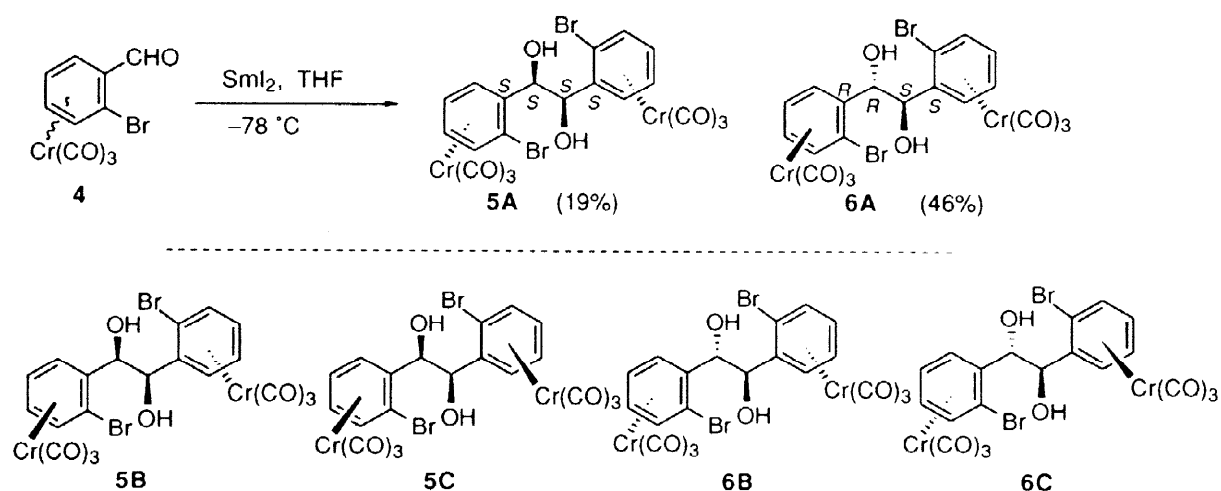### Table 1. Pinacol Coupling of (benzaldehyde)Cr(CO)₃ Complexes

Entry	Complex 1	Temp (°C)	Additive	Yields (%) *a*; *b*;	Ratio of 3 (*threo* : *erythro*)
1	$R^1 = R^2 = H$	-78	none	78, 92	91 : 9
2	$R^1 = R^2 = H$	0	none	78, 92	90 : 10
3	$R^1 = R^2 = H$	0	HMPA	80, 87	60 : 40
4	$R^1 = Me, R^2 = H$	-78	none	85, 91	95 : 5
5	$R^1 = Me, R^2 = H$	0	none	83, 91	95 : 5
6	$R^1 = Me, R^2 = H$	0	HMPA	80, 85	20 : 80
7	$R^1 = OMe, R^2 = H$	0	none	81, 91	80 : 20
8	$R^1 = OMe, R^2 = H$	0	HMPA	81, 89	8 : 92
9	$R^1 = OPr^i, R^2 = H$	rt	none	79, 90	79 : 21
10	$R^1 = NMe_2, R^2 = H$	-78	none	74, 92	73 : 27
11	$R^1 = Br, R^2 = H$	rt	none	84, 89	16 : 84
12	$R^1 = Br, R^2 = H$	0	none	85, 89	34 : 66
13	$R^1 = H, R^2 = Me$	0	none	78, 93	98 : 2
14	$R^1 = H, R^2 = OMe$	0	none	73, 91	91 : 9
15	$R^1 = H, R^2 = OMe$	-78	none	73, 91	92 : 8
16	$R^1 = H, R^2 = Br$	-78	none	75, 82	71 : 29

a; Pinacol coupling. *b*; Demetalation step with iodine.

essential for the pinacol coupling. Thus, the chromium free *o*-bromobenzaldehyde produced a carbonyl-phenyl coupling product having a linkage between the *para*-position of the phenyl ring and carbonyl groups, (3-bromo-4-formylphenyl)-2-bromophenylmethanol, in 35 % yield as the major product along with 7 % yield of the desired pinacol coupling product by treatment with samarium diiodide in THF.[14] On the other hand, the pinacol coupling of (benzaldehyde)Cr(CO)₃ complexes in the presence of 5 eq of HMPA resulted in an increase of the *erythro* 1,2-diols (entries 3,6,8). Thus, tricarbonyl(*o*-methoxy benzaldehyde)chromium gave predominantly the corresponding *erythro* 1,2-di-*o*-methoxyphenyl-1,2-ethanediol in a ratio of 92 : 8 by the reductive coupling in a mixture of HMPA and THF solvent. These results indicate that the *threo* coupling products can be predominantly obtained by a simple chromium complexation of benzaldehydes except of *o*-bromobenzaldehyde, and the addition of HMPA into the reaction solvent was changed to the *erythro* predominance.

In order to clarify a reaction mechanism of the pinacol coupling of tricarbonylchromium-complexed benzaldehydes, the relative stereochemistry of both *threo* and *erytho* tricarbonylchromium-complexed pinacols obtained from a *racemic* (*o*-brombenzaldehyde)Cr(CO)₃ was next investigated. The tricarbonylchromium complexes of both *threo* and *erytho* pinacols could possibly exist as three stereoisomers based on two chiral planes and two stereogenic centers, respectively. However, the samarium diiodide-mediated reductive coupling of the *racemic* (*o*-brombenzaldehyde)Cr(CO)₃ (4) at -78 °C in THF gave a single *threo* pinacol 5A among three possible *threo* isomers, 5A - 5C, and a single *erytho* pinacol 6A in 19 % and 46 % yields, respectively (Scheme 1). Proton signals of both *threo* pinacol 5A and *erythro* isomer 6A exhibit a symmetry. Thus, two benzylic protons of *O,O'*-dimethyl ether derived from the *threo* compound 5A appeared at 4.44 ppm as a sharp singlet and the corresponding protons of dimethyl ether of 6A showed a sharp singlet at 4.57 ppm. Methyl protons of the dimethyl ether compounds appeared at 3.34 ppm for the *threo*-isomer, and at 3.71 ppm for the *erythro*-isomer as a sharp singlet, respectively.

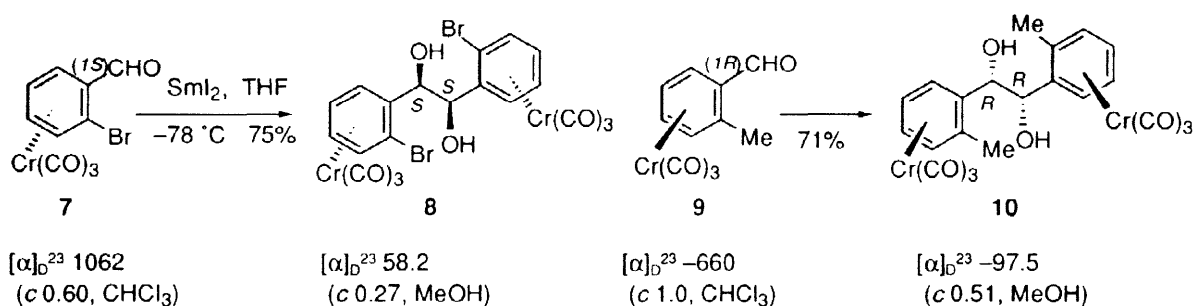**Scheme 1. Pinacol Coupling of *Racemic* (*o*-Bromobenzaldehyde)Cr(CO)₃** [a]

a; one enantiomer is shown for clarity

The relative stereochemistry of both chromium-complexed *threo*- and *erythro*-pinacol coupling products was finally determined by X-ray crystallography.[15] The *threo* pinacol 5A has 1(*S**),α(*S**),α'(*S**),1'(*S**)-configuration,[16] while the stereochemistry of *erythro* pinacol 6A is found to be 1(*R**),α(*R**),α'(*S**),1'(*S**)-configuration.[16] These stereochemical results indicate that each benzylic stereogenic center of both coupling products 5A and 6A is controlled by its adjacent chromium-complexed planar chirality, respectively. And, the *threo* pinacol 5A is consistent by the both rings with identical planar chirality, while the both rings of *erythro* pinacol 6A have different planar chirality. In other words, the *threo* pinacol 5A was obtained by a homo-

coupling of the same planar chiral (o-bromobenzaldehyde)Cr(CO)₃, while the *erythro* pinacol 6A was formed by a hetero-coupling of different planar chiral (η⁶-arene)chromium complex to each other.
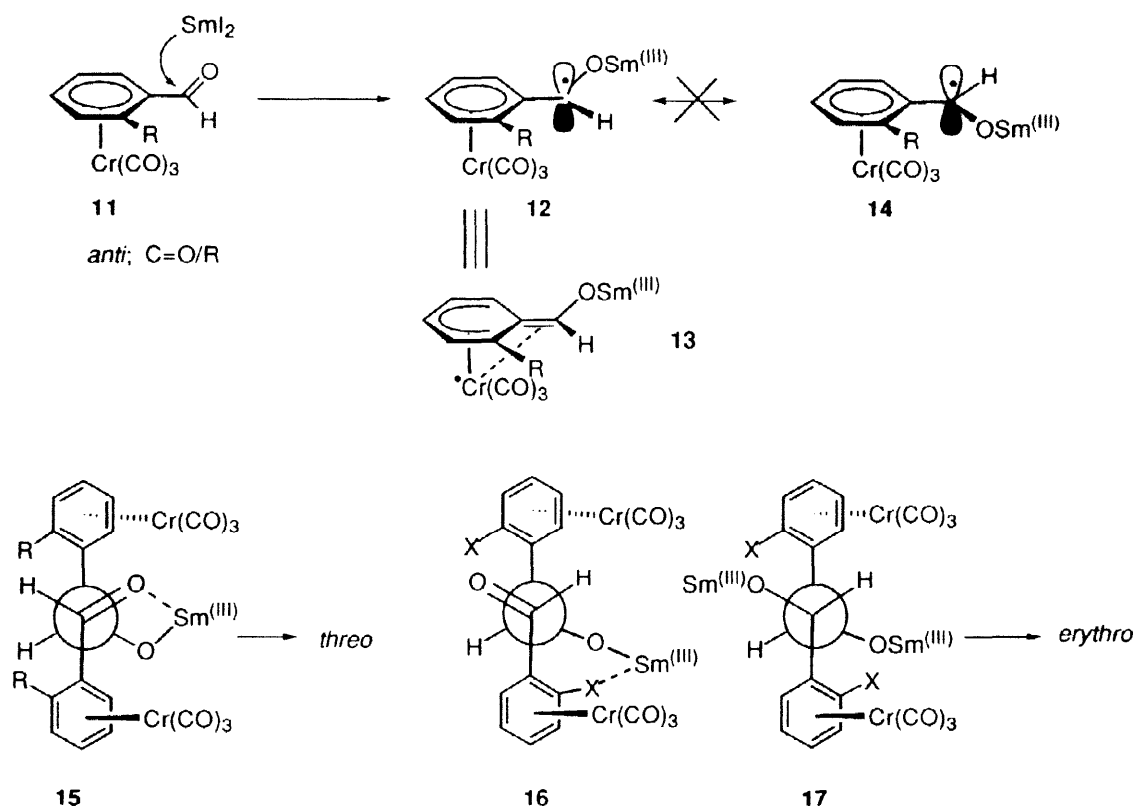
These stereochemical results of the chromium-complexed pinacols predict that an enantiomerically pure (o-substituted benzaldehyde)Cr(CO)₃ could produce only *threo* 1,2-diol as a single coupling product. Indeed, the enantiomerically pure (1S)-(+)-tricarbonyl(o-bromobenzaldehyde)chromium (7)[17] was treated with samarium diiodide in THF at -78°C to produce a single *threo* pinacol complex 8 in 75 % yield without formation of the *erythro* isomer (Scheme 2). Similarly, the optically pure (1R)-(−)-(o-methylbenzaldehyde)Cr(CO)₃ (9) gave the corresponding *threo* pinacol complex 10 in 71% yield. In this way, the enantiomerically pure 1,2-diols could be synthesized by the pinacol coupling of the planar chiral (benzaldehyde)chromium complex with SmI₂. Furthermore, these chiral 1,2-diols and the corresponding ethers would be expected to be the characteristic chiral ligand in the asymmetric reactions, since these compounds have both planar and central chiralities with C₂-symmetry.

Scheme 2. Pinacol Coupling of *Enantiomerically Pure* (Arene)Cr(CO)₃

7	8	9	10
$[\alpha]_D^{23}$ 1062	$[\alpha]_D^{23}$ 58.2	$[\alpha]_D^{23}$ −660	$[\alpha]_D^{23}$ −97.5
(c 0.60, CHCl₃)	(c 0.27, MeOH)	(c 1.0, CHCl₃)	(c 0.51, MeOH)

Reaction mechanism of the pinacol coupling of the benzaldehyde tricarbonylchromium complexes would be proposed as follows (Fig. 1).[18] A carbonyl oxygen of the chromium-complexed *ortho* substituted benzaldehydes possessing an electron-donating substituent tends to be an *anti*-conformation to the *ortho* substituents 11 in both solid and solution states due to the stereoelectronic effect.[19]. An *exo*-attack of the samarium to the *anti* carbonyl gave a ketyl radical 12 which incorporates a substantial amount of the exocyclic double bond character 13 owing to an interaction of d-orbital on the chromium with p-orbital of the benzylic carbon. This, in turn, implies that a rotation about the Cα-Cipso bond giving 14 will be restricted. Then, the generated tricarbonylchromium-complexed ketyl intermediate is coupled with the carbonyl group of other (benzaldehyde)Cr(CO)₃ from the opposite side to the tricarbonylchromium fragment, in which both tricarbonylchromium-complexed arene rings are located in *anti*-orientation to each other due to a dipole-dipole and steric repulsions. Similar dipole-dipole interaction has been proposed in highly enantioselective reactions of the metalcarbonyl coordinated substrates.[20] Taking into account the Newman model, the both arenes coupled via an intermolecular coordinated transition state 15 of the samarium with the carbonyl oxygen to give the *threo* pinacol. In the case of the chromium complexes possessing O- and N-hetero-atoms at the *ortho* position, the alternative coordination structure 16 of the samarium with the *ortho* hetero atom would compete with the transition state 15, giving the pinacol coupling products in a various ratio. The presence of HMPA, however, precludes such coordination of the samarium with carbonyl or o-hetero-atoms. Therefore, it seems reasonable to assume that the *erythro* pinacols would be formed by the bimolecular coupling of the generated radical 12 via the transition state 17 with minimized stereo-electronic conformation. In any event, it is interesting that the tricarbonylchromium-complexed benzyl radicals could be generated stereoselectively, and caused pinacol coupling giving the *threo* 1,2-diols without stereochemical isomerization at the benzylic position.

Fig. 1. Proposed reaction mechanism

Pinacol Coupling of 2-Substituted Ferrocenecarboxaldehydes and (Dienal)Fe(CO)₃

We demonstrated that the pinacol coupling of enantiomerically pure tricarbonylchromium complexes of *o*-substituted benzaldehydes produced single 1,2-diol with the *threo*-configuration. As part of our asymmetric exploration of the transition metal-cooordinated planar substrates, we next studied the intermolecular pinacol coupling of the planar chiral α-substituted ferrocenecarboxyaldehydes and tricarbonyl(dienal)iron complex. The reaction results of samarium diiodide-mediated pinacol coupling of ferrocenecarboxaldehydes are summarized in Table 2. 2-Unsubstituted ferrocenecarboxaldehyde (**18**) (R = H) produced a 1 : 1 diastereomeric mixture of *threo* (*dl*) and *erythro* (*meso*)-pinacols in 95 % yield. Racemic 2-methylferrocenecarboxaldehyde gave a complexed mixture of the 1,2-diols based on the central and planar chiralities. However, an *enantiomerically pure* (*R*)-2-methylferrocenecarboxaldehyde (**18**) (R = Me) was reacted with samarium diiodide at 0 °C to give the corresponding three pinacol coupling products **19, 20** and **21** in a ratio of 92 : 4 : 4 in 98 % yield (entry 2). The reductive coupling at lower reaction temperature (-78 °C) produced a single pinacol coupling **19** (R = Me) with the *threo*-configuration in 92 % yield (entry 3). Similarly, the planar chiral 2-trimethylsilyl, bromo or iodo substituted ferrocenecarboxaldehydes afforded the corresponding 1,2-diols **19** with extremely high diastereoselectivity under same reaction conditions (entries 6–8).

The relative stereochemistry of the major coupling product **19** (R = I) was determined by a single crystal X-ray analysis[15] after conversion of the diol to the corresponding acetonide, and found to be the (S_Fc,1S,2S,S_Fc')-configuration. The structures of the other stereoisomeric coupling products could be easily assigned by NMR spectra. The compounds **19** and **20** have a C₂-symmetry, while **21** has a C₁-symmetry conformation.[21] However, no obvious diastereoselectivity was observed for the samarium diiodide-mediated

Table 2. Pinacol Coupling of Enantiomerically Pure Ferrocenecarboxyaldehydes

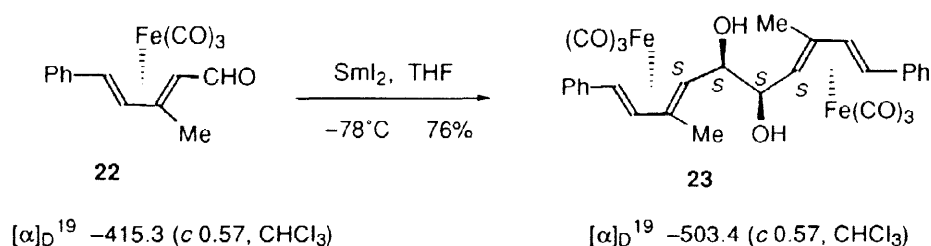| Entry	R	Temp (°C)	Yield	Ratio (19 : 20 : 21)	19 $[\alpha]_D$ (CHCl$_3$)
1[a]	H	0	95	25 : 25 : 50	
2	Me	0	98	92 : 4 : 4	
3	Me	-78	92	100 : 0 : 0	+89.5
4	TMS	0	88	91 : 8 : 1	
5	TMS	-78	87	93 : 6 : 1	+69.5
6	I	0	94	92 : 4 : 4	
7	I	-78	92	100 : 0 : 0	+37.4
8	Br	-78	93	100 : 0 : 0	+44.2
9[b]	PPh$_2$	0	41	52 : 24 : 24	–
10[c]	PPh$_2$	rt	80	30 : 40 : 30	c

a; The compounds 19 and 20 are enantiomer to each other when R is hydrogen.

b; No pinacol coupling of 18 with 2-diphenylphosphino substituent proceeded at -78 °C.
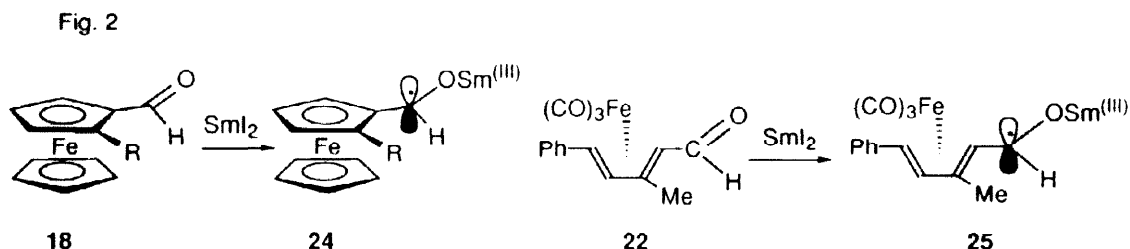
c; Ref. 22.

pinacol coupling of 2-(diphenylphosphino)ferrocenecarboxaldehyde. Thus, (S)-2-diphenylphosphino ferrocene **18** (R = PPh$_2$) produced all possible stereoisomers of the pinacol coupling products **19, 20** and **21** in a ratio of 52 : 24 : 24 in only 41 % yield along with ferrocenylmethyl alcohol of 20 % yield (entry 9). A similar result was recently reported by Kagan et al,[22] in which the ratio of the diols was 30 : 40 : 30 (entry 10).

Similarly, enantiomerically pure planar chiral (E-3-methyl-5-phenyl-2,4-pentadienal)Fe(CO)$_3$ complex **(22)** was treated with samarium diiodide to produce a single coupling product with the *threo*-configuration in 76 % yield (Scheme 3). The stereochemistry of the coupling product **23** was determined as 1(S),α(S),α'(S),1'(S)-configuration by X-ray crystallographical analysis[15].

Scheme 3. Pinacol Coupling of Enantiomerically Pure (Dienal)Fe(CO)$_3$

The reaction mechanism of stereoselective pinacol coupling of the planar chiral 2-substituted ferrocenecarboxaldehydes and tricarbonyl(dienal)iron complex would be analogous to the samarium-mediated reductive coupling of the planar chiral (o-substituted benzaldehyde)Cr(CO)$_3$ complexes, because the relative stereochemical relationship between the pseudo benzylic stereogenic center and the metal-complexed adjacent planar center of **19** and **23** are identical with those of the pinacol product **8** derived from enantiomerically pure
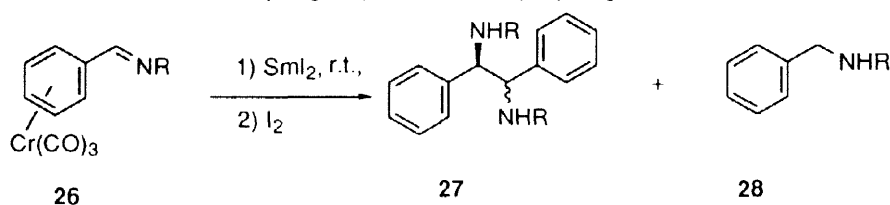
(o-bromobenzaldehyde)chromium complex. The carbonyl oxygen atom of **18** and **22** would be an *anti*-configuration to the α-substituent due to stereoelectronic effect. Then, the samarium metal attacks the *anti*-carbonyl[23] from the *exo*-side to generate the corresponding ketyl radical intermediates **24** and **25**, respectively, which incorporate a substantial amount of the exocyclic double bond character owing to an interaction of *d*-orbital of the metal with *p*-orbital of the carbon. But, with 2-diphenylphosphino substituent of ferrocenyl compound, the initially formed ketyl intermediate **24** might be isomerized to diastereoisomerically configuration.

Fig. 2

18   **24**   **22**   **25**

Pinacol Coupling of Tricarbonyl(benzaldimine)chromium Complexes

One of the most straightforward methods for the preparation of 1,2-diamines is an inter- or intramolecular reductive coupling of the aldimine compounds.[24] As a further extension of the pinacol coupling of the planar chiral arene chromium complexes, we next investigated a reductive coupling of the planar chiral (benzaldimine)Cr(CO)₃ complexes giving 1,2-diamines.[25] The effect of *N*-substituent in the aldimine chromium complexes **26** was initially evaluated for the reductive coupling with samarium diiodide (Table 3). From the reaction results, it can be seen that *N*-alkyl substituted benzaldimine chromium complexes produced the desired coupling products as diastereomeric mixtures along with benzylamine in a various ratio. The aldimine chromium complexes having an electron-withdrawing substituent gave the C-N double bond reduced product without formation of the coupling product (entries 5,6), and *N*-heteroatom substituents resulted in a complexed mixture (entries 7,8). Therefore, we next investigated stereoselectivity of the pinacol coupling of (*N*-alkyl *o*-substituted benzaldimine)Cr(CO)₃ complexes.

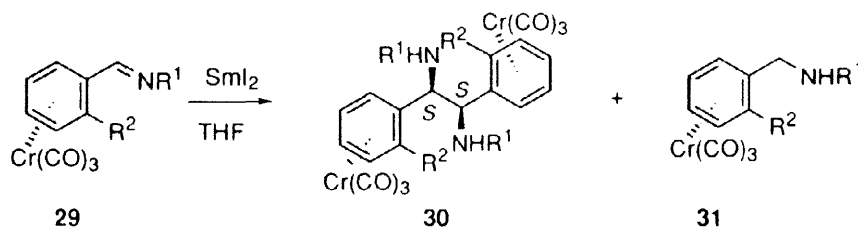### Table 3. Pinacol Coupling of (Benzaldimine)Cr(CO)₃

26   **27**   **28**

Entry	R	27 (%)	Ratio of 27 (*threo : erythro*)	28 (%)
1	Me	71	41 : 59	14
2	Buⁿ	31	50 : 50	48
3	Prⁱ	48	50 : 50	41
4	CH₂Ph	42	50 : 50	48
5	Ph	–		80
6	SO₂Ph	–		95
7[a]	OMe	–		10
8[a]	NMe₂	–		10

a: Complexed mixture.

Racemic tricarbonyl(*N*-methyl *o*-methoxybenzaldimine)chromium was treated with samarium diiodide in THF at 0°C to give the corresponding coupling products, *threo*- and *erythro*-diamines, in 63% yield as a mixture (ratio 43 : 57) accompanied with 17% yield of *N*-methyl *o*-methoxybenzylamine complex. Although a high diastereoselectivity was not observed in the pinacol coupling 1,2-diamine product of the *racemic* (*o*-substituted benzaldimine)Cr(CO)₃ complex, particular attention should be given to the relative stereochemistry of the tricarbonylchromium-complexed 1,2-diamine. Either *threo*- or *erythro*-1,2-diamine chromium complex derived from the *racemic* (*o*-substituted benzaldimine)chromium complex was obtained as a single compound, respectively, as well as the pinacol coupling of *racemic* (*o*-substituted benzaldehyde)chromium complexes. Both the chromium-complexed *threo*- and *erythro* 1,2-diamines have the symmetrical structure, as evidenced by NMR spectra. A symmetry of the coupling products and an analogy of (*o*-substituted benzaldehyde)chromium as mentioned above, it can be easily proposed that the tricarbonylchromium-complexed *threo* 1,2-diamine (C₂ symmmetry) would possess the identical planar chirality in the chromium-complexed arene rings, while the corresponding *erythro* (*meso*-) complex (Cᵢ symmetry) would be formed by a hetero-coupling of the (benzaldimine)chromium complexes with distinguishable chirality to each other.

As expected, the enantiomerically pure tricarbonyl(benzaldimine)chromium complex[26] could produce only *threo* coupling product as a single compound by the reductive coupling, irrespective of the *ortho* substituents as follows. For example, an enantiomerically pure (1S)-(*N*-methyl *o*-methoxybenzaldimine)chromium (29) (R¹ = Me, R² = OMe) was treated with SmI₂ to give the corresponding *threo* 1,2-diamine 30 as a single coupling product in 67% yield along with 10% of the benzylamine chromium complex 31 (Table 4). No *erythro* 1,2-diamine was observed by using enantiomerically pure complex. The absolute stereochemistry of 30 (R¹ = Me, R² = OMe) was confirmed by X-ray crystallography[15] and the benzylic center was found to be the *S*-configuration. Similarly, other enantiomerically pure benzaldimine chromium complexes gave the corresponding *threo* 1,2-diamines as a single pinacol coupling compound. Thus, the 1,2-diamines can be prepared as an enantiomerically pure form by the reductive pinacol coupling of planar chiral tricarbonyl(*o*-substituted benzaldimine)chromium complexes. These enantiomerically pure 1,2-diamines would be useful compounds for the asymmetric reactions.

Table 4. Pinacol Coupling of Enantiomerically Pure (Benzaldimine)Cr(CO)₃

entry	R¹	R²	30 (%)	30 [α]_D (CHCl₃)	31 (%)
1	Me	Me	65	+86.2	25
2	Me	OMe	67	–234	10
3	Me	Br	45	–31.3	41
4	Me	Cl	48	–6.7	46
5ᵃ	CH₂Ph	Me	54	+20.9	38
6ᵃ	CH₂Ph	OPrⁱ	51	+126	29

a: The antipode of 29 was used as a starting material and the coupling product was an enantiomer of 30.

The reaction mechanism for the stereoselective coupling of the planar chiral (*o*-substituted benzaldimine)Cr(CO)₃ complexes would be analogous to the samarium(II)-mediated pinacol coupling of the (*o*-substituted benzaldehyde)chromium complexes. The samarium attacks an *anti* C=N double bond to generate

configurationally stable radical intermediate which react with imine double bond of the arene chromium complexes.

In conclusion we demonstarted that the planar chiral tricarbonylchromium complexes of benzaldehydes, benzaldimines, 2-substituted ferrocenecarboxaldehydes and (dienal)Fe(CO)$_3$ gave the corresponding metal-stabilized ketyl radicals stereoselectively without racemization at the radical carbon positions, and produced pinacol coupling products with the *threo*-configuration by treatment with samarium diiodide.

Experimental Section

All manipulations involving organometallics were performed under argon atmosphere using standard Schlenk techniques. Solvents were distilled under an argon atmosphere from sodium benzophenone ketyl (THF), CaH$_2$ (HMPA) or P$_2$O$_5$ (CH$_2$Cl$_2$). Melting points were uncorrected. ^{1}H NMR spectra were recorded on JEOL GX-400 (400 MHz), JEOL LA-300 (300 MHz) and JEOL EX (270 MHz) spectrometer with Me$_4$Si as an internal standard. IR spectra were taken with a JASCO A-100 spectrometer. Mass spectra were measured on a JEOL D-300 instrument in the EI mode (70 eV). Elemental analysis was performed on a Perkin-Elmer Model 240 elemental analyzer. Optical rotations were obtained on JASCO DIP-370 automatic polarimeter at 589 nm (sodium D line) using a 1.0-dm cell with a total volume of 3 mL.

Typical Procedure for Pinacol Coupling of Tricarbonyl(benzaldehyde)chromium Complexes with Samarium Diiodide. A solution of tricarbonyl(benzaldehyde)chromium (100 mg, 0.41 mmol) and SmI$_2$ (0.1 M in THF, 10 mL, 1.0 mmol) was stirred at –78 °C for 30 min under argon atmosphere. The reaction mixture was quenched with saturated aqueous NaHCO$_3$ and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether, and the extract was washed with brine, dried over MgSO$_4$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with ether/hexane) to give 78 mg (78%) of pinacol coupling product, a mixture of *threo* and *erythro* isomers 2 (R^1 = R^2 = H). mp 160-163 °C (dec.); ^{1}H NMR (400 MHz, CD$_3$OD) δ 1.15 (brs, 2H for *threo*), 1.23 (brs, 2H for *erythro*), 4.25 (s, 2H for *erythro*), 4.42 (s, 2H for *threo*), 5.23-5.58 (m, 10H); IR (CHCl$_3$) 3350, 1980, 1910 cm^{-1}; MS (relative intensities) m/z 486 (M$^+$, 15), 430 (48), 402 (39), 374 (27), 346 (36), 318 (76), 300 (50), 266 (100), 230 (84), 179 (74). Anal. calcd for C$_{20}$H$_{14}$O$_8$Cr$_2$: C, 49.39; H, 2.90. Found: C, 48.99; H, 2.80. The demetalation of the chromium-complexed pinacols was carried out with iodine. To a solution of the pinacol 2 (R^1 = R^2 = H) (78 mg, 0.16 mmol) in CH$_2$Cl$_2$ (3 mL) was added iodine (40 mg, 0.32 mmol) at room temperature. After the reaction mixture was stirred for 30 min, saturated aqueous NaHSO$_3$ was added. The resulting mixture was stirred for a few minute and extracted with ether. 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 column chromatography on silica gel (eluted with ether/hexane) to give 32 mg (92%) of demetalated pinacol 3 (R^1 = R^2 = H) as a colorless crystal. The ratio (91:9) of *threo*- and *erythro* isomers was determined by the proton area of methyne (CHOH): 4.72 ppm for methyne protons of *threo* pinacol 3 (R^1 = H, R^2 = H) [12b] and 4.84 ppm for the corresponding protons of *erythro* pinacol 3 (R^1 = H, R^2 = H).[16b] ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.85 (brs, 2H), 4.72 (s, 2H for *threo*), 4.84 (s, 2H for *erythro*), 7.12-7.30 (m, 10H). The methyne protons in *threo* isomer 3 appears at ca. 0.1-0.2 ppm higher field than the corresponding ones in *erythro* isomer 3.[6a,12] The physical data of the other pinacol coupling products are as follows.

2 (R^1 = Me, R^2 = H): mp 210–213 °C (dec.); ^{1}H NMR (300 MHz, CDCl$_3$) for *threo* δ 2.01 (s, 6H,), 2.45 (br, 2H), 4.77 (s, 2H), 5.06 (d, J = 6.4 Hz, 2H), 5.19 (t, J = 6.4 Hz, 2H), 5.45 (t, J = 6.4 Hz, 2H), 5.65 (d, J = 6.4Hz, 2H); for *erythro* δ 2.09 (br, 2H,), 2.17 (s, 6H), 4.68 (s, 2H), 5.10 (d, J = 6.5 Hz, 2H), 5.23 (t, J = 6.5 Hz, 2H), 5.47 (t, J = 6.5 Hz, 2H), 5.67 (d, J = 6.5 Hz, 2H); IR (CHCl$_3$) 3350, 1980, 1910 cm^{-1}; MS (relative intensity) m/z 514 (M$^+$ 15), 430 (48), 402(39), 374 (27), 346 (36), 318 (76), 300 (50), 266 (100), 230 (84), 179 (74); Anal. calcd for C$_{22}$H$_{18}$O$_8$Cr$_2$: C, 51.37; H, 3.52. Found; C, 51.34; H, 3.56.

2 (R^1 = OMe, R^2 = H): mp 167–169 °C (dec.); ^{1}H NMR (300 MHz, CD$_3$OD) for *erythro* δ 2.04 (br, 2H), 3.43 (s, 6H), 4.96 (t, J = 6.3 Hz, 2H), 5.07 (s, 2H), 5.08 (d, J = 6.3 Hz, 2H), 5.50 (t, J = 6.3 Hz, 2H), 5.59

(d, J = 6.3 Hz, 2H); for *threo* δ 3.56 (br, 2H), 3.72 (s, 6H), 4.87 (s, 2H), 5.06 (t, J = 6.4 Hz, 2H), 5.31 (d, J = 6.4 Hz, 2H), 5.64 (t, J = 6.4 Hz, 2H), 6.04 (d, J = 6.4 Hz, 2H); IR (CHCl₃) 3300, 1960, 1890 cm⁻¹; MS (relative intensity) m/z 546 (M⁺ 2), 378 (18), 360 (14), 326 (30), 173 (74), 52 (100). Anal. calcd for $C_{22}H_{18}O_{10}Cr_2$: C, 48.36; H, 3.32. Found; C, 48.68; H, 3.10.

2 (R^1 = O^{i}Pr, R^2 = H): mp 165–167 °C; ¹H NMR (270 MHz, CDCl₃) for *threo* δ 1.31 (d, J = 6.0 Hz, 6H), 1.32 (d, J = 6.0 Hz, 6H), 2.38 (br, 2H), 4.21–4.26 (m, 2H), 5.21 (s, 2H), 5.49–5.56 (m, 4H), 5.67 (d, J = 6.2 Hz, 2H),6.01 (d, J = 6.2 Hz, 2H); for *erythro* δ 1.21 (d, J = 5.9 Hz, 6H), 1.29 (d, J = 5.9 Hz, 6H), 2.20 (br, 2H), 4.19–4.30 (m, 2H), 4.79–4.86 (m, 4H), 4.91 (s, 2H), 5.54 (t, J = 6.4 Hz, 2H), 6.03 (d, J = 6.4 Hz, 2H); IR (CHCl₃) 3350, 1980, 1910 cm⁻¹; MS (relative intensity) m/z 602 (M⁺, 0.4), 434 (2), 382 (3), 173 (38), 121 (100). Anal. calcd for $C_{26}H_{26}O_{10}Cr_2$: C, 51.83; H, 4.35. Found; C, 52.07, H, 4.66.

2 (R^1 = NMe₂, R^2 = H): mp 128–130 °C (dec.); ¹H NMR (300 MHz, CDCl₃) for *threo* δ 1.92 (br, 2H), 2.76 (s, 12H), 4.92 (s, 2H), 4.99 (t, J = 6.4 Hz, 2H), 5.28 (d, J = 6.4 Hz, 2H), 5.45 (t, J = 6.4 Hz, 2H), 5.65 (d, J = 6.4 Hz, 2H); for *erythro* δ 1.86 (br, 2H), 2.71 (s, 12H), 4.68 (s, 2H), 5.10 (d, J = 6.5 Hz, 2H), 5.23 (t, J = 6.5 Hz, 2H), 5.47 (t, J = 6.5 Hz, 2H), 5.67 (d, J = 6.5 Hz, 2H); IR (CHCl₃) 3350, 1950, 1890 cm⁻¹; MS (relative intensity) m/z 572 (M⁺ 1), 516 (48), 402 (13), 460 (25), 404 (15), 352 (100), 334 (15). Anal. calcd for $C_{24}H_{24}O_8N_2Cr_2$: C, 50.35; H, 4.23, N, 4.89. Found: C, 50.17; H, 4.18, N, 4.95.

2 (R^1 = H, R^2 = Br): mp 182–184 °C (dec.); ¹H NMR (300 MHz, CDCl₃) δ 2.25 (br, 2H for *threo*), 4.30 (s, 2H for *erythro*), 4.33 (s, 2H for *threo*), 5.25 (d, J = 6.6 Hz, 2H for *threo*), 5.39 (d, J = 6.6 Hz, 2H for *threo*), 5.46–5.56 (m, 4H for *threo*); IR (CHCl₃) 3300, 1970, 1910 cm⁻¹; MS (relative intensity) m/z 644 (M⁺ 0.6), 588 (7), 476 (20), 390 (18), 338 (15), 178 (37), 52 (100). Anal. calcd for $C_{20}H_{12}O_8Cr_2Br_2$: C, 37.29; H, 1.88. Found: C, 36.99; H, 1.91.

2 (R^1 = H, R^2 = Me): for *threo*; mp 182–184 °C (dec.); ¹H NMR (300 MHz, CDCl₃) δ 2.20 (s, 6H), 2.46 (br, 2H), 4.37 (s, 2H), 5.10 (d, J = 6.8 Hz, 2H), 5.14 (d, J = 6.8 Hz, 2H), 5.29 (d, J = 6.8 Hz, 2H), 5.47 (d, J = 6.8 Hz, 2H); IR (CHCl₃) 3300, 1960, 1900 cm⁻¹; MS (relative intensity) m/z 514 (M⁺ 1), 480 (4), 346 (10), 276 (12), 260 (61), 208 (28), 172 (44), 52(100). Anal. calcd for $C_{22}H_{18}O_8Cr_2$: C, 51.37; H, 3.52. Found: C, 51.18; H, 3.57.

2 (R^1 = H, R^2 = OMe): for *threo*; mp 165–167 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.41 (br, 2H), 3.72 (s, 6H), 4.28 (s, 2H), 5.04–5.06 (m, 4H), 5.45 (d, J = 6.8 Hz, 2H), 5.56 (d, J = 6.8 Hz, 2H); IR (CHCl₃) 3300, 1970, 1930 cm⁻¹; MS (relative intensity) m/z 546 (M⁺, 2), 378 (30), 344 (8), 292 (92), 240 (100), 225 (62). Anal. calcd for $C_{22}H_{18}O_{10}Cr_2$: C, 48.36; H, 3.32. Found: C, 48.22; H, 3.31.

Pinacol Coupling of *dl*-Tricarbonyl(*o*-bromobenzaldehyde)chromium (4): The crude product obtained by pinacol coupling of *racemic* tricarbonyl(*o*-bromobenzaldehyde)chromium (4) (300 mg, 0.93 mmol) with SmI₂ (0.1 M in THF, 18.6 mL, 1.86 mmol) at –78 °C for 1 h under argon atmosphere was purified by column chromatography on silica gel (eluted with ether/hexane) to give 57 mg (19%) of *threo* pinacol **5A** and 138 mg (46%) of *erythro* pinacol **6A**. *threo* pinacol **5A**. yellow crystals, mp 158-160 °C (dec.); ¹H NMR (300 MHz, CDCl₃) δ 2.59 (brs, 2H), 4.95 (s, 2H), 5.20 (t, J = 7.3 Hz, 2H), 5.41 (t, J = 7.3 Hz, 2H), 5.53 (d, J = 7.3 Hz, 2H), 5.94 (d, J = 7.3 Hz, 2H); IR (CHCl₃) 3300, 1990, 1940 cm⁻¹; MS (relative intensities) m/z 644 (M⁺, 3), 476 (4), 378 (4), 236 (28), 178 (77), 157 (67), 52 (100). Anal. calcd for $C_{20}H_{12}O_8Br_2Cr_2$: C, 37.29; H, 1.88. Found: C, 37.25; H, 1.99. *erythro* pinacol **6A**. yellow crystals, mp 150-153 °C (dec.); ¹H NMR (400 MHz, CDCl₃) δ 2.74 (brs, 2H), 5.16 (t, J = 6.1 Hz, 2H), 5.36 (s, 2H), , 5.37 (t, J = 6.1 Hz, 2H), 5.41 (d, J = 6.1 Hz, 2H), 5.53 (d, J = 6.1 Hz, 2H); IR (CHCl₃) 3300, 1990, 1930 cm⁻¹. Anal. calcd for $C_{20}H_{12}O_8Br_2Cr_2$: C, 37.29; H, 1.88. Found: C, 37.49; H, 2.00.

Pinacol Coupling of (1S)-Tricarbonyl(*o*-bromobenzaldehyde)chromium (7): (1S)-Tricarbonyl(*o*-bromobenzaldehyde)chromium (7) {[α]$_D^{23}$ +1062.5° (c 0.60, CHCl₃)} (100 mg, 0.31 mmol) was reacted with SmI₂ (0.1 M in THF, 6.2 mL, 0.62 mmol) at 0 °C for 30 min under usual conditions, and the

crude coupling product was purified by column chromatography on silica gel (eluted with ether/hexane) to give 75 mg (75%) of enantiomerically pure *threo* pinacol **8** as a single product; $[\alpha]_D^{23}$ +58.2° (*c* 0.27, MeOH).

Pinacol Coupling of (1*R*)-Tricarbonyl(*o*-methylbenzaldehyde)chromium (9): (*R*)-Tricarbonyl(*o*-methylbenzaldehyde)chromium (9) {$[\alpha]_D^{25}$ –660.6° (*c* 1.00, CHCl₃)} (100 mg, 0.39 mmol) was reacted with SmI₂ (0.1 M in THF, 9.8 mL, 0.98 mmol) and the product was purified by column chromatography on silica gel (eluted with ether/hexane) to give 71 mg (71%) of enantiomerically pure *threo* pinacol **10** as a single product; yellow crystals, $[\alpha]_D^{25}$ –97.6° (*c* 0.51, CHCl₃), mp 210-213 °C (dec.); ¹H NMR (300 MHz, CDCl₃) δ 2.01 (s, 6H), 2.44 (brs, 2H), 4.77 (s, 2H), 5.06 (d, *J* = 6.4 Hz, 2H), 5.19 (t, *J* = 6.4 Hz, 2H), 5.44 (t, *J* = 6.4 Hz, 2H), 5.65 (d, *J* = 6.4 Hz, 2H); IR (CHCl₃) 3300, 1950, 1870 cm⁻¹; MS (relative intensities) *m/z* 514 (M⁺, 1), 346 (2), 294 (4), 172 (35), 120 (53), 91 (100), 65 (31), 52 (62). Anal. calcd for C₂₂H₁₈O₈Cr₂: C, 51.37; H, 3.53. Found: C, 51.66; H, 3.62.

Pinacol Coupling of 2-Methylferrocenecarboxyaldehyde (18) (R = Me). To a solution of (*R*-α-methylferrocenecarboxaldehyde (18) (R = Me) (128 mg, 0.56 mmol) in dry THF (0.5 mL) was added a solution of SmI₂ (0.15 M, 9.3 mL, 1.40 mmol) in THF at -78 °C, and the solution was stirred at the same temperature for 30 min under argon atmosphere. The reaction mixture was quenched with saturated aqueous NH₄Cl and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether. The extract was washed with brine, dried over MgSO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with Et₂O/hexane) to give 116 mg (91%) of **19** (R = Me): mp 210–211 °C; ¹H NMR (270 MHz, CDCl₃) δ 1.32 (s, 6H), 2.66 (br, 2H), 3.93–3.97 (m, 4H), 4.07 (s, 10H), 4.20–4.21 (m, 2H), 4.24 (s, 2H); $[\alpha]_D^{19}$ +89.5 (*c* 0.39, CHCl₃). Anal. calcd for C₂₄H₂₆O₂Fe₂: C, 62.78; H, 5.79. Found C, 62.91; H, 5.72.

19 (R = TMS): mp 41 °C; ¹H NMR (270 MHz, CDCl₃) δ 0.28 (s, 18H), 1.60 (br, 2H), 4.11–4.12 (m, 2H), 4.15 (s, 10H), 4.29–4.31 (m, 2H), 4.34 (s, 2H), 4.38-4.39 (m, 2H); $[\alpha]_D^{19}$ +69.4 (*c* 0.55, CHCl₃). Anal. calcd for C₂₈H₃₀O₂Si₂Fe₂: C, 58.54; H, 6.67. Found C, 58.61; H, 6.69.

19 (R = Br): mp 174 °C; ¹H NMR (270 MHz, CDCl₃) δ 2.44 (br, 2H), 4.14–4.16 (m, 2H), 4.22 (s, 10H), 4.32–4.34 (m, 2H), 4.42-4.44 (m, 2H), 4.54 (s, 2H); $[\alpha]_D^{20}$ +44.2 (*c* 0.12, CHCl₃). Anal. calcd for C₂₂H₂₀O₂Fe₂Br₂: C, 44.95; H, 3.43. Found C, 45.10; H, 3.44.

19 (R = I): mp 170 °C; ¹H NMR (270 MHz, CDCl₃) δ 2.47 (br, 2H), 4.19 (s, 10H), 4.25-4.26 (m, 2H), 4.39 (s, 2H), 4.40-4.44 (m, 4H); $[\alpha]_D^{24}$ +37.4 (*c* 0.38, CHCl₃). Anal. calcd for C₂₂H₂₀O₂Fe₂I₂: C, 44.95; H, 3.43. Found C, 45.10; H, 3.44.

Preparation of 23: ¹H NMR (270 MHz, CDCl₃) δ 1.42 (d, 2H, *J* = 8.9 Hz), 2.07 (d, 2H, *J* = 8.9 Hz), 2.23 (s, 2H), 2.26 (s, 6H), 3.73-3.77 (m, 2H), 5.70 (d, 2H, *J* = 8.9Hz), 7.15-7.27 (m, 10H); IR (CHCl₃) 3250, 2030, 1950 cm⁻¹; $[\alpha]_D^{19}$ –503.4 (*c* 0.58, CHCl₃). MS (relative intensities) *m/z* 626 (M⁺, 2), 609 (8), 570 (16), 542 (20), 458 (10), 368 (48), 154 (100).

Typical Procedure of Pinacol Coupling of Tricarbonyl(benzaldimine)chromium: To a solution of **26** (R = Me) (100 mg, 0.39 mmol) in THF (2.5 mL) was added a solution of SmI₂ prepared from samarium metal (294 mg, 1.96 mmol) and 1,2-diiodoethane (552 mg, 1.96 mmol) in THF (1.5 mL) at room temperature and the mixture was stirred for 1 h. The reaction mixture was quenched with saturated aqueous NaHCO₃ and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether, and the extract was washed with brine, dried over MgSO₄ and evaporated under reduced pressure. To a solution of the residue in CH₂Cl₂ (2 mL) was added iodine (49.0 mg, 0.39 mmol) at room temperature and stirred for 30 min. The reaction mixture was quenched with saturated aqueous NaHSO₃ and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether, and the extract was washed with brine, dried over MgSO₄ and evaporated under reduced pressure. The residue was treated with iodine, and then purified by column chromatography on silica gel (eluted with ether/hexane) to give 33.4 mg (71%) of **27** (R = Me) and 6.5 mg (14%) of *N*-methylbenzylamine. **27** (R = Me).²⁷ ¹H NMR (270 MHz, CDCl₃) δ 1.30 (s, 2H for *threo*),

1.90 (s, 2H for *erythro*), 2.08 (s, 6H for *erythro*), 2.20 (s, 6H for *threo*), 3.48 (s, 2H for *threo*), 3.58 (s, 2H for *erythro*), 6.97-7.48 (m, 10H); IR(CHCl₃) 3400, 1230 cm⁻¹. **28 (R = Me)**. ¹H NMR (270 MHz, CDCl₃) δ 2.45 (s, 3H), 3.74 (s, 2H), 4.68 (s, 1H), 7.27-7.37 (m, 5H); IR (CHCl₃) 3200, 1430 cm⁻¹; MS (relative intensity) *m/z* 121 (M⁺ 62), 91 (100); HRMS calcd for C₈H₁₁N 121.0891. found 121.0905.

Pinacol Coupling of *Enantiomerically Pure* Tricarbonyl(*N*-methyl *o*-substituted benzaldimine)chromium (29) (R¹ = Me, R² = OMe): Pinacol couping was carried out under the same conditions. **30** (R¹ = Me, R² = OMe). mp 150-152 °C (dec.); ¹H NMR (270 MHz, CDCl₃) δ 1.43 (s, 2H), 2.48 (s, 6H), 3.68 (s, 6H), 3.88 (s, 2H), 4.87 (t, *J* = 6.2 Hz, 2H), 4.94 (d, *J* = 6.2 Hz, 2H), 5.52 (t, *J* = 6.1 Hz, 2H), 5.84 (d, *J* = 6.1 Hz, 2H); IR (CHCl₃) 3300, 1960, 1890 cm⁻¹; [α]$_D^{28}$ -234 (*c* 0.27, CHCl₃). Anal. calcd for C₂₄H₂₄N₂O₈Cr₂: C, 50.36; H, 4.23; N, 4.89. Found: C, 50.28; H, 4.24; N, 4.75. **31** (R¹ = Me, R² = OMe). ¹H NMR (270 MHz, CDCl₃) 1.40 (br, 1H), 2.51 (s, 3H), 3.21 (d, *J* = 12.7 Hz, 1H), 3.76 (s, 1H), 3.84 (d, *J* = 12.7 Hz, 1H), 4.92 (t, *J* = 6.0 Hz, 1H), 5.06 (d, *J* = 6.2 Hz, 1H), 5.48 (t, *J* = 6.2 Hz, 1H), 5.71 (d, *J* = 6.0 Hz, 1H); IR (CHCl₃) 1950, 1870 cm⁻¹. MS (relative intensity) *m/z* 287 (M⁺ 2), 285 (20), 257 (55), 230 (98), 149 (100); HRMS calcd for C₁₂H₁₃O₄NCr 287.0998, found 287.0978.

30 (R¹ = Me, R² = Me): mp 150-152 °C (dec.); ¹H NMR (300 MHz, CDCl₃) δ 1.24 (br,2H), 2.27 (s, 6H), 2.58 (s, 6H), 3.69 (s, 2H), 4.97 (t, *J* = 5.9 Hz, 2H), 5.11 (d, *J* = 5.9 Hz, 2H), 5.22 (d, *J* = 5.9Hz, 2H), 5.39 (t, *J* = 5.9 Hz, 2H); IR (CHCl₃) 3350, 2980, 1940, 1880 cm⁻¹; [α]$_D^{22}$ +86.1 (*c* 0.61, CHCl₃). Anal. calcd for C₂₄H₂₄N₂O₆Cr₂: C, 53.34; H, 4.48; N, 5.18. Found: C, 53.18; H, 4.49; N, 5.05. **31** (R¹ = Me, R² = Me). ¹H NMR (300 MHz, CDCl₃) δ 1.25 (s, 1H), 2.22 (s, 3H), 2.52 (s, 3H), 3.41 (d, *J* = 13.7 Hz, 1H), 3.65 (d, *J* = 13.7 Hz, 1H), 5.21-5.25 (m, 2H), 5.34 (d, *J* = 6.1 Hz, 1H), 5.58 (d, *J* = 6.1 Hz, 1H); IR (CHCl₃) 1950, 1870 cm⁻¹. MS (relative intensity) *m/z* 271 (M⁺ 20), 215 (20), 187 (60), 134 (100); HRMS calcd for C₁₂H₁₃O₃NCr 271.0892, found 271.0905.

30 (R¹ = Me, R² = Br): mp 147-149 °C (dec.); ¹H NMR (300 MHz, CDCl₃) δ 1.25 (br, 2H), 2.54 (s, 6H), 3.72 (s, 2H), 5.04 (t, *J* = 5.9 Hz, 2H), 5.41 (d, *J* = 5.9 Hz, 2H), 5.43 (t, *J* = 6.1 Hz, 2H) 5.91 (d, *J* = 6.1Hz, 2H); IR (CHCl₃) 3350, 1980, 1890, 1410 cm⁻¹; [α]$_D^{26}$ -31.3 (*c* 0.41, CHCl₃). Anal. calcd for C₂₂H₁₈N₂O₆Cr₂Br₂: C, 39.43; H, 2.71; N, 4.18. Found: C, 39.31; H, 2.72; N, 4.04. **31** (R¹ = Me, R² = Br). ¹H NMR (300 MHz, CDCl₃) δ 1.26 (s, 1H), 2.54 (s, 3H), 3.54 (d, *J* = 13.5 Hz, 1H), 3.80 (d, *J* = 13.5 Hz, 1H), 5.20 (d, *J* = 6.1 Hz, 1H), 5.28 (d, *J* = 6.2 Hz, 1H), 5.60-5.66 (m, 2H); IR (CHCl₃) 1960, 1890 cm⁻¹. MS (relative intensity) *m/z* 336 (M⁺ 5), 334 (18), 278 (52), 250(95), 198 (100); HRMS calcd for C₁₁H₁₀O₃NCrBr 336.0154, found 336.0161.

30 (R¹ = Me, R² = Cl): mp 150-152 °C (dec.); ¹H NMR (270 MHz, CDCl₃) δ 1.47 (s, 2H), 2.49 (s, 6H), 3.82 (s, 2H), 5.03 (t, *J* = 6.8 Hz, 2H), 5.32 (d, *J* = 6.6 Hz, 2H), 5.49 (t, *J* = 6.6 Hz, 2H), 5.90 (d, *J* = 6.8 Hz, 2H); IR (CHCl₃) 3320, 1960, 1890 cm⁻¹; [α]$_D^{26}$ -6.7 (*c* 0.22, CHCl₃). Anal. calcd for C₂₂H₁₈N₂O₆Cl₂Cr₂: C, 45.44; H, 3.12; N, 4.82. Found: C, 45.73; H, 3.40; N, 4.69. **31** (R¹ = Me, R² = Cl). ¹H NMR (270 MHz, CDCl₃) δ 1.43 (s, 1H), 2.54 (s, 3H), 3.52 (d, *J* = 14.0 Hz, 1H), 3.86 (d, *J* = 14.0 Hz, 1H), 5.12 (t, *J* = 6.1 Hz, 1H), 5.36 (t, *J* = 6.2 Hz, 1H), 5.52 (d, *J* = 6.1 Hz, 1H), 5.36 (d, *J* = 6.2 Hz, 1H); IR (CHCl₃) 1960, 1890 cm⁻¹. MS (relative intensity) *m/z* 291 (M⁺ 5), 289 (59), 261(90), 153 (100); HRMS calcd for C₁₁H₁₀O₃NClCr 291.0346, found 291.0350.

Antipode of 30 (R¹ = Bn, R² = Me): the corresponding antipode of **29** was used as a starting material; mp 175-176 °C (dec.); ¹H NMR (270 MHz, CDCl₃) δ 2.16 (s, 6H), 2.31 (s, 2H), 3.63 (d, *J* = 13.2 Hz, 2H), 3.83 (s, 2H), 3.95 (d, *J* = 13.2 Hz, 2H), 4.98 (d, *J* = 6.4 Hz, 2H), 5.11 (t, *J* = 6.3 Hz, 2H), 5.49 (t, *J* = 6.4 Hz, 2H), 5.75 (d, *J* = 6.3 Hz, 2H), 7.14-7.38 (m, 10H); IR (CHCl₃) 3300, 2980, 1940, 1870 cm⁻¹. [α]$_D^{26}$ +20.9 (*c* 0.22, CHCl₃); Anal. calcd for C₃₆H₃₂N₂O₆Cr₂: C, 62.42; H, 4.66; N, 4.04. Found: C, 62.16; H, 4.48; N, 3.99. **31** (R¹ = Bn, R² = Me). mp 72-73 °C; ¹H NMR (270 MHz, CDCl₃) δ 1.41 (br, 1H), 2.18 (s, 3H), 3.48 (d, *J* = 13.7 Hz, 1H), 3.65 (d, *J* = 13.7 Hz, 1H), 3.83 (d, *J* = 8.5 Hz, 1H), 3.93 (d, *J* = 8.5 Hz, 1H), 5.19-5.23 (m, 2H), 5.33 (t, *J* = 6.1 Hz, 1H), 5.63 (d, *J* = 6.1 Hz, 1H), 7.27-7.36 (m, 5H); IR (CHCl₃)

1950, 1870 cm⁻¹. Anal. calcd for $C_{18}H_{17}NO_3Cr$: C, 62.24; H, 4.93; N, 4.03. Found: C, 62.06, H, 4.96; N, 4.01.

Antipode of 30 (R^1 = Bn, R^2 = O^{i}Pr): the corresponding antipode of **29** was used as a starting material; mp 90–91 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 1.18 (d, J = 6.1Hz, 6H), 1.36 (d, J = 6.1 Hz, 6H), 1.43 (s, 2H), 3.68 (d, J = 13.1Hz, 2H), 4.05 (d, J = 13.1 Hz, 2H), 4.18-4.26 (m, 2H), 4.29 (s. 2H), 4.85 (t, J = 6.4 Hz, 2H), 4.87 (d, J = 6.4 Hz, 2H), 5.56 (t, J = 6.4 Hz, 2H), 5.96 (d, J = 6.4 Hz, 2H), 7.15–7.29 (m, 10H); IR (CHCl₃) 3350, 3020, 1970, 1410 cm⁻¹; $[\alpha]_D^{26}$ +126 (c 0.50, CHCl₃). Anal. calcd for $C_{40}H_{40}N_2O_8Cr_2$: C, 61.53; H, 5.16; N, 3.59. Found: C, 61.28; H, 5.46; N, 3.35. **31** (R^1 = Bn, R^2 = O^{i}Pr). ^1H NMR (270 MHz, CDCl₃) δ 1.36 (d, J = 6.1 Hz, 6H), 1.40 (br, 1H), 3.41 (d, J = 14.0 Hz, 1H), 3.83 (d, J = 13.7 Hz, 2H), 3.94 (d, J = 14.0 Hz, 1H), 4.32-4.37 (m, 1H), 4.88 (t, J = 6.6 Hz, 1H), 5.02 (d, J = 6.7 Hz, 1H), 5.48 (t, J = 6.6 Hz, 1H), 5.78 (d, J = 6.7 Hz, 1H), 7.27–7.36 (m, 5H). IR (CHCl₃) 1950, 1870 cm⁻¹; MS (relative intensity) m/z 391 (M⁺ 5), 333 (20), 305 (100), 253 (15); HRMS calcd for $C_{20}H_{21}O_4NCr$ 391.0570, found 391.0563.

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