Preparation of Enantiomerically Pure [3]Ferrocenophane-Based Chelate Bis-Phosphane Ligands and Their Use in Asymmetric Alternating Carbon Monoxide/Propene Copolymerization

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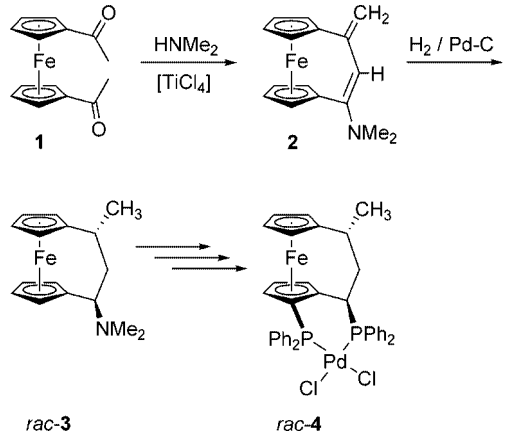
An intramolecular Mannich reaction ($HNMe_2$, $TiCl_4$) was used to convert 1,1′-diacetylferrocene to the unsaturated amino[3]ferrocenophane **2**. Subsequent hydrogenation gave **3**. To obtain enantiomerically pure chelate *P,P*-[3]ferrocenophane ligands the readily available pure dimethylamino[3]ferrocenophane enantiomers (*R,R*)-**3** and (*S,S*)-**3** each were treated with butyllithium followed by chlorodiphenylphosphane to yield the chelate *P,N*-[3]ferrocenophanes (R,R,R_{pl})-**10** and (S,S,S_{pl})-**10**, respectively. Their treatment with $HPPh_2$ in glacial acetic acid resulted in substitution of the $–NMe_2$ group by $–PPh_2$ with overall retention of configuration to yield (R,R,R_{pl})-**11** and (S,S,S_{pl})-**11**, respectively (both characterized by X-ray diffraction). Similarly, the reaction of (R,R,R_{pl})-**10** or (S,S,S_{pl})-**10** with dicyclohexylphosphane/HOAc yielded the pure (R,R,R_{pl})-**12** and (S,S,S_{pl})-**12** enantiomers, respectively. Both these compounds were also characterized by X-ray crystal structure analyses. (R,R,R_{pl})-**12** was employed in catalytic asymmetric hydrogenation and also in asymmetric alternating carbon monoxide/propene copolymerization. A catalyst that was generated in situ from the chelate *P,P*-[3]ferrocenophane ligand and palladium acetate gave the CO/propene alternating copolymer with a good activity and high asymmetric induction. The catalyst derived from the reaction of (R,R,R_{pl})-**11** with $[Rh(cod)_2]BF_4$ was employed in the enantioselective hydrogenation of dimethyl itaconate (DMI) (**13**, ca. 95 % *ee*, *R*-configured product) and methyl α-acetamidocinnamate (MAC) **14** (ca. 24 % *ee*, *R*-configured product).

Introduction

Optically active chelate bis(phosphanyl)ferrocene-derived ligand systems have played an important role in asymmetric catalysis.[1,2] Weissensteiner et al. have developed a variety of such ligands derived from the [3]ferrocenophane framework,[3] among them enantiomerically pure examples.[4,5] They had further shown that the chiral bis(phosphanyl)[3]-ferrocenophane ligands appeared to be inferior with regard to asymmetric induction, e.g. in some hydrogenation reactions as compared e.g. to the JOSIPHOS system and related less rigid ligands.[4] Recently we have found that bis(phosphanyl)[3]ferrocenophane ligands may be of some use in alternating CO/olefin copolymerization.[6] We had developed a very simple way to synthesize such systems starting from 1,1′-diacetylferrocene (**1**) by a reaction sequence that was initiated by an intramolecular Mannich-type coupling reaction[7,8] (see Scheme 1). We had prepared the corresponding *P,P*-[3]ferrocenophane and characterized its $PdCl_2$ complex *rac*-**4** by X-ray diffraction.[6] The Pd complex *rac*-**4** was employed in CO/ethene alternating copolymerization using different activation protocols and found to give a very active catalyst system. Since the racemic chelate bis(phosphanyl)[3]ferrocenophane ligands showed such a promising catalytic performance it was tempting to see



Scheme 1.

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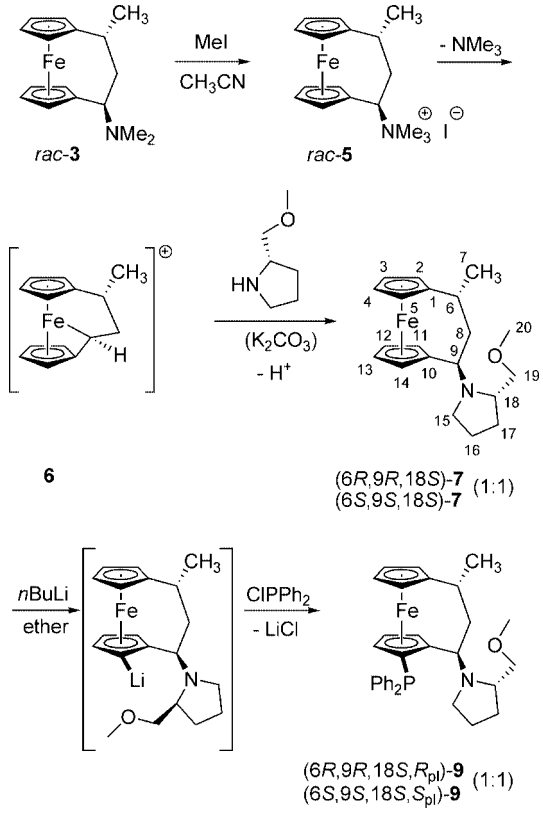
whether they would give rise to a considerable asymmetric induction in a related CO/1-alkene alternating copolymerization. Therefore, we have developed a short synthetic pathway to both enantiomers of optically active examples of such ligand systems to investigate their potential in asymmetric CO/propene alternating copolymerization and enantioselective catalytic hydrogenation.[1,9]

Results and Discussion

We first tried to solve this synthetic problem by reacting the racemic [3]ferrocenophanylamine (*rac*-**3**)[6] with the enantiomerically pure proline-derived reagent (*S*)-methoxymethylpyrrolidine (SMP). The amine *rac*-**3** was quaternized by treatment with methyliodide in acetonitrile, followed by treatment with SMP (1.1 equiv.) in the presence of K_2CO_3 (2 equiv.). Under these conditions, the substitution reaction at the α-position to the Cp-ring of the [3]ferrocenophane proceeds with retention of configuration, utilizing a strong anchimeric assistance of the Fe metal atom.[10] This reaction probably proceeds through the reactive cationic intermediate (**6**).[5,11] Complex **7** was isolated as a 1:1 mixture of the respective (6*S*,9*S*,18*S*)- and (6*R*,9*R*,18*S*)-diastereoisomers (isolated in a total yield of 98%), (Scheme 2).



Scheme 2.

We have obtained a few single crystals of one of the diastereoisomers [(6*S*,9*S*,18*S*)-**7**] and characterized it by X-ray diffraction (see Figure 1). The X-ray crystal structure analyses revealed the *trans* positions of the methyl substituent at C6 and the SMP substituent at C9. The [3]ferrocenophane bridging framework features a "cycloheptane boat-like" conformation of the atoms C5, C1, C6, C8, C9, C10, and C14 with the small 6-CH_3 group being oriented axially and the bulky SMP substituent equatorially. The corresponding dihedral angles of the framework amount to –60.1(3)° (C5–C1–C6–C8), –66.7(3)° (C1–C6–C8–C9), +61.1(3)° (C7–C6–C8–C9) and –157.6(2)° (C6–C8–C9–N).

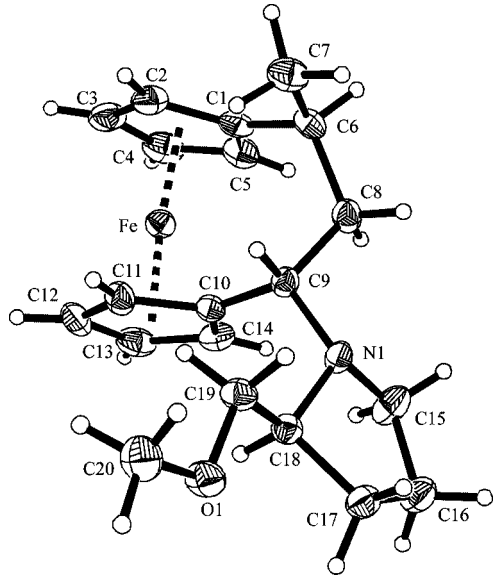


Figure 1. A view of the molecular structure of the diastereomer (6*S*,9*S*,18*S*)-**7**. Selected bond lengths [Å] and angles [°]: C1–C6 1.516(3), C6–C7 1.528(3), C6–C8 1.545(3), C8–C9 1.541(3), C9–C10 1.523(3), C9–N1 1.479(3); C1–C6–C7 112.5(2), C1–C6–C8 112.3(2), C7–C6–C8 112.0(2), C6–C8–C9 115.1(2), C8–C9–C10 112.9(2), C8–C9–N1 109.3(2), C10–C9–N1 115.5(2).

We tried to separate the (*R*,*R*,*S*)- and (*S*,*S*,*S*)-**7** isomers by fractional crystallization.[12] Twofold recrystallization from ether at –18 °C eventually resulted in an enrichment of 87% *de*, but the obtained yields after the separation process were too low to make this a practical procedure. Therefore, we submitted the 1:1 mixture of (*R*,*R*,*S*)- and (*S*,*S*,*S*)-**7** directly to the directed *ortho*-metallation reaction.[13] Complexes **7** turned out to be rather active in this reaction. Treatment with *n*-butyllithium at +4 °C in ether followed by treatment with chlorodiphenylphosphane gave a 1:1 mixture of (*R*,*R*,*S*,R_{pl})-**9** and (*S*,*S*,*S*,S_{pl})-**9** in a combined yield of 76% (see Scheme 2). Recrystallization from ether again resulted in a marked enrichment of one of the diastereoisomers [here: (*R*,*R*,*S*,R_{pl})-**9**] to ca. 71% *de*, but the losses in yield during this separation process again were too high for a practical application. Complex (*R*,*R*,*S*,S_{pl})-**9** was characterized by X-ray diffraction. In principle, this chelate *P*,*N*-[3]ferrocenophane shows a similar framework as **7**. However, the introduction of the bulky PPh_2 ligand has resulted in a slight "flattening" of the framework. Thus, in **9** the C14–C10–C9–N dihedral angle amounts to 58.8(2)°, which is >15° smaller than found in **7**. The angle between the C9–N1 [1.467(2) Å] and C14–P1 [1.825(2) Å] vectors in **9** amounts to 59.0°. The bonding angles at phosphorus are 98.29(9)° (C14–P–C27), 101.40(9)° (C21–P–C27), and

103.72(9)° (C14–P–C21). The bond angles at nitrogen are larger; they amount to 112.74(16)° (C9–N1–C15), 119.22(15)° (C9–N1–C18), and 106.54(15)° (C15–N1–C18) (Figure 2).

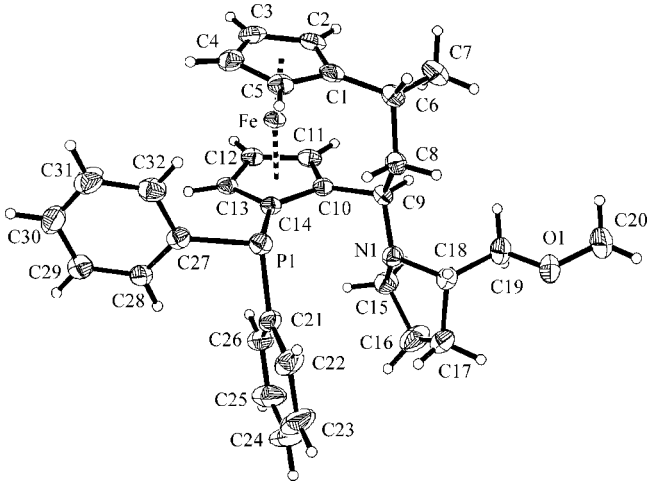


Figure 2. A view of the molecular structure of the diastereomer **9**. Selected bond lengths [Å] and angles [°]: C1–C6 1.508(3), C6–C7 1.524(4), C6–C8 1.540(3), C8–C9 1.546(2), C9–C10 1.521(2), C9–N1 1.467(2), C10–C14 1.449(3), C14–P1 1.825(2); C1–C6–C7 112.9(2), C1–C6–C8 113.1(2), C7–C6–C8 112.3(2), C6–C8–C9 115.8(2), C8–C9–C10 112.7(2), C8–C9–N1 111.4(2), C10–C9–N1 107.6(1), C9–C10–C14 127.4(2), C10–C14–P1 126.4(1).

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In the solid state, complex (R,R,S,R_{pl})-**9** attains a conformation that has oriented the CH_2OCH_3 group at the SMP substituent away from the ferrocenophane core. It seems that the bonding sites at P and at N face each other in the chelate *P,N*-[3]ferrocenophane system **9** (the P1···N1 separation is 3.444 Å).

Since the systems **9** were only obtained diastereomerically enriched, we chose another route for the preparation of enantiomerically pure chelate *P,N*- and *P,P*-[3]ferrocenophane ligand systems. We had previously shown that the (6*R*,9*R*)-**3** and (6*S*,9*S*)-**3** enantiomers were rather easily available on a preparative scale, using methyl(1-phenylethyl)amine as a chiral auxiliary, and employing a simple chromatographic separation of the respective diastereomers.[14] After hydrogenolytic removal of the auxiliary followed by *N*-methylation, each of the enantiomers of **3** was obtained in ca. 30% overall yield (of a possible max. 50%) by this method.

For the directed metallation of **3** we first used *n*-butyllithium followed by quenching with $ClPPh_2$ and chromatographic separation, which lead to the formation of *ortho*-substituted product **10** in ca. 40% yield. Treatment of (6*R*,9*R*)-**3** with *tert*-butyllithium instead of *n*-butyllithium gave (6*R*,9*R*,R_{pl})-**10** in 73% yield. Analogously, (6*S*,9*S*,S_{pl})-**10** was obtained, but in both cases some residual starting material (*R,R*)-**3** or (*S,S*)-**3**, respectively, could be obtained from the chromatographic column by elution with methanol. The obtained products showed optical rotations of $[a]_D^{20}$ = +244 [(*R,R,R*$_{pl}$)-**10**] and $[a]_D^{20}$ = –242 [(*S,S,S*$_{pl}$)-**10**], respectively. They feature a typical set of NMR signals of the [3]ferrocenophane bridge [^{1}H: δ = 2.31 (8-H_{eq}), 2.68 (9-H), 2.84 (6-H), 3.16 (8-H_{ax}); ^{13}C: 27.7 (C6), 45.3 (C8), 59.1 (C9) ppm] and a ^{31}P NMR resonance at δ = –21.7 ppm. Both enantiomers were characterized by their CD spectra (see Figure 3 and Scheme 3).

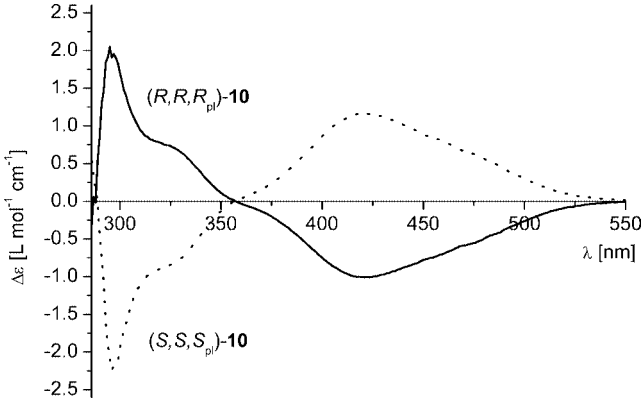

Figure 3. CD-spectra of (R,R,R_{pl})-**10** (solid line) and (S,S,S_{pl})-**10** (dotted line) (c = 4 10^{-4} g·mL^{-1} in CH_2Cl_2).

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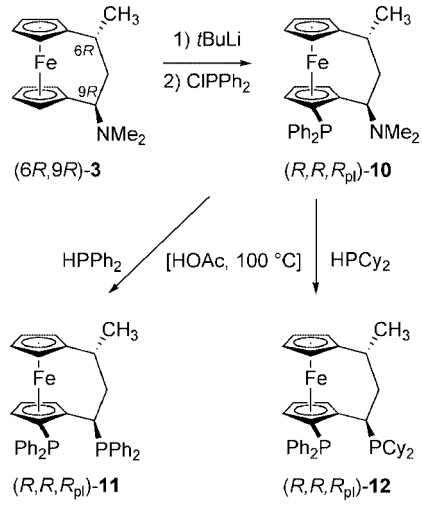

Scheme 3.

The complexes (R,R,R_{pl})-**10** and (S,S,S_{pl})-**10** were used as relay starting materials for the synthesis of optically active chelate *P,P*-[3]ferrocenophanes. For this transformation we took advantage of the strong neighboring group effect of the iron atom in nucleophilic substitution reactions that were carried out at the periphery of this specific ligand framework. For the –NMe_2 vs. –PR_2 exchange reaction we applied a protocol that had previously been used by Weissensteiner et al.[3] Thus, complex (S,S,S_{pl})-**10** was treated with diphenylphosphane for 20 h at 100 °C in glacial acetic acid. Under these conditions the substitution reaction is practically complete to give the chelate *P,P*-[3]ferrocenophane product (S,S,S_{pl})-**11** (93% isolated). As expected, substitution of the –NMe_2 group by –PPh_2 took place with

complete retention of configuration under these conditions. The product shows two ^{31}P NMR signals[15] at δ = –22.2 (d, $J_{P,P}$ = 79.6 Hz, 14-PPh_2) and δ = –7.9 (9-PPh_2) ppm. It features a typical set of $^1H/^{13}C$ NMR resonances of the C3-ferrocenophane bridge {^1H: δ = 1.91 (8-H_{eq}), 2.59 (6-H), 3.13 (9-H), 3.19 (8-H_{ax}) ppm; ^{13}C: δ = 26.0 [d, J(P,C) = 10.6 Hz, C6], 29.3 (dd, $J_{P,C}$ = 12.9 Hz and 2.7 Hz, C9), 45.3 (dd, $J_{P,C}$ = 23.5 Hz and 10.2 Hz, C8)}.

The reaction of the enantiomer (R,R,R_{pl})-**10** with $HPPh_2$ under the same conditions gave (R,R,R_{pl})-**11**. The optical rotations of the enantiomers were determined as $[\alpha]_D^{20}$ = +259 [(R,R,R_{pl})-**11**] and –260 [(S,S,S_{pl})-**11**], respectively.

The reaction of (R,R,R_{pl})-**10** and(S,S,S_{pl})-**10** with HP(cyclohexyl)$_2$ [$HPCy_2$] was carried out analogously to yield the pure enantiomers of the chelate *P,P*-[3]ferrocenophane products (R,R,R_{pl})-**12** ($[\alpha]_D^{20}$ = +344) and (S,S,S_{pl})-**12** ($[\alpha]_D^{20}$ = –346). Both the pairs of enantiomers of the chelate *P,P*-[3]ferrocenophane systems **11** and **12** were characterized by their CD spectra (see Figure 4 for **11**), and we have obtained single crystals for all these four complexes that have allowed them to be characterized by X-ray crystal structure analyses (see Figures 5 and 6).

Figure 5 shows a view of the two enantiomers of complex **11** that were synthesized and crystallized separately. The framework of the complexes **11** is characterized by dihedral angles of 49.7(3)° (C5–C1–C6–C8) and 72.0(2)° (C1–C6–C8–C9). The methyl substituent at C6 is oriented almost ideally in an axial position at the folded bridge conformation [C2–C1–C6–C7: 2.9(3)°], whereas the bulky –PPh_2 group at C9 is arranged equatorially [C6–C8–C9–P1: 173.5(1)°]. The angles around the Cp-bonded phosphorus atom P2 amount to 99.81(9)° (C14–P2–C33), 100.47(10)° (C27–P2–C33) and 101.80(9)° (C14–P2–C27); those around P1 to 98.48(9)° (C15–P1–C21), 101.80(11)° (C9–P1–C15) and 105.29(10)° (C9–P1–C21). The angle between the C14–P2 [1.829(2) Å] and C9–P1 [1.868(2) Å] vectors amounts to 49.6°. The P1···P2 separation in **11** is 3.491(1) Å, and the cone angle of this chelate *P,P*-[3]ferrocenophane ligand was calculated at 97.8°.

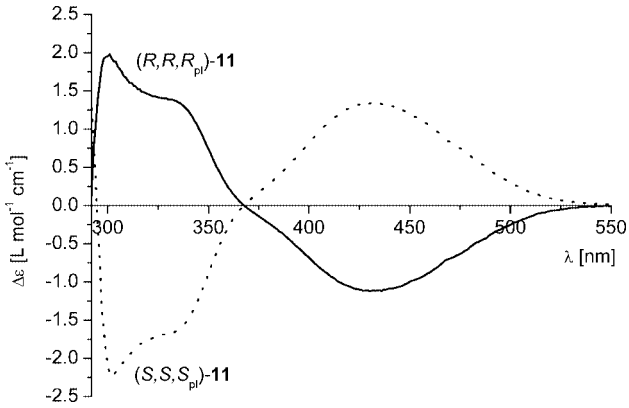

Figure 4. CD spectra of (R,R,R_{pl})-**11** (solid line) and (S,S,S_{pl})-**11** (dotted line) ($c = 4\times10^{-4}$ g·mL^{-1} in CH_2Cl_2).

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The ligand **12** enantiomers show similar structures in the solid state (see Figure 6), although there are a few noteworthy differences as compared to **11**. In **12** the bridging framework is slightly less folded – the dihedral angle C1–C6–C8–C9 (65.4(4)°] is by ca. 7° smaller than found in **11**. Consequently, the absolute values of the C5–C1–C6–C8 (57.2(4)°] and C7–C6–C8–C9 [–62.9(4)°] dihedral angles of **12** are similarly enlarged (≈ 7°) and the C6–C8–C9–P1 value (169.6(2)°] is slightly smaller for **12**. The methyl group at carbon atom C6 of the bridge is still axially oriented [C2–C1–C6–C7: 10.4(4)°] and the –PCy_2 group at C9 is in an equatorial position [C14–C10–C9–P1: 63.9(3)°]. The angle between the C14–P2 [1.837(3) Å] and C9–P1 [1.881(3) Å] vectors in the complexes **12** amounts to 58.0°. The P1···P2

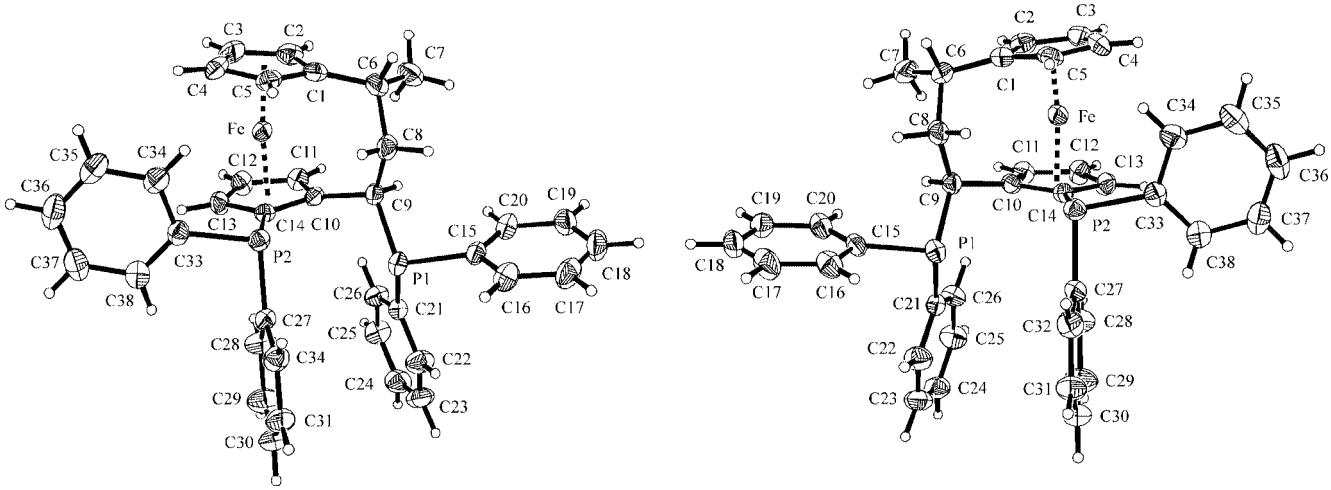


Figure 5. Views of the molecular structures of the enantiomers of the chelate *P,P*[3]ferrocenophane ligands (R,R,R_{pl})-**11** (right) and (S,S,S_{pl})-**11** (left). Selected bond lengths [Å] and angles [°]: (R,R,R_{pl})-**11**: C1–C6 1.506(3), C6–C7 1.536(4), C6–C8 1.550(3), C8–C9 1.548(3), C9–C10 1.524(3), C9–P1 1.868(2), C10–C14 1.444(3), C14–P2 1.829(2); C1–C6–C7 113.0(2), C1–C6–C8 112.1(2), C7–C6–C8 111.5(2), C6–C8–C9 115.7(2), C8–C9–C10 113.5(2), C8–C9–P1 106.6(1), C10–C9–P1 111.0(1), C9–C10–C14 128.6(2), C10–C14–P2 126.5(1); (S,S,S_{pl})-**11**: C1–C6 1.508(4), C6–C7 1.533(4), C6–C8 1.547(4), C8–C9 1.544(4), C9–C10 1.529(3), C9–P1 1.868(2), C10–C14 1.444(3), C14–P2 1.826(2); C1–C6–C7 112.8(2), C1–C6–C8 111.8(2), C7–C6–C8 111.7(2), C6–C8–C9 115.8(2), C8–C9–C10 113.5(2), C8–C9–P1 106.8(2), C10–C9–P1 110.8(2), C9–C10–C14 128.6(2), C10–C14–P2 126.5(2). For additional values see the text.

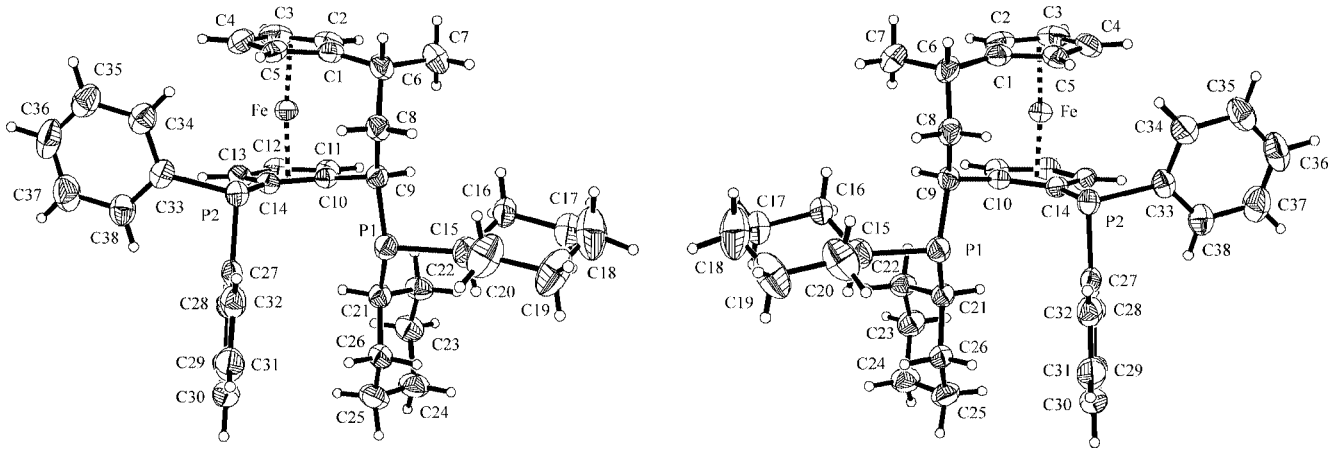


Figure 6. A projection of the molecular structures of (R,R,R_{pl})-**12** (right) and (S,S,S_{pl})-**12** (left). Selected bond lengths [Å] and angles [°]: (R,R,R_{pl})-**12**: C1–C6 1.509(5), C6–C7 1.531(5), C6–C8 1.555(4), C8–C9 1.541(4), C9–C10 1.516(4), C9–P1 1.881(3), C10–C14 1.451(4), C14–P2 1.837(3); C1–C6–C7 112.4(3), C1–C6–C8 113.0(2), C7–C6–C8 112.2(3), C6–C8–C9 116.4(3), C8–C9–C10 114.2(2), C8–C9–P1 107.9(2), C10–C9–P1 110.7(2), C9–C10–C14 129.5(3), C10–C14–P2 125.5(2); (S,S,S_{pl})-**12**: C1–C6 1.514(4), C6–C7 1.528(4), C6–C8 1.549(4), C8–C9 1.540(4), C9–C10 1.514(4), C9–P1 1.878(3), C10–C14 1.453(4), C14–P2 1.831(3); C1–C6–C7 111.9(3), C1–C6–C8 113.0(2), C7–C6–C8 112.2(2), C6–C8–C9 116.6(2), C8–C9–C10 114.3(2), C8–C9–P1 108.1(2), C10–C9–P1 110.6(2), C9–C10–C14 129.2(2), C10–C14–P2 125.7(2). For additional values see the text.

separation is slightly larger in **12** [3.689(1) Å] as compared to **11**. The cone angle of **12** was calculated at 105.7°.

We explored the chelate *P,P*-[3]ferrocenophane ligand (R,R,R_{pl})-**11** and (R,R,R_{pl})-**12** for its potential in asymmetric catalysis.

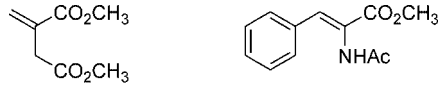
Catalytic hydrogenations were carried out with the substrates dimethyl itaconate (DMI, **13**) and methyl (*Z*)-acetamidocinnamate (MAC, **14**) using catalysts that were prepared in situ from $[(cod)_2Rh^+]\,BF_4^-$ and the ligands (R,R,R_{pl})-**11** and (R,R,R_{pl})-**12**, respectively.[3,16] Both substrates were hydrogenated with appreciable reaction rates with both ligands (Table 1).

Table 1. Enantioselective hydrogenation reactions using chelate phosphane Rh^I catalysts.

Entry	Substrate	Ligand / Rh^+[a]	Conv. [%]	*ee* [%]	Config.[d]
1	DMI (**13**)[b]	(R,S_{pl})-JOSIPHOS	100	99	(*S*)
2		(R,R,R_{pl})-**11**	100	95	(*R*)
3		(R,R,R_{pl})-**12**	100	52	(*R*)
4	MAC (**14**)[c]	(R,S_{pl})-JOSIPHOS	100	74	(*S*)
5		(R,R,R_{pl})-**11**	100	22	(*R*)
6		(R,R,R_{pl})-**12**	100	42	(*S*)

[a] Catalyst precursor: $[(cod)_2Rh]BF_4$; *c* (catalyst) = 1 mol-%. [b] Solvent: methanol, *ee* determination by GC on Lipodex-E (H_2 1.2 bar, 70 °C, isothermic). [c] Solvent: methanol, *ee* determination by GC on Lipodex-E (H_2 2.4 bar, 110 °C, isothermic) and by HPLC on Chiralcel OJ (heptane/2-propanol, 85:15, flow: 1 mL/min). [d] For determination of absolute configuration see Supporting Information (see also the footnote on the first page of this article).

Hydrogenation of **14** gave much lower asymmetric inductions than the $[(R,S_{pl})$JOSIPHOS/$Rh^+]$ reference, which we have used for comparison.[17] For this substrate only (R,R,R_{pl})-**12**/Rh^+ produces the same enantiomer as the $[(R,S_{pl})$-JOSIPHOS/$Rh^+]$ reference, whereas (R,R,R_{pl})-**11**/Rh^+ yielded the opposite enantiomer. Dimethylitaconate (**13**) was converted into the opposite enantiomer, dimethyl (*R*)-(+)-methylsuccinate, with the Rh complexes of both ligands. With (R,R,R_{pl})-**11**/Rh^+ this reaction gave rather high enantioselectivities [95% *ee* (*R*)]. Weissensteiner had used a related chelate (R,R_{pl})-[3]ferrocenophane/Rh^I catalyst for the hydrogenation of **13** and described that the (*S*)-configured product was obtained with ca. 65% *ee*.[4] It seems that the (R,R,R_{pl})-**11**/Rh^+ catalyst represents an effective complementary catalyst system as compared to the (R,S_{pl})-JOSIPHOS/Rh^+ system, which yielded a 98% *ee* (*S*) hydrogenation product in the DMI (**13**) case under our conditions (Scheme 4).



13 **14**

Scheme 4.

We had previously shown that *rac*-**11**/Pd^{II} systems are highly active catalysts for alternating CO/ethene copolymerization.[6] Therefore, we have now employed the enantiomerically pure (R,R,R_{pl})-**12** ligand system for the generation of palladium catalysts to be used in the related CO/propene alternating copolymerization[18,19] in order to investigate the ability of this rigid ligand type for asymmetric induction in such a reaction.[20]

We have generated an active CO/propene copolymerization catalyst in situ by treatment of a solution of palladium acetate and the chelate *P,P*-[3]ferrocenophane ligand (R,R,R_{pl})-**12** in dichloromethane with BF_3–diethyl ether and then methanol (as an initiator). Propene was condensed into the reaction mixture and the autoclave pressurized with CO (30 or 75 bar). In a couple of typical experiments carried out at 50 °C using 10 mg of palladium acetate we isolated ca. 6.5 g of the CO/propene-copolymer, which corre-

sponds to an averaged catalyst activity of ca. 155 g polymer/mmol [Pd]. The [(R,R,R_{pl})-**12**/Pd^{II}] catalyst system is actually slightly more active than the [(JOSIPHOS)/Pd^{II}] reference[19] [a = 117], and it seems to show a slightly higher asymmetric induction {$[\alpha]_D^{20}$ = –30, (R,R,R_{pl})-**12** vs. $[\alpha]_D^{20}$ = –25 for the reference system}. The CO/propene copolymer obtained with the new (R,R,R_{pl})-**12**-derived [3]ferrocenophane catalyst features an intense CD band at 277 nm ($\Delta\varepsilon$ = 1.5) (see Figure 7). In $(CF_3)_2CHOH$ solution it features the typical ^{13}C NMR resonances of the polyketone form [δ = 15.5 (CH_3), 40.8 (CH), 44.5 (CH_2) and 217.0 (C=O) ppm]. A $^{13}C\{^1H\}$ CP-MAS spectrum of a sample of the copolymer that was not previously dissolved in hexafluoroisopropanol to break up the structure, actually showed the signals of both the polyketone and the polyspiroketal sections to be present (see Figure 8) (Scheme 5)[21]

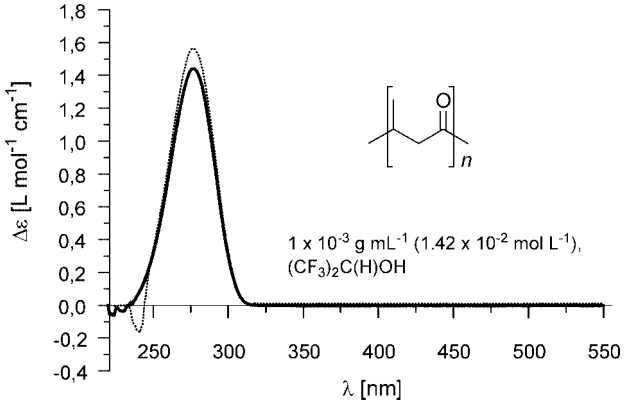


Figure 7. CD spectra of two samples (solid and dotted lines) of the alternating CO/propene polyketone polymer that was obtained with an in situ generated (R,R,R_{pl})-**12**/Pd^{II} catalyst (c = 1.42 ·10^{-2} mol l^{-1} in $(CF_3)_2CHOH$).

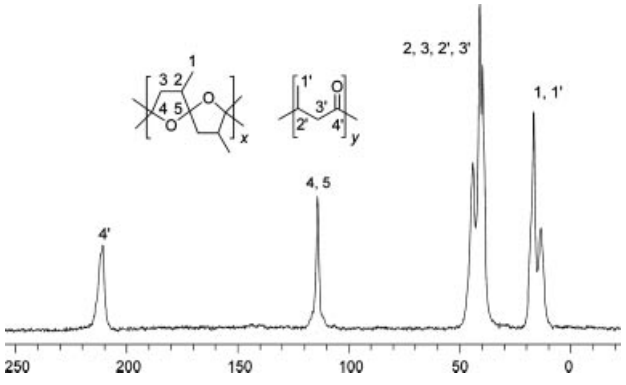


Figure 8. ^{13}C-CP-MAS NMR spectrum of a CO/propene copolymer obtained with the (R,R,R_{pl})**12**/Pd^{II} catalyst system.

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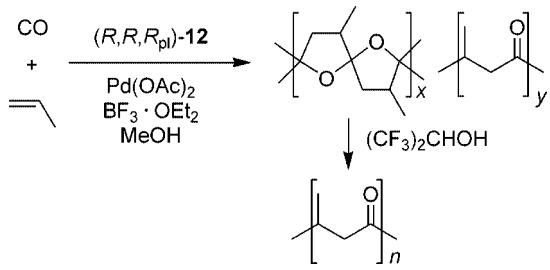
Conclusions

This study shows that the enantiomers of the chelate P,P-[3]ferrocenophane ligand systems are easily synthesized starting from the readily available dimethylamino[3]ferrocenophanes (R,R)-**3** and (S,S)-**3**, respectively. These chelate



Scheme 5.

ligands are characterized by having their pairs of –PR_2 donor functionalities attached to a rigid ferrocenophane framework. This rigidity may in some cases indeed create an unfavorable situation for some specific asymmetric catalytic reactions, as we and others have observed, but the rigid close to gauche-like arrangement of the C-PR_2 vectors at these frameworks seems to be of advantage for both the catalyst activities and its stereocontrol in other reactions. Our exploratory work has shown that the use of the (R,R,R_{pl})-**12** ligand gives good activities *and* good absolute as well as relative stereoselectivities in the formation of the alternating CO/propene copolymers. This is a promising result for the search for further reaction types where the characteristic features of the chelate P,P-[3]ferrocenophane ligands might result in an improved catalyst performance. Furthermore the enantiomerically pure P,P-[3]ferrocenophane ligands were shown to form highly active hydrogenation catalysts. These complexes represent catalysts which in some cases gave high enantioselectivities and in comparison to the reference systems useful complementary absolute configuration of the hydrogenation products.

Experimental Section

General Remarks: Reactions with air- and moisture-sensitive compounds or reagents were carried out under argon using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under argon prior to use. For additional general information, including a list of the instruments used for physical characterization of the compounds see refs.[6,14]. The starting materials *rac*-**3**, (R,R)-**3** and (S,S)-**3** were prepared as described previously by us in the literature.[14] For the atom numbering Scheme used for the NMR listings, see Scheme 2. Most NMR assignments were secured by additional 2D NMR experiments.[22]

X-ray Crystal Structure Analyses: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN,[23] absorption correction SORTAV,[24] structure solution SHELXS-97,[25] structure refinement SHELXL-97,[26] graphics XP (Bruker AXS, **2000**).

CCDC-241633 to -241638 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Preparation of (S,S,S)-7 and (R,R,S)-7: Amine Exchange Reaction of *rac*-3 with (S)-2-Methoxymethylpyrrolidine: Methyl iodide

(11.3 mL, 182 mmol, 64 equiv.) was added to a solution of *rac*-**3** (800 mg, 2.82 mmol, 6.7:1 *trans*:*cis* mixture) in 15 mL of acetonitrile. The mixture was stirred for 1 h at room temperature and then all volatiles removed in vacuo. The residue was taken up in acetonitrile (40 mL), potassium carbonate (780 mg, 5.64 mmol, 2 equiv.) was added and then (*S*)-2-methoxymethylpyrrolidine (0.4 mL, 3.1 mmol, 1.1 equiv.). The reaction mixture was refluxed for 18 h. The volatiles were then removed at room temperature in vacuo. The solid residue was taken up in *n*-hexane and filtered through Celite. Concentration of the clear filtrate in vacuo gave 980 mg (98%) of a solid. Twofold recrystallization from diethyl ether at –18 °C gave an enrichment of (*S*,*S*,*R*)-**7** of 87% *de*, but only at the expense of loosing the majority of the material. The physical characterization was carried out using the obtained 74:26 mixture of (*S*,*S*,*S*)-**7** and (*R*,*R*,*S*)-**7**, m.p. 90 °C. $C_{20}H_{27}FeNO$ (353.3): calcd. C 68.00, H 7.70, N 3.96; found C 67.75, H 7.22, N 3.60. MS (EI, 70 eV): *m*/*z* (%) = 353.2 (18) [M^+], 239.0 (100) [M^+ – amine], 120.9 (11). IR (KBr): $\tilde{\nu}$ = 3098 cm^{-1} (w), 3065 (w), 2979 (m), 2940 (m), 2887 (m), 2815 (m), 1663 (w), 1617(w), 1466 (m), 1374 (m), 1196 (m), 1123 (s), 808 (s), 538 (m) cm^{-1}. ^1H NMR (599.9 MHz, CD_2Cl_2, 298 K, (*S*,*S*,*S*)-**7**): δ = 1.23 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, 7-H), 1.55 (m, 1 H, 17-H), 1.59 (m, 2 H, 16-H), 1.65 (m, 1 H, 17-H), 2.06 (m, 1 H, 8-H_{eq}), 2.44 (m, 1 H, 8-H_{ax}), 2.50 (m, 1 H, 15-H), 2.73 (m, 2 H, 6-H, 18-H), 2.82 (m, 1 H, 15-H), 3.18 (m, 1 H, 19-H), 3.33 (s, 3 H, 20-H), 3.37 (m, 1 H, 19-H), 3.57 (dd, $^3J_{H,H}$ = 11.8 Hz, 1.9 Hz, 1 H, 9-H), 3.93, 4.04, 4.10, 4.17 (each m, each 1 H, $Cp_{1–5}$), 4.00, 4.05, 4.08, 4.21 (each m, each 1 H, $Cp_{10–14}$) ppm. The (*S*,*S*,*S*)-**7**:(*R*,*R*,*S*)-**7** ratio in the sample was determined by the corresponding well-resolved 600 MHz ^1H NMR cyclopentadienyl resonances at δ = 3.89 [m, 1H (*R*,*R*,*S*)-**7**] ppm and δ = 3.93 [m, 1 H (*S*,*S*,*R*)-**7**] ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 17.1 (C-7), 23.4 (C-16), 28.3 (C-6), 28.7 (C-17), 48.8 (C-8), 49.7 (C-15), 53.2 (C-9), 59.1 (C-20), 60.1 (C-18), 67.1, 68.5, 68.6, 69.2, 93.2 ($Cp_{1–5}$), 67.8, 68.1, 69.5, 72.2, 81.4 ($Cp_{10–14}$), 77.0 (C-19) ppm.

X-ray Crystal Structure Analysis of (*S*,*S*,*S*)-7: Single crystals were obtained from ether at –18 °C. formula $C_{20}H_{27}FeNO$, M = 353.28, yellow crystal 0.35 × 0.25 × 0.03 mm, a = 8.936(1), b = 9.802(1), c = 9.977(1) Å, β = 104.46(1)°, V = 846.2(2) $Å^3$, $\rho_{calcd.}$ = 1.386 g cm^{-3}, μ = 8.96 cm^{-1}, empirical absorption correction (0.745 ≤ T ≤ 974), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, T = 198 K, ω and φ scans, 5606 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 $Å^{-1}$, 3525 independent (R_{int} = 0.045) and 3274 observed reflections [$I \geq 2\ \sigma(I)$], 210 refined parameters, R = 0.032, wR_2 = 0.069, max. residual electron density 0.26 (–0.28) e·$Å^{-3}$, Flack parameter –0.010(15), hydrogen atoms calculated and refined as riding atoms.

Formation of 9. Directed Phosphorylyation of 7: *n*-Butyllithium (1.7 mL of a 1.96 M solution in hexane, 3.3 mmol, 1.2 equiv.) was added dropwise with stirring at 4 °C to a solution of 0.95 g (2.7 mmol) of the 1:1 mixture of the (*R*,*R*,*S*)-**7** and (*S*,*S*,*S*)-**7** diastereoisomers. The cooling bath was then removed and the mixture stirred for 3 h at room temperature. During this time an orange-colored precipitate appeared. The mixture was then re-cooled to 4 °C and $ClPPh_2$ (0.74 g, 0.6 mL, 3.4 mmol, 1.3 equiv.) was added dropwise with stirring. The reaction mixture was then stirred at room temperature for 12 h. The reaction was quenched by adding saturated aqueous sodium hydrogencarbonate solution (20 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined original phases were washed with water (2 × 10 mL) and brine (10 mL) and dried with magnesium sulfate. Filtration and removal of the solvent in vacuo gave an orange-colored solid (1.22 g). Chromatography (silica gel, $CHCl_3/CH_3OH/NEt_3$, 400:50:1) gave a 1:1 mixture of the diastereomers of **9** (1.10 g, 76%). Recrystallization from dichloromethane/diethyl ether at +8 °C gave an enrichment of the (*R*,*R*,*S*,R_{pl})-**9** isomer (71% *de*) but at the expense of a great loss of material. The analytical data were obtained from this (*R*,*R*,*S*,R_{pl})-**9** enriched sample (m. p. 192 °C). $C_{32}H_{36}FeNOP$ (537.5): calcd. C 71.51, H 6.75, N 2.61; found C 70.99, H 6.95, N 2.43. MS (EI, 70 eV): *m*/*z* (%) = 537.2 (33.1) [M^+], 423.1 (100) [M^+ – amine]. ^1H NMR (599.9 MHz, $CDCl_3$, 298 K): δ = 0.53 (m, 1 H, 16/17-H), 1.10 (m, 1 H, 16/17-H), 1.25 (d, 3 H, $^3J_{H,H}$ = 7.3 Hz, 7-H), 1.29 (m, 2 H, 16/17-H), 2.27 (m, 2 H, 15-H), 2.47 (m, 1 H, 8-H_{eq}), 2.84 (m, 1 H, 6-H), 2.86 (m, 1 H, 19-H), 3.23 (s, 3 H, 20-H), 3.25 (m, 2 H, 18, 19-H), 3.31 (m, 2 H, 8-H_{ax}, 9-H), 3.64, 3.84, 4.11, 4.41 (each m, each 1 H, $Cp_{1–5}$), 3.69, 4.14, 4.18 (each m, each 1 H, $Cp_{10–14}$), 7.26 (m, 6 H, Ph), 7.38 (m, 2 H, Ph), 7.43 (m, 2 H, Ph) ppm. The (*R*,*R*,*S*,R_{pl})-**9**:(*S*,*S*,*S*,S_{pl})-**9** ratio was determined by the ^1H NMR Cp signals at δ = 4.41 [m, 1 H (*R*,*R*,*S*,R_{pl})-**9**] ppm and δ = 4.45 [m, 1 H (*S*,*S*,*S*,S_{pl})-**9**] ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$, 298 K): δ = 16.4 (C-7), 21.0 (C-16/17), 27.5 (C-6), 27.9 (C-16/17), 44.9 (d, $J_{P,C}$ = 10.9 Hz, C-8), 50.5 (C-15), 53.3 (C-9), 59.0 (C-20), 59.5 (C-18), 67.3, 68.6, 70.0, 72.3, 93.3 (d, $J_{P,C}$ = 5.7 Hz) ($Cp_{1–5}$), 68.9, 73.9 (d, $J_{P,C}$ = 5.2 Hz), 74.2 (d, $J_{P,C}$ = 5.8 Hz), 74.1 (d, $^1J_{P,C}$ = 13.5 Hz), 92.0 (d, $^2J_{P,C}$ = 18.3 Hz) ($Cp_{10–14}$), 71.9 (C-19), 127.7 (Ph*p*, Ph*p*), 127.7 (d, $J_{P,C}$ = 15.1 Hz, Pho/*m*), 128.1 (d, $J_{P,C}$ = 19.3 Hz, Pho/*m*), 133.4 (d, $J_{P,C}$ = 21.0 Hz, Pho/*m*), 134.3 (d, $J_{P,C}$ = 20.1 Hz, Pho/*m*), 138.6 (d, $^1J_{P,C}$ = 12.1 Hz, Ph*i*), 138.9 (d, $^1J_{P,C}$ = 9.1 Hz, Ph*i*) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 298 K): δ = –22.2 ppm.

X-ray Crystal Structure Analysis of (*R*,*R*,*S*,R_{pl})-9: Single crystals were obtained by slow evaporation of a solution in dichloromethane/diethyl ether: Formula $C_{32}H_{36}FeNOP$, M = 537.44, yellow crystal 0.50 × 0.30 × 0.15 mm, a = 7.200(1), b = 8.828(1), c = 21.233(1) Å, β = 91.31(1)°, V = 1349.3(3) $Å^3$, $\rho_{calcd.}$ = 1.323 g·cm^{-3}, μ = 6.44 cm^{-1}, empirical absorption correction (0.739 ≤ T ≤ 0.910), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, T = 198 K, ω and φ scans, 10520 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 $Å^{-1}$, 5716 independent (R_{int} = 0.028) and 5488 observed reflections [$I \geq 2\ \sigma(I)$], 327 refined parameters, R = 0.026, wR_2 = 0.072, max. residual electron density 0.25 (–0.29) e·$Å^{-3}$, Flack parameter –0.001(10), hydroge atoms calculated and refined as riding atoms.

Formation of the Enantiomeric Products (*R*,*R*,R_{pl})-10 and (*S*,*S*,S_{pl})-10. Directed Phosphorylation of (*R*,*R*)-3 and of (*S*,*S*)-3: *tert*-Butyllithium (10.6 mL of a 1.5 M hexane solution, 15.9 mmol, 1.5 equiv.) was added dropwise with stirring to a solution of the enantiomerically pure complex (*R*,*R*)-**3** (3.01 g, 10.6 mmol) in 20 mL of diethyl ether at 0 °C. The reaction mixture was then stirred at room temperature for 30 min. The dark orange-colored mixture was then again cooled to 0 °C, and chlorodiphenylphosphane (3.53 g, 2.94 mL, 15.9 mmol, 1.5 equiv.) was added dropwise with stirring. The mixture was then stirred at room temperature for 12 h. Saturated aqueous $NaHCO_3$ solution (60 mL) was added slowly to quench the reaction. Workup analogously as described above gave the crude product (4.74 g) as a red oil. Chromatography (silica gel, cyclohexene/ethylacetate, 1:1) yielded the product (*R*,*R*,R_{pl})-**10** (3.62 g, 73%) as a yellow solid.

Analogous treatment of (*S*,*S*)-**3** (0.88 g, 3.1 mmol) in diethyl ether (17 mL) with *tert*-butyllithium (2.4 mL of a 1.5 M solution in hexane, 4.6 mmol) and subsequent reaction with chlorodiphenylphosphane (1.03 g, 0.85 mL, 4.6 mmol) gave 0.99 g (70%) of the enantiomer (*S*,*S*,S_{pl})-**10**, m.p. 156 °C. $C_{28}H_{30}FeNP$ (467.4): calcd. C 71.96, H 6.47, N 3.00; found for (R,R,R_{pl})-**10**: C 71.72, H 6.39, N 2.67; (*S*,*S*,S_{pl})-**10**: C 71.71, H 6.56, N 2.85. MS (EI, 70 eV): *m*/*z* (%) = 467.1 (100) [M^+], 422.0 (46) [M^+ – amine]. $[\alpha]_D^{20}$ (*R*,*R*,R_{pl})-

10: +244 ($c = 2\times10^{-3}$ g·mL^{-1}, CH_2Cl_2). $[\alpha]_D^{20}$ (*S*,*S*,S_{pl})-**10**: –242 ($c = 2\times10^{-3}$ g·mL^{-1}, CH_2Cl_2). CD**:** (*R*,*R*,R_{pl})-**10**: $\Delta\varepsilon$ ($\lambda_{max.}$) = +0.67 (shoulder, 329 nm), –1.00 (420 nm) ($c = 4\times10^{-4}$ g·mL^{-1}, CH_2Cl_2); (*S*,*S*,S_{pl})-**10**: $\Delta\varepsilon$ ($\lambda_{max.}$) = –0.77 (shoulder, 329 nm), +1.15 (420 nm) ($c = 4\times10^{-4}$ g·mL^{-1}, CH_2Cl_2). ^{1}H NMR (599.9 MHz, $CDCl_3$, 298 K): δ = 1.22 (d, $^3J_{H,H}$ = 7.3 Hz, 3 H, 7-H), 1.79 (s, 6 H, 15-H), 2.31 (m, 1 H, 8-H_{eq}), 2.68 (pd, 1 H, 9-H), 2.84 (m, 1 H, 6-H), 3.16 (m, 1 H, 8-H_{ax}), 3.68 (m, 2 H, Cp_{1-5}, Cp_{10-14}), 3.85 (m, 1 H, Cp_{1-5}), 4.11 (m, 1 H, Cp_{1-5}), 4.14 (m, 2 H, Cp_{10-14}), 4.41 (m, 1 H, Cp_{1-5}), 7.22–7.47 (m, 10 H, Ph-H) ppm. ^{13}C{^{1}H} NMR (150.8 MHz, $CDCl_3$, 298 K): δ = 16.7 (C-7), 27.7 (C-6), 44.2 (C-15), 45.3 (C-8), 59.1 (C-9), 67.5, 68.8, 70.2, 72.2, 93.3 (Cp_{1-5}), 68.9, 73.9, 74.1, 75.2 (d, $^1J_{P,C}$ = 12 Hz), 91.4 (br.) (Cp_{10-14}), 127.5 (br., Ph), 127.7 (br., Ph), 128.1 (br., Ph), 133.1 (br., Ph), 133.4 (d, $^1J_{P,C}$ = 19 Hz, Ph), 134.2 (d, $^1J_{P,C}$ = 19 Hz, Ph), 138.9 (br., Ph*i*), 139.4 (br., Ph*i*) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 298 K): δ = –21.7 ppm.

Synthesis of the (*R*,*R*,R_{pl})-11 and (*S*,*S*,S_{pl})-11 Enantiomers. Reaction of the (*R*,*R*,R_{pl})-10 and (*S*,*S*,S_{pl})-10 Enantiomers with Diphenylphosphane. (*R*,*R*,R_{pl})-11: Diphenylphosphane (0.53 g, 0.53 mL, 2.9 mmol, 1.1 equiv.) was added with exclusion of light to a solution of (*R*,*R*,R_{pl})-**10** (1.22 g, 2.6 mmol) in freshly distilled glacial acetic acid (25 mL). The mixture was kept at 100 °C for 20 h. The mixture was cooled to room temperature during which time a pale yellow precipitate appeared. Control by thin layer chromatography (silica gel, chloroform) revealed the complete consumption of the starting material. Dichloromethane (20 mL) was added to the reaction mixture and then saturated aqueous $NaHCO_3$ solution was cautiously added in small portions until the gas evolution had ceased. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried with magnesium sulfate, filtered and concentrated in vacuo, then washed with pentane (3×20 mL) and ethanol (3×20 mL). The residue was suspended in ethanol (15 mL) and a few drops of dichloromethane were added until complete solution. This was stored at –18 °C overnight and the precipitate was collected to yield 1.44 g (91%) of (*R*,*R*,R_{pl})-**11**. Single crystals of (*R*,*R*,R_{pl})-**11** could be obtained by a slow evaporation of dichloromethane/pentane or dichloromethane/ethanol solutions.

(*S*,*S*,S_{pl})-11: Analogously as described above (*S*,*S*,S_{pl})-**10** (150 mg, 0.32 mmol) was reacted with $HPPh_2$ (70 mg, 0.07 mL, 0.35 mmol) in 3.5 mL of freshly distilled glacial acetic acid to yield 213 mg of a raw product. This crude product was washed with pentane (3×5 mL) and ethanol (3×5 mL). It was then suspended in 5 mL of ethanol and dissolved by adding a minimum amount of dichloromethane. The solution was concentrated in vacuo and the product precipitated overnight at –18 °C to yield 180 mg (93%) of (*S*,*S*,S_{pl})-**11**. Crystals suited for the X-ray crystal structure analysis were obtained by slow concentration of a dichloromethane/ethanol solution, m.p. 205 °C (decomp.). $C_{38}H_{34}FeP_2$ (608.5): calcd. C 75.01, H 5.63; found for (*R*,*R*,R_{pl})-**11**: C 74.41, H 5.60, for (*S*,*S*,S_{pl})-**11**: C 76.65, H 5.60. MS (EI, 70 eV): *m*/*z* (%) = 608.2 (62) [M^+], 423.0 (46) [M^+ – PPh_2]. $[\alpha]_D^{20}$ (*R*,*R*,R_{pl})-**11**: +259 ($c = 2\times10^{-3}$ g·mL^{-1}, CH_2Cl_2). $[\alpha]_D^{20}$ (*S*,*S*,S_{pl})-**11**: –260 ($c = 2\times10^{-3}$ g·mL^{-1}, CH_2Cl_2). CD**:** (*R*,*R*,R_{pl})-**11**: $\Delta\varepsilon$ ($\lambda_{max.}$) = +1.34 (shoulder, 336 nm), –1.11 (430 nm) ($c = 4\times10^{-4}$ g·mL^{-1}, CH_2Cl_2); (*S*,*S*,S_{pl})-**11**: $\Delta\varepsilon$ ($\lambda_{max.}$) = –1.60 (shoulder, 333 nm), +1.34 (432 nm) ($c = 4\times10^{-4}$ g·mL^{-1}, CH_2Cl_2). ^{1}H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 1.10 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, 7-H), 1.91 (m, 1 H, 8-H_{eq}), 2.59 (m, 1 H, 6-H), 3.13 (dd, $^3J_{H,H}$ = 12.9 Hz, 4.2 Hz, 9-H), 3.19 (m, 1 H, 8-H_{ax}), 3.40, 3.83, 4.14, 4.31 (each m, each 1 H, Cp_{1-5}), 3.71, 4.12, 4.27 (each m, each 1 H, Cp_{10-14}), 7.04–7.54 (bm, 20 H, Ph-H) ppm. ^{13}C{^{1}H} NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 15.9 (C-7), 26.0 (d, $J_{P,C}$ = 10.6 Hz, C-6), 29.3 (dd, $J_{P,C}$ = 12.9 Hz, 2.7 Hz, C-9), 45.3 (dd, $J_{P,C}$ = 23.5 Hz, 10.2 Hz, C-8), 68.0, 69.2, 70.3, 72.4 (d, $J_{P,C}$ = 4.8 Hz), 92.9 (Cp_{1-5}), 69.8 (Cp_{10-14}), 73.9 (d, $J_{P,C}$ = 15.5 Hz, C-14), 74.6 (dd, $J_{P,C}$ = 4.4 Hz, 1.7 Hz, Cp_{10-14}), 76.6 (dd, $J_{P,C}$ = 5.1 Hz, 2.6 Hz, Cp_{10-14}), 91.1 (dd, $J_{P,C}$ = 21.5 Hz, 17.2 Hz, C-10),, 127.7 (Ph), 128.1 (Ph, Ph, Ph), 128.7 (d, $J_{P,C}$ = 7.7 Hz, Ph, Ph), 129.0, 129.3, 133.2 (d, $J_{P,C}$ = 18.0 Hz, Ph), 133.7 (d, $J_{P,C}$ = 4.0 Hz, Ph), 133.8 (d, $J_{P,C}$ = 2.3 Hz, Ph), 135.5 (d, $J_{P,C}$ = 21.0 Hz, Ph), 138.2 (d, $J_{P,C}$ = 16.1 Hz, Ph*i*), 139.2 (dd, $J_{P,C}$ = 12.6 Hz, 5.4 Hz, Ph*i*), 140.2 (dd, $J_{P,C}$ = 20.7 Hz, 3.2 Hz, Ph*i*), 141.2 (d, $J_{P,C}$ = 8.2 Hz, Ph*i*) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 298 K): δ = –22.2 (d, $J_{P,P}$ = 79.6 Hz, 14-P), –7.9 (d, $J_{P,P}$ = 79.6 Hz, 9-P) ppm.

X-ray Crystal Structure Analysis of (*R*,*R*,R_{pl})-11: Formula $C_{38}H_{34}FeP_2$, M = 608.44, yellow crystal 0.35×0.35×0.25 mm, a = 9.268(1), b = 13.095(1), c = 12.691(1) Å, β = 98.32(1)°, V = 1524.0(2) Å^3, $\rho_{calcd.}$ = 1.326 g·cm^{-3}, μ = 6.26 cm^{-1}, empirical absorption correction ($0.811 \le T \le 0.859$), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, T = 198 K, ω and φ scans, 8474 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.67 Å^{-1}, 6160 independent (R_{int} = 0.028) and 5753 observed reflections [$I \ge 2\sigma(I)$], 371 refined parameters, R = 0.028, wR_2 = 0.065, max. residual electron density 0.18 (–0.21) e·Å^{-3}, Flack parameter –0.020(10), hydrogens calculated and refined as riding atoms. **X-ray Crystal Structure Analysis of (*S*,*S*,S_{pl})-11:** Formula $C_{38}H_{34}FeP_2$, M = 608.44, yellow crystal 0.35×0.20×0.15 mm, a = 9.260(1), b = 13.066(1), c = 12.681(1) Å, β = 98.18(1)°, V = 1518.7(2) Å^3, $\rho_{calcd.}$ = 1.331 g·cm^{-3}, μ = 6.28 cm^{-1}, empirical absorption correction ($0.810 \le T \le 0.912$), Z = 2, monoclinic, space group $P2_1$ (No. 4), λ = 0.71073 Å, T = 198 K, ω and φ scans, 9689 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ] = 0.66 Å^{-1}, 6074 independent (R_{int} = 0.028) and 5512 observed reflections [$I \ge 2\sigma(I)$], 371 refined parameters, R = 0.033, wR_2 = 0.067, max. residual electron density 0.21 (–0.26) e·Å^{-3}, Flack parameter –0.014(11), hydrogen atoms calculated and refined as riding atoms.

Preparation of the (*R*,*R*,R_{pl})-12 and (*S*,*S*,S_{pl})12 Enantiomers. Reaction of the (*R*,*R*,R_{pl})-10 and (*S*,*S*,S_{pl})-10 Enantiomers with $HPCy_2$. (*R*,*R*,R_{pl})-12: Analogously as described above the reaction of (*R*,*R*,R_{pl})-**10** (0.56 g, 1.2 mmol) with dicyclohexylphosphane (0.26 g, 0.27 mL, 1.3 mmol) in 15 mL HOAc (20 h, 100 °C) and a workup procedure analogously as described for the (*R*,*R*,R_{pl})-**11** enantiomer eventually yielded 0.66 g (90%) of (*R*,*R*,R_{pl})-**12**. Single crystals of (*R*, *R*,R_{pl})-**12** were obtained by diffusion of pentane vapor into a dichloromethane solution of the product.

(*S*,*S*,S_{pl})-12: Analogously as described above, the reaction of (*S*,*S*,S_{pl})-**10** (150 mg, 0.32 mmol) with $HPCy_2$ (65 mg, 0.065 mL, 0.35 mmol) in 3.5 mL HOAc (20 h, 100 °C) gave 199 mg of the crude product. Purification analogously as described above for (*S*,*S*,S_{pl})-**11** eventually yielded 180 mg (93%) of the enantiomer (*S*,*S*,S_{pl})-**12** as a yellow solid, m.p. 208 °C. Single crystals of (*S*,*S*,S_{pl})-**12** for the X-ray crystal structure analysis were obtained by slow diffusion of pentane vapor into a solution of the product in dichloromethane/ethanol. $C_{38}H_{46}FeP_2$ (620.6): calcd. C 73.55, H 7.47; found for (*R*,*R*,R_{pl})-**12**: C 73.43, H 7.54, for (*S*,*S*,S_{pl})-**12**: C 73.28, H 7.48. MS (EI, 70 eV): *m*/*z* (%) = 620.4(2) [M^+], 537.2 (100) [M^+ – C_6H_{11}]. $[\alpha]_D^{20}$ (*R*,*R*,R_{pl})-**12**: +344 ($c = 2\times10^{-3}$ g·mL^{-1}, CH_2Cl_2). $[\alpha]_D^{20}$ (*S*,*S*,S_{pl})-**12**: –346 ($c = 2\times10^{-3}$ g·mL^{-1}, CH_2Cl_2). CD**:** (*R*,*R*,R_{pl})-**12**: $\Delta\varepsilon$ ($\lambda_{max.}$) = –1.86 (427 nm) ($c = 4\times10^{-4}$ g·mL^{-1}, CH_2Cl_2); (*S*,*S*,S_{pl})-**12**: $\Delta\varepsilon$ ($\lambda_{max.}$) = +1.01 (425 nm) (c = 4 10^{-4} g·mL^{-1}, CH_2Cl_2). ^{1}H NMR (599.9 MHz, CD_2Cl_2, 298 K): δ = 0.54–1.87 (bm, 22 H, Cy–H), 1.19 (d, 3 H, $^3J_{H,H}$ = 7.2 Hz, 7–H), 2.12 (m, 1 H, 8–H_{eq}), 2.62 (ddd, $J_{H,H}$ = 12.6 Hz, 7.2 Hz, 1.8 Hz,

9–H), 2.72 (m, 1 H, 6–H), 3.12 (m, 1 H, 8–H_{ax}), 3.38 (m, 1 H, Cp_{1-5}), 3.83 (m, 2 H, Cp_{1-5}, Cp_{10-14}), 4.07 (m, 1 H, Cp_{1-5}), 4.14 (m, 1 H, Cp_{10-14}), 4.20 (m, 1 H, Cp_{10-14}), 4.29 (m, 1 H, Cp_{1-5}), 7.22–7.46 (bm, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR (150.8 MHz, CD_2Cl_2, 298 K): δ = 16.1 (C-7), 22.9 (dd, $J_{P,C}$ = 18.8 Hz, 3.9 Hz, C-9), 26.4 (d, $J_{P,C}$ = 10.2 Hz, C-6), 26.9 (d, $J_{P,C}$ = 0.7 Hz, Cy), 27.0 (d, $J_{P,C}$ = 0.9 Hz, Cy), 28.2 (d, $J_{P,C}$ = 1.8 Hz, Cy), 28.3–28.5 (2d, without exact assignment, 2 × Cy), 28.7–28.8 (2d, without exact assignment, 2 × Cy), 30.9 (d, $J_{P,C}$ = 2.3 Hz, Cy), 31.0 (d, $J_{P,C}$ = 22.5 Hz, Cy), 33.7 (dd, $J_{P,C}$ = 24.9 Hz, 3.4 Hz, P*C*yC), 34.5 (d, $J_{P,C}$ = 23.3 Hz, Cy), 35.1 (d, $J_{P,C}$ = 18.2 Hz, P*C*yC), 45.7 (dd, $J_{P,C}$ = 24.0 Hz, 10.0 Hz, C-8), 67.8, 69.0, 70.1, 72.3 (d, $J_{P,C}$ = 4.8 Hz), 92.0 (Cp_{1-5}), 69.7 (Cp_{10-14}), 73.0 (d, $J_{P,C}$ = 15.9 Hz, C-14), 74.8 (dd, $J_{P,C}$ = 4.4 Hz, 1.0 Hz, Cp_{10-14}), 75.5 (dd, $J_{P,C}$ = 5.5 Hz, 2.2 Hz, Cp_{10-14}), 93.2 (dd, $J_{P,C}$ = 22.0 Hz, 12.9 Hz, C-10), 127.9 (Ph*p*), 128.0 (d, $J_{P,C}$ = 7.4 Hz, Ph*o*/*m*), 128.2 (d, $J_{P,C}$ = 7.1 Hz, Ph*o*/*m*), 128.8 (Ph*p*), 133.3 (dd, $J_{P,C}$ = 19.1 Hz, 0.6 Hz, Ph*o*/*m*), 135.3 (d, $J_{P,C}$ = 21.3 Hz, Ph*o*/*m*), 139.4 (dd, $J_{P,C}$ = 13.5 Hz, 6.1 Hz, Ph*i*), 140.9 (d, $J_{P,C}$ = 8.4 Hz, Ph*i*) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 298 K): δ = –24.4 (d, $J_{P,P}$ = 79.0 Hz, 14-P), 8.3 (d, $J_{P,P}$ = 79.0 Hz, 9–P) ppm.

X-ray Crystal Structure Analysis of (R,R,R_{pl})-12: Formula $C_{38}H_{46}FeP_2$, M = 620.54, yellow crystal 0.20 × 0.20 × 0.15 mm, a = 11.494(1), c = 48.811(1) Å, V = 6448.5(8) Å^3, $\rho_{calcd.}$ = 1.278 g·cm^{-3}, μ = 5.92 cm^{-1}, empirical absorption correction (0.891 ≤ T ≤ 0.916), Z = 8, tetragonal, space group $P4_12_12$ (No. 92), λ = 0.71073 Å, T = 198 K, ω and φ scans, 13119 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 7292 independent (R_{int} = 0.036) and 5520 observed reflections [$I \geq 2\sigma(I)$], 371 refined parameters, R = 0.048, wR_2 = 0.104, max. residual electron density 0.49 (–0.33) e·Å^{-3}, Flack parameter 0.003(17), hydrogens calculated and refined as riding atoms. **X-ray Crystal Structure Analysis of (S,S,S_{pl})-12:** Formula $C_{38}H_{46}FeP_2$, M = 620.54, yellow crystal 0.70 × 0.30 × 0.20 mm, a = 11.494(1), c = 48.823(1) Å, V = 6450.1(8) Å^3, $\rho_{calcd.}$ = 1.278 g·cm^{-3}, μ = 5.92 cm^{-1}, empirical absorption correction (0.682 ≤ T ≤ 0.891), Z = 8, tetragonal, space group $P4_32_12$ (No. 96), λ = 0.71073 Å, T = 198 K, ω and φ scans, 11662 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.66 Å^{-1}, 6850 independent (R_{int} = 0.025) and 5598 observed reflections [$I \geq 2\sigma(I)$], 371 refined parameters, R = 0.042, wR_2 = 0.097, max. residual electron density 0.54 (–0.36) e·Å^{-3}, Flack parameter 0.002(16), hydrogen atoms calculated and refined as riding atoms.

Catalytic Hydrogenation Reactions. General Procedure: A solution containing $[(cod)_2Rh]BF_4$ (12.6 mg, 0.031 mmol, 1 mol-%) and the respective chelate ligand (0.031 mmol) in dry methanol (10 mL) was stirred at room temperature for 15 min. A solution of the substrate (3.1 mmol) in 5 mL of dry methanol was added. A slight vacuum was applied and then the substrate hydrogenated under 1.0 bar H_2 pressure for 4 h with vigorous mixing. The reaction was usually complete after this time. Solvent was removed in vacuo and the crude product characterized by ^1H NMR spectroscopy (200.1 MHz, CD_2Cl_2). Before the GC or HPLC analyses the product was dissolved in diethyl ether (**14**-H_2) or pentane (**13**-H_2) and filtered through silica gel to remove the catalyst components. Each hydrogenation was carried out at least twice to ensure that the results were reproducible. Enantiomeric analyses were carried out by GC and HPLC. For (**13**-H_2): GC on LIPODEX-E (Macherey & Nagel, 50 m, ID 0.25 mm), isothermal, 70 °C, H_2 (1.2 bar), FID-detecting retention times (S)-**13**-H_2: 24.3 min, (R)-**13**-H_2: 25.5 min. For (**14**-H_2): GC on LIPODEX-E (Macherey–Nagel, 50 m, ID 0.25 mm), isothermal, 110 °C, H_2 (2.4 bar), FID-detecting retention times (R)-**14**-H_2: 287 min, (S)-**14**-H_2: 305 min, and HPLC on CHIRALCEL OJ (Daicel), heptane/2-propanol 85:15, flow: 1 mL/min, 25 °C, retention times (S)-**14**-H_2: 8.1 min, (R)-**14**-H_2: 11.1 min. Under the applied reaction conditions the catalytic hydrogenation of **13** with Rh^+ and the following chelate ligands gave **13**-H_2 [% *ee*, (major enantiomer)]: (R,S_{pl})-JOSIPHOS [99% *ee* (S)], (R,R,R_{pl})-**11** [96% *ee* (R)], (R,R,R_{pl})-**12** [52% *ee* (R)]. Hydrogenation of **14**: (R,S_{pl})-JOSIPHOS [74% *ee* (S)], (R,R,R_{pl})-**11** [24% *ee* (R)], (R,R,R_{pl})-**12** [42% *ee* (S)].

Catalytic Alternating Carbonmonoxide/propene Copolymerization: The copolymerization reactions were carried out in a 300-mL steel autoclave with a glass vessel and stirrer. BF_3–diethyl ether (20 μL of a 50 weight% solution, 86 μmol) and then methanol (2.0 mL) was added to a solution of the ligand (R,R,R_{pl})-**12** (52 μmol, 1.2 equiv.) and $Pd(OAc)_2$ (10.0 mg, 43 μmol) in dichloromethane (50 mL). Propene (ca. 14 g) was condensed into the autoclave, which was then brought to the reaction temperature (50 °C) and pressurized with CO (30 or 75 bar). After the reaction was completed the CO pressure was released and the obtained copolymer dissolved in dichloromethane. Solvent was removed in vacuo to determine the yield. The polymer was then not soluble any more in CH_2Cl_2. It was dissolved in hexafluoroisopropanol and poured into methanol to precipitate the copolymer. Four experiments were carried out independently. (a, carried out by P. L.) 14 g propene, 30 bar CO, 50 °C, 2.5 h yielded 6.9 g copolymer, activity 160 g copol./mmol [Pd], m.p. (DSC) 176 °C, $[a]_D^{20}$ = –30, CD $\Delta\varepsilon$ (c = 1 mg·mL^{-1} in HFIP) = 1.56 (2.78 nm); (b, carried out by P. L.) 14 g propene, 75 bar CO, 50 °C, 14.6 h yielded 6.4 g copolymer, activity 149 g copol./mmol [Pd], m.p. (DSC): 167 °C, $[a]_D^{20}$ = –30, CD: $\Delta\varepsilon$ ($\lambda_{max.}$) = 1.44 (277 nm); (c, carried out by L.T.) 20.7 g propene, 30 bar CO, 50 °C, 3.0 h yielded 11.7 g copolymer, activity 272 g copol./mmol [Pd], (d, carried out by L.T.) 22.3 g propene, 30 bar CO, 50 °C, 2.5 h yielded 12.2 g copolymer, activity 284 g copol./mmol [Pd]. NMR spectra were recorded by dissolving 30 mg of the respective copolymer in 0.7 mL of $(CF_3)_2CHOH$ (HFIP) and 0.3 mL of [D_6]benzene. The solutions were filtered through Celite. ^1H NMR (200.1 MHz, HFIP/[D_6]benzene 7:3, 298 K): δ = 0.89 (d, 3 H, CH_3), 2.45 [m, 1 H, CH_2 (syn)], 2.77 (m, 1 H, CH), 2.85 [m, 1H CH_2 (*anti*)] ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, HFIP/[D_6]benzene 7:3, 298K): δ = 15.5 (CH_3), 40.8 (CH), 44.5 (CH_2), 217.0 (CO) ppm.

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