Synthesis and Characterization of [3]Ferrocenophane-derived P,P-Chelate Ligand Gold Complexes Featuring an Aurophilic Interaction

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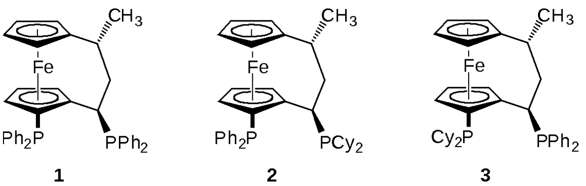
Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The P,P-chelate ligand (*rac*)-**4** was prepared starting from the α-dimethylamino-[3]ferrocenophane by a series of directed *ortho*-lithiation, phosphination with $ClPPh_2$ and substituent exchange using HP^iPr_2. Treatment with two molar equivalents of $(Me_2S)AuCl$ subsequently gave the corresponding $\kappa P,\kappa P(AuCl)_2$ complex (*rac*)-**9**. In similar sequences the α-PCy_2/*o*-PPh_2 ligands (S,S,S_{pl})-**2** and the "substituent-invertomer" (R,R,R_{pl})-**3** (α-PPh_2/*o*-PCy_2) were prepared. Treatment with $(Me_2S)AuCl$ in a 1 : 2 ratio gave the chelate ligand-$(AuCl)_2$ complexes (S,S,S_{pl})-**8** and (R,R,R_{pl})-**11**, respectively. The ligand (*rac*)-**4** and the gold complexes **8**, **9** and **11** were characterized by X-ray diffraction. All three show an intramolecular Au $\cdots$ Au interaction.

Key words: Ferrocene, P,P-Chelate Ligands, Gold, Aurophilic Interaction

Introduction

We had recently described an efficient synthetic entry to P,P-chelate ligand systems based on the [3]ferrocenophane framework [1, 2]. The bis(diphenylphosphino)[3]ferrocenophane **1** turned out to be an ideal basis for the generation of a very active Pd-based catalyst system for alternating carbon monoxide/ethylene copolymerization [3]. We have described an efficient synthetic route to the respective highly enantiomerically enriched P,P-ligands based on a resolution process that made each enantiomeric series easily available in high yield [4]. The unsymmetrical P,P-chelate ligand **2** in enantiomeric form [*i. e.* (R,R,R_{pl})-**2**] provided the basis for a very efficient Pd-based catalyst for asymmetric alternating CO/propene copolymerization [5]. Subsequently we observed that the "inverse" P,P-ligand system **3** gave a Pd catalyst that featured a markedly different catalyst performance profile [6] (Fig. 1). In order to further characterize the functional differences of such chelate ligands with inverted diarylphosphino and dialkylphosphino groups, we prepared their bis(gold(I))-complexes and characterized them spectroscopically and by X-ray diffraction. This revealed some small but probably characteristic differences between these otherwise closely related systems.



1 **2** **3**

Ph = phenyl, Cy = cyclohexyl

Fig. 1. P,P-(**1**), P,P-(**2**) and its "substituent-invertomer" P,P-chelate ligand system (**3**).

Results and Discussion

We prepared the [3]ferrocenophane-derived P,P-chelate ligand systems **2** and **3** each as racemates and in both pure enantiomeric forms. In this account we will, however, only describe those systems that were actually used for the preparation of the respective $\kappa P,\kappa P$-bis(gold(I)chloride) complexes, namely the compounds (S,S,S_{pl})-**2** and (R,R,R_{pl})-**3**. In addition we will also describe the preparation of the -P(isopropyl)$_2$ analog of **2**, namely (*rac*)-**4**, and its utilization in this chemistry.

Compound (S,S,S_{pl})-**2** had previously been described by us [5]. For clarity, its synthesis is briefly outlined in Scheme 1. The preparation starts with the enantiomerically pure [3]ferrocenophane amine (S,S)-**5**. Treatment with ^{t}BuLi in hexane/ether effected a directed metallation at the adjacent "*ortho*" position at the "lower" ferrocenophane Cp ring [7] to gener-

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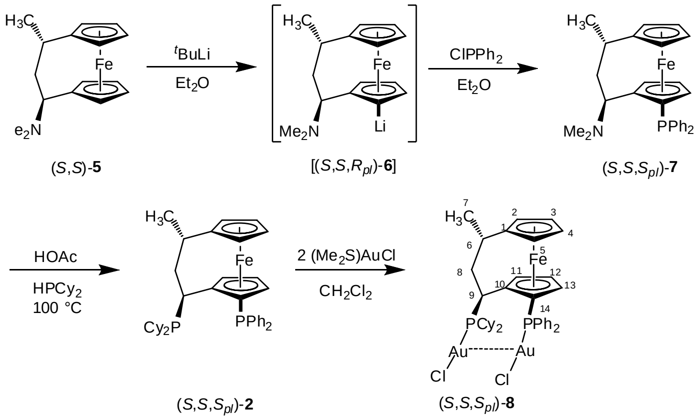


Scheme 1.

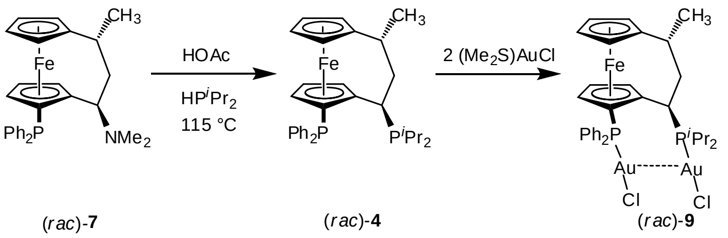
ate (*S*,*S*,*R*$_{pl}$)-**6**, which was subsequently quenched with diphenylchlorophosphine to yield (*S*,*S*,*S*$_{pl}$)-**7**. It should be noted that the pair of chiral centers in the [3]ferrocenophane system is dependent on each other, and that this directed metallation process proceeds (necessarily) with practically complete diastereoselectivity, which makes stereocontrol at the [3]ferrocenophane framework with "our" specific substitution pattern easy and straightforward.

Exchange of the -NMe$_2$ substituent in the α-position of the [3]ferrocenophane bridge is carried out stereo-controlled with overall retention of the configuration [8 – 10]. The respective two-step process is initiated by protonation of the amine in acetic acid (100 °C) followed by attack of the dicyclohexylphosphine nucleophile. The process proceeds with anchimeric assistance of the iron center which very effectively controls the specific stereochemical pathway followed here. The resulting chelate phosphine (*S*,*S*,*S*$_{pl}$)-**2** was then reacted with the (Me$_2$S)AuCl reagent in dichloromethane solution at r. t. to give the [$\kappa P,\kappa P$-(*S*,*S*,*S*$_{pl}$)-**2**](AuCl)$_2$ complex (*S*,*S*,*S*$_{pl}$)-**8** in 77 % yield as a yellow solid. Single crystals for an X-ray crystal structure analysis were obtained from pentane/toluene by the diffusion method.

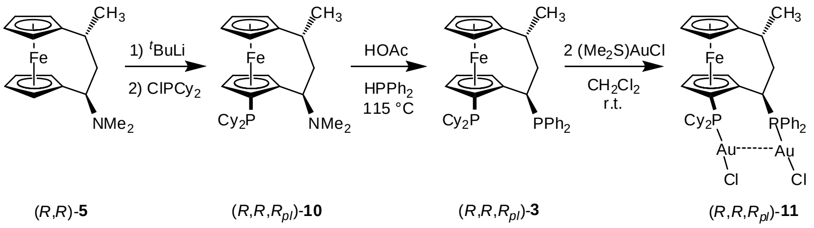
The related racemic α-P^{i}Pr$_2$-substituted Au$_2$-complex (*rac*)-**9** was prepared analogously. In this case treatment of (*rac*)-**7** with diisopropylphosphine in freshly distilled glacial acetic acid at 115 °C gave the *P,P*-chelate ligand (*rac*)-**4** in $>$ 90 % yield. The subsequent reaction of (*rac*)-**4** with two molar equivalents of (Me$_2$S)AuCl was carried out in dichloromethane solution at r. t. to yield complex (*rac*)-**9** as a yellow solid ($>$ 70 % isolated) (Scheme 2). Single crystals of (*rac*)-**9** were obtained by diffusion of ether vapor at r. t. into a solution of the compound in CH$_2$Cl$_2$.

The *P,P*-chelate ligand **3** featuring an "inverted" attachment of the -PCy$_2$ and -PPh$_2$ substituents relative to **2** (see above) was prepared by simply inverting the steps of the respective reaction scheme. In our specific case directed *ortho*-lithiation of (*R*,*R*)-**5** followed by quenching with ClPCy$_2$ gave the intermediate *P*,*N*-chelate [3]ferrocenophane system (*R*,*R*,*R*$_{pl}$)-**10**, which was then converted to the *P,P*-chelate ligand (*R*,*R*,*R*$_{pl}$)-**3** by treatment with HPPh$_2$ in glacid acetic acid. The product (*R*,*R*,*R*$_{pl}$)-**3** was isolated in 72 % yield. Its subsequent treatment with (Me$_2$S)AuCl in a 1 : 2 molar ratio in dichloromethane eventually gave the respective $\kappa P,\kappa P$(AuCl)$_2$ complex (*R*,*R*,*R*$_{pl}$)-**11** in 68 % yield as a yellow amorphous solid (Scheme 3). Single crystals were obtained by diffusion of pentane vapor into a toluene solution of this compound.

The new *P,P*-chelate ligand (*rac*)-**4** (see Scheme 2) shows the typical NMR signals of the [3]ferroceno-



Scheme 2.



Scheme 3.

Table 1. Selected ^{31}P NMR features of the *P,P*-[3]ferrocenophane ligand systems and their $\kappa P,\kappa P(\mathrm{AuCl})_2$ complexes[a].

	No.	o-^{31}P	$\Delta\delta$ (o)[b]	α-^{31}P	$\Delta\delta$ (α)[c]	J_{PP} [Hz]
Free ligand:						
o-PPh$_2$, α-P^{i}Pr$_2$	**4**	−24.6	49.3	11.7	41.8	75.5
o-PPh$_2$, α-PCy$_2$	**2**	−24.2	48.9	9.1	39.4	79.0
o-PCy$_2$, α-PPh$_2$	**3**	−16.0	51.3	−7.4	46.9	48.4
Au-complex:						
o-PPh$_2$, α-P^{i}Pr$_2$	**9**	24.7		53.5		10.3
o-PPh$_2$, α-PCy$_2$	**8**	24.7		48.5		11.2
o-PCy$_2$, α-PPh$_2$	**11**	35.3		39.5		7.0

[a] ^{31}P NMR spectra were recorded with a Varian INOVA 500 NMR spectrometer (^{31}P: 202 MHz) or a Varian Unityplus 600 NMR spectrometer (^{31}P: 243 MHz) at 298 K in [D$_2$]dichloromethane solution; [b] $\Delta\delta(o) = \delta[o\text{-}^{31}\mathrm{P(Au\ complex)}] - \delta[o\text{-}^{31}\mathrm{P(free\ ligand)}]$; [c] $\Delta\delta(\alpha) = \delta[\alpha\text{-}^{31}\mathrm{P(Au\ complex)}] - \delta[\alpha\text{-}^{31}\mathrm{P(free\ ligand)}]$.

phane framework (*e. g.* the ^{1}H NMR 6-CH$_3$ at δ = 1.19 (d), the corresponding 6-H signal at δ = 2.72 and the 8-H$_A$/H$_B$ resonances at δ = 2.12/3.12). In the $\kappa P,\kappa P(\mathrm{AuCl})_2$-complex (*rac*)-**4** these resonances do not change much, as expected. However, we observe very typical changes of the ^{31}P NMR resonances upon complexation of these *P,P*-chelate ligands to gold (see Table 1). The free *P,P*-[3]ferrocenophane system exhibits an AX pattern of ^{31}P NMR signals at δ = −24.6 (o-PPh$_2$) and δ = +11.7 (α-P^{i}Pr$_2$) with a very large coupling constant of J_{PP} = 75 Hz. Both the absolute chemical shifts and the magnitude of the J_{PP} coupling constant change drastically upon complexation of the pair of phosphorus donors to the gold atoms. The o-PPh$_2$ resonance is shifted to larger δ values by close to 50 ppm and the α-P^{i}Pr$_2$ chemical shift by > 40 ppm (see Table 1). In the same time the value of the J_{PP} coupling constant is drastically reduced (*i. e.* by *ca.* 65 Hz) upon complexation of the (*rac*)-**4** *P,P*-chelate ligand to the pair of gold atoms ((*rac*)-**9**).

Similar ^{31}P NMR features are observed for the related free *P,P*-ligand (*S,S,S$_{pl}$*)-**2**, and similar changes occur in the ^{31}P NMR spectra upon complexation to the Au atoms (see Table 1). We observe characteristic changes of the ^{31}P NMR features upon the formal mutual exchange of the positions of the attachments of the -PPh$_2$/-PCy$_2$ substituents at the [3]ferrocenophane framework. On going from ligand **2** (o-PPh$_2$/α-PCy$_2$) to ligand **3** (o-PCy$_2$/α-PPh$_2$) we note a shift of the -PCy$_2$ resonances to smaller δ values by *ca.* −16 ppm and a shift of the -PPh$_2$ signal to larger δ values by *ca.* −8 ppm (see Table 1). This is as it is expected for a "transition" from a trialkylphosphine to an aryldialkylphosphine or a triarylphosphine to an alkyldiarylphosphine, respectively [11]. We must, however, note that the value of the J_{PP} coupling constant is also affected by this exchange – here we observe a marked decrease of the J_{PP} value of about 30 Hz upon going from **2** to **3**. This probably indicates some differences in the stereoelectronic features between the individual systems of the "substituent-inverted" *P,P*-ligand pair **2**/**3**.

In the gold complexes the ^{31}P NMR resonances in the o-PCy$_2$/α-PPh$_2$ system **11** are close together ($\Delta\delta \approx 4$ ppm), whereas in the "substituent-inverted" o-PPh$_2$/α-PCy$_2$ complex **8** they are markedly separated ($\Delta\delta \approx$ 24 ppm). In both complexes the value of the J_{PP} coupling constants were found markedly reduced relative to the observed values of the respective free ligands (see Table 1).

Both the *P,P*-chelate ligand (*rac*)-**4** and the corresponding gold complex (*rac*)-**9** were characterized by X-ray diffraction (Fig. 2). The ligand system **4** shows the typical structural features of the [3]ferrocenophane framework. The bridge shows a folded "chair-like" geometry. This places the *trans*-1,3-substituents in pseudo-axial and pseudo-equatorial positions. The smaller of the two, the methyl group at C6, is oriented pseudo-axially and, consequently, the bulky -P^{i}Pr$_2$ substituent at C9 (the "α-position") is found in an equatorial position at the bridge. The phosphorus center P1 shows a sum of C–P–C bond angles of 308.2°. Its conformation is characterized by the dihedral angle C10–C9–P1–C31 of 54.6(2)° (C10–C9–P1–C21 = 160.4(2)°).

The -PPh$_2$ substituent is attached at the adjacent "*ortho*-position" at the ferrocene moiety. It features a sum of C–P–C bond angles of 302.3° and an orientation

Table 2. Selected structural data of ligand **4** and Au_2-complexes **8**, **9** and **11** (distances in Å, angles in deg).

	Lig. **4**	**9** (*o*-PPh_2/α-P^iPr_2)	**8** (*o*-PPh_2/α-PCy_2)	**11** (*o*-PCy_2/α-PPh_2)
C9–P1	1.877(2)	1.87(2)	1.851(6)	1.867(7)
P1–Au1	–	2.247(5)	2.247(2)	2.241(2)
Au1–Cl1	–	2.307(6)	2.311(2)	2.299(2)
C14–P2	1.827(2)	1.81(2)	1.804(7)	1.811(7)
P2–Au2	–	2.234(5)	2.238(2)	2.248(2)
Au2–Cl2	–	2.305(6)	2.290(2)	2.304(2)
Au1–Au2	–	3.278(1)	3.274(1)	3.076(1)
P1 ··· P2	3.601(1)	4.067(8)	4.123(2)	4.185(3)
P1–Au1–Cl1	–	172.5(2)	171.7(1)	174.5(1)
P1–Au1–Au2	–	99.2(1)	101.3(1)	99.5(1)
P2–Au2–Cl2	–	171.5(2)	169.5(1)	173.2(1)
P2–Au2–Au1	–	89.0(1)	83.5(1)	88.9(1)
C9–P1–Au1	–	115.9(6)	115.5(2)	117.0(2)
C14–P2–Au2	–	117.2(7)	117.2(2)	114.4(3)
P1–C9 ··· C14–P2	54.3(1)	−52.7(12)	−55.7(4)	56.6(5)
P1–Au1 ··· Au2–P2	–	−50.3(2)	−60.9(1)	66.3(1)

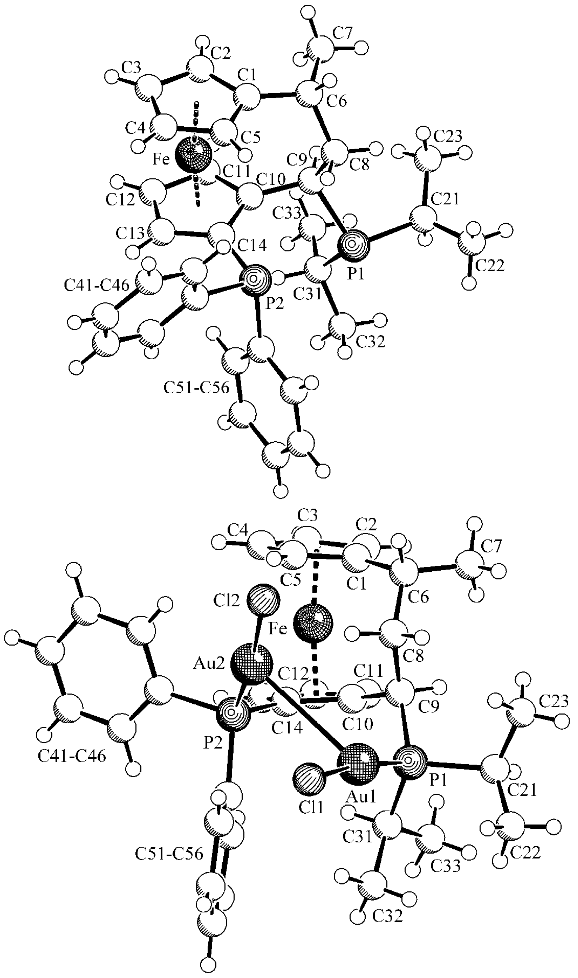


Fig. 2. Views of the free *P,P*-ligand (*rac*)-**4** (top) and its corresponding κ*P*,κ*P*$(AuCl)_2$ complex (*rac*)-**9** (bottom) in the crystal.

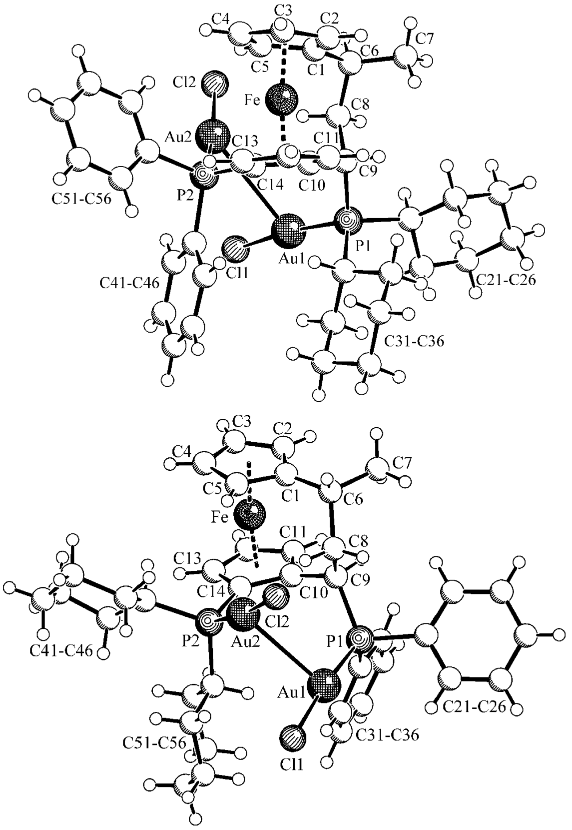


Fig. 3. Views of the complexes (S,S,S_{pl})-**8** (top) and (R,R,R_{pl})-**11** (bottom) in the crystal.

characterized by the dihedral angles C10–C14–P2–C41 of 159.7(2)° and C10–C14–P2–C51 of −98.2(2)°.

Compound (*rac*)-**4** takes up two equivalents of gold(I)chloride from the $(Me_2S)AuCl$ reagent to form the chelate κ*P*,κ*P*$(AuCl)_2$ complex (*rac*)-**9**. In the crystal this features a pair of close to linear -P(R)$_2$-Au-Cl units that are oriented toward the same sector at the [3]ferrocenophane framework. They are found in a conformational situation that allows for the formation of a weak aurophilic Au ··· Au interaction [12 – 15]. We find an Au ··· Au distance of 3.278(1) Å in (*rac*)-**9**. The resulting arrangement is non-planar. It features dihedral angles Cl1–Au1–Au2–Cl2 of −56.7(2)° and P1–Au1–Au2–P2 of −50.3(2)°. To allow for this interaction it was necessary to adjust the -PR$_2$ conformations. We find corresponding dihedral angles C10–C9–P1–C31 of −26.8(16)° and C10–C9–P1–C21 of −139.1(14)° to characterize the geometric situation at P1 in the complex. The corresponding dihedral angles at the other phosphorus center in (*rac*)-**9** C10–C14–P2–C41 and C10–C14–P2–C51 amount to −165.5(19)° and 85.0(20)°, respectively. Overall, we note that relatively small geometrical changes are necessary within the ligand system to go from (*rac*)-**4** to (*rac*)-**9**.

The pair of "substituent-invertomeric" complexes **8** and **11** was also characterized by X-ray diffraction (Fig. 3). Complex (*S*,*S*,*S$_{pl}$*)-**8** shows a very similar structure as (*rac*)-**9**. It features a rotational arrangement of the -PCy$_2$ substituent at C9 (C10–C9–P1–C31 = −37.1(5)°, C10–C9–P1–C21 = −156.6(5)°) and the -PPh$_2$ group at C14 (C10–C14–P2–C41 = 89.7(6)°, C10–C14–P2–C51 = −160.6(6)°) that easily allows for an aurophilic Au ··· Au interaction to be built up. With an Au ··· Au distance of 3.274(1) Å that is almost identical in strength to that found in (*rac*)-**9**. The geometric situation around the gold-gold vector in (*S*,*S*,*S$_{pl}$*)-**8** is characterized by dihedral angles C10–C9–P1–Au1 of 85.6(4)°, P1–Au1–Au2–P2 of −60.9(1)°, Cl1–Au1–Au2–Cl2 of −61.6(1)°, and C10–C14–P2–Au2 of 40.8(6)° (for additional data see Table 2.)

Complex (*R*,*R*,*R$_{pl}$*)-**11** shows a similar overall structure, but the formal exchange of the positions of the attachment of the -PPh$_2$ and -PCy$_2$ substituents has resulted in some noteworthy differences in detail. The system features a number of changes in a variety of parameters that make the Au ··· Au contact markedly more favorable as compared to its congener **8** (or **9**). We observe a complex geometry of (*R*,*R*,*R$_{pl}$*)-**11** in the solid state that is characterized *e. g.* by the dihedral angles around the phosphorus atoms C10–C9–P1–C31 of 46.0(6)°, C10–C9–P1–C21 of 153.6(5)°, C10–C14–P2–C41 of 155.7(7)°, and C10–C14–P2–C51 of −87.7(8)°. The Au ··· Au distance in (*R*,*R*,*R$_{pl}$*)-**11** amounts to 3.076(1) Å, which is 0.2 Å shorter as observed for the "substituent-invertomer" (*S*,*S*,*S$_{pl}$*)-**8**. In complex **11** the angle between the P1–Au1 and P2–Au2 vectors is 66.3(1)°.

Conclusion

We have prepared the [3]ferrocenophane-based *P,P*-chelate ligands **2**, **3** and **4**, the former pair of "substituent-invertomers" in optically active form. All of them form $\kappa P,\kappa P$(AuCl)$_2$ complexes when treated with (Me$_2$S)AuCl in a 1 : 2 molar ratio. The X-ray crystal structure analyses have shown that these chelates are geometrically suited for building up intramolecular aurophilic interactions between the respective pairs of gold atoms, quite different as it was recently observed by us for a remotely related zirconocene-based *P,P*-chelate ligand [16].

A comparison of the X-ray crystal structure analyses of the "substituent-invertomeric" complexes **8** and **11** has revealed geometrically similar frameworks. Nevertheless, the *o*-PCy$_2$/α-PPh$_2$ system **11** exhibits a markedly shorter – and hence probably stronger – intramolecular Au ··· Au contact, indicating that such effects may result from an accumulation of a number of small differences in framework geometries, which also seem to be responsible for the considerably better performance of the *o*-PPh$_2$/α-PCy$_2$ *P,P*-chelate ligand system **2** in Pd-catalyzed asymmetric CO/propene copolymerization as compared to its "substituent-invertomer" **3** [5, 6].

Experimental Section

All reactions with air- and moisture-sensitive compounds were carried out under dry argon (Argon 5.0; Westfalen AG) in Schlenk-type glassware. Diethyl ether, dichloromethane, pentane, and toluene were dried using a Grubbs-type system [17], with activated alumina (basic) or molecular sieves as drying agents. [D$_2$]Dichloromethane was dried over calciumhydride and distilled under vacuum. Commercially available reagents were used as received. NMR spectra were recorded with a Varian 500 MHz INOVA (^{1}H: 500 MHz, ^{13}C: 126 MHz, ^{31}P: 202 MHz) and a Varian UNITY*plus* 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{31}P: 243 MHz) spectrometer. IR spectra were recorded for solids in pure form on an ATR unit using a Varian 3100 FT-IR (Excalibur Series) spectrometer. For the determination of melting points a DSC Q 20 and a DSC 2910 CE (both of TA Instruments) were employed. Mass spectra were collected using a MAT 312 spectrometer from Finnigan (EI) or a MicroTof instrument from Bruker (ESI). Elemental analyses were performed using a CHNO-Rapid analyzer (Foss-Heraeus). The compounds (*rac*)-**7**, (*S,S,S$_{pl}$*)-**7**, (*R,R,R$_{pl}$*)-**10** and (*S,S,S$_{pl}$*)-**2** were prepared as previously described by us [2, 5, 18].

X-Ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT [19], data reduction DENZO-SMN [20], absorption correction SORTAV [21] and DENZO [22], structure solution SHELXS-97 [23], structure refinement SHELXL-97 [24], graphics SCHAKAL [25].

CCDC 750384–750387 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

*Preparation of compound (rac)-**4***

Diisopropylphosphine (0.974 g, (10 % solution in hexane), 0.825 mmol, 1.1 eq.) was added to a solution of (*rac*)-**7** (350 mg, 0.75 mmol, 1.0 eq.) in freshly distilled glacial acetic acid (15 mL). The mixture was kept at 115 °C for 48 h and afterwards cooled down to r. t. After addition of dichloromethane (20 mL), saturated aqueous sodium bicarbonate (400 mL) 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 over magnesium sulfate, filtered and concentrated *in vacuo*. The residue was dissolved in dichloromethane (3 mL) and precipitated with *n*-pentane (10 mL). Purification of the crude material was obtained by column chromatography on silica gel (cyclohexane, ethyl acetate, 1 : 1; R_f = 0.8) to give pure (*rac*)-**4** (380 mg, 0.70 mmol, 93 %). Single crystals suitable for X-ray diffraction, were obtained by slow diffusion of a saturated dichloromethane solution. – ^{1}H NMR (600 MHz, 298 K, [D$_2$]dichloromethane): δ = 7.47 (m, 2H, *o*-PPh_2), 7.31 (m, 5H, *o*, *m*, *p*-PPh_2), 7.25 (m, 3H, *m*, *p*-PPh_2), 4.29 (m, 1H, H-5), 4.19 (m, 1H, H-12), 4.18 (m, 1H, H-11), 4.08 (m, 1H, H-2), 3.84 (m, 1H, H-3), 3.82 (m, 1H, H-13), 3.39 (m, 1H, H-4), 3.12 (m, 1H, H-8$_\mathrm{B}$), 2.72 (m, 1H, H-6), 2.46 (ddd, $^{3}J_{\mathrm{H,H}}$ = 12.8 Hz, 4.7 Hz, 1.9 Hz, 1H, H-9), 2.12 (m, 1H, H-8$_\mathrm{A}$), 1.73 (sept, $^{3}J_{\mathrm{H,H}}$ = 6.4 Hz, 1H, $^{\mathrm{CH}}\mathrm{P}^{i}\mathrm{Pr}$), 1.20 (sept, $^{3}J_{\mathrm{H,H}}$ = 6.4 Hz, 1H, $^{\mathrm{CH}}\mathrm{P}^{i}\mathrm{Pr}'$), 1.19 (d, $^{3}J_{\mathrm{H,H}}$ = 7.7 Hz, 1H, H-7), 1.18 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.9 Hz, 7.3 Hz, 1H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}_2$), 1.17 (dd, $^{3}J_{\mathrm{H,H}}$ = 14.7 Hz, 7.4 Hz, 1H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}_2$), 0.90 (dd, $^{3}J_{\mathrm{H,H}}$ = 7.2 Hz, 5.4 Hz, 1H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}'_2$), 0.40 (dd, $^{3}J_{\mathrm{H,H}}$ = 15.6 Hz, 7.4 Hz, 1H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}'_2$). – ^{13}C{^{1}H} NMR (151 MHz, 298 K, [D$_2$]dichloromethane): δ = 140.6 (d, $^{1}J_{\mathrm{P,C}}$ = 8.9 Hz, *i*-PPh_2), 139.2 (dd, $^{1}J_{\mathrm{P,C}}$ = 13.9 Hz, 5.7 Hz, *i*-PPh_2), 135.3 (d, $J_{\mathrm{P,C}}$ = 21.4 Hz, *o*-PPh_2), 133.4 (d, $J_{\mathrm{P,C}}$ = 19.4 Hz, *o*-PPh_2), 128.8 (*p*-PPh_2), 128.2 (d, $J_{\mathrm{P,C}}$ = 7.3 Hz, *m*-PPh_2), 128.03 (d, $J_{\mathrm{P,C}}$ = 7.0 Hz, *m*-PPh_2), 127.97 (*p*-PPh_2), 93.1 (dd, $J_{\mathrm{P,C}}$ = 22.3, 12.5 Hz, C-10), 92.0 (C-1), 75.6 (dd, $J_{\mathrm{P,C}}$ = 5.3, 2.1 Hz, C-11), 74.8 (d, $J_{\mathrm{P,C}}$ = 4.6, C-13), 73.2 (d, $J_{\mathrm{P,C}}$ = 15.8 Hz, C-14), 72.3 (d, $J_{\mathrm{P,C}}$ = 4.8 Hz, C-5), 70.1 (C-4), 69.6 (C-12), 69.1 (C-2), 67.9 (C-3), 45.8 (dd, $J_{\mathrm{P,C}}$ = 22.8 Hz, 9.7 Hz, C-8), 26.4 (d, $J_{\mathrm{P,C}}$ = 10.2 Hz, C-6), 25.2 (dd, $J_{\mathrm{P,C}}$ = 20.2 Hz, 3.3 Hz, C-9), 24.1 (d, $J_{\mathrm{P,C}}$ = 18.6 Hz, $^{\mathrm{CH}}\mathrm{P}^{i}\mathrm{Pr}'_2$), 23.5 (d, $J_{\mathrm{P,C}}$ = 24.3 Hz, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}_2$), 22.2 (dd, $J_{\mathrm{P,C}}$ = 22.2 Hz, 3.5 Hz, $^{\mathrm{CH}}\mathrm{P}^{i}\mathrm{Pr}_2$), 20.9 (d, $J_{\mathrm{P,C}}$ = 23.7 Hz, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}'_2$), 20.3 (d, $J_{\mathrm{P,C}}$ = 3.8 Hz, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}_2$), 17.6 (d, $J_{\mathrm{P,C}}$ = 2.9 Hz, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}'_2$), 16.1 (C-7). – ^{31}P{^{1}H} NMR (202 MHz, 298 K, [D$_2$]dichloromethane): δ = 11.7 (d, $J_{\mathrm{P,P}}$ = 75.5 Hz, $\mathrm{P}^{i}\mathrm{Pr}$), –24.6 (d, $J_{\mathrm{P,P}}$ = 75.5 Hz, PPh). – MS (ES, 70 eV): *m/z* (%) = 541.2 (100) $[\mathrm{M+H}]^{+}$. – M. p. 166 °C. – IR (film): ν = 2960 (m), 2862 (m), 1466 (m), 1433 (s), 1261 (m), 1095 (m), 1039 (s), 1024 (m), 806 (s), 741 (s), 697 (s). – $\mathrm{C_{32}H_{38}FeP_2}$ (540.2): calcd. C 71.12, H 7.09; found C 71.07, H 7.11.

X-Ray crystal structure analysis of (*rac*)-**4**: Formula $\mathrm{C_{32}H_{38}FeP_2}$, M_r = 540.41, yellow crystal 0.40 × 0.30 × 0.20 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 11.2050(2), b = 14.4166(2), c = 17.7884(3) Å, β = 91.332(1)°, V = 2872.73(8) Å^3, Z = 4, ρ_calc = 1.25 g cm^{-3}, μ = 0.7 mm^{-1}, empirical absorption correction ($0.780 \le T \le 0.880$), λ = 0.71073 Å, T = 223 K, ω and φ scans, 18115 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.67 Å^{-1}, 7047 independent (R_int = 0.037) and 4736 observed reflections [$I \ge 2\sigma(I)$], 321 refined parameters, R = 0.049, wR^2 = 0.126, max. (min.) residual electron density 0.65 (–0.60) e Å^{-3}. Comments: Hydrogen atoms calculated and refined as riding atoms.

*Synthesis of complex (rac)-**9***

A reaction flask was charged with 54.5 mg $(\mathrm{Me_2S})\mathrm{AuCl}$ (0.19 mmol, 2.0 eq.) and $\mathrm{CH_2Cl_2}$ (15 mL). After the dropwise addition of a $\mathrm{CH_2Cl_2}$ (10 mL) solution of 50 mg (0.095 mmol, 1.0 eq.) of (*rac*)-**4**, the solution was stirred for 1 h at r. t. Then the solvent was reduced to 3 mL *in vacuo*. After the addition of 15 mL of diethyl ether the product precipitated as a yellow powder (75 mg, 0.07 mmol, 74 %). Yellow single crystals were obtained by slow diffusion of diethyl ether into a dichloromethane solution of (*rac*)-**9** at r. t. – ^{1}H NMR (500 MHz, 298 K, [D$_2$]dichloromethane): δ = 7.73 (m, 2H, *o*-PPh_2), 7.55 (m, 2H, *o*-PPh'_2), 7.55 (m, 1H, *p*-PPh_2), 7.51 (m, 1H, *p*-PPh'_2), 7.51 (m, 2H, *m*-PPh_2), 7.45 (m, 2H, *m*-PPh'_2), 5.03 (m, 1H, H-5), 4.44 (m, 1H, H-13), 4.42 (m, 1H, H-11), 4.34 (m, 1H, H-8$_\mathrm{B}$), 4.25 (m, 1H, H-2), 4.03 (m, 1H, H-3), 3.82 (m, 1H, H-4), 3.78 (m, 1H, H-12), 2.99 (m, 1H, H-6), 2.88 (m, 1H, H-9), 2.37 (m, 1H, H-8$_\mathrm{A}$), 2.36 (m, 1H, $^{\mathrm{CH}}\mathrm{P}^{i}\mathrm{Pr}$), 1.57 (m, 1H, $^{\mathrm{CH}}\mathrm{P}^{i}\mathrm{Pr}'$), 1.34 (d, $J_{\mathrm{H,H}}$ = 7.2 Hz, 3H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}_2$), 1.31 (d, $J_{\mathrm{H,H}}$ = 7.3 Hz, 3H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}_2$), 1.24 (d, $J_{\mathrm{H,H}}$ = 7.3 Hz, 3H, H-7), 1.05 (dd, $J_{\mathrm{H,H}}$ = 13.0 Hz, 7.3 Hz, 3H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}'_2$), 0.63 (dd, $J_{\mathrm{H,H}}$ = 18.0 Hz, 7.0 Hz, 3H, $^{\mathrm{Me}}\mathrm{P}^{i}\mathrm{Pr}'_2$). – ^{13}C{^{1}H} NMR (125.6 MHz, 298 K, [D$_2$]dichloromethane): δ = 135.6 (d, $J_{\mathrm{P,C}}$ = 13.0 Hz, *o*-PPh_2), 134.9 (d, $J_{\mathrm{P,C}}$ = 14.3 Hz, *o*-PPh'_2), 132.3 (d, $J_{\mathrm{P,C}}$ = 2.6 Hz, *p*-PPh_2), 131.8 (d, $J_{\mathrm{P,C}}$ = 2.3 Hz, *p*-PPh'_2), 131.2 (d, $J_{\mathrm{P,C}}$ = 61.7 Hz, *i*-PPh'_2), 129.6 (d, $J_{\mathrm{P,C}}$ = 63.0 Hz, *i*-PPh_2), 129.4 (d, $J_{\mathrm{P,C}}$ = 12.0 Hz, *m*-PPh_2), 128.9

(d, $J_{P,C}$ = 11.5 Hz, *m*-PPh′$_2$), 92.8 (C-1), 86.2 (dd, $J_{P,C}$ = 13.3 Hz, 2.9 Hz, C-10), 79.4 (dd, $J_{P,C}$ = 8.4 Hz, 3.7 Hz, C-11), 79.0 (d, $J_{P,C}$ = 5.7 Hz, C-12), 73.8 (d, $J_{P,C}$ = 2.0 Hz, C-5), 72.5 (C-4), 71.9 (d, $J_{P,C}$ = 7.1 Hz, C-13), 70.4 (C-2), 70.1 (C-3), 68.6 (d, $J_{P,C}$ = 62.8 Hz, C-14), 47.0 (dd, $J_{P,C}$ = 8.6 Hz, 2.0 Hz, C-8), 28.5 (dd, $J_{P,C}$ = 28.0 Hz, 1.6 Hz, C-9), 27.4 (d, $J_{P,C}$ = 31.7 Hz, ^{CH}P^{i}Pr′), 27.0 (d, $J_{P,C}$ = 27.5 Hz, ^{CH}P^{i}Pr), 26.1 (d, $J_{P,C}$ = 11.5 Hz, C-6), 22.2 (d, $J_{P,C}$ = 6.2 Hz, ^{Me}P^{i}Pr′$_2$), 21.8 (d, $J_{P,C}$ = 1.2 Hz, ^{Me}P^{i}Pr$_2$), 21.0 (^{Me}P^{i}Pr$_2$), 17.6 (d, $J_{P,C}$ = 4.9 Hz, ^{Me}P^{i}Pr′$_2$), 16.2 (C-7). – ^{31}P{^{1}H} NMR (202 MHz, 298 K, [D$_2$]dichloromethane): δ = 53.5 (d, $J_{P,P}$ = 10.3 Hz, P^{i}Pr), 24.7 (d, $J_{P,P}$ = 10.3 Hz, PPh). – HRMS ((+)-ESI): *m/z* = 1027.0387 (calcd. 1027.0400 for $C_{32}H_{38}Au_2FeP_2Cl_2Na$, [M+Na]$^+$). – M. p. 259 °C. – IR (film): ν = 2957 (m), 2870 (m), 1458 (s), 1458 (m), 1436 (s), 1384.5 (m), 1146 (s), 1096 (s), 1054 (w), 1030 (w), 815 (w), 753 (s), 696 (s). – $C_{32}H_{38}Au_2Cl_2FeP_2$ (1004.1): calcd. C 38.23, H 3.81; found C 37.87, H 3.77.

X-Ray crystal structure analysis of (*rac*)-**9**: Formula $C_{32}H_{38}Au_2Cl_2FeP_2 \cdot 1/2\, CH_2Cl_2$, M_r = 1047.71, yellow crystal $0.30 \times 0.03 \times 0.02$ mm^3, monoclinic, space group $P2_1/n$ (no. 14), a = 9.0973(3), b = 16.0397(4), c = 23.7200(8) Å, β = 90.456(2)°, V = 3461.1(2) Å^3, Z = 4, ρ_{calc} = 2.01 g cm^{-3}, μ = 9.2 mm^{-1}, empirical absorption correction ($0.169 \le T \le 0.837$), λ = 0.71073 Å, T = 223 K, ω and φ scans, 27171 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.54 Å^{-1}, 4451 independent (R_{int} = 0.124) and 3465 observed reflections [$I \ge 2\sigma(I)$], 369 refined parameters, R = 0.078, wR^2 = 0.190, max. (min.) residual electron density 1.96 (−2.90) e Å^{-3}. Comments: Hydrogen atoms calculated and refined as riding atoms; due to the shape and the size of the investigated crystal the quality of the analysis is limited.

*Synthesis of complex (S,S,S$_{pl}$)-**8***

47 mg (Me$_2$S)AuCl (0.16 mmol, 2.0 eq.) was dissolved in CH$_2$Cl$_2$ (15 mL). After the addition of 50 mg (0.08 mmol, 1.0 eq.) of (*S,S,S$_{pl}$*)-**2**, the solution was stirred for 1 h at r. t. Then the solvent was reduced to 5 mL *in vacuo*. After the addition of 8 mL of diethyl ether the product was precipitated as a yellow powder (67 mg, 0.062 mmol, 77 %). – ^{1}H NMR (500 MHz, 298 K, [D$_2$]dichloromethane): δ = 7.69 (m, 2H, *o*-PPh$_2$), 7.55 (m, 2H, *o*-PPh′$_2$), 7.53 (m, 1H, *p*-PPh$_2$), 7.52 (m, 2H, *m*-PPh$_2$), 7.50 (m, 1H, *p*-PPh′$_2$), 7.44 (m, 2H, *m*-PPh′$_2$), 5.01 (m, 1H, H-5), 4.45 (m, 1H, H-12), 4.39 (m, 1H, H-11), 4.37 (m, 1H, H-8$_B$), 4.24 (m, 1H, H-2), 4.01 (m, 1H, H-3), 3.82 (m, 1H, H-13), 3.75 (m, 1H, H-4), 3.00 (m, 2H, H-9, H-6), 2.35 (m, 1H, H-8$_A$), 2.09 (m, 1H, ^{CH}PCy), 1.36 (m, 1H, ^{CH}PCy′), 2.17/1.56, 2.08/1.48, 1.87/1.32, 1.84/1.32, 1.82/1.24, 1.74/0.92, 1.71/1.24, 1.59/1.09, 1.58/0.97, 1.18/1.18 (each m, each 1H, ^{CH2}PCy$_2$), 1.23 (d, $J_{H,H}$ = 7.2 Hz, 3H, H-7). – ^{13}C{^{1}H} NMR (126 MHz, 298 K, [D$_2$]dichloromethane): δ = 135.3 (d, $J_{P,C}$ = 13.2 Hz, *o*-PPh$_2$), 135.0 (d, $J_{P,C}$ = 14.3 Hz, *o*-PPh′$_2$), 132.1 (d, $J_{P,C}$ = 2.6 Hz, *p*-PPh$_2$), 131.8 (d, $J_{P,C}$ = 2.5 Hz, *p*-PPh′$_2$), 131.6 (d, $J_{P,C}$ = 61.3 Hz, *i*-PPh′$_2$), 130.3 (d, $J_{P,C}$ = 63.5 Hz, *i*-PPh$_2$), 129.4 (d, $J_{P,C}$ = 11.5, *m*-PPh$_2$), 128.8 (d, $J_{P,C}$ = 11.8 Hz, *m*-PPh′$_2$), 92.8 (C-1), 86.1 (dd, $J_{P,C}$ = 13.2 Hz, 3.2 Hz, C-10), 79.3 (dd, $J_{P,C}$ = 8.8 Hz, 3.8 Hz, C-11), 79.0 (d, $J_{P,C}$ = 5.5 Hz, C-13), 73.7 (d, $J_{P,C}$ = 1.8 Hz, C-5), 72.5 (C-4), 72.1 (d, $J_{P,C}$ = 7.2 Hz, C-12), 70.4 (C-2), 70.0 (C-3), 68.2 (d, $J_{P,C}$ = 62.7 Hz, C-14), 46.5 (dd, $J_{P,C}$ = 8.2 Hz, 2.0 Hz, C-8), 37.8 (d, $J_{P,C}$ = 30.8 Hz, ^{CH}PCy′), 37.2 (d, $J_{P,C}$ = 26.2 Hz, ^{CH}PCy), 33.2 (^{CH2}PCy$_2$), 32.3 (d, $J_{P,C}$ = 4.8 Hz, ^{CH2}PCy$_2$), 31.2 (^{CH2}PCy$_2$), 29.1 (d, $J_{P,C}$ = 5.3 Hz, ^{CH2}PCy$_2$), 27.9 (d, $J_{P,C}$ = 12.7 Hz, ^{CH2}PCy$_2$), 27.7 (d, $J_{P,C}$ = 11.2 Hz, ^{CH2}PCy$_2$), 27.5 (d, $J_{P,C}$ = 9.3 Hz, ^{CH2}PCy$_2$), 27.4 (d, $J_{P,C}$ = 14.9 Hz, ^{CH2}PCy$_2$), 26.5 (dd, $J_{P,C}$ = 28.2 Hz, 1.8 Hz, C-9), 26.4 (d, $J_{P,C}$ = 1.5 Hz, ^{CH2}PCy$_2$), 26.2 (d, $J_{P,C}$ = 1.3 Hz, ^{CH2}PCy$_2$), 26.1 (d, $J_{P,C}$ = 11.5 Hz, C-6), 16.4 (C-7). – ^{31}P{^{1}H} NMR (202 MHz, 298 K, [D$_2$]dichloromethane): δ = 48.5 (d, $J_{P,P}$ = 11.2 Hz, PCy), 24.7 (d, $J_{P,P}$ = 11.2 Hz, PPh). – HRMS ((+)-ESI): *m/z* = 1049.1423 (calcd. 1049.1439 for $C_{38}H_{46}Au_2FeP_2Cl$, [M]$^+$). – M. p. decomposition at 267 °C. – IR (film): ν = 2923 (s), 2852 (s), 2360 (w), 1436 (s), 1176 (m), 1150 (m), 1095 (s), 999 (s), 812 (m), 747 (s), 695 (s), 642 (s). – $C_{38}H_{46}Au_2Cl_2FeP_2$ (1084.1): calcd. C 42.05, H 4.27; found C 42.49, H 4.16. – $[\alpha]_D^{20}$ (589 nm) = −74 (c = $1 \cdot 10^{-3}$ g mL^{-1}, CH$_2$Cl$_2$).

X-Ray crystal structure analysis of **8**: formula $C_{38}H_{46}Au_2Cl_2FeP_2 \cdot 2\ C_7H_8$, M_r = 1269.64, yellow crystal $0.60 \times 0.10 \times 0.10$ mm^3, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.6050(1), b = 20.9797(3), c = 24.4364(4) Å, V = 4924.18(12) Å^3, Z = 4, ρ_{calc} = 1.71 g cm^{-3}, μ = 6.4 mm^{-1}, empirical absorption correction ($0.113 \le T \le 0.565$), λ = 0.71073 Å, T = 223 K, ω and φ scans, 27573 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 11333 independent (R_{int} = 0.054) and 9652 observed reflections [$I \ge 2\sigma(I)$], 441 refined parameters, R = 0.036, wR^2 = 0.090, Flack parameter: −0.023(6), max. (min.) residual electron density 0.96 (−1.06) e Å^{-3}. Comments: Hydrogen atoms calculated and refined as riding atoms; solvent molecules refined with geometrical restraints and isotropic thermal parameters.

*Preparation of compound (R,R,R$_{pl}$)-**3***

Diphenylphosphine (0.13 mL, 0.71 mmol, 1.1 eq.) was added with exclusion of light to a solution of (*R,R,R$_{pl}$*)-**10** (310 mg, 0.65 mmol, 1.0 eq.) in freshly distilled glacial acetic acid (15 mL). The mixture was kept at 115 °C for 20 h and afterwards cooled to r. t. After addition of dichloromethane (20 mL), saturated aqueous sodium bicarbonate (400 mL) was added in small portions until the gas evolution ceased. The aqueous phase was extracted with dichloromethane. The combined organic phases were dried (magnesium sulfate), filtered and concentrated *in vacuo*. The residue was suspended in ethanol (15 mL), and a few drops of dichloromethane were added until complete solution. This was stored at −32 °C for 12 h, and the precipitate was collected. Purification of the crude material was carried out by column chromatography with silica gel (cyclohexane, ethyl acetate, 1 : 1; R_f = 0.4) to give pure (R,R,R_{pl})-**3** (286 mg, 0.46 mmol, 72 %). By slow diffusion of *n*-pentane in a saturated dichloromethane solution single crystals suitable for X-ray diffraction were obtained. ^{1}H NMR (500 MHz, 298 K, [D$_2$]dichloromethane): δ = 7.65 (m, 2H, *o*-PPh), 7.46 (m, 2H, *o*-PPh′), 7.38 (m, 3H, *m*/*p*-PPh), 7.21 (m, 3H, *m*/*p*-PPh′), 4.16 (m, 1H, H-13), 4.15 (m, 1H, H-11), 4.11 (m, 1H, H-2), 4.05 (m, 1H, H-12), 4.00 (m, 1H, H-3), 3.98 (m,1H, H-5), 3.92 (m, 1H, H-4), 3.07/1.75 (each m, each 1H, H-8$_{A/B}$), 3.05 (m, 1H, H-9), 2.46/1.39, 1.97/1.37, 1.84/1.37, 1.83/1.35, 1.75/1.35, 1.73/1.33, 1.60/1.23, 1.57/0.81, 1.56/1.09, 1.55/1.10 (each m, each 1H, ^{CH2}PCy$_2$), 2.45 (m, 1H, H-6), 2.04 (m, 1H, ^{CH}PCy), 1.67 (m, 1H, ^{CH}PCy′), 0.97 (d, $^3J_{H,H}$ = 7.2 Hz, 3H, H-7). – ^{13}C{^{1}H} NMR (126 MHz, 298 K, [D$_2$]dichloromethane): δ = 140.2 (dd, $J_{P,C}$ = 19.6 Hz, 1.7 Hz, *i*-PPh), 139.4 (dd, $J_{P,C}$ = 17.9 Hz, 1.8 Hz, *i*-PPh′), 134.3 (d, $J_{P,C}$ = 22.2 Hz, *o*-PPh), 133.3 (d, $J_{P,C}$ = 18.3 Hz, *o*-PPh′), 129.5 (d, $J_{P,C}$ = 1.0 Hz, *p*-PPh), 128.7 (d, $J_{P,C}$ = 7.8 Hz, *m*-PPh), 128.5 (*p*-PPh′), 128.2 (d, $J_{P,C}$ = 6.2 Hz, *m*-PPh′), 93.4 (C-1), 89.4 (dd, $J_{P,C}$ = 18.5 Hz, 16.6 Hz, C-10), 78.7 (d, $J_{P,C}$ = 25.9 Hz, C-14), 75.7 (dd, $J_{P,C}$ = 4.3 Hz, 2.2 Hz, C-11), 72.4 (dd, $J_{P,C}$ = 4.5 Hz, 1.0 Hz, C-12), 72.3 (d, $J_{P,C}$ = 2.7 Hz, C-5), 71.1 (C-4), 68.8 (C-2), 68.7 (C-13), 67.8 (C-3), 45.2 (dd, $J_{P,C}$ = 23.6 Hz, 11.8 Hz, C-8), 39.3 (dd, $J_{P,C}$ = 13.5 Hz, 7.8 Hz, ^{CH}PCy′), 34.7 (dd, $J_{P,C}$ = 14.1 Hz, 2.3 Hz, ^{CH}PCy), 33.3 (d, $J_{P,C}$ = 20.2 Hz, ^{CH2}PCy$_2$), 32.7 (dd, $J_{P,C}$ = 18.9 Hz, 3.4 Hz, ^{CH2}PCy$_2$), 31.1 (d, $J_{P,C}$ = 11.0 Hz, ^{CH2}PCy$_2$), 30.7 (dd, $J_{P,C}$ = 14.1 Hz, 2.0 Hz, C-9), 28.4 (d, $J_{P,C}$ = 5.1 Hz, ^{CH2}PCy$_2$), 28.4 (d, $J_{P,C}$ = 12.7 Hz, ^{CH2}PCy$_2$), 28.1 (d, $J_{P,C}$ = 12.5 Hz, ^{CH2}PCy$_2$), 27.8 (d, $J_{P,C}$ = 5.4 Hz, ^{CH2}PCy$_2$), 27.7 (d, $J_{P,C}$ = 8.2 Hz, ^{CH2}PCy$_2$), 26.9 (m, 2C, ^{CH2}PCy$_2$), 26.0 (d, $J_{P,C}$ = 11.1 Hz, C-6), 16.1 (C-7). – ^{31}P{^{1}H} NMR (202 MHz, 298 K, [D$_2$]dichloromethane): δ = −7.4 (d, $^4J_{P,P}$ = 48.4 Hz, $\nu_{1/2}$ ~ 3 Hz, PPh), −16.0 (d, $^4J_{P,P}$ = 48.4 Hz, $\nu_{1/2}$ ~ 15 Hz, PCy). – $C_{38}H_{46}FeP_2$ (620.2): calcd. C 73.55, H 7.47; found C 73.20, H 7.24. – $[\alpha]_D^{20}$ (589 nm) = 52 (c = 1 · 10^{-3} g mL^{-1}, CH$_2$Cl$_2$). [From (*rac*)-**3**: HRMS ((+)-ESI): *m/z* = 621.2493 (calcd. 621.2498 for $C_{38}H_{46}FeP_2H$, [M+H]$^+$). – M. p. 220 °C. – IR (film): ν = 3088 (m), 2922 (s), 2842 (m), 1441 (m), 1263 (w), 1086 (w), 1026 (w), 812 (w), 741 (w), 698 (w) cm^{-1}].

*Synthesis of complex (R,R,R$_{pl}$)-**11***

47 mg (Me$_2$S)AuCl (0.16 mmol, 2.0 eq.) was dissolved in CH$_2$Cl$_2$ (15 mL). After the dropwise addition of 50 mg (0.08 mmol, 1.0 eq.) of (R,R,R_{pl})-**3** in a CH$_2$Cl$_2$ (10 mL) solution, the reaction was stirred for 1 h at r. t. The solvent was reduced to 5 mL *in vacuo*. After the addition of 10 mL of pentane the product was precipitated as a yellow powder (59 mg, 0.05 mmol, 68 %). Yellow single crystals were obtained by slow diffusion of pentane into a toluene solution of (R,R,R_{pl})-**11** at r. t. – ^{1}H NMR (600 MHz, 298 K, [D$_2$]dichloromethane): δ = 7.96 (m, 2H, *o*-PPh$_2$), 7.93 (m, 2H, *o*-PPh′$_2$), 7.53 (m, 1H, *p*-PPh$_2$), 7.52 (m, 2H, *m*-PPh$_2$), 7.45 (m, 1H, *p*-PPh′$_2$), 7.42 (m, 2H, *m*-PPh′$_2$), 4.49 (m, 1H, H-5), 4.46 (m, 1H, H-12), 4.45 (m, 1H, H-11), 4.28 (m, 1H, H-8$_B$), 4.24 (m, 1H, H-2), 4.18 (m, 1H, H-13), 4.17 (m, 1H, H-3), 4.02 (m, 1H, H-4), 3.41 (dd, J = 18.8 Hz, 12.0 Hz, 1H, H-9), 2.81/1.68, 2.46/1.65, 2.08/1.65, 1.93/1.40, 1.90/1.37, 1.74/1.14, 1.72/1.35, 1.49/1.15, 1.43/0.23, 1.24/1.24 (each m, each 1H, ^{CH2}PCy$_2$), 2.68 (m, 1H, H-6), 2.30 (m, 1H, ^{CH}PCy), 2.12 (m, 2H, H-8$_A$), 1.75 (m, 1H, ^{CH}PCy′), 0.81 (d, $J_{H,H}$ = 7.2 Hz, 3H, H-7). – ^{13}C{^{1}H} NMR (151 MHz, 298 K, [D$_2$]dichloromethane): δ = 134.7 (d, $J_{P,C}$ = 13.1 Hz, *o*-PPh′$_2$), 134.5 (d, $J_{P,C}$ = 14.1 Hz, *o*-PPh$_2$), 132.5 (d, $J_{P,C}$ = 2.6 Hz, *p*-PPh$_2$), 132.3 (d, $J_{P,C}$ = 2.7 Hz, *p*-PPh′$_2$), 131.9 (d, $J_{P,C}$ = 55.4 Hz, *i*-PPh$_2$), 129.9 (d, $J_{P,C}$ = 55.4 Hz, *i*-PPh′$_2$), 129.6 (d, $J_{P,C}$ = 11.4, *m*-PPh$_2$), 129.3 (d, $J_{P,C}$ = 10.6 Hz, *m*-PPh′$_2$), 94.2 (C-1), 83.0 (m, C-10), 79.2 (m, C-11), 76.3 (d, $J_{P,C}$ = 4.9 Hz, C-13), 73.5 (C-4), 72.6 (C-5), 71.3 (d, $J_{P,C}$ = 51.9 Hz, C-14), 71.0 (d, $J_{P,C}$ = 6.0 Hz, C-12), 70.14 (C-2), 70.09 (C-3), 46.5 (dd, $J_{P,C}$ = 13.2 Hz, 1.9 Hz, C-8), 42.3 (dd, $J_{P,C}$ = 33.0 Hz, 1.0 Hz, ^{CH}PCy′), 37.2 (d, $J_{P,C}$ = 33.6 Hz, ^{CH}PCy), 34.6 (dd, $J_{P,C}$ = 32.6 Hz, 1.5 Hz, H-9), 33.8 (d, $J_{P,C}$ = 3.4 Hz, ^{CH2}PCy$_2$), 31.8 (d, $J_{P,C}$ = 2.4 Hz, ^{CH2}PCy$_2$), 31.3 (d, $J_{P,C}$ = 1.8 Hz, ^{CH2}PCy$_2$), 28.0 (d, $J_{P,C}$ = 14.9 Hz, ^{CH2}PCy$_2$), 27.8 (d, $J_{P,C}$ = 3.2 Hz, ^{CH2}PCy$_2$), 27.2 (d, $J_{P,C}$ = 14.4 Hz, ^{CH2}PCy$_2$), 27.1 (d, $J_{P,C}$ = 13.4 Hz, ^{CH2}PCy$_2$), 26.7 (d, $J_{P,C}$ = 11.0 Hz, ^{CH2}PCy$_2$), 26.1 (d, $J_{P,C}$ = 1.5 Hz, ^{CH2}PCy$_2$), 26.0 (d, $J_{P,C}$ = 1.9 Hz, ^{CH2}PCy$_2$), 25.6 (d, $J_{P,C}$ = 13.0 Hz, H-6), 15.5 (C-7). – ^{31}P{^{1}H} NMR (202 MHz, 298 K, [D$_2$]dichloromethane): δ = 39.5 (d, $J_{P,P}$ = 7.0 Hz, PPh), 35.3 (d, $J_{P,P}$ = 7.0 Hz, PCy). – HRMS ((+)-ESI): *m/z* = 1107.1019 (calcd. 1107.1026 for $C_{38}H_{46}Au_2FeP_2Cl_2Na$, [M+Na]$^+$). – M. p. decomposition at 290 °C. – IR (film): ν = 2927 (s), 2851 (s), 1436 (s), 1177 (m), 1147 (m), 1099 (s), 999 (w), 746 (s), 692 (s), 545 (m). – $C_{38}H_{46}Au_2FeP_2Cl_2$ (1004.1): calcd. C 42.05, H 4.27; found C 42.23, H 4.12. – $[\alpha]_D^{20}$ (589 nm) = −93 (c = 1 · 10^{-3} g mL^{-1}, CH$_2$Cl$_2$).

X-Ray crystal structure analysis of **11**: formula $C_{38}H_{46}Au_2Cl_2FeP_2 \cdot CH_2Cl_2$, M_r = 1170.30, yellow crystal 0.30 × 0.30 × 0.03 mm^3, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.6258(1), b = 18.5462(3), c = 21.9882(3) Å, V = 3925.38(9) Å^3, Z = 4, ρ_{calc} = 1.98 g cm^{-3}, μ = 8.2 mm^{-1}, empirical absorption correction ($0.192 \le T \le 0.791$), λ = 0.71073 Å, T = 223 K, ω and φ scans, 31688 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda]$ = 0.66 Å^{-1}, 9352 independent (R_{int} = 0.094) and 8120 observed reflections $[I \geq 2\sigma(I)]$, 434 refined parameters, $R = 0.043$, $wR^2 = 0.109$, Flack parameter: $-0.019(7)$, max. (min.) residual electron density 1.34 (-1.90) e Å^{-3}. Comments: Hydrogen atoms calculated and refined as riding atoms.

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