New chiral tricarbonyl(η^6-arene)chromium(0) complexes: synthesis and preliminary application in asymmetric catalysis

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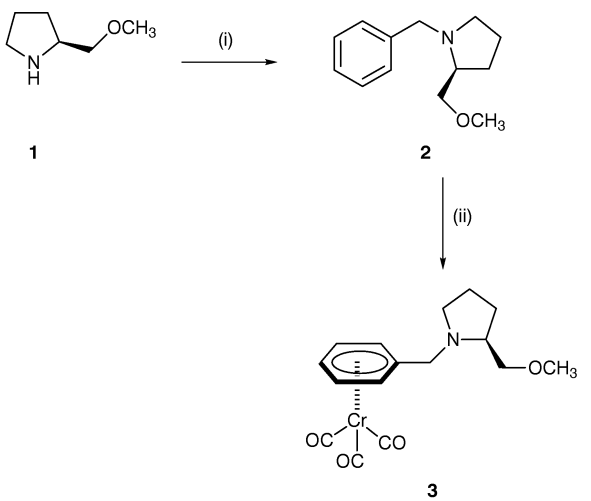
The synthesis of new enantiomerically pure tricarbonyl(η^6-arene)chromium(0) complexes having both planar and central chirality is reported. The procedure for their preparation involves a directed *ortho*-lithiation as the key step using (*S*)-2-methoxymethylpyrrolidine (SMP) as a suitable anchor group. The absolute configuration of the newly generated element of planar chirality was determined *via* chemical correlation. The potential use of the new complexes in asymmetric catalysis was briefly examined in dialkylzinc additions to ferrocenecarbaldehyde and benzaldehyde

Planar chiral complexes have found various applications[1,2] and their stereoselective synthesis remains a major challenge. While there are numerous reports on the asymmetric generation of unsymmetrical 1,2-disubstituted ferrocenes,[3] the structurally closely related tricarbonyl(η^6-arene)chromium(0) complexes have attracted less attention.[4] This is quite surprising taking into account that their arene ligands are usually more easily accessible than the comparable cyclopentadienyl structures which are required for the corresponding ferrocene derivatives.

Several methods for the preparation of optically pure tricarbonyl(η^6-arene)chromium(0) complexes are known, including kinetic resolution by enzymatic[5] and chemical[6] means, diastereoselective complexation,[7] chiral-ligand-mediated nucleophilic addition and hydride abstraction,[8] diastereoselective benzannulation reaction,[9] and enantioselective deprotonation with chiral bases[10] or by directed *ortho*-metallation *via* enantiopure directing groups.[11,12] The major advantage of the latter strategy[12] lies in the easy accessibility of 1,2-disubstituted compounds.



(i): Benzyl chloride, NaI, Na_2CO_3, toluene, reflux, 14h, 87%.

(ii): $Cr(CO)_6$, $(n\text{-}C_4H_9)_2O$/THF, 120-140°C, 48h, 96%.

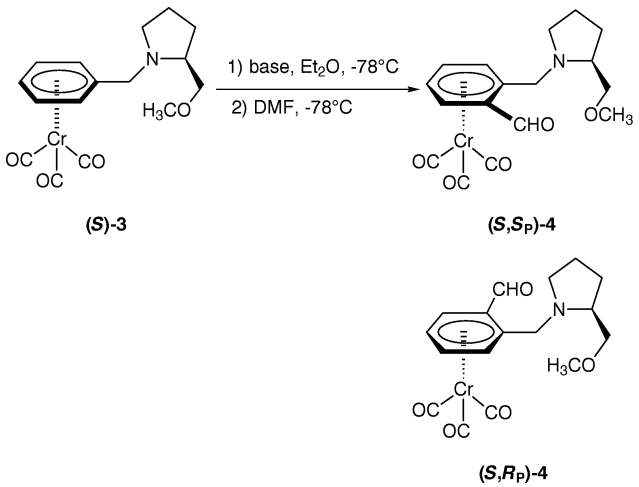
Scheme 1

Results and Discussion

Given our ongoing interest in planar chiral ligands for asymmetric catalysis,[13,14] we developed a diastereoselective synthesis of new 1,2-disubstituted tricarbonyl(η^6-arene)chromium(0) complexes *via* a convenient two-step procedure using readily available *N*-benzyl-(*S*)-2-methoxymethylpyrrolidine (**2**) as starting material. Pyrrolidine **2** can easily be obtained from (*S*)-2-methoxymethylpyrrolidine (**1**) (SMP), which is known to be a powerful chiral auxiliary and which has been used in a number of impressive transformations in asymmetric synthesis.[15] It has also been introduced into organometallic chemistry[16] and a previous report by one of us demonstrated its usefulness in the synthesis of optically active SMP-containing ferrocenes.[14]

Organometallic species **3** is prepared from SMP **1**[17] by benzylation followed by complexation of the resulting *N*-benzyl-SMP with hexacarbonylchromium(0) under standard conditions in the dark giving **3** as a viscous yellow oil in very good overall yield (Scheme 1).

Selective deprotonation of **3** (Scheme 2) was then investigated employing different bases and DMF as electrophile (Table 1). Comparing the characteristic signals of the formyl



Scheme 2

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Table 1 Determination of the stereochemical outcome in the preparation of **4** using different bases for the asymmetric deprotonation of **3** and DMF as electrophile

Entry	Base	Diastereomeric ratio (S,S_p)-**4** : (S,R_p)-**4** [a]	Diastereomeric excess/%	Chemical yield/%
1	Bu^nLi	16 : 1	88	*ca.* 30
2	Bu^sLi	42 : 1	95	*ca.* 70 (54[b])
3	Bu^tLi	67 : 1	97	>90 (74[b])

[a] Determined from the set of signals in the crude ^{1}H NMR spectra. [b] After purification and recrystallization.

protons in the ^{1}H NMR spectra of the resulting diastereomeric aldehydes **4** allowed an accurate determination of the reaction outcome.[18]

It is noteworthy that even with Bu^nLi a good diastereodifferentiation was observed, indicating the good directing power of the SMP group. However, with this base the chemical yield remained rather low. Both diastereomeric excess and yield were improved by using the sterically more hindered bases Bu^sLi and Bu^tLi. The latter was found to be the most effective, affording the product in almost quantitative yield and with an excellent diastereomeric ratio of 67 : 1.

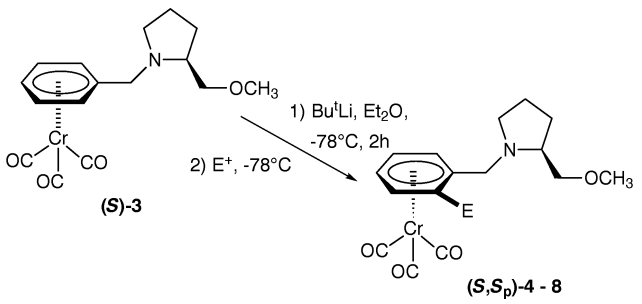
Having established the optimal reaction conditions for the asymmetric *ortho*-functionalization of (*S*)-**3**, various electrophiles were employed in order to show the general applicability of this process. Thus, new tricarbonyl(η^6-arene)chromium(0) complexes **5**–**8** with excellent diastereomeric excesses having the (S,S_p) configuration were also prepared (Scheme 3, Table 2).

It is further noteworthy that the lithiation of (*S*)-**3** is highly chemoselective. In all cases, only the desired 1,2-disubstituted complexes were isolated, accompanied by different amounts of unreacted starting material (and sometimes slight amounts of decomplexed arene). However, no other products such as, for example, those derived from metallation in the benzylic position, were ever detected.

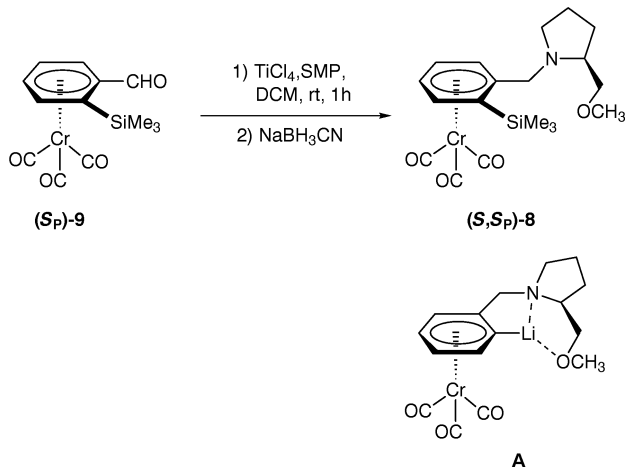
The absolute planar chirality was unambiguously determined *via* chemical correlation: enantiopure planar chiral compound (S_p)-**9** was synthesized according to the procedure by Davies and Goodfellow[19] and transformed into the corresponding diastereomerically pure complex (S,S_p)-**8** by reductive amination. ^{13}C NMR spectroscopy and optical rotation revealed that this compound was identical with the one obtained from the *ortho*-functionalization sequence. This observation makes it most probable that the intermediate arising from the deprotonation has a chelated structure **A** as depicted in Scheme 4. Such a species contains a favourable coordination of the lithium and is similar to the one that has been proposed for the corresponding ferrocene complexes, yielding identical absolute planar chirality.[14]

With the new chromium complexes in hand, we briefly examined the asymmetric addition of dialkylzincs to aldehydes as a first catalytic application.[20,21] A variety of amino alcohols is known to catalyse this reaction effectively *via* coordination of the bidentate ligand to the zinc atom.[22,23] Two such amino alcohols appeared to be of interest here: complex (S,S_p)-**5**, which was obtained directly *via* the above described *ortho*-functionalization, and complex (S,S_p)-**10**, which could be synthesized by reduction of the enantiopure arene complex (S,S_p)-**4** (Scheme 5).

The results of various catalyses are listed in Table 3. Two aromatic aldehydes, ferrocenecarbaldehyde and benzaldehyde, were used as substrates. Dimethylzinc and diethylzinc were the organometallic reagents. In the presence of 5 mol% of (S,S_p)-**5** the reaction of ferrocenecarbaldehyde and dimethylzinc afforded an addition product with 77% enantiomeric excess (ee) (entry 1). Increasing the catalyst loading to 10 mol% raised the ee to 83% and improved the chemical yield (entry 2). Use of larger quantities of (S,S_p)-**5** had no further positive effect. Both aldehydes performed nearly identically, implying



Scheme 3

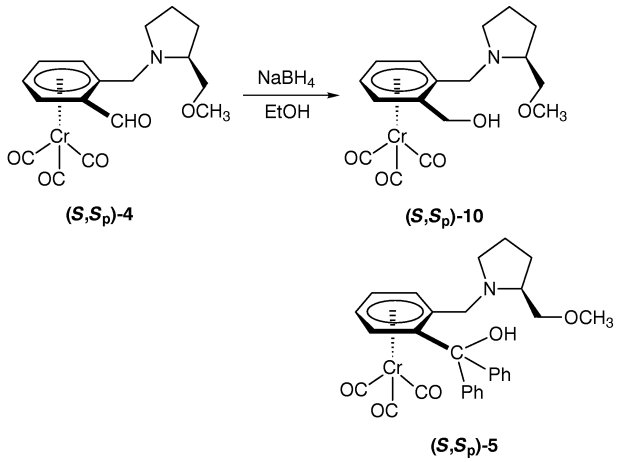


Scheme 4

Table 2 Preparation of various complexes derived from (S,S_p)-**3**

Entry	Electrophile E^+	Product	Diastereomeric excess/%[a]	Chemical yield/%[b]
1	DMF	(S,S_p)-**4**	>96	74
2	Ph_2CO	(S,S_p)-**5**	>96	91
3	Bu_3SnCl	(S,S_p)-**6**	>96	89
4	Ph_2PCl	(S,S_p)-**7**	>96	77
5	Me_3SiCl	(S,S_p)-**8**	n.d.	54

[a] Determined from the set of signals in the crude ^{1}H NMR spectra; n.d. = not determined. [b] After purification and/or recrystallization.



Scheme 5

that there were no significant differences between the aromatic ferrocenyl or phenyl moities (entries 2,4).

Comparison of the results of catalyses with (S,S_p)-**5** and (S,S_p)-**10** reveals that the latter performed less effectively (compare entries 2,4 to entries 6,7). Apparently, the presence of the diphenylhydroxymethyl group in (S,S_p)-**5** is of major importance for chemical yield and enantioselectivity.[24] In catalyses with (S,S_p)-**10** both were much lower compared to reactions with (S,S_p)-**5**. Observations of this kind have also been reported by Uemura *et al.* for their catalysts.[20a]

The absolute configuration of the products was found to be *S* in all cases, which is in accordance with the generally accepted transition states proposed by Noyori and Kitamura[22a] and by Corey and Hannon.[25]

In conclusion, we have introduced a highly diastereoselective synthesis of new 1,2-disubstituted tricarbonyl(η^6-arene)chromium(0) complexes starting from tricarbonyl(η^6-benzyl-SMP)chromium(0) (*S*)-**3**. We have further proven that complex (S,S_p)-**5** is a suitable ligand for the asymmetric addition of dialkylzincs to aldehydes, giving the corresponding secondary alcohols in very good yield and with enantiomeric excesses of up to 86%.

The application of the phosphino derivative (S,S_p)-**7** as a bidentate ligand in asymmetric catalysis is currently under investigation.

Experimental

All reactions were carried out in dried glassware under an atmosphere of argon. Manipulations were performed in the absence of light using common Schlenk techniques in order to guarantee an inert atmosphere. Chromium hexacarbonyl was obtained from Merck–Schuchardt and used as received. *P*-Chlorodiphenylphosphine was purchased from Merck–Schuchardt, distilled and stored under argon. Bu^{n}Li and Bu^{t}Li were obtained from Merck–Schuchardt, Bu^{s}Li from Aldrich. SMP **1** was synthesized according to the published procedure.[16] Diethyl ether, THF and toluene were distilled from sodium–benzophenone ketyl radical prior to use. $CDCl_3$ was distilled and stored under argon. All other solvents and reagents were used as received from commercial suppliers. Dimethylzinc was used as 2 M solution in toluene and was purchased from Aldrich. Neat diethylzinc was obtained from Witco and used as such.

Synthesis

(*S*)-(2-Methoxymethylpyrrolidin-1-yl-methyl)benzene, (2). To a solution of 4.00 g (34.7 mmol) of (*S*)-2-methoxymethylpyrrolidine (**1**) in 50 mL freshly distilled toluene were subsequently added 5.2 mL (45.2 mmol) benzyl chloride, 3.6 g (26.0 mmol) anhydrous potassium carbonate and a catalytic amount of sodium iodide. The mixture was gently refluxed overnight at 120 °C oil bath temperature. After cooling to room temperature the resulting yellow solution was quenched with water. A 2 M solution of HCl was added and the mixture was extracted with diethyl ether. The aqueous layer was then neutralized by addition of solid potassium carbonate and extracted with dichloromethane. The combined organic phases were dried over $MgSO_4$, filtered, and the solvents were subsequently removed *in vacuo* at a bath temperature of 35 °C to yield an orange oil, which was distilled under vacuum to give 6.2 g (30.2 mmol, 87%) of **2** as a colourless liquid. Compound **2** was stored under argon at −24 °C.

T_b = 70 °C/3 × 10^{-3} bar. $[\alpha]_D$ = −87.4 (c = 3.5, CH_2Cl_2). MS [70 eV, m/z (%)]: 205 ([M^+], 1); 160 (86); 91 (100); 65 (12); 45 (14). GC-MS (column HP-5-MS, He, const. flow 1.2 ml min^{-1}, 260 °C): 37.67 min (205 [M^+]). IR: 2873, 2807, 1453, 1118, 738, 699 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.60–1.75 (m, 3H); 1.86–1.95 (m, 1H); 2.21 (ddd, J = 9.1, 7.7, 1.4 Hz, 1H); 2.66–2.75 (m, 1H); 2.89–2.96 (m, 1H); 3.31 (dd, J = 9.3, 5.1 Hz, 1H); 3.34 (s, 3H); 3.35 (dd, J = 9.3, 4.9 Hz, 1H); 3.39 (d, J = 13.1 Hz, 1H); 4.09 (d, J = 13.1 Hz, 1H); 7.20–7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.43; 29.29; 55.23; 59.68; 60.30; 63.57; 77.12; 127.38; 128.75; 129.57; 140.39. Anal. calcd. for $C_{13}H_{19}NO$: C 76.06; H 9.33; N 6.82. Found: C 75.77; H 9.50; N 7.20.

(*S*)-Tricarbonyl[η^6-(2-methoxymethylpyrrolidin-1-yl-methyl) benzene]chromium(0) [(*S*)-3]. In a well ventilated fume cupboard, 6.00 g (29 mmol) of (*S*)-(2-methoxymethylpyrrolidin-1-yl-methyl)benzene (**2**) were placed in a well-dried Schlenk tube under an inert atmosphere of argon. Freshly distilled di-*n*-butyl ether (160 mL) was added followed by addition of 16 mL of freshly distilled THF. The resulting mixture was stirred at room temperature while 12.9 g (59 mmol) of chromium hexacarbonyl were carefully added against a positive stream of argon. The Schlenk tube was then fitted with air and water condensers on top. The whole system was degassed three times and the resulting slightly yellow solution was heated under reflux in the dark for 48 h. The reaction mixture was then cooled down to 0 °C and filtered through a Celite layer, eluated with diethyl ether, and finally concentrated under

Table 3 Catalyzed asymmetric dialkylzinc additions

Entry	Substrate	ZnR_2/ [mol%]	Complex	Reaction time/h	Yield/ %[a]	ee/ %[b]	Absol. config.[c]
1	Ferrocenecarbaldehyde	$ZnMe_2$ [5]	**5**	33	83	77	*S*
2	Ferrocenecarbaldehyde	$ZnMe_2$ [10]	**5**	24	96	83	*S*
3	Ferrocenecarbaldehyde	$ZnMe_2$ [20]	**5**	20	98	81	*S*
4	Benzaldehyde	$ZnMe_2$ [10]	**5**	26	86	84	*S*
5	Benzaldehyde	$ZnEt_2$ [10]	**5**	18	91	86	*S*
6	Ferrocenecarbaldehyde	$ZnMe_2$ [10]	**10**	34	54	17	*S*
7	Benzaldehyde	$ZnMe_2$ [10]	**10**	38	59	24	*S*

[a] After purification. [b] Determined by HPLC. [c] Determined by correlation of the optical rotation with literature values.

reduced pressure. Purification of the residue by column [silica gel, diethyl ether–hexanes (90 : 10)] gave 9.5 g (27.8 mmol) of **3** as an orange oil, which slowly solidified at −24 °C.

$[\alpha]_D = -96.5$ ($c = 0.8$, CH_2Cl_2). MS [70 eV, *m/z* (%)]: 341 ([M^+], 3); 313 (4); 285 (20); 257 (30); 165 (100); 91 (33); 52 (26). IR: 1963, 1876, 664, 632 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 1.38–1.65 (m, 4H); 1.88–1.97 (m, 1H); 2.54–2.59 (m, 1H); 2.80–2.83 (m, 1H); 2.82 (d, $J = 14.0$ Hz, 1H); 3.04–3.08 (m, 1H); 3.08 (s, 3H); 3.11–3.18 (m, 1H); 3.78 (m, $J = 14.0$ Hz, 1H); 4.31–4.35 (m, 1H); 4.49–4.53 (m, 1H); 4.78–4.81 (m, 1H); 4.87–4.89 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.56; 28.62; 55.31; 58.87; 59.69; 63.46; 76.99; 91.96; 93.54; 94.17; 94.55; 110.67; 233.68. EI-HRMS: Calcd. for $C_{16}H_{19}CrNO_4$: 341.0719. Found: 341.0720.

General procedure for the asymmetric deprotonation of complex (*S*)-3

A dry Schlenk tube under an argon atmosphere was charged with complex **3**, which was dissolved in freshly distilled diethyl ether (10 mL per mmol of **3**). The resulting yellow solution was cooled to −78 °C and Bu^{t}Li (1.1 to 1.2 equiv as a 1.6 M solution in *n*-pentane) was added dropwise *via* syringe. Stirring was continued for a period of 2 h. The cooling bath was then removed and the reaction mixture was briefly warmed to room temperature. It was recooled to −78 °C and the electrophile (1.2 to 1.3 equiv.) was added neat. The reaction mixture was allowed to warm to room temperature overnight and was then quenched with water. The aqueous layer was extracted with diethyl ether, the combined etheral phases were subsequently washed with brine and distilled water and were dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure by distillation into a cold trap. An NMR spectrum of the crude product was obtained in order to determine the diastereomeric ratio. Further purification steps in order to obtain analytically pure compounds were carried out as stated below.

(S,S_p)-Tricarbonyl[η^6-2-(2-methoxymethylpyrrolidin-1-ylmethyl)formylbenzene]chromium(0), [(S,S_p)-4]. Standard work-up left a red oil, which was purified by column chromatography [silica gel, diethyl ether–*n*-hexane (90 : 10)]. Recrystallization from pure *n*-hexane yielded the title complex as an orange to red air-stable solid.

$[\alpha]_D = -561.5$ ($c = 0.3$, CH_2Cl_2). MS [70 eV, *m/z* (%)]: 369 ([M^+], 1); 313 (8); 285 (30); 165 (100); 52 (42). IR: 1968, 1905, 1886, 1678 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.33–1.44 (m, 1H); 1.51–1.68 (m, 2H); 1.78–1.90 (m, 1H); 2.16 (ddd, $J = 9.1$, 7.4, 1.7 Hz, 1H); 2.71–2.80 (m, 1H); 2.83–2.89 (m, 1H); 2.98 (d, $J = 13.2$ Hz, 1H); 3.27–3.36 (m, 2H); 3.31 (s, 3H); 4.69 (d, $J = 13.2$ Hz, 1H); 5.06–5.08 (m, 1H); 5.17–5.21 (m, 1H); 5.59–5.63 (m, 1H); 6.02–6.04 (m, 1H); 9.94 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.59; 28.38; 55.25; 57.23; 59.62; 63.74; 77.96; 89.00; 91.62; 93.92; 95.46; 95.61; 114.08; 189.07; 231.21. Anal. calcd. for $C_{17}H_{19}CrNO_5$: C 55.28; H 5.18; N 3.79. Found: C 55.20; H 5.11; N 3.75.

(S,S_p)-Tricarbonyl[η^6-2-(2-methoxymethylpyrrolidin-1-ylmethyl)(diphenylhydroxymethyl)benzene]chromium(0), [(S,S_p)-5]. Standard work-up followed by recrystallization from *n*-hexane–diethyl ether afforded the title complex as a yellow air-stable solid.

$[\alpha]_D = -136.7$ ($c = 1.0$, CH_2Cl_2). MS [70 eV, *m/z* (%)]: 523 ([M^+], 3); 467 (3); 439 (59); 421 (100); 342 (80); 164 (72); 52 (35). IR: 3362, 1950, 1875 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.06–1.27 (m, 1H); 1.40–1.47 (m, 2H); 1.75–1.80 (m, 1H); 2.16 (ddd, $J = 9.1$, 7.3, 1.7 Hz, 1H); 2.36–2.40 (m, 1H); 2.52–2.57 (m, 1H); 2.79 (d, $J = 12.9$ Hz); 3.19–3.22 (m, 2H); 3.31 (s, 3H); 4.55 (d, $J = 12.9$ Hz); 4.80–4.85 (m, 1H); 5.00–5.08 (m, 1H); 5.44–5.48 (m, 1H); 7.24–7.38 (m, 10H); 7.55–7.58 (m, 2H); 7.81 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 22.58; 22.18; 53.94; 59.53; 60.01; 64.12; 74.75; 81.79; 89.21; 93.95; 95.09; 98.08; 108.81; 119.52; 127.89; 128.02; 128.10; 128.20; 128.51; 129.00; 146.40; 147.55; 233.39. EI-HRMS: Calcd. for $C_{26}H_{29}CrNO_2$ ([M^+ − 3 CO]): 439.1603. Found: 439.1606.

(S,S_p)-Tricarbonyl[η^6-2-(2-methoxymethylpyrrolidin-1-ylmethyl)(tributylstannyl)benzene]chromium(0), [(S,S_p)-6]. Standard work-up gave a yellow to orange oil, which was purified by column chromatography [silica gel, *n*-hexane–diethyl ether (50 : 50)] to yield the title complex as a slightly unstable light orange oil.

$[\alpha]_D = -84.6$ ($c = 1.9$, CH_2Cl_2). MS [70 eV, *m/z* (%)]: 631 ([M^+], 1); 574 (1); 450 (31); 438 (100); 158 (32). IR: 2957, 2925, 1961, 1884, 1459, 665, 629 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.86–1.10 (t, $J = 6.9$ Hz, 9H); 1.23–1.87 (m, 21H); 1.90–2.00 (m, 1H); 2.25–2.34 (m, 1H); 2.66–2.71 (m, 1H); 3.00–3.03 (m, 1H); 3.14 (d, $J = 14.0$ Hz, 1H); 3.23–3.28 (m, 1H); 3.28 (s, 3H); 3.34–3.40 (m, 1H); 3.92 (d, $J = 14.0$ Hz, 1H); 5.11–5.15 (m, 1H); 5.36–5.38 (m, 1H); 5.46–5.51 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.92; 14.24; 23.30; 28.00; 28.94; 29.54; 55.45; 59.51; 61.16; 64.81; 76.99; 92.03; 94.03; 95.48; 102.89; 118.50; 234.65. EI-HRMS: Calcd. for $C_{28}H_{45}CrNO_4Sn$: 631.1775. Found: 631.1774.

(S,S_p)-Tricarbonyl[η^6-2-(2-methoxymethylpyrrolidin-1-ylmethyl)(diphenylphosphino)benzene]chromium(0), [(S,S_p)-7]. Standard work-up leaves a yellow foam, which was purified by column chromatography [silica gel, *n*-hexane–diethyl ether (70 : 30)]. Recrystallization from pure *n*-hexane yielded the title complex as an orange solid.

$[\alpha]_D = -314.3$ ($c = 1.8$, CH_2Cl_2). MS [70 eV, *m/z* (%)]: 525 ([M^+], 2); 485 (3); 457 (97); 344 (100); 165 (63); 52 (88). IR: 1965, 1883 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.94–1.03 (m, 1H); 1.08–1.23 (m, 1H); 1.35–1.46 (m, 1H); 1.60–1.70 (m, 1H); 2.04–2.12 (m, 1H), 2.53–2.61 (m, 1H), 2.66–2.72 (m, 1H), 3.06 (dd, $J = 6.3$, 9.3 Hz, 1H); 3.14 (d, $J = 13.5$ Hz, 1H); 3.29 (s, 3H); 3.57 (dd, $J = 5.5$, 9.4 Hz, 1H); 4.55 (dd, $J = 2.5$, 13.5 Hz, 1H); 4.79–4.81 (m, 1H), 5.07–5.09 (m, 1H), 5.35–5.38 (m, 1H), 5.46–5.50 (m, 1H), 7.28–7.37 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.24; 28.33; 53.81; 57.42 (d, $J_{C\text{-}P} = 16.1$ Hz); 58.85; 63.40; 76.04; 89.99; 91. 59 (d, $J_{C\text{-}P} = 4.6$ Hz); 94.09; 98.62; 102.94 (d, $J_{C\text{-}P} = 25.2$ Hz); 116.24 (d, $J_{C\text{-}P} = 21.1$ Hz); 128.32 (d, $J_{C\text{-}P} = 6.6$ Hz); 128.55 (d, $J_{C\text{-}P} = 6.3$ Hz); 129.32; 132.85 (d, $J_{C\text{-}P} = 19.4$ Hz); 134.68 (d, $J_{C\text{-}P} = 20.0$ Hz); 135.09 (d, $J_{C\text{-}P} = 13.7$ Hz); 136.96 (d, $J_{C\text{-}P} = 9.1$ Hz); 232.48. Anal. calcd. for $C_{28}H_{28}CrNO_4P$: C 64.00; H 5.32; N 2.67. Found: C 64.27; H 5.35; N 2.38.

(S,S_p)-Tricarbonyl[η^6-2-(2-methoxymethylpyrrolidin-1-ylmethyl)(trimethylsilyl)benzene]chromium(0), [(S,S_p)-8]. A solution of complex (S,S_p)-**2** (250 mg, 0.7 mmol) in 10 mL of freshly distilled diethyl ether was cooled to −78 °C and Bu^{t}Li (0.53 mL, 0.84 mmol, 1.6 M-solution in *n*-pentane) was added dropwise *via* syringe. Stirring was continued for a period of 2 h. The cooling bath was then removed and the reaction mixture was warmed to room temperature for a short period of time. It was recooled to −78 °C and chlorotrimethylsilane (0.9 mL, 7.1 mmol) was added directly. Stirring was continued for a further period of 2 h and the solvent was then directly removed into a trap under reduced pressure. The residue was purified by column chromatography [silica gel, *n*-hexane–dichloromethane (20 : 80)] to afford the title complex (214 mg, 5.2 mmol, 74%) as a highly unstable orange oil.

$[\alpha]_D = -104.9$ ($c = 0.2$, CH_2Cl_2). MS [70 eV, *m/z* (%)]: 413 ([M^+], 2); 329 (13); 232 (29); 165 (100). IR: 2957, 1963, 1883, 1450, 844, 665, 629 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.38 (s, 9H); 1.51–1.95 (m, 3H); 2.28–2.37 (m, 1H); 2.71–2.73 (m, 1H); 3.01–3.03 (m, 1H); 3.25 (s, 3H); 3.26–3.48 (m, 4H); 4.11 (d, $J = 14.3$ Hz, 1H); 5.09–5.21 (m, 1H); 5.39–5.56 (m,

3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.40; 22.80; 28.13; 55.01; 58.47; 58.78; 64.33; 76.33; 89.55; 92.12; 95.58; 98.26; 101.14; 118.15; 233.58. EI-HRMS: Calcd. for $C_{19}H_{27}CrNO_4Si$: 413.1115. Found: 413.1115.

Independent synthesis of (S,S_p)-8 from (S_p)-tricarbonyl[η^6-2-(trimethylsilyl)benzaldehyde]chromium(0), [(S_p)-9]

To a solution of (S_p)-**9** (105 mg, 0.33 mmol) in 5 mL of freshly distilled dichloromethane were subsequently added 0.04 mL titanium tetrachloride (0.33 mmol), 0.09 mL triethylamine (0.66 mmol) and 38 mg (*S*)-2-methoxymethylpyrrolidine (0.33 mmol). The resulting solution was stirred for 1 h, then sodium cyanoborohydride (40 mg, 0.64 mmol) was added in one portion, and the mixture was stirred for a further 5 h. After this, 10 mL of methanol and water were added to quench the reaction. Extraction with dichloromethane, drying over $MgSO_4$, and removal of the solvents under reduced pressure left a dark residue, which was purified by column chromatography [silica gel, *n*-hexane–dichloromethane (20 : 80)] to leave the complex (44 mg, 0.11 mmol, 32%) as an orange oil.

(S,S_p)-Tricarbonyl[η^6-2-(2-methoxymethylpyrrolidin-1-yl-methyl)(hydroxymethyl)benzene]chromium(0), [(S,S_p)-10]

In a dry Schlenk tube under an argon atmosphere, complex (S,S_p)-**4** (520 mg, 1.41 mmol) was dissolved in 10 mL of dry ethanol. Sodium borohydride (800 mg, 2.11 mmol) was then added and the reaction mixture was stirred for about 30 s until the originally deep red solution had turned yellow. The reaction mixture was quenched by careful addition of 20 mL of distilled water. It was extracted with diethyl ether, washed with brine and water. After drying over $MgSO_4$ the solvent was removed under reduced pressure by distillation into a cold trap, leaving an oil. This was purified by column chromatography (silica gel, diethyl ether) to afford a quantitative yield of the title complex (520 mg, 1.40 mmol) as a yellow oil.

$[\alpha]_D = -127.3$ ($c = 0.7$, CH_2Cl_2). MS [70 eV, m/z (%)]: 371 ([M^+], 2); 287 (11); 190 (100); 91 (52). IR: 1965, 1880, 1450, 669, 629 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46–1.86 (m, 3H); 1.90–2.07 (m, 1H); 2.11–2.16 (m, 1H); 2.65–2.90 (m, 3H); 3.05–3.46 (m, 2H); 3.36 (s, 3H); 3.81–3.84 (m, 1H); 4.59 (d, $J = 12.4$ Hz, 1H); 4.67 (d, $J = 12.4$ Hz, 1H); 5.20–5.28 (m, 4H); 6.7 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.32; 28.16; 54.84; 59.11; 59.57; 64.16; 76.97; 92.17; 92.58; 95.53; 95.62; 108.38; 110.98; 233.01. EI-HRMS: Calcd. for $C_{17}H_{21}CrNO_5$: 371.0825. Found: 371.0825.

General procedure for the asymmetric alkylation in the presence of (S,S_p)-5 and (S,S_p)-10

A well-dried Schlenk flask under argon was charged with 5 mol% of the complex. The flask was evacuated twice and flushed with argon. After this, 5 mL of freshly distilled toluene were added and the solution was cooled to 0 °C followed by addition of 1.5 equiv. of the dialkylzinc species. The resulting solution was stirred for 20 min and 1.0 equiv. of benzaldehyde was added. The reaction mixture was then sealed and the process of the reaction monitored by TLC. The reaction was worked-up by careful addition of 10 mL of water and subsequent fourfold extraction with 25 mL of dichloromethane each. The combined organic phases were washed with brine, dried over $MgSO_4$ and the solvent was removed *in vacuo*. Following steps were as stated below.

1-Ferrocenylethanol. Column chromatography [silica gel, *n*-hexane–ethyl acetate (75 : 25)] gave an orange fraction, which was collected in a Schlenk flask. Evaporation of the solvents under reduced pressure yielded the product in pure form. The optical purity of the product was determined by analytical HPLC analysis: Chiralpak AD, *n*-hexane–*iso*-propanol 95 : 5, 0.5 mL min^{-1}; retention times: 39.5 min (*R* enantiomer), 42.6 min (*S* enantiomer).

1-Phenylethanol and 1-phenylpropanol. The crude product was purified by column chromatography [silica gel, hexanes–MTBE (90 : 10)] followed by Kugelrohr distillation, which yielded the title compounds as colourless oils. The optical purity of the product was determined by analytical HPLC analysis. 1-Phenylethanol: Chiralcel OD, *n*-hexane–*iso*-propanol 98.5:1.5, 1.0 mL min^{-1}; retention times: 27.0 min (*R* enantiomer), 34.7 min (*S* enantiomer); 1-phenylpropanol: Chiralcel OD, *n*-hexane–*iso*-propanol 98 : 2, 0.5 mL min^{-1}; retention times: 15.5 min (*R* enantiomer), 17.7 min (*S* enantiomer).

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