Chiral Phosphoramidite Ligands Based on 8-Chloroquinoline and Their Rhodium(III), Palladium(II), and Platinum(II) Complexes

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Keywords: Phosphoramidite / Chiral ligands / Platinum / Rhodium

The new chiral ligands 2-butyl-8-chloro-1-(4,8-di-*tert*-butyl-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)-1,2-dihydroquinoline (BIPHENPHOSHQUIN, **3**) and 2-butyl-8-chloro-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]-dinaphthalen-4-yl)-1,2-dihydroquinoline (BINAPHOSHQUIN, **4**; **4a**: S_aR_C, **4b**: S_aS_C) have been synthesized starting from the rigid backbone of 8-chloroquinoline. The reactions of **3** and **4** with rhodium(I), palladium(II), and platinum(II) substrates are reported. The reaction of **3** with $[Rh(CO)_2Cl]_2$ in a 2:1 molar ratio in hexane afforded a binuclear chloro-bridged rhodium(III) species by intramolecular oxidative addition of the C–Cl bond of ligand **3** across the rhodium(I) centers. The rhodium(III) complex **5**, incorporating the enantiomers S_aR_C-**3** and R_aS_C-**3**, has been fully characterized by X-ray diffractometry. Reactions of $[Pd(PhCN)_2Cl_2]$ with the ligands **3** and **4a** in 1:2 molar ratio in toluene afforded the products *cis*-$[Pd(\mathbf{3})_2Cl_2]$ (**9**) and *cis*-$[Pd(\mathbf{4a})_2Cl_2]$ (**10**). Similarly, reaction of $[Pt(COD)I_2]$ with **4a** in a 1:2 molar ratio afforded the complex *cis*-$[Pt(\mathbf{4a})_2I_2]$ (**11**). An X-ray analysis has been carried out to obtain information on the effect of the ligand **4a** on the overall structure of **11**.

Introduction

Recently, much attention has been focused on the development of chiral ligand-modified catalysts for application in asymmetric synthesis.[1] Attempts have been made to correlate structural and electronic characteristics of the coordinated ligands with the catalytic activities of the resulting metal complexes. The structural features of the ligands, such as the "natural bite angle",[2] the rigidity, and the presence of bulky substituents, drastically influence the chemo- and regioselectivity of the catalytic process.[3] Recent contributions[4] have shown that diphosphites or a mixed phosphane/phosphite containing a chiral bridging moiety are efficient ligands in the rhodium-catalyzed asymmetric hydroformylation of olefinic substrates. Several mono- and bidentate phosphane ligands have been prepared starting from molecules with rigid polyaromatic backbones.[5] Their abilities in determining unusual geometries when coordinated to a metal center are of great interest.

The present work stems from our interest in developing large chiral mono- and bidentate ligands starting from the rigid backbone of quinolines, and to study the properties of their d^8-metal complexes, particularly in homogeneous catalysis. We report here the synthesis of large chiral monodentate phosphoramidites, and of their rhodium(III), palladium(II), and platinum(II) complexes, together with the X-ray structures of some representative compounds of this series. Recently,[6] phosphoramidite ligands have been used in homogeneous catalysis. Several metal complexes incorporating ligands based on quinolines, such as 8-(dimethylphosphanyl)quinoline, 8-(dimethylarsanyl)quinoline, 8-(diphenylphosphanyl)quinoline, 8-(diphenylarsanyl)quinoline, bis(6-methylquinolin-8-yl)phenylarsane, tris(6-methylquinolin-8-yl)phenylarsane, (*R*)- and (*S*)-methylphenyl(8-quinolyl)phosphane, and (*R*)- and (*S*)-methylphenyl(8-quinolyl)-arsane, have previously been reported.[7] Application of ligands **3** and **4** in copper-catalyzed enantioselective Michael addition will soon be reported.[8]

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Results and Discussion

Synthesis of the Ligands

Reaction of 8-chloroquinoline with *n*BuLi[9] in a 1:1 molar ratio in tetrahydrofuran at −78 °C involves addition of the butyl group to the carbon atom in the 2-position and lithiation of the nitrogen atom. Consequently, the ring containing the nitrogen atom loses its aromaticity and the carbon atom in the 2-position becomes a stereogenic center. Addition of an excess of neat PCl_3 to the THF solution of anion **1** affords, after removal of the unreacted PCl_3 under reduced pressure, compound **2** (Scheme 1). Subsequent treatment of a solution of **2** in toluene at 0 °C with equimolar amounts of 3,3′-di-*tert*-butyl-2,2′-dihydroxy-5,5′-dimethoxybiphenyl and NEt_3 affords the ligand 2-butyl-8-chloro-1-(4,8-di-*tert*-butyl-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)-1,2-dihydroquinoline (BIPHENPHOSHQUIN, **3**) (Scheme 1).

Compound **3** was also obtained by treating 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo-

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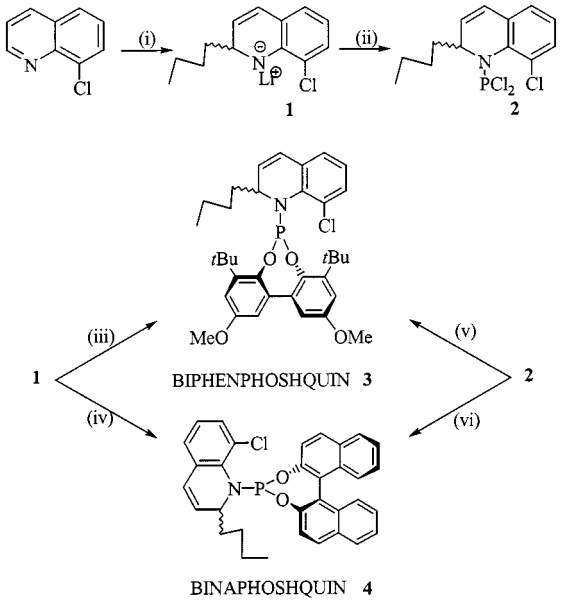


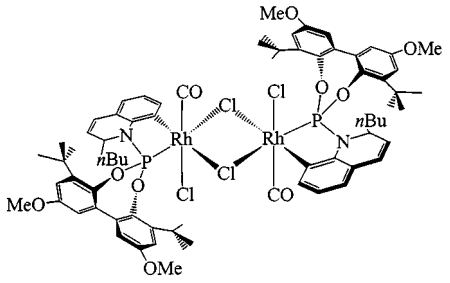
Scheme 1. (i) thf, −78°C, BuLi; (ii) thf, −78°C, PCl_3; (iii) thf, −78°C, 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene; (iv) thf, −78°C, (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene; (v) toluene, 0°C, Et_3N, 3,3′-di-*tert*-butyl-2,2′-dihydroxy-5,5′-dimethoxybiphenyl; (vi) toluene, 0°C, Et_3N, (*S*)-2,2′-dihydroxybinaphthyl

[*a*,*c*]cycloheptene with the anion **1** in THF solution. Because of the atropoisomerism of the biphenyl moiety and the presence of a stereogenic carbon atom, compound **3** may be obtained as a racemic mixture of two diastereoisomers [(S_aR_C), (R_aS_C), (S_aS_C), and (R_aR_C)]. The $^{31}P\{^1H\}$-NMR spectra in CD_2Cl_2 solution at 293 K and 193 K show a singlet at δ = 141.1 and are consistent with either the presence of only one of the two possible enantiomeric pairs, or with rapid atropoisomerization of the biphenyl moiety on the NMR time scale. In some cases, $^{31}P\{^1H\}$-NMR spectroscopy does not allow a distinction of species present in solution.[10] In the ^1H-NMR spectrum in $CDCl_3$, the *tert*-butyl groups display two different chemical shifts due to their diastereotopicity.

The ligand 2-butyl-8-chloro-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-1,2-dihydroquinoline (BINAPHOSHQUIN, **4**) was similarly obtained either by addition of the enantiomer (S_a)-(−)-2,2′-dihydroxy-1,1′-binaphthyl in toluene to a solution of **2** in the same solvent, or by addition of (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene in THF to a solution of the anion **1** in the same solvent (Scheme 1). An improved procedure[4a] was utilized for the synthesis of (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (see Experimental Section). Compound **4** was found to be moisture-sensitive and was obtained as a mixture of the two diastereoisomers [(S_aR_C)and (S_aS_C)]. Thus, the $^{31}P\{^1H\}$-NMR spectrum in $CDCl_3$ solution shows two peaks at δ = 137.6 and 145.1, while in the ^1H-NMR spectrum two sets of signals are seen. The synthesis method had an effect on the diastereoisomer ratio. Starting from **2**, the diastereoisomers were formed in a 50:50 ratio, whereas starting from the anion **1** an excess (70:30) of the (S_aS_C) diastereoisomer was obtained. The (S_aR_C) and (S_aS_C) diastereoisomers (**4a** and **4b**, respectively) could be separated as white solids by virtue of their different solubilities in hexane and were characterized by microanalysis and spectroscopic data. By comparison with the structure of *cis*-[Pt(**4a**)$_2$I$_2$] (**11**) (see below), it can be inferred that the diastereomer exhibiting a $^{31}P\{^1H\}$-NMR resonance at δ = 137.6 has the absolute configuration (S_aR_C).

Syntheses of the Complexes

We treated the ligands **3** and **4** with rhodium(I), palladium(II), and platinum(II) precursors. Addition of a hexane solution of ligand **3** to $[Rh(CO)_2Cl]_2$ in the same solvent in a 2:1 molar ratio afforded a yellow solid, which was recrystallized from CH_2Cl_2/hexane. The air-stable product **5** proved to be non-conducting in benzene solution and its structure was fully elucidated by an X-ray analysis of crystals of its hexane solvate (see below).



5

The IR spectrum (Nujol mull) of **5** shows a ν(CO) band at 2112 cm^{-1}, consistent with an oxidative process on the starting rhodium(I) center. It is noteworthy that the ^1H-NMR spectrum in $CDCl_3$ solution features two signals with very different shifts (δ = 1.75 and 1.08) due to the *tert*-butyl groups; a slight difference in the methoxy group resonances is also observed (δ = 3.86 and 3.87). The $^{31}P\{^1H\}$-NMR spectrum in $CDCl_3$ solution shows a single resonance at δ = 127.7 (J_{RhP} = 197 Hz).

In the crystals of **5** · 2 C_6H_{14}, dimeric rhodium(III) complexes, having an imposed C_i symmetry, are present, together with disordered molecules of hexane. A view of the dimer showing the atomic numbering system is presented in Figure 1. Selected bond lengths and angles are given in Table 1. Two Cl atoms bridge the two rhodium atoms in an asymmetric manner.

The metal has an octahedral coordination sphere, involving three Cl atoms (two bridging and one terminal), a carbonyl group, and the P1 and C3 atoms of the chelating ligand, derived from oxidative addition of **3**. The five-membered Rh−P1−N1−C2−C3 chelating ring is approximately planar. The Rh−Cl2 bond length, 2.328(4) Å, is much shorter than those involving the bridging Cl1 and Cl1′ atoms, which amount to 2.454(4) and 2.536(4) Å. In accordance with the *trans* influence, the Rh−Cl1 bond length (Cl1 *trans* to P1) is shorter than the Rh−Cl1′ bond length (Cl1′

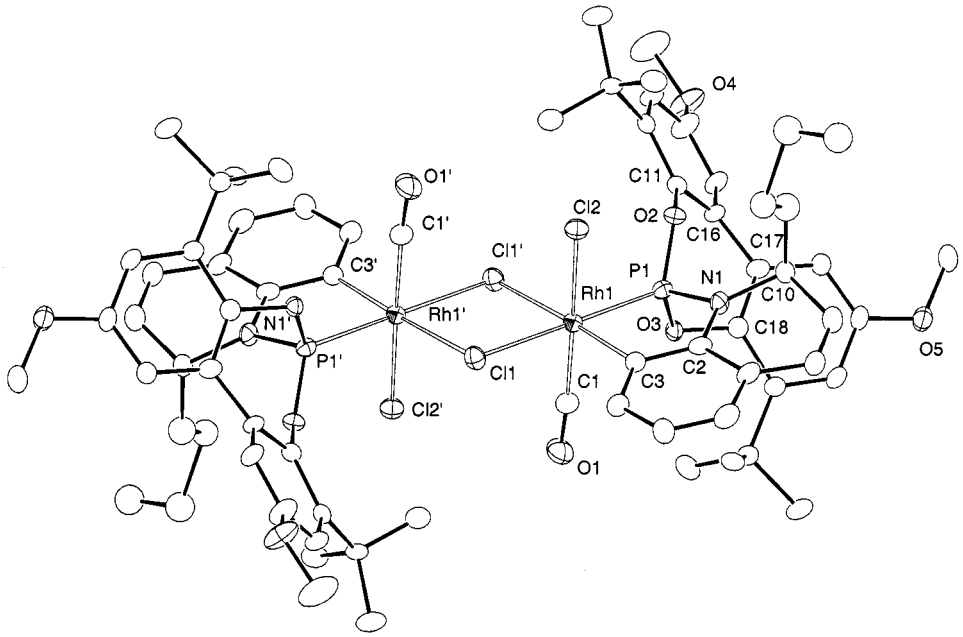


Figure 1. ORTEP view of the structure of complex **5** showing the atomic numbering scheme; thermal ellipsoids are drawn at a 30% probability level

Table 1. Selected bond lengths [Å] and angles [°] in $\mathbf{5} \cdot 2\,C_6H_{14}$; symmetry transformation used to generate equivalent atoms: $-x + 1, -y + 1, -z + 1$

Bond lengths			
Rh(1)−C(1)	1.89(2)	O(2)−C(11)	1.43(2)
Rh(1)−C(3)	2.02(2)	O(3)−C(18)	1.45(2)
Rh(1)−P(1)	2.206(4)	O(4)−C(14)	1.37(2)
Rh(1)−Cl(2)	2.328(4)	O(4)−C(31)	1.43(2)
Rh(1)−Cl(1)	2.454(4)	O(5)−C(21)	1.39(2)
Rh(1)−Cl(1′)	2.536(4)	O(5)−C(32)	1.45(2)
P(1)−O(2)	1.59(1)	N(1)−C(2)	1.45(2)
P(1)−O(3)	1.60(1)	N(1)−C(10)	1.50(2)
P(1)−N(1)	1.64(1)	C(9)−C(10)	1.52(2)
O(1)−C(1)	1.11(2)	C(16)−C(17)	1.47(2)
Bond angles			
C(1)−Rh(1)−C(3)	90.8(7)	N(1)−P(1)−Rh(1)	105.4(5)
C(1)−Rh(1)−P(1)	95.2(6)	C(11)−O(2)−P(1)	129.9(9)
C(3)−Rh(1)−P(1)	82.0(5)	C(18)−O(3)−P(1)	117.0(9)
C(1)−Rh(1)−Cl(2)	174.8(5)	C(14)−O(4)−C(31)	121(1)
C(3)−Rh(1)−Cl(2)	86.3(5)	C(21)−O(5)−C(32)	117(1)
P(1)−Rh(1)−Cl(2)	88.6(2)	C(2)−N(1)−C(10)	121(1)
C(1)−Rh(1)−Cl(1)	86.5(6)	C(2)−N(1)−P(1)	114(1)
C(3)−Rh(1)−Cl(1)	96.1(5)	C(10)−N(1)−P(1)	125(1)
P(1)−Rh(1)−Cl(1)	177.4(2)	Rh(1)−Cl(1)−Rh(1′)	96.4(1)
Cl(2)−Rh(1)−Cl(1)	89.5(2)	O(1)−C(1)−Rh(1)	175(2)
C(1)−Rh(1)−Cl(1′)	86.1(5)	C(8)−C(9)−C(10)	122(2)
C(3)−Rh(1)−Cl(1′)	176.9(5)	N(1)−C(10)−C(9)	108(1)
P(1)−Rh(1)−Cl(1′)	98.3(1)	N(1)−C(10)−C(1A)	111(1)
Cl(2)−Rh(1)−Cl(1′)	96.8(1)	C(9)−C(10)−C(1A)	111(1)
Cl(1)−Rh(1)−Cl(1′)	83.6(1)	C(15)−C(16)−C(11)	117(1)
O(2)−P(1)−O(3)	105.5(5)	C(15)−C(16)−C(17)	117(1)
O(2)−P(1)−N(1)	102.1(6)	C(11)−C(16)−C(17)	125(1)
O(3)−P(1)−N(1)	111.3(6)	C(18)−C(17)−C(22)	118(1)
O(2)−P(1)−Rh(1)	122.1(4)	C(18)−C(17)−C(16)	123(2)
O(3)−P(1)−Rh(1)	110.0(4)	C(22)−C(17)−C(16)	119(1)

trans to C3). As a result of the chelation, the mean plane of the fragment derived from the quinoline approximately bisects the O−P−O angle. The chiral C10 atom lies out of the plane formed by the other five atoms of the ring by 0.44(2) Å. The *n*-butyl groups are situated in axial positions so as to minimize steric repulsion with the biphenyl moiety and thus determine the configuration [(S_aR_C) and (R_aS_C)] of the atropoisomeric unit in complex **5**. The torsion angle, determining the axial chirality of the ligand [τ(C11−C16−C17−C18)], is 55(2)°. The nitrogen atom shows a remarkable degree of sp^2 character.

The packing of the complexes in the crystal leads to the formation of large channels that extend along the *b* axis, into which hexane molecules can insert in a disordered fashion (Figure 2).

It seems very likely that the formation of **5** occurs via an intermediate rhodium(I) species. In this way, an intramolecular redox process, due to the addition of the C−Cl bond of the coordinated ligand **3** across the rhodium(I) center, can account for the formation of the product **5**. The breaking of the C(aromatic)−Cl bond may be induced by the rigidity and steric requirements of **3**, which fix the chlorine atom in the proximity of the metal center in the rhodium(I) intermediate.

Nozaki et al.,[4a] using phosphane/phosphite ligands derived from reaction of optically active (*R*)-2-(diphenylphosphanyl)-1,1′-binaphthalen-2′-ol with the phosphorochloridite of biphenol in the rhodium(I)-catalyzed hydroformylation of olefins, found that a single species is present in solution and they proposed that the biphenyl is fixed in an (*S*) configuration. Analogously, the phosphane/phosphite ligand prepared starting from racemic 2-diphenylphosphanyl-2′-hydroxybiphenyl by reaction with the phosphorochloridite of (*R*)-binaphthol was obtained as a 55:45 equi-

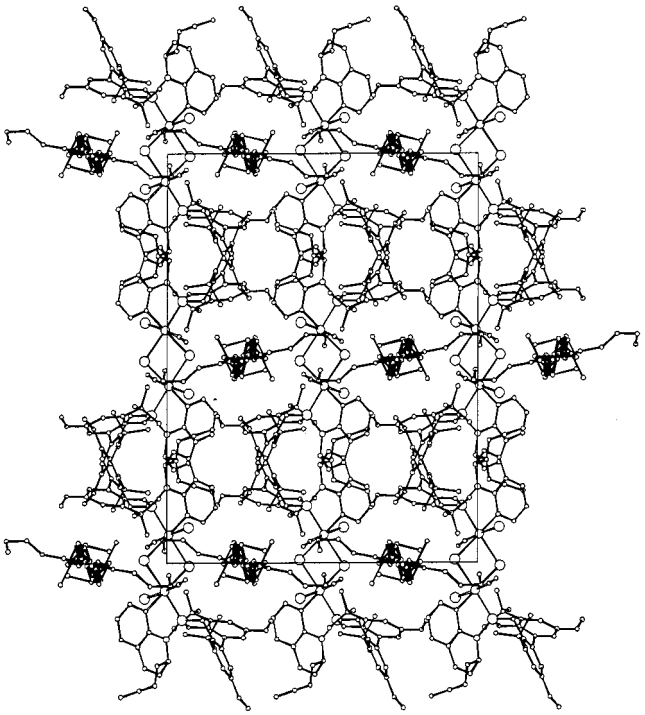
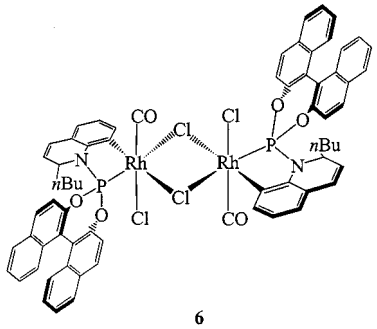


Figure 2. Projection of the structure of $\mathbf{5} \cdot 2\ C_6H_{14}$ along the *b* axis showing the channels into which the hexane molecules are inserted in a disordered manner

librium mixture of two diastereomers. Interconversion between the diastereomers seems to be inhibited by coordination to the rhodium(I) center and in the resulting compound the ligand adopts only one configuration.[4a] Other examples of the fixation of biphenyl rings following coordination to a metal center, using biphenol-derived bis(phosphites), have been reported in the literature.[11] Fixation of the biphenyl rings also occurs in compound **5** due to the presence of the substituents and the rigidity of the chelate quinoline ring.

The reaction of $[Rh(CO)_2Cl]_2$ with **4** proceeds differently to that with **3**. Addition of a twofold molar excess of diastereomer **4a** (S_aR_C) in hexane to a solution of $[Rh(CO)_2Cl]_2$ in the same solvent afforded a yellow solid. The IR spectrum shows ν(CO) bands at 2106 and 2012 cm^{-1}, indicating the presence of the rhodium(III) species **6** as the major product, together with the rhodium(I) species **7** (ratio 10:1.5). The $^{31}P\{^1H\}$-NMR spectrum of the mixture in $CDCl_3$ solution features a resonance at δ = 134.8 (J_{RPh} = 192 Hz) for the major product **6**, together with a resonance at δ = 135.0 (J_{RhP} = 191 Hz) of very low intensity. The similar values of the ^{31}P chemical shifts for **6** and **7** are consistent with structures in which the ligands *trans* to **4a** are the same. Assuming that **6** has a structure analogous to that of **5**, it is very likely that **7** has a binuclear structure with chloro bridges, i.e. $[Rh(CO)(\mathbf{4a})Cl]_2$. A similar intermediate, $[Rh(CO)(\mathbf{3})Cl]_2$, should be formed in the reaction of $[Rh(CO)_2Cl]_2$ with **3**. Compound **6** was obtained in an analytically pure state by several crystallizations from benzene/hexane. The ^1H-NMR spectrum of **6** in $CDCl_3$ solution shows a multiplet at δ = 5.15 and a doublet at δ = 6.28 (^3J = 10.2 Hz) due to the olefinic protons, while a multiplet at δ = 3.24 can be assigned to the proton on the stereogenic carbon atom.



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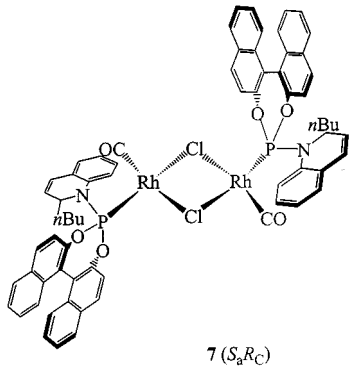


7 (S_aR_C)

8 (S_aS_C)

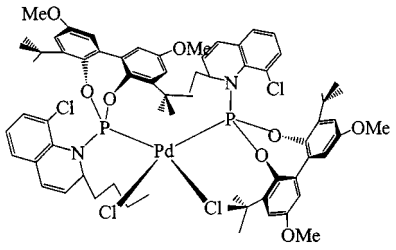
The reaction of $[Rh(CO)_2Cl]_2$ with **4b** in hexane gave only the rhodium(I) species, i.e. $[Rh(CO)(\mathbf{4b})Cl]_2$ (**8**) with the ν(CO) appearing at low wavenumbers. With this diastereoisomer, the intramolecular redox process of addition of the C−Cl bond across the rhodium(I) center seems to be hindered.

Binuclear chloro-bridged compounds, such as **7** and **8**, have been detected previously by NMR spectroscopy.[12] In the reactions with $[Rh(CO)_2Cl]_2$, the rigidity and steric requirements of the ligands **3**, **4a**, and **4b** might be a factor determining the nature of the reaction products. Thus, in reactions of $[Rh(CO)_2Cl]_2$ with sterically hindered ligand molecules, a CO substitution reaction might be preferred to cleavage of the chloro bridges. The C−Cl bond in haloarenes is rather inert. Unlike alkyl halides, haloarenes exhibit low reactivities toward nucleophiles.[13] The use of rhodium(I) complexes in catalytic transformations of chloroarenes is limited to a few examples of C−Cl bond hydrogenolysis.[13] Intramolecular activation of the C−Cl bonds in $[Rh(CO)(\mathbf{3})Cl]_2$, **7** and **8**, requires a proximity of the chlorine atom to the metal center. The diastereoisomers **4a** and **4b** behave differently in the intermediate, most probably because with the (S_aS_C) diastereomer **4b**, the C−Cl bond is positioned away from the rhodium(I) center.

Overnight stirring of $[Pd(PhCN)_2Cl_2]$ and ligand **3** in a 1:2 molar ratio in toluene led to a bright-yellow solution. Workup of the reaction mixture furnished the product $[Pd(\mathbf{3})_2Cl_2]$ (**9**) as a yellow solid, which was found to be stable in air in the solid state and soluble in dichlorometh-

ane. In this case, in contrast to the situation in the rhodium(I) complex **5**, the ligand **3** acts as a monodentate ligand. Compound **9** was characterized by microanalysis and spectroscopic data. The $^{31}P\{^1H\}$-NMR spectrum in CD_2Cl_2 solution shows two partially overlapped singlets at $\delta = 134.1$ and $\delta = 134.2$, with an intensity ratio of ca. 1:0.7. This supports the presence of only two diastereomers, i.e. [Pd(R_C-**3**)(R_C-**3**)Cl_2] {[Pd(S_C-**3**)(S_C-**3**)Cl_2]} and [Pd(S_C-**3**)(R_C-**3**)Cl_2], assuming that the rapid atropoisomerism of the biphenyl moiety is still possible. In the ^1H-NMR spectrum in CD_2Cl_2 solution, at either 298 K or 193 K, only one set of signals is observed, hence there is no discrimination between the two diastereomers. The *tert*-butyl groups give rise to singlets with markedly different chemical shift values ($\delta = 0.95$ and 1.61), whereas only a slight difference is seen in the δ values of the methoxy groups ($\delta = 3.78$ and 3.84).

The reaction of [Pd$(PhCN)_2Cl_2$] with ligand **4a** in a 1:2 molar ratio proceeded similarly and the complex [Pd(**4a**)$_2Cl_2$] (**10**) was obtained in high yield as a yellow solid. The product was found to be stable in air in the solid state and soluble in benzene, acetone, and chlorinated solvents. Its $^{31}P\{^1H\}$-NMR spectrum in $CDCl_3$ shows a single peak at $\delta = 117.5$. In the ^1H-NMR spectrum in $CDCl_3$, the olefinic protons give rise to a double-doublet at $\delta = 4.50$ ($^3J = 5.4$ Hz, $^3J = 9.4$ Hz) and a doublet at $\delta = 6.40$ ($^3J =$ 9.4 Hz). The proton at the stereogenic center appears as a multiplet at $\delta = 3.95$. The appearance of two ν(PdCl) bands at about 335 and 300 cm^{-1} in the IR spectrum (Nujol mull) is indicative of a *cis* configuration for **9** and **10**.



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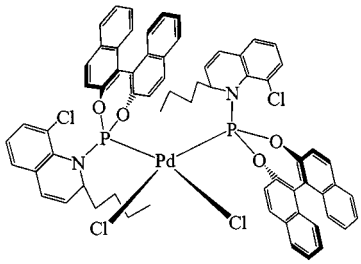

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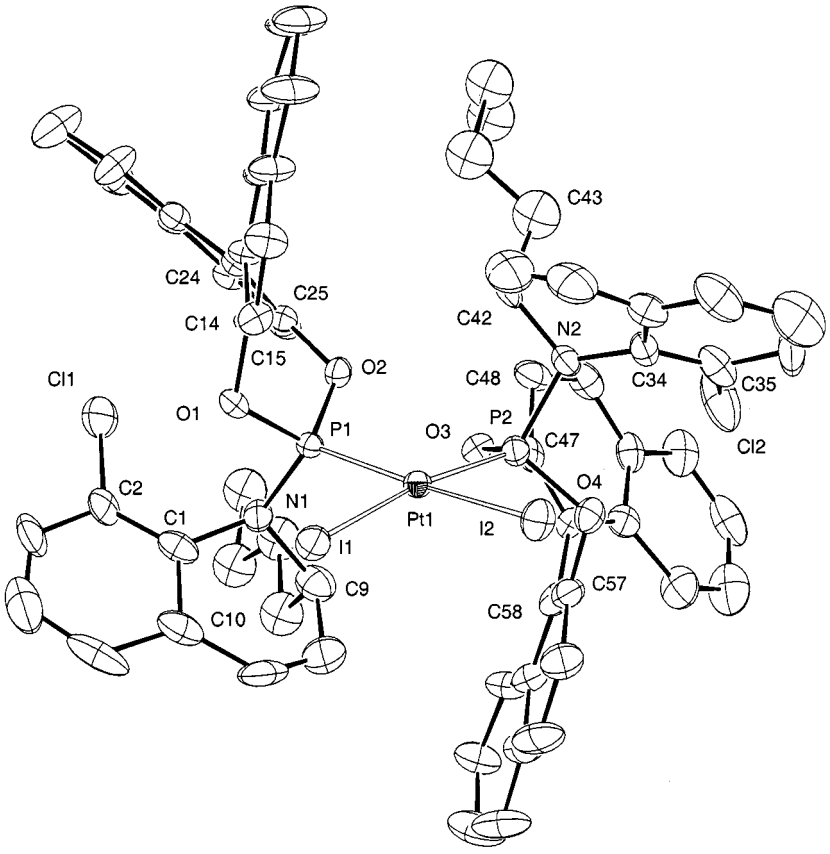
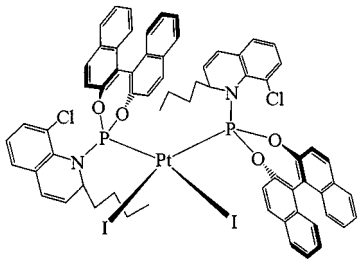


Figure 3. ORTEP view of the structure of complex **11** showing the atomic numbering scheme; thermal ellipsoids are drawn at a 30% probability level

Similarly, reaction of $[Pt(COD)I_2]$ with **4a** in a 1:2 molar ratio afforded *cis*-$[Pt(\mathbf{4a})_2Cl_2]$ (**11**) as a yellow crystalline solid. The compound was characterized by microanalysis and spectroscopic data. The effect of the coordinated ligand **4a** on the overall structure of **11** was assessed by X-ray analysis.



11

Table 2. Selected bond lengths [Å] and angles [°] in **11**

Bond lengths			
Pt(1)−P(2)	2.229(4)	O(2)−C(25)	1.42(2)
Pt(1)−P(1)	2.235(3)	O(3)−C(47)	1.43(1)
Pt(1)−I(1)	2.655(1)	O(4)−C(57)	1.44(2)
Pt(1)−I(2)	2.670(1)	N(1)−C(1)	1.47(2)
P(1)−O(1)	1.584(9)	N(1)−C(9)	1.55(2)
P(1)−O(2)	1.586(9)	N(2)−C(34)	1.42(2)
P(1)−N(1)	1.66(1)	N(2)−C(42)	1.51(2)
P(2)−O(4)	1.59(1)	Cl(1)−C(2)	1.70(2)
P(2)−O(3)	1.613(9)	Cl(2)−C(35)	1.77(2)
P(2)−N(2)	1.67(1)	C(23)−C(24)	1.49(2)
O(1)−C(14)	1.45(1)	C(56)−C(58)	1.49(2)
Bond angles			
P(2)−Pt(1)−P(1)	98.1(1)	C(10)−C(9)−C(8)	109(1)
P(2)−Pt(1)−I(1)	172.1(1)	C(10)−C(9)−N(1)	110(1)
P(1)−Pt(1)−I(1)	87.86(9)	C(23)−C(14)−C(15)	124.8(12)
P(2)−Pt(1)−I(2)	86.8(1)	C(23)−C(14)−O(1)	119.3(12)
P(1)−Pt(1)−I(2)	172.56(9)	C(15)−C(14)−O(1)	115.5(12)
I(1)−Pt(1)−I(2)	87.80(4)	C(14)−C(23)−C(22)	116.3(13)
O(1)−P(1)−O(2)	102.5(5)	C(14)−C(23)−C(24)	120.3(11)
O(1)−P(1)−N(1)	98.1(5)	C(22)−C(23)−C(24)	123.1(12)
O(2)−P(1)−N(1)	108.5(6)	C(25)−C(24)−C(33)	117.8(13)
O(1)−P(1)−Pt(1)	118.2(3)	C(25)−C(24)−C(23)	120.7(12)
O(2)−P(1)−Pt(1)	108.2(3)	C(33)−C(24)−C(23)	121.5(13)
N(1)−P(1)−Pt(1)	119.8(4)	C(24)−C(25)−O(2)	120.3(12)
O(4)−P(2)−O(3)	104.0(5)	C(24)−C(25)−C(26)	123.5(13)
O(4)−P(2)−N(2)	101.3(6)	O(2)−C(25)−C(26)	116.2(12)
O(3)−P(2)−N(2)	106.8(6)	C(35)−C(34)−N(2)	125.5(15)
O(4)−P(2)−Pt(1)	115.8(4)	C(35)−C(34)−C(39)	116.8(16)
O(3)−P(2)−Pt(1)	109.6(4)	N(2)−C(34)−C(39)	117.5(15)
N(2)−P(2)−Pt(1)	118.2(5)	C(41)−C(42)−N(2)	110.6(18)
C(14)−O(1)−P(1)	115.8(8)	C(41)−C(42)−C(43)	116.6(17)
C(25)−O(2)−P(1)	123.7(8)	N(2)−C(42)−C(43)	103.1(17)
C(47)−O(3)−P(2)	120.3(8)	C(56)−C(47)−O(3)	122.4(14)
C(57)−O(4)−P(2)	114.2(9)	C(56)−C(47)−C(48)	124.1(13)
C(1)−N(1)−C(9)	115(1)	O(3)−C(47)−C(48)	113.5(13)
C(1)−N(1)−P(1)	121.2(9)	C(47)−C(56)−C(55)	117.9(14)
C(9)−N(1)−P(1)	112(1)	C(47)−C(56)−C(58)	118.6(13)
C(34)−N(2)−C(42)	112(1)	C(55)−C(56)−C(58)	123.5(13)
C(34)−N(2)−P(2)	127(1)	C(58)−C(57)−C(66)	123.7(16)
C(42)−N(2)−P(2)	111.0(9)	C(58)−C(57)−O(4)	121.4(13)
C(2)−C(1)−C(6)	120(2)	C(66)−C(57)−O(4)	114.9(15)
C(2)−C(1)−N(1)	126(1)	C(57)−C(58)−C(59)	117.7(15)
C(6)−C(1)−N(1)	115(2)	C(57)−C(58)−C(56)	119.8(14)
C(8)−C(9)−N(1)	111(1)	C(59)−C(58)−C(56)	122.4(14)

A view of complex **11** showing the atomic numbering system is depicted in Figure 3. Selected bond lengths and angles are given in Table 2. The Pt atom has a distorted square-planar coordination sphere involving two iodine atoms and the P atoms of two **4a** ligands.

The *cis* arrangement of these very bulky ligands leads to a remarkable distortion of the coordination geometry. The two P atoms deviate above and below the mean square plane by about 0.20(1) Å. The absolute configuration of both ligands is (S_aR_C). The two binaphthyl fragments reside on opposite sides with respect to the coordination plane, and the torsion angles determining the axial chirality [τ(C14−C23−C24−C25) and τ(C47−C56−C58−C57)] are 48(2)° and −54(2)°, respectively. In contrast to the nitrogen atoms in ligand **3** in complex **5**, the nitrogen atoms of the coordinated ligand **4a** in complex **11** show a remarkable degree of sp^3 hybridization, such that these atoms can be considered as chiral centers. In both ligands, the nitrogen atoms are of (*S*) configuration. In accordance with the observed structure, the $^{31}P\{^1H\}$-NMR spectrum shows a single resonance at δ = 94.5 (J_{PtP} = 5296 Hz), while the ^1H-NMR spectrum in $CDCl_3$ solution features a double-doublet at δ = 4.36 and a doublet at δ = 6.20 due to the vinylic protons, and a multiplet at δ = 4.05 attributable to the proton at the stereogenic center.

Surprisingly the compound $[Pt(COD)I_2]$ does not react with **3** in solution, even if an excess of the ligand is used. Most probably, the presence of OMe and *t*Bu substituents on the biphenyl ring of the ligand **3** prevents the formation of a *cis* square-planar platinum(II) complex.

Experimental Section

The compounds 3,3′-di-*tert*-butyl-2,2′-dihydroxy-5,5′-dimethoxybiphenyl and 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a,c*]cycloheptene were prepared according to literature procedures.[5a,14] 8-Chloroquinoline was purchased from Tokyo Kasei Organic Chemicals, whereas all other reagents were purchased from Sigma/Aldrich and were used as supplied. Solvents were dried by standard procedures. All experiments were performed under purified nitrogen. − IR spectra were obtained from Nujol mulls on KBr plates using a Perkin−Elmer FT-IR 1720 spectrophotometer. − ^1H- and $^{31}P\{^1H\}$-NMR spectra were recorded with a Bruker AMX R300 instrument. ^1H-NMR spectra are referenced to internal tetramethylsilane and $^{31}P\{^1H\}$-NMR spectra to external 85% H_3PO_4; positive chemical shifts for all nuclei refer to higher frequencies. − Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

2-Butyl-8-chloro-*N*-(dichlorophosphanyl)-1,2-dihydroquinoline (2): To a solution of 8-chloroquinoline (1.00 g, 6.1 mmol) in tetrahydrofuran (20 mL) at −78°C, 3.9 mL of a 1.6 M hexane solution of *n*-butyllithium was added dropwise. The reaction mixture was allowed to warm to −50°C, stirred for 1 h, then cooled to −78°C once more. Excess PCl_3 (8.37 g, 61.1 mmol) was then rapidly added to the lithium reagent. The reaction mixture was slowly allowed to warm to room temperature and then stirred for 2 h. After removal of the solvents and the excess PCl_3, the residue was extracted with toluene (40 mL). Evaporation of the solvent from the combined extracts afforded the product as a pale-yellow oil, which was used without further purification. Yield: 1.47 g (75%). − ^1H NMR

($CDCl_3$): δ = 6.94 (d, ^3J = 6.0 Hz, 1 H, Ar-H), 6.56 (m, 2 H, Ar-H), 6.05 (d, ^3J = 9.6 Hz, 1 H, CH=CH), 5.80 (dd, ^3J = 9.6 Hz, ^3J = 5.6 Hz, 1 H, CH=CH), 4.68 (m, 1 H, CH), 1.38−1.13 (m, 6 H, CH_2), 0.82 (t, ^3J = 7.2 Hz, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 160.7 (s).

(*S*)-4-Chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene: A suspension of (*S*)-2,2′-dihydroxybinaphthyl (1.00 g, 3.5 mmol) and 1-methyl-2-pyrrolidone (0.001 g, 0.01 mmol) in PCl_3 (7.21 g, 52.5 mmol) was warmed to 75°C and then stirred for 5 min. After this time, a clear solution was obtained. The bulk of the excess PCl_3 was removed under reduced pressure and then the final traces were removed by azeotropic distillation with toluene (10 mL) in vacuo. A white solid corresponding to the title compound was obtained.

2-Butyl-8-chloro-1-(4,8-di-*tert*-butyl-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)-1,2-dihydroquinoline (3). − Method A: A solution of 3,3′-di-*tert*-butyl-2,2′-dihydroxy-5,5′-dimethoxybiphenyl (1.11 g, 3.1 mmol) and Et_3N (1.57 g, 15.5 mmol) in toluene (10 mL) was added dropwise over a period of 1 h to a solution of **2** (1.00 g, 3.1 mmol) in the same solvent (20 mL) at 0°C. The mixture was stirred at room temp. for 40 min and then the precipitate of $Et_3N \cdot HCl$ formed was removed by filtration. The toluene was evaporated from the filtrate and the residue was extracted with hexane (50 mL). Removal of the solvent from the combined extracts afforded **3** (1.69 g, 90%) as a white foam. − ^1H NMR ($CDCl_3$): δ = 7.34 (d, ^4J = 3.0 Hz, 1 H, Ar-H), 7.23 (d, ^4J = 3.0 Hz, 1 H, Ar-H), 6.89 (d, ^4J = 3.0 Hz, 1 H, Ar-H), 6.86 (d, ^4J = 3.0 Hz, 1 H, Ar-H), 6.75 (m, 3 H, Ar-H), 6.33 (d, ^3J = 9.5 Hz, 1 H, CH=CH), 5.83 (dd, ^3J = 9.5 Hz, ^3J = 5.7 Hz, 1 H, CH=CH), 4.48 (m, 1 H, CH), 3.49 (s, 3 H, OCH_3), 3.47 (s, 3 H, OCH_3), 1.83 [s, 9 H, $C(CH_3)_3$], 1.45 [s, 9 H, $C(CH_3)_3$], 1.56−1.53 (m, 2 H, CH_2), 1.24−1.12 (m, 4 H, CH_2), 0.84 (t, ^3J = 7.2 Hz, 3 H, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 141.1 (s). − $C_{35}H_{43}ClNO_4P$ (608.16): calcd. C 69.12, H 7.13, Cl 5.83, N 2.30; found C 68.85, H 7.01, Cl 5.59, N 2.15. − **Method B:** To a solution of 8-chloroquinoline (1.00 g, 6.1 mmol) in tetrahydrofuran (20 mL) cooled in an acetone/dry-ice bath, 3.9 mL of a 1.6 M hexane solution of *n*-butyllithium was added dropwise. The reaction mixture was allowed to warm to −50°C, stirred for 1 h, and cooled to −78°C once more. A precooled solution of 4,8-di-*tert*-butyl-6-chloro-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cycloheptene (2.58 g, 6.1 mmol) in THF (3 mL) was then rapidly added to the lithium reagent (anion). The reaction mixture was slowly allowed to warm to room temperature and then stirred for 2 h. After removal of the THF, the residue was extracted with hexane (50 mL). Removal of the solvent from the combined extracts afforded **3** as a white foam. Yield: 2.97 g, 80%.

2-Butyl-8-chloro-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]-dinaphthalen-4-yl)-1,2-dihydroquinoline (4). Method A: In analogy to Method A for the preparation of compound **3**, compound **4** was synthesized from (*S*)-2,2′-dihydroxybinaphthyl (1.00 g, 3.5 mmol), Et_3N (1.76 g, 17.5 mmol), and **2** (1.13 g, 3.5 mmol). The ^1H- and $^{31}P\{^1H\}$-NMR spectra of the crude reaction mixture were consistent with the formation of an approximately 1:1 mixture of two diastereoisomers. Recrystallization from hexane allowed the components to be separated. The compound more soluble in hexane (0.56 g, 30%) proved to be the (S_aR_C) diastereoisomer **4a** (assignment based on X-ray studies of the corresponding diiodoplatinum complex). − ^1H NMR ($CDCl_3$): δ = 8.04−7.88 (m, 3 H, Ar-H), 7.64 (m, 1 H, Ar-H), 7.44−7.28 (m, 9 H, Ar-H), 7.23−7.03 (m, 2 H, Ar-H), 6.52 (d, ^3J = 9.5 Hz, 1 H, CH=CH), 5.74 (dd, ^3J = 9.5 Hz, ^3J = 5.6 Hz, 1 H, CH=CH), 4.35 (m, 1 H, CH), 1.48−1.20 (m, 6 H, CH_2), 0.61 (t, ^3J = 7.2 Hz, 3 H). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 137.6 (s). − $C_{33}H_{27}ClNO_2P$ (536.01): calcd. C 73.95, H 5.08, N 2.61, Cl 6.61; found C 73.75, H 5.02, N 2.71, Cl 6.45. − The compound less soluble in hexane (0.75 g, 40%) proved to be the (S_aS_C) diastereomer **4b**. − ^1H NMR ($CDCl_3$): δ = 7.96−7.89 (m, 3 H, Ar-H), 7.65 (m, 1 H, Ar-H), 7.45−7.26 (m, 9 H, Ar-H), 7.28−7.26 (m, 2 H, Ar-H), 6.36 (d, ^3J = 9.3 Hz, 1 H, CH=CH), 5.92 (dd, ^3J = 9.3 Hz, ^3J = 5.6 Hz, 1 H, CH=CH), 3.72 (m, 1 H, CH), 1.52−1.22 (m, 6 H, CH_2), 0.72 (t, ^3J = 7.2 Hz, 3 H, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 145.1 (s). − $C_{33}H_{27}ClNO_2P$ (536.01): calcd. C 73.95, H 5.08, Cl 6.61, N 2.61; found C 73.78, H 5.07, Cl 6.55, N 2.63. − **Method B:** In analogy to Method B for the preparation of compound **3**, compound **4** was synthesized from 8-chloroquinoline (0.3 g, 0.18 mmol), *n*BuLi (1.6 M in hexane, 0.56 mL), and (*S*)-4-chloro-3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalene (0.643 g, 0.18 mmol). In this case, the diastereomeric ratio was 70:30, with the (S_aS_C) diastereomer constituting the major product.

[Rh(CO)(P−C)Cl$_2$]$_2$ [P−C = 2-Butyl-1-(4,8-di-*tert*-butyl-2,10-dimethoxy-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)-1,2-dihydro-8-quinolyl] (5): A solution of **3** (0.317 g, 0.52 mmol) in hexane (15 mL) was added to a stirred solution of $[Rh(CO)_2Cl]_2$ (0.100 g, 0.26 mmol) in the same solvent (15 mL) at room temp. A yellow precipitate was deposited during the course of the addition. This solid was collected, washed with petroleum ether, and dried. Yield 0.382 g (95%). − IR (KBr, Nujol): ν(CO) = 2112 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 7.19 (d, ^4J = 2.9 Hz, 1 H, Ar-H), 6.97 (d, ^4J = 2.9 Hz, 1 H, Ar-H), 6.72 (m, 3 H, Ar-H), 6.68 (d, ^4J = 2.9 Hz, 1 H, Ar-H), 6.62 (d, ^4J = 2.9 Hz, 1 H, Ar-H), 6.19 (d, ^3J = 9.6 Hz, 1 H, CH=CH), 5.33 (br. dd, 1 H, CH=CH), 3.87 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 3.60 (br. m, 1 H, CH), 1.75 [s, 9 H, $C(CH_3)_3$], 1.08 [s, 9 H, $C(CH_3)_3$], 1.82−0.86 (m, 6 H, CH_2), 0.71 (t, ^3J = 7.3 Hz, 3 H, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 127.7 (d, J_{RhP} = 197 Hz). − $C_{36}H_{43}Cl_2NO_5PRh$ (774.53): calcd. C 55.83, H 5.60, Cl 9.15, N 1.81; found C 55.78, H 5.68, Cl 8.91, N 2.01.

[Rh(CO)(P′−C)Cl$_2$]$_2$ [P′−C = (S_aR_C)-2-Butyl-1-(3,5-dioxa-4-phosphacyclohepta[2,1-*a*;3,4-*a*′]dinaphthalen-4-yl)-1,2-dihydro-8-quinolyl] (6): A solution of **4a** (0.279 g, 0.52 mmol) in hexane was slowly added at room temp. to a stirred solution of $[Rh(CO)_2Cl]_2$ (0.100 g, 0.26 mmol) in the same solvent (15 mL) until the CO stretching bands of the reagent disappeared from the IR spectrum. A yellow precipitate was deposited during the course of the addition. This solid was collected and washed with petroleum ether. After repeated recrystallization from benzene/hexane, the pure title compound was obtained. Yield: 0.255 g (70%). − IR (KBr, Nujol): ν(CO) = 2106 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.08−7.36 (m, 12 H, Ar-H), 6.91−6.86 (m, 3 H, Ar-H), 6.28 (d, ^3J = 10.2 Hz, 1 H, CH=CH), 5.15 (m, 1 H, CH=CH), 3.24 (m, 1 H, CH), 1.24−0.76 (m, 6 H, CH_2), 0.54 (t, ^3J = 7.3 Hz, 3 H, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 134.8 (d, J_{RhP} = 192 Hz). − $C_{34}H_{27}Cl_2NO_3PRh$ (702.38): calcd. C 58.14, H 3.87, Cl 10.10, N 1.99; found C 58.35, H 3.93, Cl 9.89, N 2.03.

***cis*-[Pd(3)$_2$Cl$_2$] (9):** A solution of **3** (0.475 g, 0.78 mmol) in toluene (10 mL) was added to a solution of $[Pd(PhCN)_2Cl_2]$ (0.150 g, 0.39 mmol) in the same solvent (20 mL) cooled in an ice bath. The reaction mixture was then stirred overnight at room temperature. The yellow solution was subsequently concentrated to a volume of 5 mL and upon addition of 30 mL of diethyl ether a lemon-yellow solid was deposited. This solid was collected, washed with diethyl ether, and dried in vacuo. Yield: 0.489 g (90%). − IR (CsI, Nujol): ν(PdCl) = 335, 302 cm^{-1}. − ^1H NMR (CD_2Cl_2): δ = 7.62−7.54 (m, 3 H, Ar-H), 7.29 (d, ^3J = 7.4 Hz, 1 H), 7.13 (br., 1 H), 7.07

(d, ^4J = 3.0 Hz, 1 H, Ar-H), 6.86 (d, ^4J = 3.0 Hz, 1 H, Ar-H), 6.71 (d, ^4J = 3.0 Hz, 1 H, Ar-H), 6.65 (d, ^4J = 3.0 Hz, 1 H, Ar-H), 4.55 (m, 1 H, CH), 3.84 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 1.61 [s, 9 H, $C(CH_3)_3$], 1.48−1.22 (m, 6 H, CH_2), 0.95 [s, 9 H, $C(CH_3)_3$], 0.85 (t, ^3J = 7.1 Hz, 3 H, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 131.6 (s). − $C_{70}H_{86}Cl_4N_2O_8P_2Pd$ (1393.6): calcd. C 60.33, H 6.22, Cl 10.18, N 2.01; found C 60.45, H 6.28, Cl 9.96, N 2.03.

***cis*-[Pd(4a)$_2$Cl$_2$] (10):** A solution of **4a** (0.418 g, 0.78 mmol) in toluene (10 mL) was added to a stirred solution of $[Pd(PhCN)_2Cl_2]$ (0.150 g, 0.39 mmol) in the same solvent (20 mL) cooled in an ice bath. The reaction mixture was then stirred overnight at room temperature, resulting in the deposition of an orange precipitate. This was filtered off, washed with toluene (in which the product is slightly soluble), and dried. Yield: 0.195 g (40%). − IR (CsI, Nujol): ν(PdCl) = 335, 301 cm^{-1}. − ^1H NMR ($CDCl_3$): δ = 8.33 (d, ^3J = 9.2 Hz, 1 H, Ar-H), 8.08−7.98 (m, 3 H, Ar-H), 7.55−7.35 (m, 9 H, Ar-H), 6.87 (m, 1 H, Ar-H), 6.80−6.76 (m, 2 H, Ar-H), 6.40 (d, ^3J = 9.4 Hz, 1 H, CH=CH), 4.50 (dd, ^3J = 9.4 Hz, ^3J = 5.4 Hz, 1 H, CH=CH), 3.95 (m, 1 H, CH), 0.88−0.68 (m, 6 H, CH_2), 0.56 (t, ^3J = 7.2 Hz, 3 H, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 117.5 (s). − $C_{66}H_{54}Cl_4N_2O_4P_2Pd$ (1249.3): calcd. C 63.45, H 4.36, Cl 11.35, N 2.24; found C 63.35, H 4.28, Cl 11.12, N 2.15.

***cis*-[Pt(4a)I$_2$] (11):** At room temp. a solution of **4a** (0.097 g, 0.18 mmol) in toluene was added to a stirred solution of $[Pt(COD)I_2]$ (0.050 g, 0.09 mmol) in the same solvent (20 mL). After 4 h, the bright-yellow solution was concentrated to a volume of ca. 5 mL and upon addition of 30 mL of diethyl ether a light-yellow solid was deposited. This solid was collected, washed with diethyl ether, and dried in vacuo. Yield: 0.123 g (90%). Recrystallization from $CHCl_3$/hexane gave yellow single crystals suitable for X-ray diffraction analysis. − ^1H NMR ($CDCl_3$): δ = 8.49 (d, ^3J = 9.2 Hz, 1 H, Ar-H), 8.04−7.95 (m, 3 H, Ar-H), 7.51−7.31 (m, 8 H, Ar-H), 6.89 (m, 1 H, Ar-H), 6.80−6.75 (m, 2 H, Ar-H), 6.20 (d, ^3J = 9.6 Hz, 1 H, CH=CH), 4.36 (dd, ^3J = 9.6 Hz, ^3J = 5.4 Hz, 1 H, CH=CH), 4.05 (m, 1 H, CH), 0.95−0.74 (m, 6 H, CH_2), 0.51 (t, ^3J = 7.2 Hz, 3 H, CH_3). − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 94.5 (J_{PtP} = 5296 Hz). − $C_{66}H_{54}Cl_2I_2N_2O_4P_2Pt$ (1520.9): calcd. C 52.12, H 3.58,, Cl 4.66, I 16.69 N 1.84; found C 52.26, H 3.60, Cl 4.76, I 16.47, N 1.89.

Crystal Structure Determination of Complexes 5 · 2 C$_6$H$_{14}$ and 11: Intensity data for **5** · 2 C_6H_{14} were collected at room temperature (22°C) with an Enraf-Nonius CAD-4 single-crystal diffractometer using graphite-monochromated Cu-K_α radiation. Intensity data for **11** were collected at room temperature (22°C) with a Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo-K_α radiation. In both cases, the θ/2θ scan technique was employed. Final unit-cell parameters were obtained from least-squares refinements using 24 (**5** · 2 C_6H_{14}) and 30 (**11**) reflections. Crystallographic and experimental details pertaining to both structures are summarized in Table 3.

Data were corrected for Lorentz and polarization effects in the usual manner. A correction for absorption was made for both complexes [maximum and minimum values for the transmission coefficients 1.000 and 0.7101 (**5** · 2 C_6H_{14}) and 1.000 and 0.3741 (**11**)].[15] Both structures were 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 final cycles of the refinement for all non-hydrogen atoms other than the carbon atoms of the *n*-butyl moiety and of the solvent molecules in **5** · 2 C_6H_{14}. The *n*-butyl group was found to be disordered and distributed over two positions with the first carbon atom (C1A) in common, with occupancy factors of 0.62 and 0.38, respectively. The

Table 3. Crystal data and structure refinement for **5** · 2 C_6H_{14} and **11**; $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Formula	$C_{72}H_{86}Cl_4N_2O_{10}P_2Rh_2 \cdot 2\ C_6H_{14}$	$C_{66}H_{54}Cl_2I_2N_2O_4P_2Pt$
Formula weight	1721.34	1520.84
Temperature	293(2) K	293(2) K
Wavelength	1.54184 Å	0.71073 Å
Crystal system	orthorhombic	orthorhombic
Space group	*Pbca*	$P2_12_12_1$
Unit cell dimensions	a = 26.499(5) Å	a = 20.479(5) Å
	b = 17.869(3) Å	b = 20.546(5) Å
	c = 20.200(4) Å	c = 16.757(4) Å
Volume	9565(3) Å^3	7051(3) Å^3
Z	4	4
Density (calculated)	1.195 Mg/m^3	1.433 Mg/m^3
Absorption coefficient	45.30 cm^{-1}	30.29 cm^{-1}
F(000)	3600	2976
Crystal size [mm]	0.32 × 0.25 × 0.21	0.18 × 0.24 × 0.27
θ range (°)	3.34−60.02	3.06−28.00
Index ranges	$0 \le h \le 29$,	$0 \le h \le 27$,
	$0 \le k \le 20$,	$0 \le k \le 27$,
	$-22 \le l \le 0$	$0 \le l \le 22$
Reflections collected	6802	9215
Independent reflections	6802	9215
Obsd. reflns. [$I > 2\sigma(I)$]	2638	4729
Refinement method	Based on F^2	Based on F^2
Data/restr./param.	6798/27/486	9215/0/677
Flack index	−	−0.04(1)
Goodness-of-fit on F^2	0.818	0.928
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0659,	$R1$ = 0.0450,
	$wR2$ = 0.1728	$wR2$ = 0.1162
R indices (all data)	$R1$ = 0.1841,	$R1$ = 0.1196,
	$wR2$ = 0.2520	$wR2$ = 0.1411
Largest diff. peak and hole	0.701 and −0.715 eÅ^{-3}	0.958 and −1.364 eÅ^{-3}

hexane molecules of solvation were found to be disordered over three different positions within the channels present in the crystal structure. The hydrogen atoms (other than those of the disordered *n*-butyl group and of the hexane molecules in **5** · 2 C_6H_{14}) were placed in geometrically calculated positions and were refined riding on the corresponding carbon atoms. In the final cycles of the refinement, weighting schemes $w = 1/[\sigma^2F_o^2 + (0.1275P)^2]$ (**5** · 2 C_6H_{14}) and $w = 1/[\sigma^2F_o^2 + (0.0668P)^2]$ (**11**), where $P = (F_o^2 + 2F_c^2)/3$, were used. All calculations were carried out with the CNRDIF computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, using the SHELXS-86 and SHELXL-92 packages of crystallographic computer programs.[16,17] Supplementary material available for both structures includes lists of atomic coordinates for the non-H atoms, of calculated coordinates for the hydrogen atoms, and of anisotropic thermal parameters. Details of the crystal structure determinations have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-110254 (**5** · 2 C_6H_{14}) and -110253 (**11**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] [1a] G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis*, Wiley-Interscience Publications, New York, **1992**. – [1b] *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), VCH, Weinheim, **1995**. – [1c] R. Noyori, *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, Jr., D. R. Powell, *J. Am. Chem. Soc.* **1992**, *114*, 5535. – [2b] C. P. Casey, G. T. Whiteker, *Isr. J. Chem.* **1990**, *30*, 299.

[3] [3a] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062. – [3b] S. Cserépi, J. Bakos, *J. Chem. Soc., Chem. Commun.* **1997**, *635*. – [3c] 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. – [3d] 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.

[4] [4a] K. Nozaki, N. Sakai, T. Nanno, T. Higashijima, S. Mano, T. Horiuchi, H. Takaya, *J. Am. Chem. Soc*. **1997**, *119*, 4413. – [4b] K. Nozaki, T. Nanno, H. Takaya, *J. Organomet. Chem*. **1997**, *527*, 103. – [4c] T. Horiuchi, E. Shirakawa, K. Nozaki, H. Takaya, *Organometallics* **1997**, *16*, 2981.

[5] [5a] S. D. Pastor, S. P. Shum, R. K. Rodebaugh, A. D. Debellis, *Helv. Chim. Acta* **1993**, *76*, 900. – [5b] S. D. Pastor, J. L. Hyun, P. A. Odorisio, R. K. Rodebaugh, *J. Am. Chem. Soc*. **1988**, *110*, 6547. – [5c] M. W. Haenel, D. Jakubik, E. Rothenberger, G. Schroth, *Chem. Ber*. **1991**, *124*, 1705. – [5d] S. D. Pastor, J. D. Spivack, L. P. Steinhuebel, *J. Heterocycl. Chem*. **1984**, *21*, 1285. – [5e] S. D. Pastor, S. P. Shum, *Tetrahedron: Asymmetry* **1998**, *9*, 543. – [5f] N. J. De Stefano, D. K. Johnson, L. M. Venanzi, *Angew. Chem. Int. Ed. Engl.* **1974**, *86*, 133. – [5g] U. Baltensperger, J. R. Gunther, S. Kagi, G. Kahr, W. Marty, *Organometallics* **1983**, *2*, 571. – [5h] M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* **1995**, *14*, 3081. – [5i] M. Stolmàr, C. Floriani, G. Gervasio, D. Viterbo, *J. Chem. Soc., Dalton Trans.* **1997**, 1119. – [5j] J. Sakaki, W. B. Schweizer, D. Seebach, *Helv. Chim. Acta* **1993**, 76, 2654. – [5k] S. D. Pastor, A. Togni, *Inorg. Chim. Acta* **1989**, *159*, 3. – [5l] S. D. Pastor, R. K. Rodebaugh, P. A. Odorisio, *Helv. Chim. Acta* **1991**, *74*, 1175.

[6] [6a] A. H. M. de Vries, A. Meetsma, B. L. Feringa, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2374. – [6b] B. L. Feringa, M. Pineschi, L. A. Arnold, R. Imbos, A. H. M. de Vries, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2620. – [6c] A. K. H. Knobel, I. H. Escher, A. Pfaltz, *Synlett* **1997**, 1429. – [6d] N. Sewald, V. Wendisch, *Tetrahedron: Asymmetry* **1998**, *9*, 1341. – [6e] N. Krause, *Angew. Chem. Int. Ed. Engl*. **1998**, *37*, 283.

[7] [7a] D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem, S. B. Wild, *Inorg. Chem*. **1982**, *21*, 1007. – [7b] R. D. Feltham, H. G. Metzger, *J. Organomet. Chem.* **1971**, *33*, 347. – [7c] G. L. Roberts, B. W. Skelton, A. H. White, S. B. Wild, *Aust. J. Chem*. **1982**, *35*, 2193. – [7d] H. A. Hudali, J. V. Kingston, H. A. Tayim, *Inorg. Chem*. **1979**, *18*, 1391. – [7e] G. A. Barclay, M. A. Collard, C. M. Harris, J. V. Kingston, *J. Chem. Soc. A* **1969**, 830. – [7f] G. Salem, S. B. Wild, *Inorg. Chem.* **1992**, *31*, 581. – [7g] T. Suzuki, K. Kashiwabara, J. Fujita, *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1619.

[8] F. Faraone et al., work in progress.

[9] J. W. Suggs, G. D. N. Pearson, *J. Org. Chem*. **1980**, *45*, 1514.

[10] G. T. Whiteker, A. M. Harrison, A. G. Abatjoglou *J. Chem. Soc., Chem. Commun.* **1995**, 1805.

[11] M. J. Baker, K. N. Harrison, A. G. Orpen, P. G. Pringle, G. Shaw, *J. Chem. Soc., Chem. Commun.* **1991**, 803.

[12] E. Rotondo, G. Battaglia, G. Giordano, F. Priolo Cusmano, *J. Organomet. Chem.* **1993**, *450*, 245 and references therein.

[13] V. V. Grushin, H. Alper, *Chem. Rev.* **1994**, *94*, 1047.

[14] F. R. Hewgill, D. G. Hewitt, *J. Chem. Soc. C* **1967**, 726.

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

[16] G. M. Sheldrick, *SHELXS-86, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1986**.

[17] G. M. Sheldrick, *SHELXL-93, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1993**.

Received December 9, 1998
[I98420]