Rhodium(I), Palladium(II), and Platinum(II) Complexes Containing New Mixed Phosphane−Phosphite Ligands − Effect of the Catalytic System Stability on the Enantioselective Hydroformylation of Styrene

Carmela G. Arena,[a] Felice Faraone,*[a] Claudia Graiff,[b] and Antonio Tiripicchio[b]

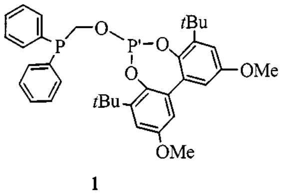
Keywords: Rhodium / Palladium / Platinum / Chirality / P ligands / Hydroformylation

The new mixed phosphane–phosphite ligands **1** and **2**, derived from 3,3′-di-*tert*-butyl-2,2′-dihydroxy-5,5′-dimethoxybiphenyl and (*S*)-binaphthol, respectively, reacted with $[Rh(COD)(THF)_2]CF_3SO_3$ to give the compounds $[Rh(COD)(\mathbf{1})]CF_3SO_3$ and $[Rh(COD)(\mathbf{2})]CF_3SO_3$ in which the ligands **1** and (*S*)-**2** are chelated to the rhodium centre. The reaction with $[Rh(CO)_2Cl]_2$ gave two different products, $[Rh(CO)_2(L)Cl]$ and $[Rh(CO)(L)Cl]$ [L = **1** and (*S*)-**2**], containing L as a chelate. On the basis of the IR and NMR spectroscopic data, the proposed structure of the pentacoordinate species is a trigonal bipyramide in which the phosphane–phosphite ligand assumes an equatorial-axial coordination. The reactions of **1** and **2** with $[Pd(C_6H_5CN)_2Cl_2]$ and $[Pt(COD)I_2]$ gave the corresponding compounds $[Pd(L)Cl_2]$ and $[Pt(L)I_2]$ in which the ligands are chelated to the metal centre. The crystal structure of the chloroform solvate of $[Pd(L)Cl_2]$ was fully characterised by an X-ray study. The chiral ligands (*S*)-**2** and (*S*)-**3** [derived from the *ortho*-bis(trimethylsilyl)-substituted (*S*)-binaphthol] were tested in the hydroformylation of styrene. The results obtained were discussed in light of the catalytic system stability.

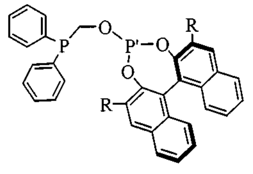
Introduction

In the last twenty years great efforts have been made in the design of chiral ligands due to their role in enantioselective catalysis.[1] Attempts have been made to correlate structural and electronic characteristics of the coordinated chiral ligands with catalytic regio- and enantioselectivity. The structural features of the coordinated ligands, viz. the geometry, rigidity, asymmetry, natural bite angle, presence of sterically hindered groups, type of chirality and distance of the chiral centre from the metal centre have been considered to be factors determining the asymmetric induction.[2] However, in spite of the number of works produced, the crucial factors in designing ligands able to induce high enantioselectivity are not clear. As concerns the electronic characteristics of bidentate ligands, the presence of donor atoms with different properties seems to afford an advantageous effect on the regio- and enantioselectivity of the catalytic process. For example, Takaya et al.[3] have reported excellent chemo- and regioselectivities in the rhodium(I)-catalysed hydroformylation of vinylarenes using the phosphane−phosphito mixed chiral ligand binaphos. Some of us,[4] using (R_a,S_C)-quinaphos, a phosphane−phosphoramidite ligand derived from quinoline, in the rhodium(I)-catalysed hydroformylation of styrene, obtained the branched aldehyde with 74% *ee* in the (*S*) form. Using the same ligand, in the (R_a,R_C) configuration, in the rhodium(I)-catalysed enantioselective hydrogenation of dimethyl itaconate and methyl 2-acetamidoacrylate the products have been obtained with a conversion higher than 99% and 98.8 and 97.8% of *ee*, respectively.

Recently we reported[5] on the synthesis of the new phosphane−phosphite ligands **1−3** and on their applications in the Pd-catalysed enantioselective allylic alkylation of 1,3-diphenyl-2-propen-1-yl acetate by dimethyl malonate. Using the complexes $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{2})]CF_3SO_3$ and $[Pd(\eta^3\text{-}C_3H_5)(\mathbf{3})]CF_3SO_3$ as catalyst precursors, the allylic substitution product was obtained with up to 71% *ee*.



1



R = H (*S*)-**2**
R = $SiMe_3$ (*S*)-**3**

Here we describe the synthesis of rhodium(I), palladium(II) and platinum(II) complexes containing the ligands **1** and (*S*)-**2**, together with the X-ray structure of the compound $[Pd(\mathbf{1})Cl_2]$. The results obtained in the hydroformyl-

---

[a] Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina,
Salita Sperone, 31 Vill. S. Agata, 98166 Messina, Italy
Fax: (internat.) + 39-090/393756
E-mail: faraone@chem.unime.it
[b] Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR,
Parco Area delle Scienze 17A, 43100 Parma, Italy

ation of styrene using ligands (*S*)-**2** and (*S*)-**3** are also briefly reported. This study stems from our interest in developing the synthesis of d^8-metal complexes able to act as efficient catalyst precursors in homogeneous catalysis.

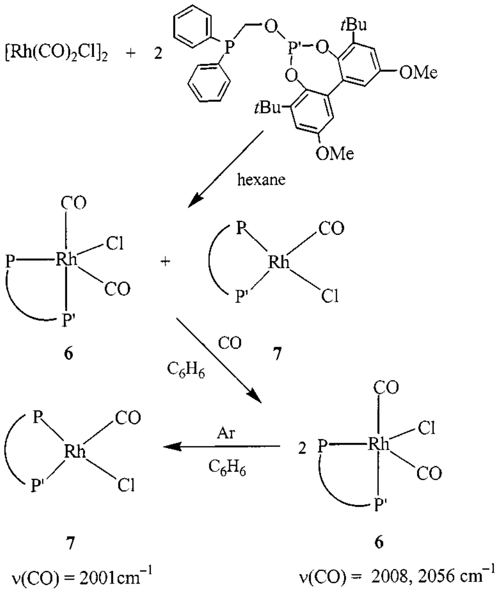
Results and Discussion

As previously reported,[5] the ligands **1** and (*S*)-**2** have been easily prepared by treating (hydroxymethyl)diphenylphosphane (Ph_2PCH_2OH)[6] with 1 equiv. of 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene and (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*:3,4-*a*′]dinaphthalene, respectively, in the presence of NEt_3 in toluene at 0 °C. They were obtained as white solids and are air-sensitive in both the solid state and in solution. The ligand (*S*)-**3** was used only in the hydroformylation.

Rhodium(I) Complexes

The addition of an equimolar THF solution of **1** or (*S*)-**2** to a solution of $[Rh(COD)(THF)_2]CF_3SO_3$ {prepared in situ by treating $[Rh(COD)Cl]_2$ in THF solution with $AgCF_3SO_3$ in a 1:2 molar ratio and filtration of AgCl precipitate} affords a yellow solution. Addition of hexane leads to the compounds [Rh(COD)(**1**)]CF_3SO_3 (**4**) and [Rh(COD)(**2**)]CF_3SO_3 (**5**). They are yellow solids that are soluble in chlorinated solvents, acetone, benzene and methanol; conductivity measurements performed on methanol solutions of **4** or **5** ($5 \cdot 10^{-4}$ to 10^{-3} M) are in accordance with their formulation as 1:1 electrolytes. As expected, the $^{31}P\{^1H\}$ NMR spectrum of **4** (C_6D_6 solution) shows two doublets of doublets at $\delta = 162.29$ [$J(RhP') = 256.0$ Hz; $J(PP') = 37.0$ Hz] and $\delta = 63.89$ [$J_{RhP} = 148.0$ Hz; $J(PP') = 37.0$ Hz]. Analogously, compound **5** exhibits two doublets of doublets at $\delta = 167.0$ [$J(RhP') = 260.0$ Hz; $J(PP') = 41.3$ Hz] and $\delta = 64.77$ [$J_{RhP} = 149.0$ Hz; $J(PP') = 41.3$ Hz]. The signals at higher frequencies are due to the phosphite moiety.[3] Of interest is that the phosphorus−phosphorus coupling constant appears in the $^{31}P\{^1H\}$ NMR spectra of **4** and **5**, but was not observed in the free ligands **1** and (*S*)-**2**. In the complexes containing **1** and **2**, the rigidity of the five-membered ring formed by chelation of the ligand to the rhodium centre promotes the coupling between the phosphorus atoms that are now only separated by the metal atom.

The slow addition of a hexane solution of the ligand **1** to a solution of $[Rh(CO)_2Cl]_2$ in the same solvent, in a 1:2 molar ratio, affords a yellow precipitate; its $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ solution shows two signals as doublets of doublets of different intensity, centred at $\delta = 62.25$ [$J(RhP') = 195$ Hz, $J(PP') = 53.1$ Hz] and $\delta = 84.5$ [$J_{RhP} = 133.5$ Hz, $J(PP') = 49.1$ Hz] for the phosphane group and two signals as doublets of doublets, centred at $\delta = 163.76$ [$J(RhP') = 266.7$ Hz, $J_{P'P} = 49.1$ Hz] and 167.97 [$J(RhP') = 325.9$ Hz, $J_{P'P} = 53.1$ Hz] for the phosphite moiety. The IR spectrum of the solid in Nujol mull exhibits in the CO stretching region bands at 2001, 2008 and 2056 cm^{-1}. These spectroscopic data support the presence, in the crude product, of both the five-coordinated $[Rh(CO)_2$(**1**)Cl] (**6**) and tetra-coordinated [Rh(CO)(**1**)Cl] (**7**) species, containing ligand **1** as the chelate. When CO was bubbled for 10 min into a benzene solution of the yellow crude product, the $^{31}P\{^1H\}$ NMR spectrum only showed the signals centred at $\delta = 62.25$ and 167.97. In the IR spectrum of the solution the ν(CO) bands occur at 2056 and 2008 cm^{-1}. This supports the presence in solution, under these conditions, of only the five-coordinated species **6** (Scheme 1). When argon was bubbled into the benzene solution containing **6**, the tetracoordinated square-planar species **7** was almost quantitatively formed; the ν(CO) at 2001 cm^{-1} is a high wave number value for a neutral rhodium(I) species and supports a structure in which the CO ligand is in the *trans* position to the phosphite moiety of **1**, with the phosphite group having a greater *trans* influence than the phosphane one.



Scheme 1

The reaction of the ligand **1** with $[Rh(CO)_2Cl]_2$, in the molar ratio 2:1, was also undertaken in toluene solution; under these conditions the precipitate formed contained only the five-coordinated species **6**, while in solution both the tetra-coordinated **7** and five-coordinated species (the latter as minor product) were detected. By adding a solution of the ligand (*S*)-**2** in hexane dropwise to a solution of $[Rh(CO)_2Cl]_2$ in the same solvent, in a 2:1 molar ratio, a yellow precipitate was formed and the solution turned yellow. The solid, separated by filtration, on the basis of analytical data and spectroscopic properties, was formulated as the five-coordinated $[Rh(CO)_2$(**2**)Cl] (**8**).

In accordance, the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6 solution shows two signals as doublets of doublets at $\delta = 61.27$ [$J_{RhP} = 133$ Hz, $J(PP') = 49.1$ Hz] and $\delta = 177.34$ [$J(RhP') = 266.7$ Hz, $J_{P'P} = 49.1$ Hz] and the IR spectrum (Nujol) exhibits two bands in the ν(CO) stretching region at 1998 and 2064 cm^{-1}. A yellow solid was recovered from the mother liquor, the square-planar rhodium(I) species [Rh(CO)(**2**)Cl] (**9**). In accordance with its formulation the $^{31}P\{^{1}H\}$ NMR spectrum shows two signals as doublets of doublets at $\delta = 84.2$ [$J_{RhP} = 190$ Hz, $J(PP') = 54.2$ Hz] and $\delta = 170.75$ [$J(RhP') = 325$ Hz, $J_{P'P} = 54.2$ Hz] and the IR spectrum (Nujol) exhibits a ν(CO) band at 2003 cm^{-1}. The ν(CO) value results are high for a neutral square-planar rhodium(I) species and supports a structure in which the CO ligand is in the *trans* position to a group with a high *trans* influence, such as the phosphite group.

For compounds **6** and **8**, the high values of the ν(CO) allows a trigonal bipyramide structure containing the CO and Cl ligands in the *trans* position to be ruled out and supports a structure in which the phosphite moiety of **1** or (*S*)-**2** and CO occupy the axial positions. The ligands **1** and (*S*)-**2** assume an equatorial-axial coordination as expected if their natural bite angle is nearly 90°.[3a] Moreover, the presence of two ν(CO) bands allowed us to rule out structures with both the CO ligands in the equatorial position.

The reactions of [Rh(acac)$(CO)_2$] with the ligands **1** and (*S*)-**2** in hexane afforded the complexes [Rh(acac)(**1**)] (**10**) and [Rh(acac)(**2**)] (**11**) as yellow solids. Compound **11** was not obtained in a pure form owing to the presence of a very minor unidentified carbonyl product. However, the IR spectra indicate that the reactions occur by displacement of the CO ligands. The $^{31}P\{^{1}H\}$ NMR spectra of **10** and **11** show the phosphorus resonances as two doublets of doublets. The observed $J(PP')$ coupling value supports for **10** and **11** structures in which the ligands **1** and **2** are chelated to the rhodium atom.

Palladium(II) and Platinum(II) Complexes

The reactions of [Pd$(C_6H_5CN)_2Cl_2$] with **1** and (*S*)-**2** in toluene solution afford the corresponding compounds [Pd(**1**)Cl_2] (**12**) and [Pd(**2**)Cl_2] (**13**) as pale yellow crystals, soluble in acetone and chlorinated solvents and slightly soluble in benzene. As expected the $^{31}P\{^{1}H\}$ NMR spectra of **12** and **13** in $CDCl_3$ solution show the phosphorus resonances as doublets at very different δ values [138.2 and 74.88, $J(PP') = 23.7$ Hz for **12**; 134.48 and 74.71, $J(PP') = 25.0$ Hz for **13**]. The crystal structure of the chloroform solvate of **12** was fully characterized by an X-ray study.

The reactions of [Pt(COD)I_2] with **1** and (*S*)-**2** in toluene solution afford the compounds [Pt(**1**)I_2] (**14**) and [Pt(**2**)I_2] (**15**), respectively, as white solids that are stable in air. In the $^{31}P\{^{1}H\}$ NMR spectra of **14** and **15** in $CDCl_3$ solution the phosphorus resonances appear as singlets at higher fields than those of **12** and **13** along with peaks due to $^{195}Pt-P$ coupling.

Description of the Crystal Structure of [Pd(1)Cl_2]·$CHCl_3$ (12·$CHCl_3$)

Chloroform molecules of solvation were found in the crystals. A view of the structure of complex **12** together with the atomic numbering system is shown in Figure 1. Selected bond lengths and angles are given in Table 1.

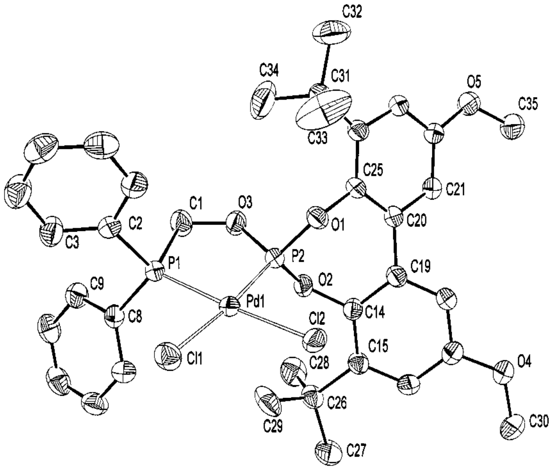


Figure 1. View of the molecular structure of complex **12** with the atomic numbering system; the ellipsoids are drawn at the 30% probability level

Table 1. Selected bond lengths [Å] and angles [°] for **12**·$CHCl_3$

Bond lengths	
Pd(1)−P(2) 2.192(1)	P(1)−C(1) 1.863(6)
Pd(1)−P(1) 2.227(1)	O(1)−C(25) 1.404(6)
Pd(1)−Cl(1) 2.341(2)	O(2)−C(14) 1.404(6)
Pd(1)−Cl(2) 2.354(1)	O(3)−C(1) 1.384(7)
O(1)−P(2) 1.573(4)	C(14)−C(19) 1.391(7)
O(2)−P(2) 1.585(4)	C(19)−C(20) 1.501(7)
O(3)−P(2) 1.590(4)	C(20)−C(25) 1.394(7)
Bond angles	
P(2)−Pd(1)−P(1) 85.95(5)	O(1)−P(2)−O(2) 106.3(2)
P(2)−Pd(1)−Cl(1) 173.39(5)	O(1)−P(2)−O(3) 107.3(2)
P(1)−Pd(1)−Cl(1) 87.47(6)	O(2)−P(2)−O(3) 96.2(2)
P(2)−Pd(1)−Cl(2) 90.87(6)	O(3)−C(1)−P(1) 113.4(4)
P(1)−Pd(1)−Cl(2) 176.43(5)	C(19)−C(14)−O(2) 117.8(5)
Cl(1)−Pd(1)−Cl(2) 95.69(6)	C(14)−C(19)−C(20) 124.1(5)
C(1)−O(3)−P(2) 122.9(4)	C(25)−C(20)−C(19) 124.1(5)
C(1)−P(1)−Pd(1) 105.8(2)	C(20)−C(25)−O(1) 118.2(4)
O(3)−P(2)−Pd(1) 111.6(1)	

The metal ion is square-planarly coordinated by two Cl atoms and two P atoms from the phosphane−phosphite chelating ligand **1** [maximum deviation from the mean plane through the five atoms 0.026(1) Å for Cl2]. The five-membered Pd1P1C1O3P2 ring [the P1−Pd1−P2 bite angle is 85.95(5)°] is roughly planar with only the Pd1 atom being significantly displaced from the mean plane [0.114(1) Å]. The two Pd1−P1 and Pd1−P2 bond lengths [2.227(1) and 2.192(1) Å] are comparable, as well as the two Pd1−Cl1 and Pd1−Cl2 ones [2.341(2) and 2.354(1) Å], as expected. The P and the N atoms are in the *trans* position.

In ligand **1** the P−O bond lengths are practically equal, in the range 1.573(4)−1.590(4) Å, whereas the O−P−O angles are in the range 96.2(2)−107.3(2)°. In the diphenyl moiety the C14−C19−C20−C25 torsion angle is +47.1(1)° with a C19−C20 bond length of 1.501(7) Å.

Catalysis

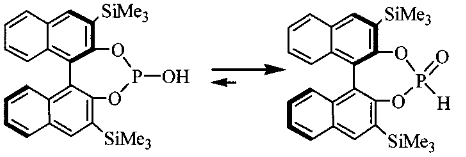
The catalytic systems formed by [Rh(acac)(CO)$_2$] and ligands (*S*)-**2** and (*S*)-**3** at variable ligand/metal ratios were used in the hydroformylation of styrene: The catalytic runs were carried out in benzene solution using an equimolar hydrogen/carbon monoxide mixture. The catalytic system with ligand (*S*)-**3** turned out to be the most efficient. Indeed, almost quantitative conversion ($>$ 99%) of styrene could be attained within 66 h at 100 atm and 40 °C with a 1:4 Rh/ligand molar ratio. Also the chemo- and regioselectivity results are very high with the linear (L) and branched (B) aldehydes being about 99.9% of the reaction products with a B/L ratio of 32.3. Under these experimental conditions only a 20% *ee* of the branched aldehyde in the (*S*) form was obtained. No influence of the ligand/Rh ratio on the enantioselectivity was found. The stability of the catalytic system [Rh(acac)(CO)$_2$]/(*S*)-**2** was very low under the same experimental conditions.

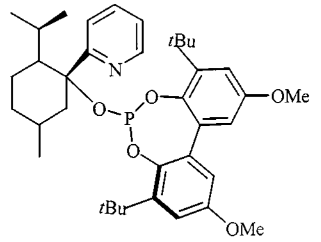
The poor hydroformylation results are surprising in view of the high enantioselectivity reached by catalytic rhodium systems containing chiral diphosphites[2f] or phosphane−phosphite[3] mixed ligands in the styrene hydroformylation. However, in the literature examples of catalytic rhodium systems containing good ligands affording high conversion and chemo- and regioselectivity, but low or zero values of enantioselectivity from the styrene hydroformylation, have been reported.[7] Generally, these situations have been found when the chelate ligand is not strongly bonded to the rhodium centre. Thus, under elevated CO/H$_2$ pressure displacement of the chelate ligand by CO can take place to give [RhH(CO)$_4$] or [RhH(CO)$_3$L] (L = bidentate ligand acting as monodentate) as the catalytic species.[8] The use of a high ligand/Rh ratio can also modify the hydride−rhodium catalyst affording species containing two bidentate ligands which are monodentate or bridging (in a binuclear species) coordinated.

We attempted to obtain information about the catalytic system on leaving [Rh(acac){(*S*)-**3**}] to stand for36 h under CO/H$_2$ of 50 atm at 40 °C in C_6D_6. The resulting solution, transferred under H$_2$/CO to an NMR tube showed two doublets centred at δ = 120.1 (J_{RhP} = 193.6 Hz) and at δ = 11.7 in the ^{31}P{^{1}H} NMR spectrum along with some signals of low intensity in the δ = 12−18 region due to the presence of phosphane oxide.

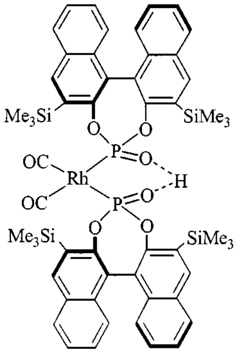
The lack of the phosphorus−phosphorus coupling in the signal at δ = 120.1 supports the presence of a monodentate ligand coordinated to the rhodium(I) centre; the shift in the δ value from 169.7 as dd, to 120.1 is indicative of a modification at the phosphite group. Moreover the ^{31}P NMR ^{1}H-coupled spectrum showed the signal at δ = 11.7 as a doublet; the J_{PH} value of 729 Hz and the chemical shift values support the presence of a P−H bond of a phosphonate group.[9] This can be formed by hydrolysis of the ligand (*S*)-**3** in a tautomeric equilibrium, shifted towards the phosphonate, with the corresponding phosphite form. A similar process[9] was observed by hydrolysis of phosphite **15**.

Thus, considering the spectroscopic data and our previously reported results,[9] coordination of the hydrolysis product to the rhodium ion could occur in both phosphite and phosphonate forms affording a rhodium−phosphonate complex. This is further supported by the presence of the phosphorus signal at δ = 120.1 (J_{RhP} = 205 Hz) and of two ν(CO) bands at 2095 and 2050 cm^{-1}. We suggest that species **16** is prevalent in solution. This species can participate in a catalytic process affording the aldehydes but, since only monodentate ligands are present in the catalyst, it cannot bring about an asymmetric induction.





15



16

Experimental Section

General: All reagents were purchased and used as supplied. Solvents were dried by standard procedures. All experiments were performed under purified nitrogen. IR spectra were obtained as Nujol mulls on KBr plates using a Perkin−Elmer FT-IR 1720 spectrophotometer. ^{1}H, and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker AMX R300. ^{1}H NMR spectra were referenced to internal tetramethylsilane and ^{31}P{^{1}H} spectra to external 85% H_3PO_4; positive chemical shifts for all nuclei are at higher frequencies. Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

[Rh(COD)(1)]CF$_3$SO$_3$ (4): Solid AgCF$_3$SO$_3$ (0.063 g, 0.249 mmol) was added to a stirred solution of [Rh(COD)Cl$_2$]$_2$ (0.061 g, 0.124 mmol) in tetrahydrofuran (10 mL). After 10 min, the precipitate of AgCl was separated by filtration and ligand **1** (0.149 g, 0.248 mmol) was added to the filtrate. The yellow-orange solution was stirred for 30 min and was then reduced to ca. 2 mL. On addition of 30 mL of hexane a yellow solid separated. It was removed by filtration, washed with hexane and vacuum-dried. Yield 85% (0.203 g, 0.211 mmol). $C_{44}H_{52}F_3O_8P_2RhS$ (962.8): calcd. C 54.89, H 5.44; found C 54.78, H 5.37. ^1H NMR ($CDCl_3$): δ = 1.58 [s, 18 H, $C(CH_3)_3$], 3.44 (s, 6 H, OCH_3), 4.35 [d, 2 H, $J_{P'H}$ = 22.4, CH_2], 5.35 (br. s, 2 H, CH), 5.62 (br. s, 2 H, CH), 6.76 [d, 2 H, J = 3.0 Hz, CH], 7.10 [d, 2 H, J = 3.0 Hz, CH], 7.25−7.62 (m, 10 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 162.29 [dd, $J(RhP')$ = 256 Hz, $J_{P'P}$ = 37 Hz], 63.89 [dd, J_{RhP} = 148 Hz, $J(PP')$ = 37 Hz].

[Rh(COD)(2)]CF$_3$SO$_3$ (5): The yellow compound **5** was prepared from $[Rh(COD)Cl_2]_2$ (0.070 g, 0.142 mmol) and the ligand (*S*)-**2** (0.154 g, 0.284 mmol) as described above for the compound **4**. Yield 80% (0.202 g, 0.227 mmol). $C_{42}H_{36}F_3O_6P_2RhS$ (890.6): calcd. C 56.64, H 4.07; found C 56.49, H 4.15. ^1H NMR ($CDCl_3$): δ = 4.30 [d, 2 H, $J_{P'H}$ = 21, CH_2], 5.30 (br. s, 2 H, CH), 5.59 (br. s, 1 H, CH), 6.76 [d, 2 H, J = 3 Hz, CH], 7.01−7.95 (m, 22 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 167 [dd, $J(RhP')$ = 260 Hz, $J_{P'P}$ = 41.3 Hz], 64.77 [dd, J_{RhP} = 149 Hz, $J(PP')$ = 41.3 Hz].

[Rh(CO)$_2$(1)Cl] (6) and [Rh(CO)(1)Cl] (7): To a stirred solution of $[Rh(CO)_2Cl]_2$ (0.080 g, 0.205 mmol) in hexane (30 mL) was added ligand **1** (0.247 g, 0.41 mmol). Immediately a yellow solid, containing both the products [Rh(CO)$_2$(**1**)Cl] and [Rh(CO)(**1**)Cl], precipitated. The solid was filtered, washed with hexane, and dried. Attempts to separate compounds **6** and **7** failed. Data for **7**: IR (KBr, Nujol): ν_{CO} = 2001 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.65 [s, 18 H, $C(CH_3)_3$], 3.27 (s, 6 H, OCH_3), 4.12 [d, 2 H, $J_{P'H}$ = 20 Hz, CH_2], 6.67 [d, 2 H, J = 3.0 Hz, CH], 7.05 (m, 2 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 163.76 [dd, $J(RhP')$ = 266.7 Hz, $J_{P'P}$ = 49.1], 84.5 [dd, J_{RhP} = 133.5 Hz, $J(PP')$ = 49.1 Hz].

[Rh(CO)$_2$(1)Cl] (6): Compound **6** was obtained by the following procedure: To a stirred solution of $[Rh(CO)_2Cl]_2$ (0.040 g, 0.103 mmol) in toluene (10 mL) was added dropwise a solution of **1** (0.124 g, 0.206 mmol) in the same solvent (2 mL). A yellow precipitate was deposited during the course of the addition. This was collected, washed with toluene (1 mL) and hexane, and then dried. Yield 87% (0.143 g, 0.179 mmol). $C_{37}H_{40}ClO_7P_2Rh$ (797.0): calcd. C 55.76, H 5.06, Cl 4.45; found C 55.69, H 5.10, Cl 4.39. IR (KBr, Nujol): ν_{CO} = 2033, 2072 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.49 [s, 18 H, $C(CH_3)_3$], 3.30 (s, 6 H, OCH_3), 4.24 [d, 2 H, $J(PH)$ = 20 Hz, CH_2], 6.71 [d, 2 H, J = 3.0 Hz, CH], 7.09 [d, 2 H, J = 3.0 Hz, CH], 7.83−7.90 (m, 10 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 167.97 [dd, $J(RhP')$ = 325.9 Hz, $J_{P'P}$ = 53.1 Hz], 62.25 [dd, J_{RhP} = 195 Hz, $J(PP')$ = 53.1 Hz].

[Rh(CO)$_2$(2)Cl] (8) and [Rh(CO)(2)Cl] (9): A solution of ligand **2** (0.318 g, 0.6 mmol) in toluene (6 mL) was added dropwise to a stirred solution of $[Rh(CO)_2Cl]_2$ (0.120 g, 0.3 mmol) in hexane (30 mL). A yellow solid immediately precipitated. This was collected washed with toluene (1 × 1 mL) and hexane, and then dried. By IR and NMR spectroscopy the yellow solid was identified as [Rh(CO)$_2$(2)Cl] (**8**). Data of **8**: $C_{35}H_{24}ClO_5P_2Rh$ (724.8): calcd. C 57.99, H 3.34, Cl, 4.89; found C 57.78, H 3.29, Cl 4.93. IR (KBr, Nujol): ν_{CO} = 1995, 2064 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.24 [d, 2 H, $J_{P'H}$ = 21 Hz, CH_2], 7.65−7.95 (m, 22 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 177.34 [dd, $J(RhP')$ = 266.7 Hz, $J_{P'P}$ = 49.1 Hz], 61.27 [dd, J_{RhP} = 133 Hz, $J(PP')$ = 49.1 Hz]. Compound **9** was recovered, as a yellow powder, from the mother liquor by addition of hexane. Data of **9**: $C_{34}H_{24}ClO_4P_2Rh$ (708.9): calcd. C 58.60, H 3.47, Cl 5.09; found C 58.71, H 3.51; Cl 5.02. IR (KBr, Nujol): ν_{CO} = 2003 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 4.20 [d, 2 H, $J_{P'H}$ = 21 Hz, CH_2], 7.62−7.94 (m, 22 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 170.75 [dd, $J(RhP')$ = 325 Hz, $J_{P'P}$ = 54.2 Hz], 84.2 [dd, J_{RhP} = 190 Hz, $J(PP')$ = 54.2 Hz].

[Rh(acac)(1)] (10): A stirred solution of [Rh(acac)(CO)$_2$] (0.050 g, 0.194 mmol) in hexane (15 mL) was added dropwise to a solution of **1** (0.117 g, 0.194 mmol) in the same solvent (10 mL). During the addition, a colour change from yellow to orange was observed. Monitoring the reaction by IR spectroscopy, a gradual disappearance of starting ν_{CO} bands was observed. After ca. 1 h, the solvent was removed to give an orange solid. It was washed twice with hexane and vacuum-dried. Yield 85% (0.133 g, 0.165 mmol). $C_{40}H_{47}O_7P_2Rh$ (801.7): C 59.71, H 5.89; found C 60.03, H 5.94. ^1H NMR (C_6D_6): δ = 1.25 (s, 3 H, acac-CH_3), 1.39 [s, 18 H, $C(CH_3)_3$], 1.60 (s, 3 H, acac-CH_3), 3.29 (s, 6 H, OCH_3), 4.22 (d, 2 H, $J_{P'H}$ = 20 Hz, CH_2), 5.03 (s, 1 H, acac-H), 6.61 (d, 2 H, J = 3.0 Hz, CH), 6.82 (d, 2 H, J = 3.0 Hz, CH), 7.04−7.99 (m, 10 H, CH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 168.1 [dd, $J(RhP')$ = 308 Hz, $J_{P'P}$ = 77 Hz], 78.8 [dd, J_{RhP} = 188 Hz, $J(PP')$ = 77 Hz].

[Rh(acac)(2)] (11): This compound was obtained by an analogous procedure to **10** as yellow solid starting from [Rh(acac)(CO)$_2$] (0.080 g, 0.310 mmol) and **2** (0.164 g, 0.310 mmol). Yield 80% (0.182 g, 0.248 mmol). $C_{38}H_{31}O_5P_2Rh$ (732.5): C 62.31, H 4.27; found C 62.81, H 4.29. ^1H NMR (C_6D_6): δ = 1.60 (s, 3 H, acac-CH_3), 4.22 [d, 2 H, $J_{P'H}$ = 20 Hz, CH_2], 5.03 (s, 1 H, acac-H), 7.04−7.99 (m, 10 H, CH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 168.1 [dd, $J(RhP')$ = 308 Hz, $J_{P'P}$ = 77 Hz], 78.8 [dd, J_{RhP} = 188 Hz, $J(PP')$ = 77 Hz].

[Pd(1)Cl$_2$] (12): Solid ligand **1** (0.094 g, 0.156 mmol) was added to a stirred solution of [Pd(PhCN)$_2$Cl$_2$] (0.060 g, 0.156 mmol) in toluene (10 mL). The resulting solution was stirred for ca. 30 min during which a colour change from red-orange to pale yellow occurred. The solution was reduced in volume (5 mL), and upon addition of hexane, compound **12** separated as a yellow solid. This was removed by filtration, washed with hexane and vacuum-dried. Yield 88% (0.107 g, 0.137 mmol). $C_{35}H_{40}Cl_2O_5P_2Pd$ (779.9): C 53.90, H 5.17, Cl 9.09; found C 53.65, H 5.22, Cl 9.23. ^1H NMR ($CDCl_3$): δ = 1.39 [s, 18 H, $C(CH_3)_3$], 3.81 (s, 6 H, OCH_3), 4.60 [dd, 2 H, $J_{P'H}$ = 26 Hz, $J(PH)$ = 1 Hz, CH_2], 6.71 [d, 2 H, J = 3.0 Hz, CH], 6.99 [d, 2 H, J = 3.0 Hz, CH], 7.55−7.90 (m, 10 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 138.2 [d, $J_{P'P}$ = 23.7 Hz], 74.88 [d, $J_{P'P}$ = 23.7 Hz].

[Pd(2)Cl$_2$] (13): This compound was obtained similarly to **12** as a yellow-orange solid by starting from [Pd(PhCN)$_2$Cl$_2$] (0.070 g, 0.182 mmol) and ligand **2** (0.096 g, 0.182 mmol). Yield 83% (0.107 g, 0.151 mmol). $C_{33}H_{24}Cl_2O_3P_2Pd$ (707.8): C 56.00, H 3.42, Cl, 10.02; found C 56.15, H 3.46, Cl 10.16. ^1H NMR ($CDCl_3$): δ = 4.45 (m, 1 H, CH_2), 4.71 (m, 1 H, CH_2), 7.0−7.96 (m, 22 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 144.4 [d, $J_{P'P}$ = 25 Hz], 74.71 [d, $J_{P'P}$ = 25 Hz].

[Pt(1)I$_2$] (14): Solid ligand **1** (0.064 g, 0.107 mmol) was added to a stirred solution of [Pt(COD)I$_2$] (0.060 g, 0.107 mmol) in toluene (10 mL). Upon addition of **1** a white solid precipitated. This was removed by filtration, washed with toluene and hexane, and then vacuum-dried. Yield 90% (0.101 g, 0.096 mmol). $C_{35}H_{40}I_2O_5P_2Pt$ (1051): C 39.98, H 3.83, I 24.14; found C 39.89, H 3.87, I 24.20. ^1H NMR ($CDCl_3$): δ = 1.37 [s, 18 H, $C(CH_3)_3$], 3.82 (s, 6 H, OCH_3), 4.48 [dd, 2 H, $J_{P'H}$ = 22 Hz, $J(PH)$ = 1 Hz, CH_2], 6.73 [d, 2 H, J = 3.0 Hz, CH], 6.99 [d, 2 H, J = 3.0 Hz, CH], 7.65−7.99 (m, 10 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 123 [s, $J(PtP')$ = 5682 Hz], 52.28 [d, J_{PtP} = 3180 Hz].

[Pt(2)I$_2$] (15): This compound was obtained similarly to **14** as a yellow-orange solid by starting from [Pt(COD)I$_2$] (0.100 g, 0.178 mmol) and ligand **2** (0.095 g, 0.178 mmol).Yield 89% (0.155 g, 0.158 mmol). $C_{33}H_{24}I_2O_3P_2Pt$ (979.4): C 40.47, H 2.47, I 25.92; found C 40.52, H 2.49, I 25.85. ^1H NMR ($CDCl_3$): δ = 4.37 (m, 1 H, CH_2), 4.55 (m, 1 H, CH_2), 7.1−7.95 (m, 22 H, CH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 128.42 [s, $J(PtP')$ = 5621 Hz], 54.26 [d, J_{PtP} = 3180 Hz].

Crystal Structure Determination of [Pd(1)Cl$_2$]·CHCl$_3$ (12·CHCl$_3$): The intensity data of the complex was collected at room temperature with an Enraf Nonius CAD 4 single-crystal diffractometer using a graphite-monochromated Cu-K_α radiation and the θ/2θ scan technique. Crystallographic and experimental details for the structure are summarized in Table 2. A correction for absorption was made for the complex [maximum/minimum value for the transmission coefficient was 1.000/0.677].[10] The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. In the final cycles of refinement a weighting scheme $w = 1/[\sigma^2 F_o^2 + (0.1416\,P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$, was used. All calculations were carried out with the DIGITAL AlphaStation 255 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, using the SHELX-97 systems of crystallographic computer programs.[11] Details of the crystal structure investigations are deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-166947. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

Table 2. Crystal data and structure refinement for **12**·CHCl$_3$; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Empirical formula	$C_{35}H_{40}Cl_2O_5P_2Pd \cdot CHCl_3$
Formula mass	899.28
Wavelength	1.54184 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 13.474(4) Å b = 14.214(5) Å c = 10.424(3) Å α = 93.79(3)° β = 91.45(2)° γ = 97.27(3)°
V	1974.9(11) Å^3
Z	4
Density (calculated)	1.512 Mg/m^3
Absorption coefficient	79.95 cm^{-1}
F(000)	916
Crystal size	0.21 × 0.27 × 0.39 mm
θ range [°]	3−70
Index ranges	$-16 \le h \le 16$, $-17 \le k \le 17$, $0 \le l \le 12$
Reflections collected	7415
Independent reflections	7415 [R(int) = 0.0]
Observed reflections [$I > 2\sigma(I)$]	5953
Data/restraints/parameter	7415/0/451
Goodness-of-fit on F^2	1.067
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0567, $wR2$ = 0.1777
R indices (all data)	$R1$ = 0.0676, $wR2$ = 0.1969

Hydroformylation Procedure: The air was evacuated from a 30-mL stainless steel autoclave and a benzene solution of [Rh(acac)(CO)$_2$], the ligand and the olefin were introduced by suction. The vessel was pressurised with CO/H$_2$ (1:1) at the required pressure at room temperature and thermostated. The conversion and the composition of the reaction products were determined by GLC with a Carlo Erba HRGC 5160 Mega Series apparatus (split/splitless injector, MEGA OV1 25-m column, film thickness 2 μm, carrier gas He, flame ionization detector). The enantiomeric excess was determined by the shift reagent Eu(hfc)$_3$.[12]

Acknowledgments

We thank MURST for financial support.

---

[1] [1a] *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Two Volumes* (Eds.: B. Cornils, W. A. Herrmann), VCH, New York, **1996**. [1b] G. W. Parshall in *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition-metal Complexes*, Wiley and Sons, New York, **1980**. [1c] *Catalytic Asymmetric Synthesis* (Ed: I. Ojima), VCH, Weinheim, **1995**. [1d]R. Noyori in *Asymmetric Catalysis in Organic Synthesis*, Wiley-Interscience Publications, New York, **1994**.

[2] [2a] C. P. Casey, G. T. Whiteker, M. G. Melville, L. M. Petrovich, J. A. Gavney, D. R. Powell, *J. Am. Chem. Soc.* **1992**, *114*, 5535. [2b] P. C. J. Kamer, J. N. H. Reek, P. W. N. M. van Leeuwen, *Chemtech* **1998**, *28*(9), 27 and references therein. [2c] G. Zhu, X. Zhang, *J. Org. Chem.* **1998**, *63*, 3133. [2d] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062. [2e] S. Cserépi, J. Bakos, *Chem. Commun.* **1997**, 635. [2f] G. J. H. Buisman, L. A. van der Veen, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **1997**, *16*, 5681 and references therein. [2g] A. von Rooy, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, N. Veldman, A. L. Spek, *Organometallics* **1996**, *15*, 835 and references therein. [2h] A. Togni, L. M. Venanzi, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 497. [2i] K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Gorls, M. Kessler, C. Kruger, W. Leitner, F. Lutz, *Chem. Eur. J.* **1997**, *3*, 755. [2l] B. M. Trost, B. Breit, S. Peukert, J. Zambrano, J. W. Ziller, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2386. [2m] M. P. T. Sjogren, S. Hansson, B. Akermark, A. Vitagliano, *Organometallics* **1994**, *13*, 1963. [2n] B. M. Trost, D. J. Murphy, *Organometallics* **1985**, *4*, 1143. [2o] P. W. N. M. van Leeuwen, G. J. H. Buisman, A. von Rooy, P. C. J. Kamer, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 61.

[3] [3a] N. Sakai, S. Mano, K. Nozaki, H. Takaya, *J. Am. Chem. Soc.* **1993**, *115*, 7033. [3b] N. Sakai, K. Nozaki, H. Takaya, *J. Chem. Soc., Chem. Commun.* **1994**, 395. [3c] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, *J. Am. Chem. Soc.* **1997**, *119*, 4413.

[4] G. Franciò, F. Faraone, W. Leitner, *Angew. Chem. Int. Ed.* **2000**, *39*, 1428.

[5] C. G. Arena, D. Drommi, F. Faraone, *Tetrahedron: Asymmetry* **2000**, *11*, 2765.

[6] H. Helmann, J. Badu, H. Birkner, O. Schumacher, *Justus Liebigs Ann. Chem.* **1962**, *659*, 49.

[7] See for example: Z. Freisa, M. N. Pereira, A. C. Pais, J. C. Bayon, *J. Chem. Soc., Dalton Trans.* **1999**, 3245.

[8] R. Lazzaroni, R. Settambolo, G. Uccello-Baretta, *Organometallics* **1995**, *14*, 4644 and refs. therein.

[9] C. G. Arena, F. Nicolò, D. Drommi, G. Bruno, F. Faraone, *J. Chem. Soc., Dalton Trans.* **1996**, 4357.

[10] [10a] N. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158. [10b] F. Ugozzoli, *Comput. Chem.* **1987**, *11*, 109.

[11] G. M. Sheldrick, *SHELX-97, Program for the Solution and the refinement of Crystal Structures*, Universität Göttingen, Germany, **1997**.

[12] G. Parrinello, J. K. Stille, *J. Am. Chem. Soc.* **1987**, *109*, 7122.

Received July 18, 2001
[I01266]