SUPPORTING INFORMATION

Experimental

General Comments. IR spectra were taken on a Nicolet FTIR Magna 750 and on a Digilab FTS 40 interferometers either in solid (KBr pellets) or in CH_2Cl_2 solution using CaF_2 windows. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer operating in FT mode, using as external references TMS and 85% H_3PO_4 respectively. Negative chemical shifts are upfield from the reference. Unless otherwise specified CD_2Cl_2 was used as the solvent. Conductivity measurements were performed on a Radiometer instrument using 10^{-3} M solutions at 25°C. GC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator. The following commercial columns were used: HP-5 and HP-FFAP (from Hewlett-Packard), Lipodex E (from Macherey-Nagel). GC-MS measurements were performed on a Hewlett-Packard 5971 mass selective detector connected to a Hewlett-Packard 5890 II gas chromatograph. Identification of products was made with GC or GC-MS by comparison with authentic samples.

Materials. Solvents were dried and purified according to standard methods.[26] Cyclopentadiene was obtained by thermal decomposition of dicyclopentadiene followed by distillation prior to use. Dppb, (R,R)-norphos, (from Strem), (R)-binap, (S,S)-diop, (S,S)-bppm (from Fluka) and most of the synthetic reagents were commercial products and used without purification.

The following compounds were prepared according to literature procedures: $[(CH_3CN)_2PdCl_2]$[27], $[(dppe)PdCl_2]$[28], $[(dppb)PdCl_2]$[4], $[(COD)PtCl_2]$[29], $[(dppb)PtCl_2]$[30, 31], $[(R\text{-}binap)PtCl_2]$[5], $[(norphos)PdCl_2]$[5], $[(bppm)PdCl_2]$[5], $[(diop)PdCl_2]$[5].

$[(dppb)Pd(CH_3CN)_2](ClO_4)_2$ (1ax). The complex $[(dppb)PdCl_2]$ (404 mg, 0.699 mmol) and dry CH_3CN (50 ml) were placed in a schlenk under nitrogen. To the suspension $AgClO_4$ (277 mg, 1.337 mmol) was added and the mixture was stirred for 1 hr in the dark. AgCl was filtered off and the solution was brought to dryness in vacuo to yield a pale yellow solid. (Yield 79%).

Anal. Calcd (found) for $C_{32}H_{34}N_2Cl_2O_8P_2Pd$: C 47.22 (47.05), H 4.21 (4.33).

[(dppb)Pd(THF)$_2$](ClO$_4$)$_2$ (1ay). This complex was obtained as a yellow solid with the same procedure as **1ax** starting from [(dppb)PdCl$_2$] (501 mg, 0.830 mmol), dry THF (60 ml) and AgClO$_4$ (344 mg, 1.660 mmol). (Yield 60%).

Anal. Calcd (found) for $C_{36}H_{44}Cl_2O_{10}P_2Pd$: C 49.36 (49.22), H 5.06 (4.92).

[(dppb)Pd(η^2-OTf)](OTf) (2a). The complex [(dppb)PdCl$_2$] (107 mg, 0.177 mmol) and dry, N$_2$ saturated CH$_2$Cl$_2$ (30 ml) were placed in a schlenk under nitrogen. To the suspension AgOTf (91 mg, 0.385 mmol) was added and the mixture was stirred for 1 hr in the dark. AgCl was filtered off and the solution was brought to small volume. Addition of Et$_2$O led to precipitation of a yellow solid that was filtered, washed with Et$_2$O and dried in vacuo. (Yield 70%).

Anal. Calcd (found) for $C_{30}H_{28}F_6O_6P_2PdS_2$: C 43.36 (43.51), H 3.40 (3.52).

[(R-binap)Pd(η^2-OTf)](OTf) (2b). This complex was obtained as a yellow solid with the same procedure as **2a** starting from [(R-binap)PdCl$_2$] (200 mg, 0.250 mmol), dry CH$_2$Cl$_2$ (20 ml) and AgOTf (128 mg, 0.500 mmol). (Yield 78%).

Anal. Calcd (found) for $C_{46}H_{32}F_6O_6P_2PdS_2$: C 53.78 (53.66), H 3.14 (3.25).

[(bppm)Pd(η^2-OTf)](OTf) (2c). This complex was obtained with the same procedure as **2a** starting from [(bppm)PdCl$_2$] (151 mg, 0.207 mmol), dry CH$_2$Cl$_2$ (20 ml) and AgOTf (106 mg, 0.414 mmol). Since the complex is partially soluble in Et$_2$O, it was obtained as a yellow solid by bringing the CH$_2$Cl$_2$ solution to dryness. (Yield 67%).

Anal. Calcd (found) for $C_{36}H_{37}F_6NO_8P_2PdS_2$: C 45.13 (45.01), H 3.89 (3.78).

[(diop)Pd(η^2-OTf)](OTf) (2d). This complex was obtained as an orange solid with the same procedure as **2c** starting from [(diop)PdCl$_2$] (158 mg, 0.234 mmol), dry CH$_2$Cl$_2$ (25 ml) and AgOTf (120 mg, 0.468 mmol). (Yield 73%).

Anal. Calcd (found) for $C_{33}H_{32}F_6O_8P_2PdS_2$: C 43.89 (44.05), H 3.57 (3.44).

[(norphos)Pd(η^2-OTf)](OTf) (2e). This complex was obtained as a pale yellow solid with the same procedure as **2a** starting from [(norphos)PdCl$_2$] (148 mg, 0.232 mmol), dry CH$_2$Cl$_2$ (20 ml) and AgOTf (119 mg, 0.464 mmol). (Yield 80%).

Anal. Calcd (found) for $C_{33}H_{28}F_6O_6P_2PdS_2$: C 45.71 (45.66), H 3.25 (3.09).

[(dppb)Pt(η^2-OTf)](OTf) (3a). This complex was obtained as a white solid with the same procedure as **2a** starting from [(dppb)$PtCl_2$] (161 mg, 0.232 mmol), dry CH_2Cl_2 (30 ml) and AgOTf (119 mg, 0.464 mmol). (Yield 73%).

Anal. Calcd (found) for $C_{30}H_{28}F6O_6P_2PtS_2$: C 39.18 (39.06), H 3.07 (3.00).

[(R-binap)Pt(η^2-OTf)](OTf) (3b). This complex was obtained as a white solid with the same procedure as **2a** starting from [(R-binap)$PtCl_2$] (175 mg, 0.196 mmol), dry CH_2Cl_2 (25 ml) and AgOTf (101 mg, 0.392 mmol). (Yield 54%).

Anal. Calcd (found) for $C_{46}H_{32}F_6O_6P_2PtS_2$: C 49.51 (49.73), H 2.89 (3.01).

[(dppb)Pd(μ-Cl)]$_2$(OTf)$_2$ (4ax). The complex [(dppb)$PdCl_2$] (201 mg, 0.333 mmol) and dry, N_2 saturated CH_2Cl_2 (40 ml) were placed in a schlenk under nitrogen. To the suspension AgOTf (86 mg, 0.333 mmol) was added and the mixture was stirred for 1 hr in the dark. AgCl was filtered off and the solution was brought to small volume. Addition of Et_2O led to precipitation of a yellow solid that was filtered, washed with Et_2O and dried in vacuo. (Yield 73%).

Anal. Calcd (found) for $C_{58}H_{56}Cl_2F_6O_6P_4Pd_2S_2$: C 48.55 (48.39), H 3.93 (3.81).

[(R-binap)Pd(μ-Cl)]$_2$(OTf)$_2$ (4bx). This complex was obtained as a yellow solid with the same procedure as **4ax** starting from [(R-binap)$PdCl_2$] (108 mg, 0.135 mmol), dry CH_2Cl_2 (25 ml) and AgOTf (35 mg, 0.135 mmol). (Yield 80%).

Anal. Calcd (found) for $C_{90}H_{64}Cl_2F_6O_6P_4Pd_2S_2$: C 59.16 (59.03), H 3.53 (3.46).

[(R-binap)Pd(μ-Cl)]$_2$(ClO_4)$_2$ (4by). This complex was obtained as a yellow solid with the same procedure as **4ax** starting from [(R-binap)$PdCl_2$] (131 mg, 0.164 mmol), dry CH_2Cl_2 (30 ml) and $AgClO_4$ (34 mg, 0.164 mmol). (Yield 81%).

Anal. Calcd (found) for $C_{88}H_{64}Cl_4O_8P_4Pd_2$: C 61.17 (61.11), H 3.73 (3.82).

[(R-binap)Pd(μ-Cl)]$_2$(BF_4)$_2$ (4bz). This complex was obtained as a yellow solid with the same procedure as **4ax** starting from [(R-binap)$PdCl_2$] (108 mg, 0.135 mmol), dry CH_2Cl_2 (20 ml) and 0.161 ml of a 0.84 M solution (0.135 mmol) of $AgBF_4$ in acetone. (Yield 90%).

Anal. Calcd (found) for $C_{88}H_{64}B_2Cl_2F_8P_4Pd_2$: C 62.07 (62.19), H 3.79 (3.88).

[(dppb)Pt(μ-Cl)]$_2$(BF_4)$_2$ (5az). This complex was obtained as a white solid solid with the same procedure as **4ax** starting from [(dppb)$PtCl_2$] (108 mg, 0.135

mmol), dry CH_2Cl_2 (20 ml) and 0.161 ml of a 0.84 M solution (0.135 mmol) of $AgBF_4$ in acetone. (Yield 79%).

Anal. Calcd (found) for $C_{56}H_{56}B_2Cl_2F_8P_4Pt_2$: C 45.21 (45.10), H 3.79 (3.67).

[(R-binap)Pt(μ-Cl)]$_2$(OTf)$_2$ (5bx). This complex was obtained as a very pale yellow solid with the same procedure as **4ax** starting from [(R-binap)$PtCl_2$] (121 mg, 0.135 mmol), dry CH_2Cl_2 (25 ml) and AgOTf (35 mg, 0.135 mmol). (Yield 67%).

Anal. Calcd (found) for $C_{90}H_{64}Cl_2F_6O_6P_4Pt_2S_2$: C 53.93 (53.82), H 3.22 (3.14).

[(R-binap)Pt(μ-Cl)]$_2$(ClO$_4$)$_2$ (5by). This complex was obtained as a very pale yellow solid with the same procedure as **4ax** starting from [(R-binap)$PtCl_2$] (195 mg, 0.220 mmol), dry CH_2Cl_2 (35 ml) and $AgClO_4$ (46 mg, 0.220 mmol). (Yield 78%).

Anal. Calcd (found) for $C_{88}H_{64}Cl_4O_8P_4Pt_2$: C 55.47 (55.39), H 3.39 (3.30).

[(R-binap)Pt(μ-Cl)]$_2$(BF$_4$)$_2$ (5bz). This complex was obtained as a very pale yellow solid with the same procedure as **4ax** starting from [(R-binap)$PtCl_2$] (151 mg, 0.170 mmol), dry CH_2Cl_2 (30 ml) and 0.185 ml of a 0.92 M solution (0.170 mmol) of $AgBF_4$ in acetone. (Yield 75%).

Anal. Calcd (found) for $C_{88}H_{64}B_2Cl_2F_8P_4Pt_2$: C 56.22 (56.33), H 3.43 (3.33).

References

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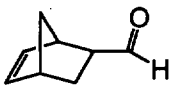
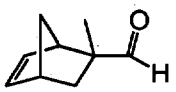
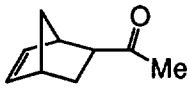
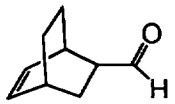
Table 6: Conditions for the GC analysis of the chiral compounds.

compound	method	retention time (min)		R_f	
		endo	exo	endo	exo
	A	25.3	21.3	1.025	1.009[a]
	B	26.2	20.3	1.042	1.011
	A	41.2	34.2	1.058	1.012
	A	38.6	36.2	1.031	1.019

Column Lipodex E; detector FID; head pressure 10 psi; helium flow 1 ml/min; split ratio 100.

Method A: initial temp. 55°C, initial time 6 min; ramp 2°C/min; intermediate temp. 80°C, intermediate time 1.5 min; ramp 0.5°C/min; final temp. 90°C.

Method B: initial temp. 60°C, initial time 6 min; ramp 2°C/min; intermediate temp. 80°C, intermediate time 1.5 min; ramp 0.5°C/min; final temp. 110°C.

Notes: a. The enantiomer separation is not complete. Experimental error ± 10%.