Palladium and Rhodium Complexes with Planar-Chiral Carborane Ligands[‡]

Henri Brunner,*[a] Andreas Apfelbacher,[a] and Manfred Zabel[a]

Dedicated to Professor Dr. Dieter Sellmann on the occasion of his 60th birthday

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Base degradation of the prochiral 1-diphenylphosphanyl-2-phenyl-1,2-dicarba-*closo*-dodecaborane (**1**) affords the planar-chiral 7-diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate anion (**2**). Resolution of the racemic anion carried out using a well-established procedure, gave the internally diastereomeric palladium complexes **3*R*-*R*** and **3*R*-*S***. These complexes were separated by fractional crystallization. A single-crystal X-ray analysis of **3*R*-*R*** established the *exo*-*nido* bonding of the carborane ligand via the phosphorus atom and the adjacent BH group, and the (*R*) configuration of the carborane ligand. The enantiomerically pure anions of **2** were liberated from the diastereomerically pure palladium complexes **3*R*-*R*** and **3*R*-*S***, respectively, by subsequent addition of HCl and NaCN. The *exo*-*nido*-rhodium–carborane complexes **4**–**8** were prepared by heating **2e*R*** or **2e*S*** with $[Rh(COD)Cl]_2$ and/or a chiral chelating phosphane, such as DIOP and BINAP, under reflux. The chiral complexes were tested under enantioselective catalysis conditions such as hydrogenation of acetamidocinnamic acid, hydrogenation of ketopantolactone, and hydrosilylation of acetophenone.

Introduction

For the realization of planar chirality, the ferrocene system is the most suitable skeleton.[1] Two different substituents in the 1,2- or 1,3-positions of the same cyclopentadienyl ring are sufficient to make the systems chiral. In the cyclopentadienyl anions $[C_5H_3RR']^-$, the symmetry plane is removed on complexation with a metal fragment. In contrast, *nido*-carboranyl anions such as $[B_9C_2H_{10}RR']^-$ or $[B_9C_2H_9RR']^{2-}$, containing two different substituents in the open face, are chiral by themselves, because the cage side and the open face are different. Until recently, there have only been a few attempts to resolve *nido*-carboranyl anions, potential ligands in enantioselective catalysts. Early reports came from the groups of Zakharkin and Hawthorne.[2–5] Meanwhile, a series of optically active boron cage compounds was described, of which four were *nido*-C_2B_9 derivatives.[6] Last year a *nido*-carboranyl anion $[B_9C_2H_{10}RR']^-$ was resolved with a SPh and a CH_2OH substituent at the adjacent carbon atoms.[7]

In this paper we report on the resolution of the chiral carboranylphosphane anion $[B_9C_2H_{10}(PPh_2)(Ph)]^-$ [8] obtained as the racemate in the base degradation of the carborane $[B_{10}C_2H_{10}(PPh_2)(Ph)]$[9] (**1**), the phenyl substituent of which is introduced in the synthesis with phenylacetylene, and the diphenylphosphanyl group by metallation. The racemic anion is incorporated into a palladium complex containing enantiopure *ortho*-metallated *N,N*-dimethyl-(*S*)-1-phenylethylamine. After separation of the diastereomers, the resolved anions are cleaved from the palladium complex and introduced into rhodium complexes. In these metal complexes, the carboranylphosphane anion binds as a chelate ligand in an *exo*-*nido*-mode via the phosphorus atom and the adjacent B–H group. The enantiomers **4*R*** and **4*S***, and the enantiomers/diastereomers **5*RR*-*R***, **5*SS*-*S*** and **5*RR*-*S*** were used as catalysts in the enantioselective hydrogenation of acetamidocinnamic acid and ketopantolactone, and in the enantioselective hydrosilylation of acetophenone with diphenylsilane.[10]

The Planar-Chiral Anion 7-Diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate

The sequence of syntheses started with the addition of phenylacetylene to decaborane(14)[11] to give 1-phenyl-1,2-dicarba-*closo*-dodecaborane. Metallation of the acidic CH group with BuLi, and reaction with $ClPPh_2$ provided 1-diphenylphosphanyl-2-phenyl-1,2-dicarba-*closo*-dodecaborane[10] (**1**) (Scheme 1), on which a single-crystal X-ray analysis was performed, as shown in Scheme 1. Both carboranes are achiral molecules. Planar chirality only comes into play after the base degradation of **1** with piperidine to yield the salt piperidinium 7-diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate (**2a**) (Scheme 1).[9] Resolution of the racemic anion of **2a** was attempted by use of enantiomerically pure counter-cations, such as *N,N,N*-trimethyl-(*S*)-1-phenylethylammonium, *N*-methylbrucinium, or *N*-methylquininium as the resolving agents in ethanol. The exchange of the piperidinium ion in **2a** for the enantiomerically pure cations to give **2b**–**d** was carried out according to literature procedures.[9] In the three series **2b**–**d**, mixtures of two diastereomers in ratios of about 1:1 were isolated. It was not possible to separate the diastereomers of the series **2b**–**d** by crystallization. For example, after 15 recrystallizations of **2b** no change in the optical rotation of the diastereomer mixture was observed.

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[a] Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany

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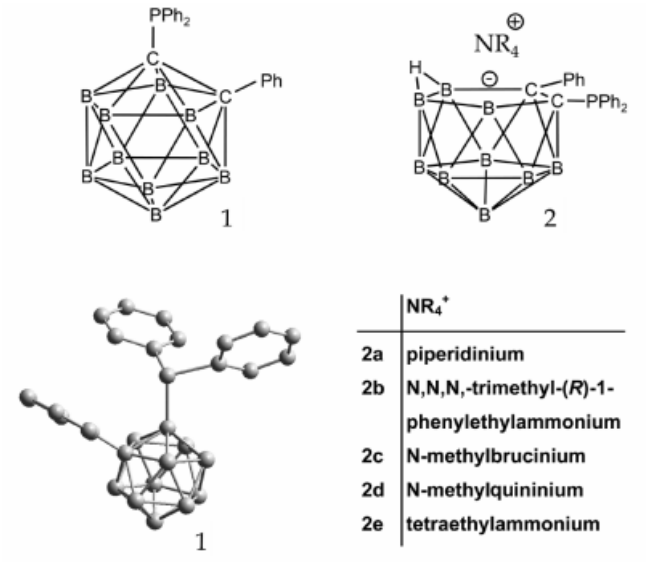


	NR_4^+
2a	piperidinium
2b	N,N,N,-trimethyl-(*R*)-1-phenylethylammonium
2c	N-methylbrucinium
2d	N-methylquininium
2e	tetraethylammonium

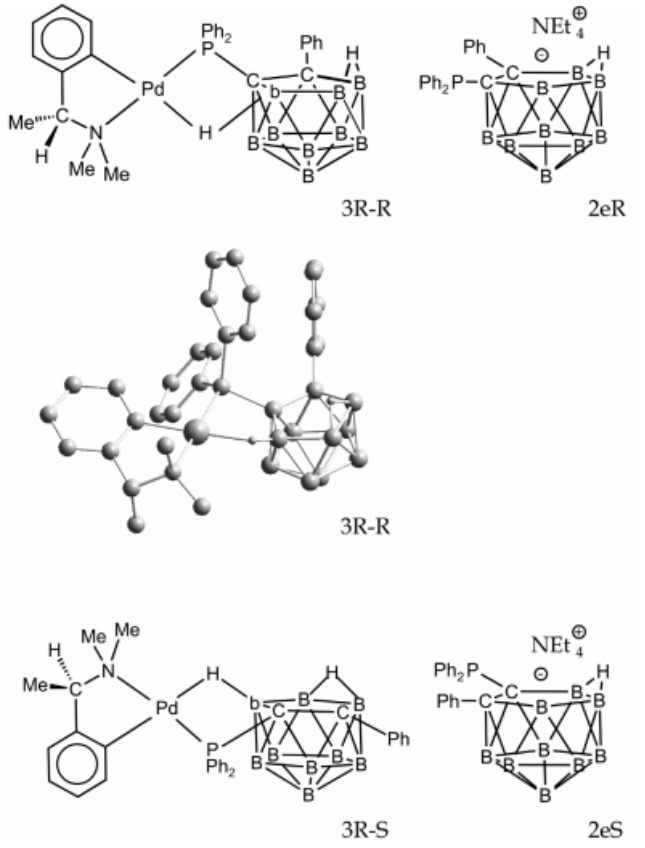
Scheme 1. The carborane **1** and the salts **2a−e** (B abbreviates BH); ORTEP diagram of **1**

Resolution of the Anion *rac*-7-Diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate Via Internally Diastereomeric Palladium Complexes

Using the well-established procedure for the resolution of racemic bis(phosphanes) via internally diastereomeric palladium complexes,[12,13] it was possible to resolve the *rac*-7-diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate anion. The diastereomers **3*R*-*R*** and **3*R*-*S*** (Scheme 2) were synthesized from **2e** and di-μ-chlorobis{(*R*)-2-[1-(dimethylamino)ethyl]phenyl-*C,N*}palladium[14] in CH_2Cl_2 at 10 °C. To remove the by-product NEt_4Cl the solvent was exchanged for $CHCl_3$ and the solution was stirred for 3 h. During this time, the mixture of the diastereomers **3*R*-*R*** and **3*R*-*S*** precipitated as a yellow-green powder in a ratio 55:45. The NEt_4Cl remained in solution.

The IR spectrum of the mixture **3*R*-*R*/3*R*-*S*** shows an intense absorption at 2570 cm^{-1}, characteristic of the B−H stretching vibrations of *nido*-carboranes. The ^{31}P NMR spectrum of the mixture of the diastereomers exhibits singlets at δ = 28.64 for **3*R*-*R*** and 31.35 for **3*R*-*S***. The ^1H NMR spectrum displays a broad resonance centered at δ = −2.3 confirming the existence of a B−H−B bridge in **3*R*-*R*** and **3*R*-*S***. Two quadruplets at δ = −0.38 for **3*R*-*R*** and 0.35 for **3*R*-*S*** are assigned to the Pd−H−B bridges. The two diastereotopic methyl groups of the $N(CH_3)_2$ groups give two doublets at δ = 2.77 and 2.89 for **3*R*-*R***, and two doublets at δ = 2.61 and 3.08 for **3*R*-*S***. A doublet at δ = 1.83 for **3*R*-*R*** and a doublet at δ = 1.45 for **3*R*-*S*** results from the CCH_3 group, and a doublet of a quadruplet at δ = 3.62 for **3*R*-*R*** and a quadruplet at δ = 4.33 for **3*R*-*S*** from the CH group.

As **3*R*-*R*** and **3*R*-*S*** differ in the chemical shifts of their NMR spectra, the ratio **3*R*-*R*:3*R*-*S*** can be determined by integration of the methyl signals in the ^1H NMR spectrum, or the phosphorus signals in the ^{31}P NMR spectrum. Furthermore, the ^1H and ^{31}P NMR spectra indicate that **3*R*-*R*** and **3*R*-*S*** are the isomers in which PPh_2 and NMe_2 as well as BH and *ortho*-C are *trans* to each other. This is in agreement with the X-ray structure analysis for **3*R*-*R***, given below.



Scheme 2. The diastereomeric Pd complexes **3*R*-*R*** and **3*R*-*S***, and the resolved salts **2e*R*** and **2e*S*** (abbreviations: B = BH and b = B); ORTEP diagram of **3*R*-*R***

The separation of the diastereomers **3*R*-*R*** and **3*R*-*S*** was first attempted by fractional crystallization from toluene/petroleum ether at −20 °C. Yellow needles were isolated containing the diastereomers in a ratio of 1:1. However, in the separation of the diastereomers **3*R*-*R*/3*R*-*S*** from the by-product NEt_4Cl it had been noticed that in a mixture of toluene and pentane the **3*R*-*R*** isomer was enriched. Based on this observation a procedure to separate the diastereomers was developed. The 1:1 mixture **3*R*-*R*/3*R*-*S*** was dissolved in toluene. Dropwise addition of pentane precipitated a light brown powder enriched in **3*R*-*R*** (**3*R*-*R*/3*R*-*S*** = 90:10), whereas the filtrate was enriched in **3*R*-*S*** (**3*R*-*R*/3*R*-*S*** = 33:66). To get the pure diastereomers **3*R*-*R*** and **3*R*-*S***, both fractions were re-dissolved in toluene. Pentane was added and the solutions were crystallized to yield pure **3*R*-*R*** and **3*R*-*S***, respectively, as light brown, rhombic crystals. The separation of the diastereomers **3*R*-*R*** and **3*R*-*S*** can be monitored by ^1H and ^{31}P NMR spectroscopy.

A single-crystal X-ray analysis of **3*R*-*R*** established the (*R*) configuration (see below) of the *nido*-carborane ligand relative to the coordinated *ortho*-metallated *N,N*-dimethyl-(*R*)-1-phenylethylamine ligand (Scheme 2). It also

showed that the carborane ligand coordinated to the palladium atom with the phosphorus atom and the adjacent BH group in an *exo-nido* fashion. Furthermore, the X-ray analysis confirmed the *trans* position of PPh_2, NMe_2, and BH, *ortho*-C in **3*R*-*R***.

The configuration of planar-chiral carborane ligands was specified according to the Schlögl convention[1,2] for planar-chiral ferrocenes. The observer looks onto the open five-membered ring of the carborane. By considering the disposition of the substituents, ordered according to the Cahn−Ingold−Prelog rules, clockwise is assigned to the (*R*) configuration, counterclockwise to the (*S*) configuration. Thus, in complex **3*R*-*R*** (Scheme 2) the priority sequence is $PPh_2 > CPh > BH$, and the carborane ligand has an (*R*) configuration.

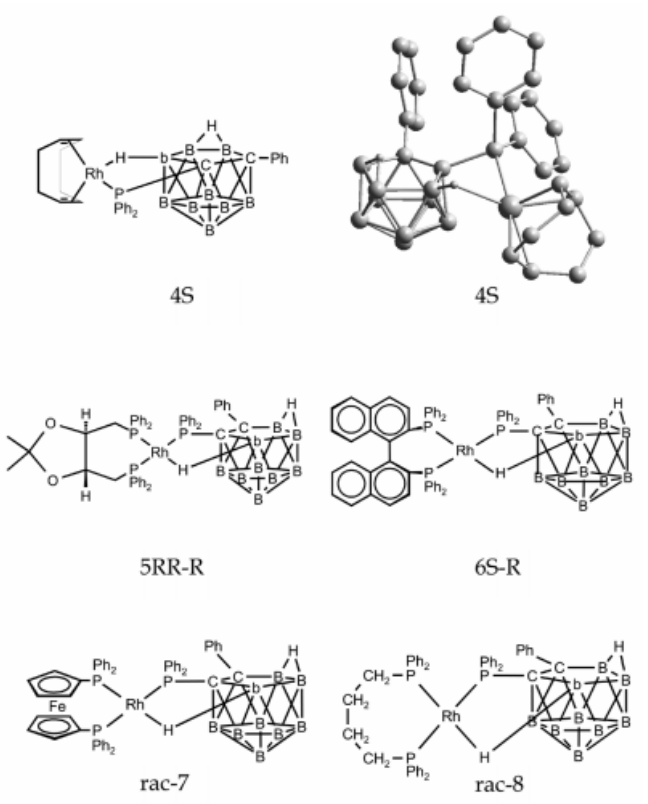
The liberation of the enantiomerically pure anions from the separated palladium complexes was performed in two steps. First, boiling solutions of the diastereomerically pure complexes **3*R*-*R*** and **3*R*-*S*** in acetone containing hydrochloric acid removed the *N*,*N*-dimethylamino-(*R*)-1-phenylethylamine ligand from the Pd complexes. Then, the carborane ligand was liberated from the palladium complex by dissolving in CH_2Cl_2 and stirring with an excess of NaCN and NEt_4Cl in water. Pure **2e*R*** and **2e*S*** (Scheme 2) were isolated from the organic phase as white powders, after discarding the water phase.

The IR spectra of **2e*R*** and **2e*S*** show an intense absorption at 2570 cm^{-1}, typical of the B−H stretching vibrations of *nido*-carboranes. The ^1H NMR spectra display a broad resonance at δ = −1.8 to −2.2, assigned to the B−H−B bridge, and a broad absorption at δ = −0.2 to −2.8 originating from the nine BH groups. The $^{31}P\{^1H\}$ NMR spectra exhibit one signal at δ = 9.45 for the PPh_2 group. The $^{11}B\{^1H\}$ NMR spectra show five peaks in a ratio of 1:1:5:1:1 at negative δ values. As expected, the optical rotations of **2e*R*** and **2e*S*** show an image/mirror image relationship. The enantiomeric purity of **2e*R*** seems to be a little higher than that of **2e*S***.

The Rhodium−Carborane Complexes 4−8

For the preparation of the Rh(COD)carborane complexes **4*R*** and **4*S*** (Scheme 3) enantiomerically pure **2e*R*** or **2e*S*** was refluxed with $[Rh(COD)Cl]_2$ in ethanol. The orange clear solution became a yellow suspension. After cooling to room temperature, the solvent was evaporated to a few mL, affording yellow **4*R*** and **4*S***, respectively. Solutions of these complexes in CH_2Cl_2 are air-sensitive. The $^{31}P\{^1H\}$ NMR spectra of **4*R*** and **4*S*** display a doublet centered at δ = 36.78 with a coupling constant $^1J_{Rh,P}$ = 114.6 Hz. Scheme 3 shows the ORTEP plot of the *exo-nido* structure of complex **4*S***.

For the syntheses of the rhodium−bis(phosphane)−carborane complexes **5**−**8** $[Rh(COD)Cl]_2$, **2e*R*** or **2e*S*** and the chelating bis(phosphane) were heated under reflux in ethanol. The rhodium complexes precipitated as orange powders in high purity. The bis(triphenylphosphane)rhodium complex containing the racemic anion 7-diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate had been described before.[15]



Scheme 3. The Rh(COD) complex **4*S*** and the ORTEP diagram of **4*S***; the [bis(phosphane)]Rh complexes **5**−**8** (abbreviations: B = BH and b = B)

With (*R*,*R*)- or (*S*,*S*)-DIOP as the chelating bis(phosphane), the enantiomers **5*RR*-*R*** and **5*SS*-*S***, as well as their diastereomer **5*RR*-*S*** were formed (Scheme 3). All the complexes were orange powders, slightly soluble, but air-stable in CH_2Cl_2 solution. The ^1H NMR spectra display the signals of the RhHB and BHB bridges at δ = −2.70 and −2.00 to −1.00 for **5*RR*-*R*** and **5*SS*-*S***, and at δ = −3.25 to −2.78 and −2.30 to −2.25 for **5*RR*-*S***, indicating the *exo-nido* structure of the complexes. The ^{31}P NMR spectra show ABX systems. The AB systems (8-line ddd structures for each P atom) are assigned to the two phosphorus atoms of the DIOP ligands, whereas the X parts of the spectra give doublets of a multiplet.

(*S*)-BINAP as the chelating bis(phosphane) afforded a 73% yield of a red-orange powder of **6*S*-*R*** (Scheme 3), for which the ^1H NMR spectrum indicates the *exo-nido* structure. The ^{31}P NMR spectrum shows an ABX system, in which the AB part is assigned to the two PPh_2 groups of BINAP (δ = 6.98 and 34.61) and the X part to the PPh_2 group of the carborane ligand (δ = 43.62).

Using racemic **2e** together with the chelating bis(phosphanes) bis(diphenylphosphanyl)ferrocene and 1,4-bis(diphenylphosphanyl)butane, racemates of the complexes **7** and **8** (Scheme 3) were formed in yields of 84% and 60%, respectively, as orange powders (*exo-nido* types). The $^{31}P\{^1H\}$ NMR spectra of both complexes exhibit ABX sys-

tems in which the AB parts are due to the two PPh_2 groups of the bis(phosphane) ligand (ddd structures) and the X parts, doublets of a multiplet, due to the carborane ligand.

Remarkably, attempts to coordinate bis(phosphanes), which form five-membered rings, such as CHIRAPHOS or NORPHOS, were not successful. Similarly, the chelating ligand (2*R*,3*R*)-1,4-dimercapto-2,3-butanediol and (*S*)-2,2′-diamino-1,1′-binaphthyl did not give the corresponding *exo-nido*-rhodium−carborane complexes. Thus, the preparation of rhodium−carborane complexes with another chelating ligand was confined to bis(phosphanes) forming seven-membered rings.

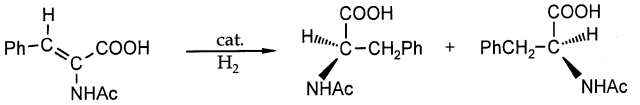
Enantioselective Catalysis

In order to explore the enantioselectivity of the new complexes **4**−**8** in asymmetric catalyses, the hydrogenation of acetamidocinnamic acid, the hydrogenation of ketopantolactone, and the hydrosilylation of acetophenone were selected for study. In all three systems it was found that only complexes **4** and **5** were catalytically active.

In a methanol solution of (*Z*)-α-*N*-acetamidocinnamic acid, containing the catalysts **4** and **5**, there was no hydrogenation while stirring under 1 atm of H_2 for 48 h at room temperature. However, complete hydrogenation resulted in an autoclave under 50 bar of H_2 at 65 °C in toluene/ethanol mixtures. The product *N*-acetylphenylalanine was converted into its methyl ester[16] in order to measure the *ee* by GC. After the hydrogenation with complexes **4*R*** and **4*S***, a black solution had formed indicating the decomposition of complexes **4*R*** and **4*S***, whereas with complexes **5*RR-R*** and **5*RR-S*** an orange solution resulted.

In 5 mL ethanol/10 mL toluene, **4*R*** gave 60−62% *ee* of *N*-acetyl-L-phenylalanine (Table 1, last column). The enantiomerically less pure **4*S*** afforded the D product in a somewhat reduced enantioselectivity. In **4*R*** and **4*S*** the planar-chiral carborane ligand is the only source of chirality, responsible for the chiral induction in the enantioselective hydrogenation reaction. Complex **5*RR-R***, containing (*R*,*R*)-DIOP in addition to the (*R*)-carborane ligand, produced 60−63% *ee* of *N*-acetyl-D-phenylalanine. Complex **5*RR-S***, containing (*R*,*R*)-DIOP in addition to the opposite (*S*)-carborane ligand, gave 50−57% *ee* with the same *N*-acetyl-D-phenylalanine in excess. Evidently, the configuration of *N*-acetylphenylalanine is controlled by the ligand (*R*,*R*)-DIOP. The small differences produced by the diastereomeric catalysts **5*RR-R*** and **5*RR-S*** could be due to the opposite configurations of the carborane ligand. Another explanation is the dissociation of the carborane ligand from the (*R*,*R*)-DIOP complexes **5*RR-R*** and **5*RR-S*** − a reasonable assumption, because empty coordination sites are needed for the binding of substrate and hydrogen during the catalysis.[17] However, the complete dissociation of the carborane ligands from the complexes **5*RR-R*** and **5*RR-S*** should give identical chiral inductions.

Table 1. Enantioselectivities (% *ee*) obtained with complexes **4** and **5** as catalysts in the hydrogenation of (*Z*)-α-*N*-acetamidocinnamic acid



Complex[a]	10 mL of ethanol 5 mL of toluene	5 mL of ethanol 5 mL of toluene	5 mL of ethanol 10 mL of toluene
4*R*	12.7, 12.0 L	48.1, (40.0), 50.1 L	61.9, 60.3, 61.7, 61.3, 62.3 L
4*S*	19.5 D	− −	55.8, 58.0, 54.8, 62.3 D
5*RR-R*	76.1, 79.6 D	(80.5) D	63.0, 60.2 D
5*RR-S*	62.6, 57.1 D	− −	56.6, 50.0, (40.4) D

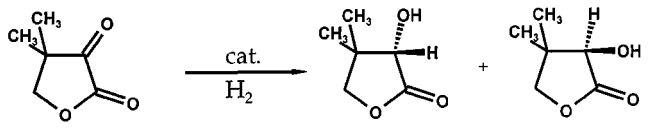
[a] Ratio catalyst/substrate = 1:100. Substrate quantity 200 mg (0.975 mmol). Reaction conditions: 50 bar H_2 pressure, 65 °C, 48 h. Quantitative hydrogenation according to ^1H NMR spectra. Enantiomeric excess determined by GC on a Chirasil-L-Val column.

It was interesting to investigate the dependence of the enantioselectivity on the composition of the solvent (Table 1, columns 2−4). The limiting factor was the solubility of acetamidocinnamic acid, which is insoluble in toluene and of the rhodium−carborane complexes, which are only sparingly soluble in ethanol. For complexes **4** with the COD/carborane ligand set, the enantioselectivity decreased appreciably with an increasing ethanol/toluene ratio. For complexes **5** the opposite trend was observed. The higher the ratio ethanol/toluene the higher was the chiral induction. For the complex **5*RR-R*** at a ratio ethanol/toluene = 10:5 the enantioselectivity was close to 80%. An *ee* of 80−81% is the value expected from the literature for the Rh(DIOP) catalyst.[18] The observed solvent dependence is therefore in agreement with a dissociation of the carborane ligand from complexes **5** during catalysis.

The hydrogenation of ketopantolactone, catalyzed by complexes **4** and **5**, was carried out in a stirred autoclave under 50 bar H_2 at 50 °C for 48 h in toluene, resulting in a complete reduction to (*R*)- and (*S*)-pantolactone.[19] The achieved enantioselectivities are given in Table 2. Complex **4*R***, consisting of the COD ligand and the enantiomerically pure (*R*)-carborane ligand, afforded (*R*)-pantolactone in 23% *ee*. The enantiomerically less pure enantiomer **4*S*** gave 16.4% *ee* of (*S*)-pantolactone. Again, the carborane ligand is the only chiral information in the complexes **4*R*** and **4*S***. Complexes **5*RR-R*** and **5*SS-S*** are enantiomers, containing the (*R*,*R*)-DIOP/(*R*)-carborane and the (*S*,*S*)-DIOP/(*S*)-carborane ligand set. These systems gave enantioselectivities of 59−66% for (*R*)- and (*S*)-pantolactone, respectively. For comparison, under the same conditions the catalyst [Rh(*R*,*R*)-DIOP-Cl]$_2$ afforded 54.4% of (*R*)-pantolac-

tone,[20] indicating a dissociation of the carborane ligand from the complexes **5*RR*-*R*** and **5*SS*-*S***.

Table 2. Complexes **4** and **5** as catalysts in the hydrogenation of ketopantolactone

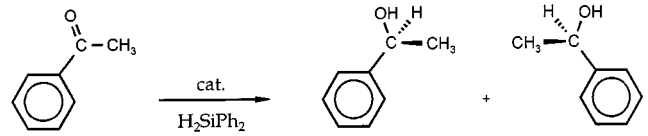


Complex[a]	*ee* [%]	Configuration
4*R*	22.5, 23.0	*R*
4*S*	(16.3)	*S*
5*RR*-*R*	63.6, 58.7, 63.4	*R*
5*SS*-*S*	58.9, 61.1, 66.6	*S*

[a] Ratio catalyst/substrate = 1:200. Ketopantolactone quantity 258 mg (2.01 mmol). Reaction conditions: 50 bar H_2 pressure, 50 °C, 48 h. Quantitative reduction and enantiomeric excess determined by GC on a Chirasil-DEX-CB column.

The hydrosilylation of acetophenone with diphenylsilane (room temperature, 48 h) was catalyzed by the complexes **4*R***, **5*RR*-*S*** and **5*SS*-*S*** to give (*R*)- or (*S*)-1-phenylethanol.[20,21] The enantioselectivities (and in addition the conversion and the enol ether content)[21] are summarized in Table 3. Complex **4*R*** induced an enantiomeric excess of 7−9% of (*R*)-1-phenylethanol, whereas the diastereomers **5*RR*-*S*** and **5*SS*-*S*** both gave 26−27% *ee* of (*R*)- and (*S*)-pantolactone, respectively. The enantioselectivity of [Rh(*R*,*R*)-DIOP-Cl]$_2$ as the chiral catalyst under the same conditions was 27% of (*R*)-1-phenylethanol,[18] compatible with a dissociation of the carborane ligand from **5*RR*-*S*** and **5*SS*-*S*** and a rhodium−DIOP species being the enantioselective catalyst.

Table 3. Complexes **4** and **5** as catalysts in the hydrosilylation of acetophenone with diphenylsilane



Complex[a]	Conversion [%]	Enol ether [%]	1-Phenylethanol Yield [%]	1-Phenylethanol *ee* [%]
4*R*	75, 83	0, 5	75, 79	8.9, 6.7 (*R*)
5*RR*-*S*	92, 92, 37	16, 9, 0	76, 83, 37	26.0, 26.3, 27.7 (*R*)
5*SS*-*S*	72, 80, 89	17, 45, 48	62, 59, 52	(20.7), 25.7, 27.5 (*S*)

[a] Ratio catalyst/acetophenone/diphenylsilane = 1:400:400. Acetophenone and diphenylsilane quantities 1.0 mL (8.5 mmol) and 1.6 mL (8.6 mmol). Reaction conditions: room temperature, 2 d. Conversion, content of enol ether and silyl ether measured by ^{1}H NMR spectroscopy. Enantiomeric excess determined by GC on a Chirasil-DEX-CB column.

In addition, the complexes **4*R*** and **4*S*** were used as catalysts in the diastereoselective hydrogenation of folic acid showing promising results.[22]

Experimental Section

General: All experiments were conducted under dry nitrogen using Schlenk techniques. Solvents were freshly distilled under nitrogen from appropriate drying agents before use. − NMR measurements: ^{1}H at 400 MHz and ^{13}C at 100.1 MHz referenced to $SiMe_4$, ^{11}B at 128 MHz referenced to external $BF_3{\cdot}OEt_3$, ^{31}P at 162 MHz referenced to external H_3PO_4 using a Bruker ARX 400 instrument (chemical shifts in units of parts per million downfield from $SiMe_4$, coupling constants in Hertz). − IR spectra: Beckman IR 4240. − Specific rotations: Perkin−Elmer polarimeter 241. Decaborane(14),[12] 1-phenylcarborane,[23] 1-diphenylphosphanyl-2-phenylcarborane[10] (**1**), tetraethylammonium 7-diphenylphosphanyl-8-phenyl-7,8-dicarba-*nido*-undecaborate[9] (**2e**), and DIOP[19,24] were synthesized according to literature procedures. BINAP, bis(diphenylphosphanyl)ferrocene, and 1,4-bis(diphenylphosphanyl)butane were commercially obtained.

Synthesis of the Mixture of Diastereomers (*R*)-{2-[1-(Dimethylamino)ethyl]phenyl-*C*,*N*}[*exo*-*nido*-(*R*)-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]palladium (3*R*-*R*) and (*R*)-{2-[1-(Dimethylamino)ethyl]phenyl-*C*,*N*}[*exo*-*nido*-(*S*)-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]palladium (3*R*-*S*): Compound **2** (7.66 g, 14.6 mmol) and (*R*)-di-μ-chlorobis{2-[1-(dimethylamino)ethyl]phenyl-*C*,*N*}palladium[15] (4.03 g, 7.03 mmol) were stirred in 200 mL of CH_2Cl_2 at −10 °C for 4 h. The solvent was evaporated and the yellow-green product was suspended in 20 mL of $CHCl_3$, while the NEt_4Cl remained in solution. After stirring for 3 h, the yellow-white diastereomers **3*R*-*R*/3*R*-*S*** were precipitated in a ratio of 55:45. The residue was filtered and washed with 3 × 5 mL of $CHCl_3$. Yield 5.48 g (58%). − $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = −6 (578 nm), −8 (546 nm), −24 (436 nm). − IR (KBr): $\tilde{\nu}$ = 2535 cm^{-1} vs (B−H). − MS (FAB-NI-LSIMS): *m*/*z* (%) = 647.7 (100) [M]$^+$, 498.3 (95) [M$^+$ − $C_{10}H_{14}N$]. − $C_{30}H_{39}B_9NPPd$ (647.7): calcd. C 55.44, H 6.06, N 2.15; found C 55.39, H 6.14, N 2.06.

Separation of the Diastereomers 3*R*-*R* and 3*R*-*S*: The diastereomeric mixture **3*R*-*R*/3*R*-*S*** (400 mg, 0.62 mmol) was dissolved in 50 mL of toluene and filtered. At 15−20 °C 150 mL of pentane was added through a dropping funnel within 5−6 h (1 drop per 3 s). 80−90 mg of a brown powder (**3$_{pow}$**) with a ratio **3*R*-*R*/3*R*-*S*** = 90:10 was precipitated and filtered off. The solvent of the filtrate was evaporated to yield 200 mg of a brown powder (**3$_{fil}$**) with a ratio **3*R*-*R*/3*R*-*S*** = 33:66. To obtain the pure diastereomers **3*R*-*R*** and **3*R*-*S***, 350 mg of **3$_{pow}$** or **3$_{fil}$** were dissolved in 50 mL of toluene. Pentane (35 mL) was added, and the solution filtered and crystallized at −20 °C to yield 200 mg (16%) of pure **3*R*-*R*** or 200 mg (23%) **3*R*-*S***.

3*R*-*R*: $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = 21 (578 nm), 30 (546 nm), 120 (436 nm). − ^{1}H NMR (CD_2Cl_2): δ = −2.4 to −2.1 (br., 1 H, BHB), −0.38 (q, $^1J_{H,B}$ = 34.1 Hz, 1 H, PdHB), 1.5−2.5 (br., 8 H, BH), 1.83 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, $CHCH_3$), 2.77 (d, $^4J_{H,P}$ = 2.0 Hz, 3 H, NCH_3), 2.89 (d, $^4J_{H,P}$ = 4.1 Hz, 3 H, NCH_3), 3.62 (dq, $^3J_{H,H}$ = 6.6 Hz, $^4J_{H,P}$ = 2.2 Hz, 1 H, CH), 6.16−6.25 (m, 1 H, Pd/CH_{ortho}), 6.45−6.55 (m, 1 H, H_{ar}), 6.69−6.91 (m, 9 H, H_{ar}), 6.94−7.09 (m, 1 H, H_{ar}), 7.11−7.19 (m, 2 H, H_{ar}), 7.39−7.63 (m, 3 H, H_{ar}), 7.81−7.92 (m, 2 H, H_{ortho} in PPh_2). − Signals different in ^{1}H{^{31}P} NMR (CD_2Cl_2): δ = 2.77 (s, 3 H, NCH_3), 2.89 (s, 3 H, NCH_3), 3.62 (q, $^3J_{H,H}$ = 6.6 Hz, 1 H, CH). − ^{11}B{^{1}H} NMR (CD_2Cl_2): δ = −34.15 (s, 1 B), −28.07 (s, 1 B), −23.31 (s, 2 B), −13.13 (s, 2 B), −10.91 (s, 1 B), −8.31 (s, 1 B), −2.70 (s, 1 B). − ^{13}C{^{1}H} NMR (CD_2Cl_2): δ = 23.41 (s, $CHCH_3$), 48.55 (s, NCH_3),

52.00 (s, NCH_3), 64.00−67.00 (br., CPh), 74.32 (s, CCH_3), 123.61 (s, C_{ar}), 125.70 (d, J =8.3 Hz, C_{ipso} in CPh, C_{ar}), 126.36 (d, $J_{C,P}$ = 7.6 Hz, C_{meta} in PPh_2), 127.20 (d, $J_{C,P}$ = 14.6 Hz, C_{meta} in PPh_2), 128.55 (m, C_{ipso} in PPh_2, C_{ar}), 129.55 (m, C_{ar}), 131.41 (d, J = 2.5 Hz, C_{ar}), 132.56 (m, C_{ar}), 134.07 (s, C_{ar}), 136.51 (d, J = 13.3 Hz, $CPPh_2$), 136.81 (d, J =13.4 Hz, C_{ar}), 155.66 (d, J =2.6 Hz, CPd). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 28.64 (s, PPh_2).

3*R*-*S*: $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = −35 (578 nm), −45 (546 nm), −149 (436 nm). − ^1H NMR (CD_2Cl_2): δ = −2.5 to −2.0 (br., 1 H, BHB), 0.35 (q, $^1J_{H,B}$ = 35.4 Hz, 1 H, PdHB), 1.45 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, $CHCH_3$), 1.5−2.5 (br., 8 H, BH), 2.61 (d, $^4J_{H,P}$ = 2.7 Hz, 3 H, NCH_3), 3.08 (d, $^4J_{H,P}$ = 3.4 Hz, 3 H, NCH_3), 4.33 (q, $^3J_{H,H}$ = 6.7 Hz, 1 H, CH), 6.20−6.28 (m, 1 H, Pd/CH_{ortho}), 6.50−6.57 (m, 1 H, H_{ar}), 6.78−6.93 (m, 8 H, H_{ar}), 7.01−7.07 (m, 1 H, H_{ar}), 7.11−7.14 (m, 2 H, H_{ar}), 7.39−7.46 (m, 1 H, H_{ar}), 7.49−7.59 (m, 3 H, H_{ar}), 7.84−7.89 (m, 2 H, H_{ortho} in PPh_2). − Signals different in $^1H\{^{31}P\}$ NMR (CD_2Cl_2): δ = 2.61 (s, 3 H, NCH_3), 3.08 (s, 3 H, NCH_3). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −35.10 (s, 1 B), −28.22 (s, 1 B), −24.67 (s, 1 B), −22.96 (s, 1 B), −13.77 (s, 1 B), −12.23 (s, 1 B), −10.40 (s, 1 B), −8.93 (s, 1 B), −3.31 (s 1 B). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.26 (s, $CHCH_3$), 44.70 (s, NCH_3), 50.96 (s, NCH_3), 64.00−67.00 (br., CPh), 71.88 (s, CCH_3), 124.31 (s, C_{ar}), 125.60 (d, J =1.4 Hz, C_{ipso} in CPh, C_{ar}), 126.77 (d, $J_{C,P}$ = 7.6 Hz, C_{meta} in PPh_2), 127.25 (d, $J_{C,P}$ = 13.0 Hz, C_{meta} in PPh_2), 128.55 (m, C_{ipso} in PPh_2, C_{ar}), 129.41 (m, $C_{ipso,}$ C_{ar}), 131.33 (d, J =3.1 Hz, C_{ar}), 132.44 (d, J =2.7 Hz, C_{ar}), 132.68 (d, J =10.7 Hz, C_{ar}), 133.84 (s, C_{ar}), 136.10 (d, J =13.5 Hz, $CPPh_2$), 137.31 (d, J =13.9 Hz, C_{ar}), 153.20 (d, J =2.7 Hz, CPd). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 31.35 (s, PPh_2).

The Enantiomerically Pure Salts Tetraethylammonium (*R*)- and (*S*)-7-Diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborate (2e*R* and 2e*S*): A solution of **3*R*-*R*** or **3*R*-*S*** (1 g, 1.544 mmol) in 50 mL of acetone was heated under reflux for 8 h with 10 mL of conc. HCl. The solvent was removed and the residue was washed with water. The product was dissolved in CH_2Cl_2 (30 mL) and a solution of NaCN (1 g) and NEt_4Cl (1 g) in water (50 mL) was added. After stirring for 24 h, the organic layer was separated, washed with water and dried with $CaCl_2$. After filtering, the solvent was evaporated to yield 0.61 g (76%) of a white powder of **2e*R*** or **2e*S***, respectively.

2e*R*: $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = 149 (578 nm), 182 (546 nm), 513 (436 nm). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2530 vs (B−H). − MS (FAB-NI-LSIMS): m/z (%) = 410.3 (30) $[MO]^+$, 394.3 (50) $[M]^+$, 306.1 (100) [M^+ − CPh]. − ^1H NMR (CD_2Cl_2): δ = −1.8 to −2.2 (br., 1 H, BHB), −0.2 to 2.8 (br., 9 H, BH), 1.33 (t, $^3J_{H,H}$ = 6.9 Hz, 12 H, CH_3), 3.35 (q, $^3J_{H,H}$ = 6.9 Hz, 8 H, CH_2), 7.8−6.9 (m, 15 H, Ph). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −34.66 (s, 1 B, BHB), −31.85 (s, 1 B, BHB), −22.55 to −12.65 (br., 5 B), −9.40 (s, 1 B), −6.62 (s, 1 B). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 9.45 (s). − $C_{28}H_{45}B_9NP$ (523.2): calcd. C 64.00, H 8.67, N 2.60; found C 63.96, H 8.63, N 2.72.

2e*S*: $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = −138 (578), −152 (546), −482 (436).

(1,5-Cyclooctadiene)[(*R*)-*exo*-*nido*-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (4*R*) and (1,5-Cyclooctadiene)[(*S*)-*exo*-*nido*-7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (4*S*): To a solution of **2e*R*** or **2e*S*** (100 mg, 0.191 mmol) in ethanol (50 mL) was added $[Rh(COD)Cl]_2$ (42 mg, 0.095 mmol). After heating under reflux for 5 h, the clear orange solution had become a yellow suspension. The reaction mixture was concentrated to 10 mL and the yellow powder was isolated. Yield 49 mg (43%) of **4*R*** or **4*S***.

4*R*: $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = −307 (578 nm), −367 (546 nm), −905 (436 nm). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2535 vs (B−H). − MS (FAB-NI-LSIMS): m/z (%) = 605.3 (100) $[M]^+$. − ^1H NMR (CD_2Cl_2): δ = −2.5 to −2.0 (br., 1 H, BHB), −1.00 to −0.10 (br., 1 H, RhHB), 0.50−2.50 (br., 8 H, BH), 1.80 (m, 2 H, CH_2), 2.00 (m, 2 H, CH_2), 2.21 (m, 3 H, CH_2), 2.56 (m, 1 H, CH_2), 3.00 (m, 1 H, CH), 3.57 (m, 1 H, CH), 5.23 (m, 1 H, CH), 5.38 (m, 1 H, CH), 6.62−6.70 (m, 2 H, CPh), 6.71−6.76 (m, 2 H, $CPPh_2$), 6.81−6.86 (m, 2 H, CPh), 6.92−6.97 (m, 1 H, CPh), 6.99−7.06 (m, 2 H, PPh_2), 7.26−7.32 (m, 1 H, PPh_2), 7.37−7.49 (m, 5 H, PPh_2). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 36.78 (d, $^1J_{Rh,P}$ = 114.6 Hz, PPh_2). − $C_{28}H_{37}B_9PRh$ (605.3): calcd. C 55.53, H 6.16; found C 55.34, H 6.32.

Synthesis of the Rhodium−Carborane Complexes. − General Procedure: To a solution of **2e*R*** or **2e*S*** (100 mg, 0.191 mmol) in ethanol (50 mL) were added $[Rh(COD)Cl]_2$ (42 mg, 0.095 mmol) and 0.191 mmol of a bis(phosphane). While heating under reflux for 5 h an orange powder precipitated. The product was filtered and washed with 3 × 10 mL of ethanol and 2 × 10 mL of pentane.

[(*R*,*R*)-DIOP][*exo*-*nido*-(*R*)-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (5*RR*-*R*), [(*S*,*S*)-DIOP][*exo*-*nido*-(*S*)-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (5*SS*-*S*), and [(*R*,*R*)-DIOP][*exo*-*nido*-(*S*)-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (5*RR*-*S*)

5*RR*-*R*: This was synthesized from **2e*R*** (120 mg, 0.229 mmol), $[Rh(COD)Cl]_2$ (55.5 mg, 0.113 mmol), and (*R*,*R*)-DIOP (116 mg, 0.233 mmol). Yield 179 mg (78%), orange powder. − $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = −102 (589 nm), −107 (578 nm), −117 (546 nm). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2535 vs (B−H). − MS (FD, CH_2Cl_2): m/z (%) = 995.1 (100) $[M]^+$. − ^1H NMR (CD_2Cl_2): δ = −2.70 to −2.10 (br., 1 H, BHRh), −2.00 to −1.00 (br., 1 H, BHB), 0.15−2.85 (br., 8 H, BH), 1.05 (s, 3 H, CH_3-DIOP), 1.13 (s, 3 H, CH_3-DIOP), 2.15 (m, 1 H, CH_2-DIOP), 2.55 (m, 3 H, CH_2-DIOP), 3.70 (m, 1 H, CH-DIOP), 4.05 (m, 1 H, CH-DIOP), 6.61 (m, 4 H, H_{ar}), 6.76 (m, 2 H, H_{ar}), 6.83 (m, 1 H, H_{ar}), 6.93 (m, 6 H, H_{ar}), 7.05 (m, 4 H, H_{ar}), 7.14 (m, 4 H, H_{ar}), 7.44 (m, 10 H, H_{ar}), 7.61 (m, 2 H, H_{ar}), 7.79 (m, 2 H, H_{ar}). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −34.2 (br., 1 B), −28.5 (br., 1 B), −26.2 (d, 1 B), −23.5 (br., 2 B), −13.7 (br., 2 B), −10.5 (br., 1 B), −2.8 (br., 1 B). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 26.81 (d, J =17.1 Hz, $C(CH_3)_2$), 30.84 (d, J = 20.2 Hz, CH_2), 34.56 (d, J = 20.2, CH_2), 65−70 (br., CPh), 77.46 (d, J = 6.2, CH), 108.72 (s, $C(CH_3)_2$), 126.54 (m, C_{ar}), 126.87 (m, C_{ar}), 127.43 (d, J =10.8 Hz, C_{ar}), 128.20 (d, J = 9.0 Hz, C_{ar}), 128.41 (m, C_{ar}), 129.60 (m, C_{ar}), 129.71 (s, C_{ar}), 130.22 (s, C_{ar}), 130.78 (m, C_{ar}), 130.90 (m, C_{ar}), 131.05 (m, C_{ar}), 132.10 (m, C_{ar}), 132.33 (d, J = 10.3 Hz, C_{ar}), 132.71 (d, J = 10.3 Hz, C_{ar}), 133.27 (d, J = 9.9 Hz, C_{ar}), 133.40 (s, C_{ar}), 133.92 (d, J = 11.9 Hz, C_{ar}), 134.40 (d, J = 11.9 Hz, C_{ar}), 135.92 (d, J = 14.4 Hz, C_{ar}), 137.51 (d, J = 3.0 Hz, C_{ar}). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 12.35 (ddd, $^2J_{P(A),P(B)}$ = 288 Hz, $^2J_{P(A),P(C)}$ = 38.5 Hz, $^2J_{P(A),Rh}$ = 117.9 Hz, 1 P, $P_{(A)}$), 16.22 (ddd, $^2J_{P(B),P(A)}$ = 288 Hz, $^2J_{P(B),P(C)}$ = 41.9 Hz, $^2J_{P(B),Rh}$ = 130.4 Hz, 1 P, $P_{(B)}$), 29.31 (dm, $^1J_{P(C),Rh}$ = 197.2 Hz, 1 P, $P_{(C)}$). − $C_{51}H_{57}B_9O_2P_3Rh$ (995.1): calcd. C 61.50, H 5.73; found C 60.43, H 5.81.

5*RR*-*S*: This was synthesized from **2e*S*** (120 mg, 0.229 mmol), $[Rh(COD)Cl]_2$ (55.5 mg, 0.113 mmol), and (*R*,*R*)-DIOP (116 mg, 0.233 mmol). Yield 179 mg (78%), orange powder. − $[\alpha]_\lambda$ (c = 1.0, CH_2Cl_2) = −158 (589 nm), −169 (578 nm), −216 (546 nm). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2535 vs (B−H). − MS (FD, CH_2Cl_2): m/z (%) = 995.1 (100) $[M]^+$. − ^1H NMR (CD_2Cl_2): δ = −3.25 to −2.78 (br., 1 H, BHRh), −2.30 to −2.25 (br., 1 H, BHB), 0.50−2.50 (br., 8 H,

BH), 1.12 (s, 3 H, CH_3-DIOP), 1.17 (s, 3 H, CH_3-DIOP), 2.25 (m, 1 H, CH_2-DIOP), 2.55 (m, 2 H, CH_2-DIOP), 2.75 (m, 1 H, CH_2-DIOP), 3.75 (m, 1 H, CH-DIOP), 3.90 (m, 1 H, CH-DIOP), 6.52 (m, 4 H, H_{ar}), 6.82 (m, 5 H, H_{ar}), 6.91 (m, 7 H, H_{ar}), 7.20 (m, 9 H, H_{ar}), 7.45 (m, 6 H, H_{ar}), 7.68 (m, 2 H, H_{ar}), 7.88 (m, 2 H, H_{ar}). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −34.0 (br., 1 B), −27.9 (br., 1 B), −25.0 (d, 1 B), −23.6 (br., 1 B), −14.1 (br., 2 B), −11.7 (br., 1 B), −8.4 (br., 1 B), −2.8 (br., 1 B). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 9.19 (ddd, $^2J_{P(A),P(B)}$ = 288.5 Hz, $^2J_{P(A),P(C)}$ = 39.2 Hz, $^2J_{P(A),Rh}$ = 117.9 Hz, 1 P, $P_{(A)}$), 18.00 (ddd, $^2J_{P(B),P(A)}$ = 288.5 Hz, $^2J_{P(B),P(C)}$ = 42.7 Hz, $^2J_{P(B),Rh}$ = 129.7 Hz, 1 P, $P_{(B)}$), 26.95 (dm, $^1J_{P(C),Rh}$ = 204.5 Hz, 1 P, $P_{(C)}$). − $C_{51}H_{57}B_9O_2P_3Rh$ (995.1): calcd. C 61.50, H 5.73; found C 60.78, H 5.62.

[(*S*)-Binap][*exo-nido*-(*R*)-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (6*S-R*): This was synthesized from compound **2e*R*** (87 mg, 0.168 mmol), $[Rh(COD)Cl]_2$ (40 mg, 0.082 mmol), and (*S*)-BINAP (100 mg, 0.160 mmol). Yield 131 mg (73%), orange powder. − $[\alpha]_\lambda$ (*c* = 1.0, CH_2Cl_2) = −70 (589 nm), −120 (578 nm), −141 (546 nm). − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2530 vs (B−H). − MS (FD, CH_2Cl_2): *m*/*z* (%) = 1119.4 (100) $[M]^+$, 725.4 (33) $[M^+ - C_{20}H_{25}B_9P]$. − ^1H NMR (CD_2Cl_2,): δ = −3.32 to −2.68 (br., 1 H, BHRh), −2.62 to −2.21 (br., 1 H, BHB), 0.05−2.48 (br., 8 H, BH), 6.37 (m, 2 H, H_{ar}), 6.62 (s, 10 H, H_{ar}), 6.74 (m, 3 H, H_{ar}), 6.91 (m, 8 H, H_{ar}), 7.21 (m, 12 H, H_{ar}), 7.59 (m, 10 H, H_{ar}), 7.95 (m, 2 H, H_{ar}). − $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ = −39.8 (br., 1 B), −28.6 (br., 1 B), −23.4 (br., 2 B), −20.6 (br., 1 B), −13.3 (br., 2 B), −8.8 (br., 1 B), −3.1 (br., 1 B). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 6.98 (ddd, $^2J_{P(A),P(B)}$ = 288.9 Hz, $^2J_{P(A),P(C)}$ = 33.3 Hz, $^1J_{P(A),Rh}$ = 119.8 Hz, 1 P $P_{(A)}$), 34.61 (ddd, $^2J_{P(B),P(A)}$ = 288.9 Hz, $^2J_{P(B),P(C)}$ = 37.8 Hz, $^1J_{P(B),Rh}$ = 133.9 Hz, 1 P, $P_{(B)}$), 43.62 (dm, $^1J_{P(C),Rh}$ = 195.3 Hz, 1 P, $P_{(C)}$). − $C_{64}H_{57}B_9P_3Rh$ (1119): calcd. C 60.55, H 5.97; found C 61.60, H 5.80.

[*rac*-1,1-Bis(diphenylphosphanyl)ferrocene][*exo-nido*-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (7): This was synthesized from *rac*-**2e** (193 mg, 0.368 mmol), $[Rh(COD)Cl]_2$ (90 mg, 0.184 mmol), and 1,1-bis(diphenylphosphanyl)ferrocene (192 mg, 0.368 mmol). Yield 325 mg (84%), orange powder. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2530 vs (B−H). − MS (FD, CH_2Cl_2): *m*/*z* (%) = 1051.1 (100) $[M]^+$, 655.1 (70) $[M^+ - C_{20}H_{25}B_9P]$. − ^1H NMR (CD_2Cl_2): δ = −4.10 to −3.05 (br., 1 H, BHRh), −2.70 to −2.35 (br., 1 H, BHB), 0.45−2.50 (br., 8 H, BH), 3.61 (s, 1 H, fc_{meta}), 3.58 (s, 1 H, fc_{meta}), 4.06 (s, 2 H, fc_{meta}), 4.34 (s, 1 H, fc_{ortho}), 4.42 (s, 1 H, fc_{ortho}), 4.51 (s, 1 H, fc_{ortho}), 4.65 (s, 1 H, fc_{ortho}), 6.71 (m, 5 H, H_{ar}), 7.06 (m, 10 H, H_{ar}), 7.35 (m, 2 H, H_{ar}), 7.68 (m, 8 H, H_{ar}), 7.45 (m, 6 H, H_{ar}), 8.11 (m, 4 H, H_{ortho} in PPh_2). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 8.06 (ddd, $^2J_{P(A),P(B)}$ = 297.8 Hz, $^2J_{P(A),P(C)}$ = 30.0 Hz, $^1J_{P(A),Rh}$ = 134.3 Hz, 1 P, $P_{(A)}$), 26.97 (ddd, $^2J_{P(B),P(A)}$ = 297.8 Hz, $^2J_{P(B),P(C)}$ = 42.0 Hz, $^1J_{P(B),Rh}$ = 120.5 Hz, 1 P, $P_{(B)}$), 43.66 (dm, $^1J_{P(C),Rh}$ = 201.4 Hz, 1 P, $P_{(C)}$). − $C_{54}H_{53}B_9FeP_3Rh$ (1051): calcd. C 61.65, H 5.05; found C 61.38, H 5.25.

[*rac*-1,4-Bis(diphenylphosphanyl)butane][*exo-nido*-(7-diphenylphosphanyl-8-phenyl-7,8-dicarbaundecaborato)]rhodium (8): This was synthesized from *rac*-**2e** (200 mg, 0.381 mmol), $[Rh(COD)Cl]_2$

Table 4. Crystal data and structure refinement for **1**, **3*R-R*** and **4*S***

Compound	**1**	**3*R-R***	**4*S***
Empirical formula	$C_{20}H_{25}B_{10}P$	$(C_{30}H_{39}B_9NPPd)\cdot 2(C_7H_8)$	$(C_{28}H_{37}B_9PRh)\cdot 0.5(C_7H_8)$
Molecular mass	404.47	832.55	650.81
Crystal size [mm]	0.94 × 0.72 × 0.12	0.49 × 0.34 × 0.22	0.50 × 0.36 × 0.20
Crystal system	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)
a [Å]	11.0599(9)	11.7316(6)	10.9388(7)
b [Å]	14.7472(13)	14.3635(8)	21.9488(16)
c [Å]	15.8620(14)	25.6339(8)	14.0388(10)
α [°]	102.948(9)	90	90
β [°]	105.009(9)	90	107.736(8)
γ [°]	104.293(9)	90	90
Volume [Å^3]	2304.0(4)	4319.5(4)	3210.4(4)
Z, $D_{calcd.}$ [Mg/m^3]	4, 1.166	4, 1.280	4, 1.347
μ [mm^{-1}]	0.13	0.50	0.60
F(000)	840	1728	1340
Data Collection			
Measurement device type	STOE-IPDS diffractometer		
Measurement method	rotation		
Temperature [K]	297(2)	123(1)	123(1)
Radiation (monochromated)	Mo-K_α (graphite), 0.71073 [Å]		
Θmin, Θmax [°]	2.09, 25.60	1.91, 25.74	1.86, 25.84
Index ranges	$-11 \le h \le 12$	$-14 \le h \le 14$	$-13 \le h \le 13$
	$-17 \le k \le 17$	$-17 \le k \le 17$	$-26 \le k \le 26$
	$-18 \le l \le 19$	$-31 \le l \le 31$	$-17 \le l \le 17$
No. refl. collected/unique	15640/8030	32170/8209	43841/6086
Reflections $I > 4\sigma(I)$	4643	7715	5342
Absorption correction	none	none	none
Refinement			
Refinement method	Full-matrix least squares on F^2		
Hydrogen treatment	constr.	mixed	all free
Data, parameters	8030, 559	8209, 697	6086, 528
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2]$ $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0270P)^2]$	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2 + 0.2487P]$
Final *R*, *wR*2, *S* [$I>4\sigma(I)$]	0.0431, 0.0954, 0.813	0.0186, 0.0412, 0.997	0.0270, 0.0693, 1.057
R, *wR*2 (all data)	0.0753, 0.1021	0.0211, 0.0417	0.0318, 0.0710
Absolute structure parameter		−0.037(11)	
Min./max. resd. density [e/Å^{-3}]	−0.156, 0.238	−0.158, 0.387	−0.340, 0.884

(94 mg, 0.184 mmol), and 1,4-bis(diphenylphosphanyl)butane (164 mg, 0.385 mmol). Yield 211 mg (60%), orange powder. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2530 vs, (B−H). − MS (FD, CH_2Cl_2): *m*/*z* (%) = 939.3 (5) $[MO]^+$, 923.4 (100) $[M]^+$. − ^1H NMR (CD_2Cl_2): δ = −2.55 to −2.15 (br., 1 H, BHRh), −1.70 to −0.70 (br., 1 H, BHB), 0.20−2.40 (br., 8 H, BH), 1.84 (m, 4 H, CH_2), 2.20 (m, 4 H, CH_2PPh_2), 6.62 (m, 4 H, H_{ar}), 6.77 (m, 2 H, H_{ar}), 6.91 (m, 9 H, H_{ar}), 7.04 (m, 2 H, H_{ar}), 7.13 (m, 4 H, H_{ar}), 7.23 (m, 3 H, H_{ar}), 7.30 (m, 1 H, H_{ar}), 7.44 (m, 6 H, H_{ar}), 7.67 (m, 4 H, H_{ar}). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 13.67 (ddd, $^2J_{P(A),P(B)}$ = 286.0 Hz, $^2J_{P(A),P(C)}$ = 35.1 Hz, $^1J_{P(A),Rh}$ = 119.0 Hz, 1 P, $P_{(A)}$), 26.97 (ddd, $^2J_{P(B),P(A)}$ = 286.0 Hz, $^2J_{P(B),P(C)}$ = 44.3 Hz, $^1J_{P(B),Rh}$ = 130.5 Hz, 1 P, $P_{(B)}$), 41.17 (dm, $^1J_{P(C),Rh}$ = 198.4 Hz, 1 P, $P_{(C)}$). − $C_{48}H_{53}B_9P_3Rh$ (923.4): calcd. C 62.40, H 5.74; found C 61.60, H 5.80.

X-ray Crystal Structure Determination of 1, 3*R*-*R*, and 4*S*: Data collection was performed on a STOE Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems Cryostream Cooler for low-temperature measurements (Table 4). All data were corrected for Lorentz and polarisation effects. Final unit cell parameters were obtained by a least-squares refinement on a set of either 2000 (**1**) or 8000 (**3*R*-*R***, **4*S***) reflections equally distributed in reciprocal space. The structures were solved by direct methods (SIR-97)[25] and subsequent difference Fourier methods. Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL97).[26] All non-H atoms were refined with anisotropic thermal parameters. H atoms were located from difference Fourier syntheses and refined with isotropic thermal parameters in three different ways: all free (**4*S***), some free, some as riding atoms (**3*R*-*R***), and all as riding atoms (**1**) with $U_{iso}(H) = 1.2U_{eq}$(C or B). The crystal structure of **3*R*-*R*** contains two toluene solvent molecules, one of them disordered between two orientations. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-147724 (**3*R*-*R***), CCDC-147725 (**4*S***) and CCDC-147726 (**1**). 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].

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