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Enantiomerically Pure Bis(phosphanyl)carbaborane(12) Compounds[‡]

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Enantiomerically pure (R_P,R_P)- and (R_P,S_P)-1,2-bis[1-adamantyloxy-(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12), 1,2-bis[bis(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) and 1,2-bis[bis(4-*tert*-butylphenyloxy)phosphanyl]-*closo*-dicarbaborane(12) were synthesised by the reaction of dilithiated 1,2-dicarba-*closo*-dodecaborane(12) with two equivalents of the corresponding chlorophosphite. The phosphonites are stable towards epimerisation, oxygen and water. P···P through-space coupling was observed, and the $^3J_{PP}$ coupling constants were determined by spectral simulation and DFT calculations. Late transition-metal complexes with molybdenum and rhodium were prepared to study the coordination properties of the bis(phosphanyl)carbaborane(12) compounds. Catalytic properties of various rhodium complexes were investigated in homogeneous catalytic hydroformylation reactions with various olefins.

Introduction

Bis(phosphanes) are versatile ligands for late transition-metal complexes in homogeneous catalytic reactions. They combine steric and electronic tunability with the stability of chelating ligands. This makes new classes of bis(phosphane) important targets for industrial and academic research focussed on developing improved catalytic processes. The class of C_2-symmetric bis(phosphanes) continues to grow, as many of these compounds were found to be excellent ligands for transition metals in homogeneous catalysis. These compounds can carry the chiral information in the carbon backbone, such as BINAP or DIOP, or at the phosphorus atom, like DIPAMP,[1] whereby the former case is more common.

1,2-Dicarba-*closo*-dodecaborane(12) [*ortho*-carbaborane(12)] is of interest as a C_2-symmetric backbone for phosphanes. Most research is focussed on disubstituted derivatives in which *ortho*-carbaborane(12) acts as rigid backbone imitating an ethylene or phenylene system. Furthermore, its unique electronic properties, with electron-withdrawing and electron-delocalising ability, change the electronic properties of the phosphanes dramatically. The hydrogen atoms at the carbon atoms of *ortho*-carbaborane(12) are acidic and can be removed by bases. Lithiated carbaboranes can be widely functionalised selectively by electrophilic substitution.[2] Therefore, an extensive field of carbaborane chemistry has developed. Tertiary phosphane derivatives of 1,2-dicarba-*closo*-dodecaborane(12) compounds were first reported in 1963, synthesised by dilithiation of *ortho*-carbaborane and subsequent reaction with chlorodiphenylphosphane.[3] Since then several derivatives with organophosphorus substituents have been prepared, and their reactivity and coordination chemistry have been investigated.[4] Several of these substances have been successfully applied as ligands in homogeneous catalysis.[5] Use of phosphanyl ligands provides a simple method for controlling steric and electronic properties through structural manipulation. The only non-chiral phosphanylcarbaborane(12), 1,2-bis(diethoxyphosphanyl)-*closo*-dicarbaborane(12), obtained starting from commercially available diethyl chlorophosphite, was reported in 1994,[6] however, no structurally characterised phosphanylcarbaborane(12) compounds have since been described.

We herein report the synthesis of phosphites with the chiral (–)-menthyl substituent and the syntheses of novel enantiomerically pure phosphanylcarbaborane(12) compounds thereof. To investigate the coordination properties, molybdenum and rhodium complexes were prepared, and the use of the latter as catalysts in hydroformylation of olefins is reported.

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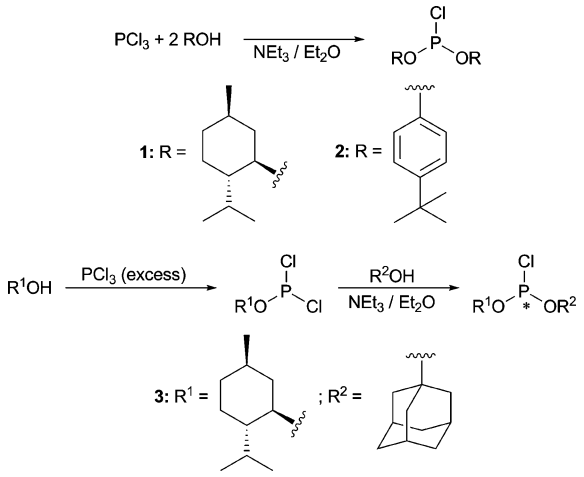
Results and Discussion

Preparation of P-Chiral Phosphites

The reaction of two equivalents of an alcohol with one equivalent of PCl_3 and two equivalents of triethylamine leads directly to the chlorophosphite.[7] In the presented work, we used the chiral alcohol (–)-menthol and the non-chiral 4-*tert*-butylphenol. During the distillation of bis(–)-menthyl chlorophosphite higher temperatures should be avoided. Above 60 °C an Arbuzov-type rearrangement occurs and dimenthylphosphonate can be observed in the ^1H and ^{31}P NMR spectra (δ_P = 4.9 ppm, $^1J_{PH}$ = 696.1 Hz).

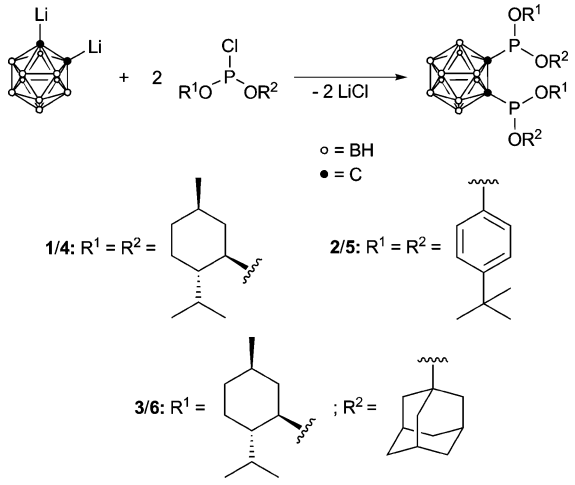
To obtain P-chiral chlorophosphites, a two-step synthesis was developed. In the first step the desired dichlorophosphite is synthesised in quantitative yield by solvent- and base-free reaction of (–)-menthol[8] with an excess of PCl_3.[9] The stoichiometric reaction in the presence of a base leads to a mixture of mono- and dichlorophosphites. In the second step (–)-menthyl dichlorophosphite is treated with 1-adamantanol in diethyl ether and triethylamine to give 1-adamantyl (–)-menthyl chlorophosphite as a single product (Scheme 1). Recrystallisation from diethyl ether gave the desired compound as a white solid. The $^{31}P\{^1H\}$ NMR spectrum showed two signals at δ = 165.5 and 170.5 ppm in a 1:1 ratio for the two diastereomers, separation of which, however, was not possible. The reverse reaction route starting from 1-adamantyl dichlorophosphite leads to a mixture of the desired product and 1-adamantyl bis(–)-menthyl phosphite as side product. It can therefore be concluded that the steric effects of 1-adamantanol are greater than those of (–)-menthol.



Scheme 1. Routes for the syntheses of chlorophosphites.

Preparation and Molecular Structures of Phosphanylcarbaborane(12) Compounds

Novel phosphanylcarbaborane(12) compounds **4**–**6** were prepared according to the synthetic pathway described by Alexander and Schroeder,[3] that is, dilithiation of 1,2-dicarba-*closo*-dodecaborane(12), followed by treatment with the corresponding chlorophosphite (Scheme 2). In the case of P-chiral phosphite **3** a racemic mixture was used. (R_P,R_P)- and (R_P,S_P)-**6** were the only enantiomers isolated, whilst the other two possible enantiomers were not obtained. The (R_P,R_P) isomer exhibits a singlet at δ =



Scheme 2. Synthesis of phosphanylcarbaborane(12) compounds.

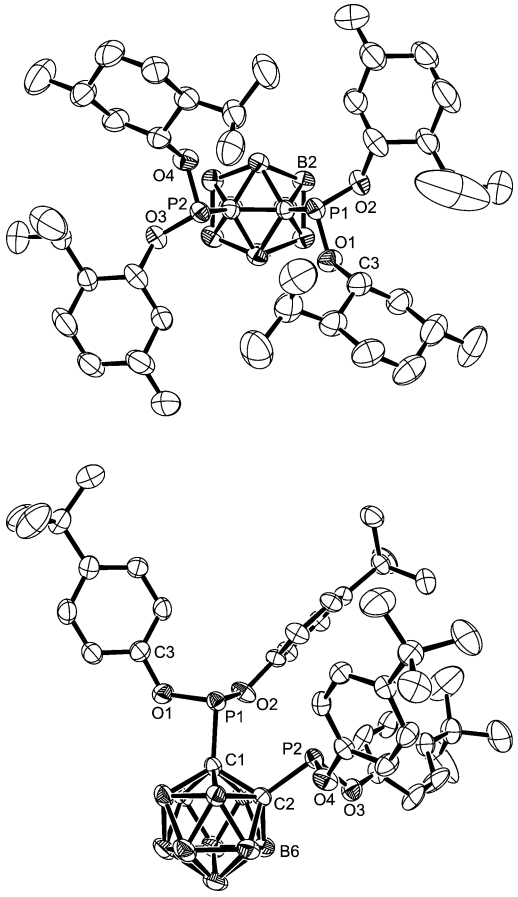


Figure 1. Molecular structures of 1,2-bis[bis(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) (**4**; top) and 1,2-bis[bis(4-*tert*-butylphenyloxy)phosphanyl]-*closo*-dicarbaborane(12) (**5**; bottom) with thermal ellipsoids at 50% probability level. H atoms have been omitted for clarity.

130.7 ppm in the $^{31}P\{^1H\}$ NMR spectrum, whilst the (R_P,S_P) isomer shows two doublets at δ = 133.1 and 137.5 ppm. The enantiomers could be separated by fractional crystallisation from *n*-hexane. The absolute configuration of all stereocentres in **4**–**6** was obtained by X-ray diffraction (Figure 1 and Figure 2, Table 1). Both enantiomers of **6** are, to the best of our knowledge, the first structurally characterised, enantiomerically pure P-chiral phosphanylcarbaborane(12) compounds.

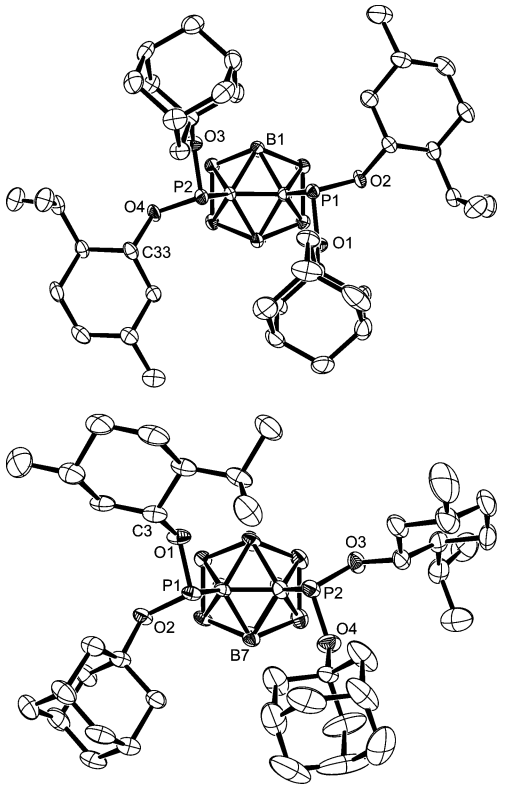


Figure 2. Molecular structures of (R_P,R_P)- (top) and (R_P,S_P)-1,2-bis[adamantyloxy-(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) (bottom) (**6**) with thermal ellipsoids at 50% probability level. H atoms and solvent molecules have been omitted for clarity.

Table 1. Selected bond lengths [pm] and angles [°] for **4**, **5** and **6**.

	4	**5**	(R_P,R_P)-**6**	(R_P,S_P)-**6**
P1–C1	189.2(2)	187.3(3)	188.5(1)	188.6(2)
P1–O1	161.1(2)	162.0(2)	160.8(1)	161.0(1)
P1–O2	161.6(1)	162.8(2)	161.6(1)	162.0(1)
P2–C2	189.4(2)	186.5(3)	188.1(2)	187.9(2)
P2–O3	161.7(1)	161.7(2)	160.3(1)	161.8(2)
P2–O4	161.7(2)	161.6(2)	161.8(1)	161.3(2)
C1–C2	168.8(2)	167.1(4)	166.0(2)	168.1(3)
P1···P2	342.18(7)	326.7(1)	331.4(1)	333.79(7)
C1–P1–O1	92.58(8)	94.0(1)	96.75(7)	97.51(8)
C1–P1–O2	98.30(7)	97.6(1)	93.74(6)	93.50(8)
O1–P1–O2	102.54(9)	100.6(1)	101.29(6)	102.37(8)
P1–C1–C2	112.2(2)	116.3(2)	117.0(1)	116.7(1)
C2–P2–O3	96.56(8)	97.2(1)	96.37(6)	92.13(8)
C2–P2–O4	93.20(8)	95.4(1)	96.20(7)	98.70(9)
O3–P2–O4	102.74(9)	98.6(1)	101.68(6)	101.17(9)
P2–C2–C1	117.2(1)	114.1(2)	115.0(1)	115.4(1)

Compounds **4**–**6** are moderately stable towards water and oxygen in both the solid state and solution, and the P-stereogenic centres in both enantiomers of **6** are stable towards epimerisation or inversion, as proved by refluxing in toluene in air for 2 d. A rearrangement of the alkyl groups to give phosphane oxides could not be detected. This phenomenon can be explained by the strongly electron-withdrawing character of the carbaborane cluster, which deactivates the electron lone pair at the phosphorus atom and stabilises the trivalent state.

In comparison to known phosphanyl-substituted carbaborane(12) compounds and phosphinites, the P–C and P–O bond lengths are in the same range.[4] The (–)-menthyl substituents have a larger steric demand than the 4-*tert*-butylphenyl groups, which can be confirmed by the slightly larger O–P–O bond angle at both phosphorus atoms and a larger P···P through-space distance in the solid state. The greater steric demand is also evident in the $^{13}C\{^1H\}$ NMR spectrum of **4**. The chemically equivalent carbon atoms become magnetically inequivalent due to hindered rotation. The phosphorus atoms of **4**–**6** show a distorted pyramidal coordination geometry, in which the electron lone pairs point towards each other. The P···P through-space distances range from 342.18(7) pm in **4** to 326.7(1) pm in **5**. Remarkably, the distances are shorter than the sum of the van der Waals radii of phosphorus. Accordingly, the P1–C1–C2 angles are smaller than expected. Both facts prove that the phosphorus atoms exhibit attraction to each other, rather than the expected repulsion.

Phosphorus–Phosphorus Coupling in Phosphanylcarbaborane(12) Compounds

To understand both phenomena, density functional theory (DFT) calculations employing the BP86 functional were carried out. The large 4-*tert*-butylphenyl substituents at the phosphorus atom were replaced with methyl groups due to the high computational effort. The geometry-optimised structure 1,2-bis(dimethoxyphosphanyl)-*closo*-dicarbaborane(12) gave a similar arrangement of the substituents at the phosphorus atoms. We further investigated the molecular orbitals and performed shared electron number (SEN) and natural bond orbital (NBO) analyses. The visualisation of the canonical molecular orbitals, which show significant overlap of the orbital fragments of the same sign, is shown in Figure 3. The lobes at the phosphorus atoms are both positive and are directed towards each other. A shared overlapping area is created and bonding interactions arise. The SEN analysis indicates electron density between the two phosphorus atoms. The value of 0.0342 is lower than those of covalent bonds (0.8–1.5), but in the range of hydrogen bonds.[10] In accordance with the X-ray data, repulsive interactions between both phosphorus atoms can be excluded. An NBO analysis was performed to study these interactions in more depth. This confirmed P···P interaction by overlap of the lone pair of one phosphorus atom with the antibonding orbital of the other phosphorus atom. Kivekäs et al. investigated this behaviour as well and verified the P···P interaction with several computational methods.[11]

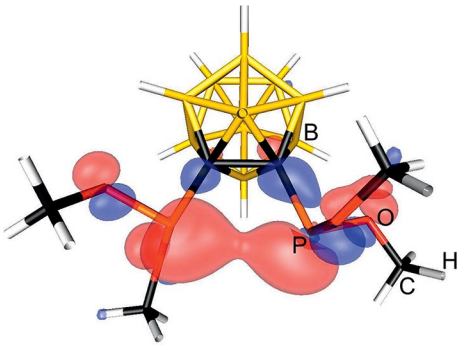


Figure 3. Canonical molecular orbitals of 1,2-bis(dimethoxyphosphanyl)-*closo*-dicarbaborane(12) with spatial probability of 95%. The red and blue spheres symbolise the positive or negative sign of the wave function.

Accordingly, multiplets appear for the phosphorus-coupled carbon atoms C1 and C2 in the $^{13}C\{^1H\}$ NMR spectra in the symmetrically P-substituted phosphanylcarbaborane(12) **5**. This is only possible if the chemically equivalent carbon atoms become magnetically inequivalent. Due to the low natural abundance of ^{13}C, the majority of these molecules detected with ^{13}C NMR spectroscopy only contain one ^{13}C atom in this position. These molecules therefore become asymmetric and the ^{13}C nucleus couples with both phosphorus nuclei ($^1J_{CP}$ and $^2J_{CP}$). This scenario results in a higher order ABX spin system. However, in the $^{31}P\{^1H\}$ NMR spectra the signal appears as a singlet, due to the chemical and magnetic equivalence of both phosphorus atoms. In the $^{13}C\{^1H,^{31}P\}$ NMR spectrum the signals appear as a singlet, which also verifies this model. This behaviour was also observed in symmetrically substituted bis(phosphanyl)carbaboranes by Hill et al., who misinterpreted this as a $^3J_{PP'}$ long-range coupling.[12] Woollins et al. also observed this behaviour in 1,8-diphosphanyl-substituted naphthalene derivatives,[13] which was confirmed by Schmidbaur et al. by spectral simulation. The signals were described as virtual triplets, caused by through-space spin coupling.[14] This corresponded to MAS NMR experiments for 1,8-bis(diphenylphosphanyl)naphthalene by Pringle et al.[15] In the solid state the bulky diphenylphosphanyl groups rotate into the most sterically unhindered position, and therefore the symmetry is eliminated.

A SpinWorks[16] simulation of the ^{13}C NMR signals of the P–C–C–P fragment in **5** verified the ABX spin system (Figure 4). The coupling constants $^3J_{PP}$, $^1J_{CP}$ and $^2J_{CP}$ were determined. If the P···P coupling is larger than the sum of the $^1J_{CP}$ and $^2J_{CP'}$ couplings – which is indicated by the outer lines of the central triplet – no $^3J_{PP}$ scalar coupling is possible. In this case only a through-space P···P coupling is possible, which is larger than 100 Hz. For all other carbon atoms, which couple with the phosphorus atoms, the distance between the outer lines also corresponds to the sum of the two coupling constants to phosphorus. For the carbon atoms, which are out of range of a phosphorus atom, the distance between the two lines is equal to the single coupling constant. The simulation of **5** results in a $^3J_{PP}$ through-space coupling constant of 104.7 Hz. The corresponding $^1J_{PC}$ coupling constant has a value of 76.0 Hz, and the $^2J_{PC}$ coupling constant is –7.0 Hz. In solution the large coupling constants are transferred by the electron lone pairs. In this case the size of the electron pair orbital depends on the σ character of the phosphorus atom. The electron lone pair is therefore forced into a repulsive overlapping position due to steric influence and forms intensive Fermi contacts (Figure 3). The $^3J_{PP}$ through-space coupling can therefore also be seen as a $^1J_{PP}$ coupling. If the electron lone pairs of the ligand coordinate in a bidentate fashion to a transition metal, such as molybdenum, the P···P through-space coupling becomes a $^2J_{PP'}$ coupling through the metal centre. For the analogous molybdenum complex of compound **5**, the $^2J_{PP'}$ coupling constant is 24.3 Hz (see below).

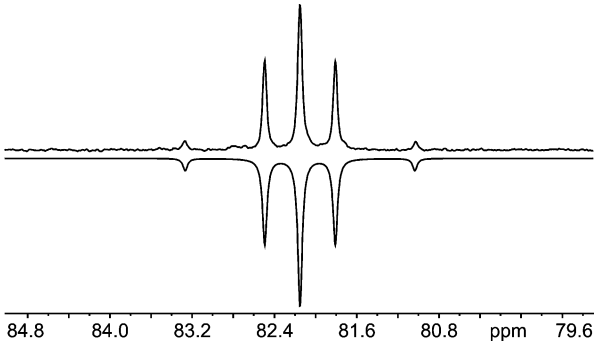


Figure 4. $^{13}C\{^1H\}$ NMR signals of the carbaborane carbon atoms of **5** (measured spectrum top, simulation bottom).

To confirm this assumption, computational studies were performed on **5** with the geometry-optimised structure mentioned above. The analysis was carried out by employing UHF calculations with a 3-21G basis set. The calculated results show a $^3J_{PP}$ coupling of 95.1 Hz, which fits well with the recorded data. $^1J_{PC}$ (39.4 Hz) and $^2J_{PC}$ (4.2 Hz) could also be determined, but these are a much poorer match. Admittedly, the natural J coupling (NJC) analysis is solely an auxiliary tool, which gives acceptable results for the elements of the first and second row, but less accurate results for those in the third row or below.

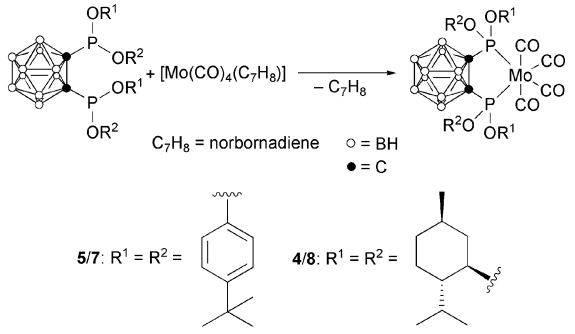
For the non-C_2-symmetric phosphanylcarbaborane (R_P,S_P)-1,2-bis[1-adamantyloxy-(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) (**6**) a doublet of doublets is obtained. This is due to the chemical inequivalence of the two phosphorus atoms. The P···P through-space coupling can be obtained directly from the ^{31}P NMR spectrum ($^3J_{PP}$ = 143.2 Hz). This pattern was observed by Pringle et al. in unsymmetrically substituted bisphosphanyl *ortho*-carbaborane(12) compounds with coupling constants of about 100 Hz.[4b] In the $^{13}C\{^1H\}$ NMR spectrum a double set of signals appears for all carbon atoms which couple with the phosphorus atom. The cluster carbon atoms appear in the same region as in the C_2-symmetric (R_P,R_P) analogue.

As mentioned above, the degree of overlap of the electron lone pair on the phosphorus atoms influences the P···P through-space coupling, and the distance between the phos-

phorus atoms has an influence on the coupling constants. In **4**, the sum of $^1J_{CP}$ and $^2J_{CP'}$ is 71.6 Hz, in the sterically less hindered compound **5** this value is 69.0 Hz, and it is 67.4 Hz in **6**. Accordingly, in the solid state the P···P distance of **4** is 342.18(7) pm as opposed to the lower values of 326.7(1) pm in **5** and 331.4(1) and 333.79(7) pm in **6**.

Synthesis, Molecular Structures and Coordination Properties of Molybdenum Complexes

The reaction of 1,2-bis[bis(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) (**4**) and 1,2-bis[bis(4-*tert*-butylphenyloxy)phosphanyl]-*closo*-dicarbaborane(12) (**5**) with tetracarbonyl norbornadienemolybdenum(0) gave the corresponding tetracarbonyl[oxyphosphanylcarbaborane(12)] molybdenum(0) complexes **8** and **7** in high yield as white solids (Scheme 3). The reactivity depends on the bulkiness of the substituents at the phosphorus atoms. Compound **5** reacted at room temperature, whereas **4** needed heating to reflux for 2 h. The complexes are quite stable in the solid state, whilst in solution they slowly decompose on exposure to air and light.



Scheme 3. Syntheses of tetracarbonyl[oxyphosphanylcarbaborane(12)]molybdenum(0) compounds.

In the $^{31}P\{^1H\}$ NMR spectra the tetracarbonyl[oxyphosphanylcarbaborane(12)]molybdenum(0) complexes **7** and **8** exhibit singlets at δ = 199.7 ppm (cf. 161.2 ppm in **5**) and 189.5 ppm (cf. 143.4 ppm in **4**), respectively. In the $^{13}C\{^1H\}$ NMR spectrum a doublet of doublets with $^2J_{CP}$ coupling constants of 12.5 and 42.1 Hz (for **7**) or 13.1 and 39.2 Hz (for **8**) can be observed for the equatorial carbonyl groups, while the axial carbonyl groups show triplets with smaller $^2J_{CP}$ coupling constants of 10.8 Hz (**7**) or 11.3 Hz (**8**). The corresponding IR spectra show shifts to higher wavenumbers for the carbonyl groups in comparison to earlier reported bis(phosphane)molybdenum(0) complexes, such as dppe, but similar to bis(phosphane)-carbaborane(12)-molybdenum(0) complexes.[17] The observed shifts indicate relatively electron-poor ligands and strong electron-withdrawing effects for the carbaborane(12) derivatives.

The molecular structures of **7** and **8** are depicted in Figure 5, and selected bond lengths and angles are given in Table 2. The molecule of **7** lies on a crystallographic mirror plane on which the axial carbonyl groups, the molybdenum atom and the centre of the C1–C1′ bond of the carbaborane cage reside. The octahedral environment of the molybdenum atom is slightly distorted due to the steric influence of the bulky substituents at phosphorus. The chelating ligands coordinate to the molybdenum atom to form an almost planar five-membered ring. The intramolecular P···P distance is shortened to 320.71(6) pm (in **7**) and 332.42(2) pm (for **8**) and the P1–Mo1–P2 angles are in the same range as in comparable complexes.[4b,d,18] The Mo–P bond length of 241.09(5) pm in **7** is slightly shorter than in earlier reported bis(phosphane) or phosphanylcarbaborane(12)-molybdenum(0) complexes.[4b,d,19] The bond lengths and angles of the coordinated ligand are not significantly changed compared to the free ligand. The strong π-acceptor and weak σ-donor properties of the phosphanyl groups influence the π back-bonding of the carbonyl groups.

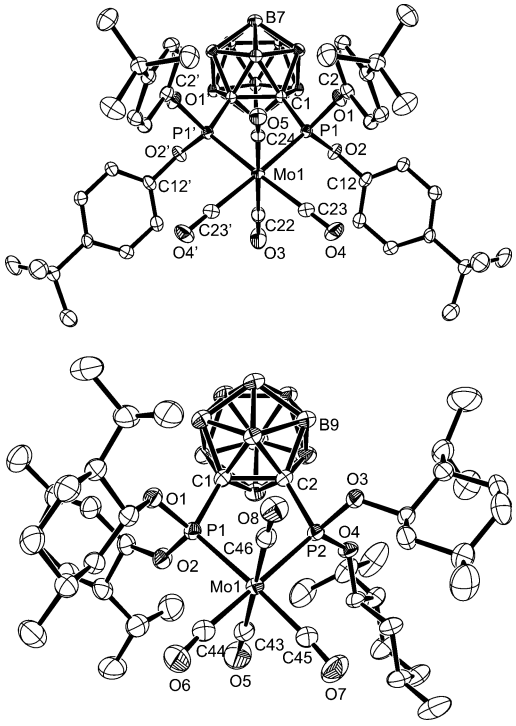


Figure 5. Molecular structures of **7** (top) and **8** (bottom) with thermal ellipsoids at 50% probability level. H atoms have been omitted for clarity. The prime (′) characters in the atom labels for **7** indicate that these atoms are in equivalent positions (x, $-y$ + 1/2, z).

An intramolecular interaction between the axial carbonyl group C24–O5 on the molybdenum atom and the π system of the C2/C2′ phenyl rings is observed. The distance of O5 to the phenyl ring is 312.67(9) pm, whilst the distance between O5 and the closest ring C atom is 329.5(3) pm. The Mo1–C24 bond length is increased to 208.4(3) pm due to this interaction. Venzo et al. first reported this behaviour for chromium tricarbonyl arene systems and described this interaction as an unconventional attractive CO···π_{arene} interaction.[20] Zabel et al. also observed these interactions for molybdenum carbonyl complexes, but the CO···π_{arene} distances are longer than those observed in this study.[21] The distance from O4 to the planes of the C12/C12′ phenyl rings is significantly larger [355.8(2) pm].

Table 2. Selected bond lengths [pm] and angles [°] for **7** and **8**.

	7		
Mo1–C22	201.0(3)	P1–Mo1–P1′	83.38(2)
Mo1–C23	203.5(2)	C22–Mo1–C23	86.95(8)
Mo1–C24	208.4(3)	C23–Mo1–C23′	91.7(1)
Mo1–P1	241.09(5)	Mo1–P1–C1	113.76(5)
P1–C1	186.4(2)	Mo1–P1–O1	123.87(5)
P1–O1	161.3(1)	Mo1–P1–O2	120.89(5)
P1–O2	161.6(1)	C1–P1–O1	98.11(7)
C1–C1′	166.3(3)	C1–P1–O2	94.05(7)
P1···P1′	320.71(6)	O1–P1–O2	100.20(7)
	8		
Mo1–C43	203.0(2)	P1–Mo1–P2	85.30(2)
Mo1–C44	202.4(2)	Mo1–P1–C1	112.07(6)
Mo1–C45	200.3(2)	Mo1–P1–O1	120.88(6)
Mo1–C46	204.9(2)	Mo1–P1–O2	113.06(6)
Mo1–P1	246.24(5)	Mo1–P2–C2	110.85(6)
Mo1–P2	244.40(5)	Mo1–P2–O3	119.30(6)
P1–C1	188.9(2)	Mo1–P2–O4	124.74(5)
P1–O1	160.1(1)	C1–P1–O1	96.36(8)
P1–O2	159.0(2)	C1–P1–O2	105.76(9)
P2–C2	188.4(2)	O1–P1–O2	106.67(8)
P2–O3	160.0(2)	C2–P2–O3	93.83(8)
P2–O4	160.6(1)	C2–P2–O4	100.59(8)
C1–C2	170.0(3)	O3–P2–O4	101.88(7)
P1···P2	332.42(2)		

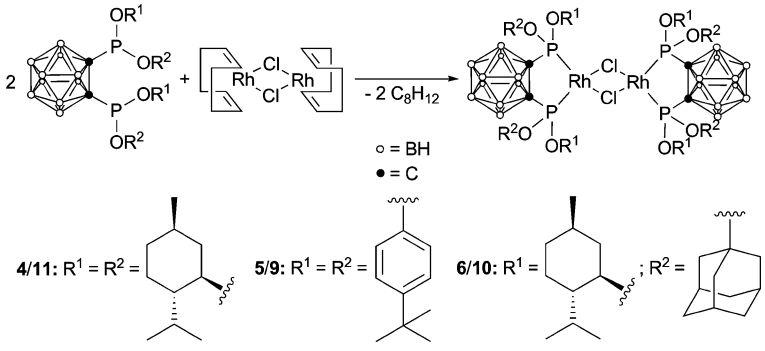
Rhodium Complexes and Catalytic Behaviour

Compounds **4**–**6** were used as ligands in homogeneous catalytic hydroformylation reactions. The rhodium complexes were first prepared to observe the configuration and steric properties of the ligands. The reaction of **4**–**6** with 0.5 equiv. of di-μ-chloro-bis(η⁴-1,5-cyclooctadiene)rhodium(I) led to the desired complexes (Scheme 4). We were able to obtain single-crystal X-ray diffraction analyses of compound **9** and both enantiomers of **10**. The products are chloro-bridged dimers, which are stable in air in the solid state. For the P-chiral complexes a formal inversion of the chirality at the phosphorus atom occurs, due to the higher priority of the rhodium atom over the electron lone pair.

While no crystal structure could be obtained for complex **11**, produced by the reaction of **4**, the compound was unambiguously characterised spectroscopically. The $^{31}P\{^{1}H\}$ NMR spectra of **9**, (S_P,S_P,S_P,S_P)-**10** and **11** show a doublet at ca. 150 ppm with a $^{1}J_{PRh}$ coupling constant of ca. 270 Hz. (R_P,S_P,R_P,S_P)-**10** shows a more complex pattern in the $^{31}P\{^{1}H\}$ NMR spectrum. Due to the coupling of two inequivalent phosphorus atoms to the rhodium atom, every ligand signal splits into a doublet.

Complex **9** crystallises in the triclinic space group $P\bar{1}$ from toluene/*n*-hexane with six molecules in the unit cell [Figure 6 (top); Table 3]. The coordination sphere of the rhodium atoms is slightly distorted square planar. The four-membered Rh–Cl–Rh–Cl ring has a butterfly conformation, wherein the angles between both of the Cl–Rh–Cl planes have values between 134.2 and 138.5°. Two of the 4-*tert*-butylphenyl groups are in almost equatorial positions, whereas the other two remain in axial positions, relative to the five-membered Rh1–P1–C1–C2–P2 ring. The rhodium complexes **10** (Figure 6, Table 3), which are to the best of our knowledge the first enantiomerically pure rhodium complexes of *ortho*-carbaboranes, exhibit an almost planar Rh–Cl–Rh–Cl four-membered ring due to the sterically demanding 1-adamantyl and (–)-menthyl groups [angle between the two Cl–Rh–Cl planes is 172.7° in the (S_P,S_P,S_P,S_P) enantiomer, 176.4° in the (R_P,S_P,R_P,S_P) enantiomer]. Theoretical calculations on chloro-bridged dimeric bis(phosphane)rhodium complexes showed that only a small energy difference of 10 kJ mol^{-1} exists between the planar and bent configurations.[22] Therefore, packing effects and/or steric interactions can effect the shape of the ring. The Rh–Cl bonds are slightly longer than in the starting material.[23] The P–C and P–O bond lengths are shorter than in the free ligand, but still in the range of other previously reported electron-poor dimeric phosphanerhodium(I) complexes.[20,24] As for the molybdenum complexes reported above, a strong π-acceptor bond to the phosphanyl phosphorus atoms can also be observed in the rhodium complexes.

Hydroformylation reactions play a major role in chemical processes to obtain aldehydes from olefins.[25] Aldehyde groups are one of the most versatile functional groups in organic synthesis and can be transformed into alcohols, amines, imines and acids.[26] A useful hydroformylation reaction needs to produce aldehydes with high productivity, and simultaneously be chemo-, regio- and stereoselective and is thus an ongoing challenge in academic and industrial research. To control the selectivity of the reaction, com-



Scheme 4. Formation of chloro-bridged rhodium(I) complexes of phosphanylcarbaborane(12) compounds.

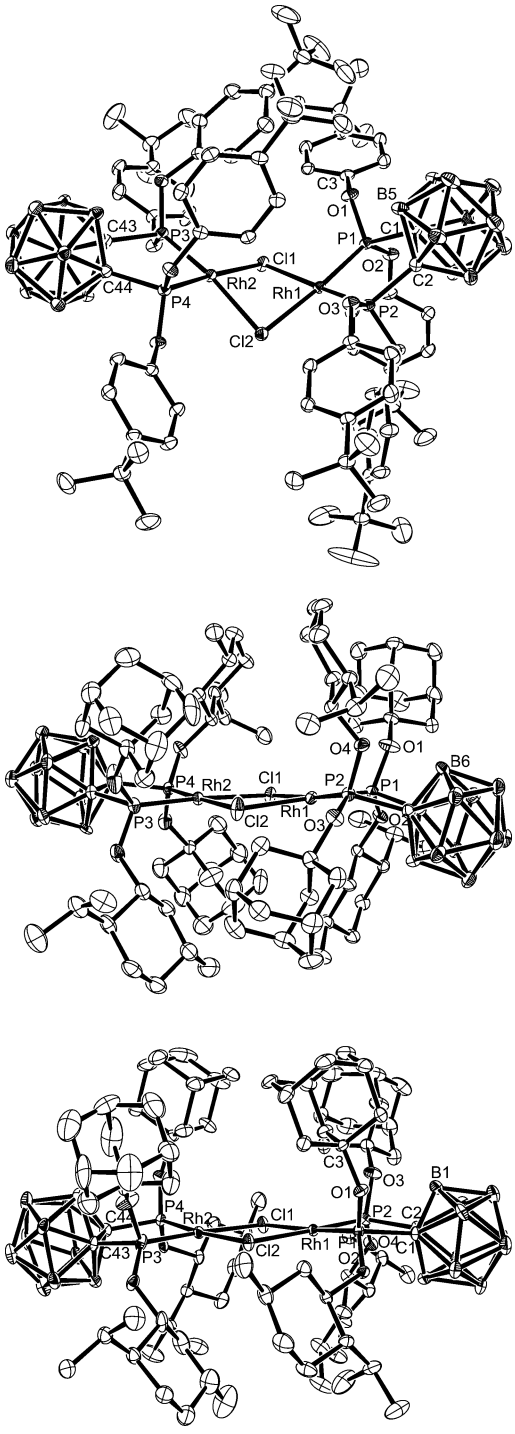


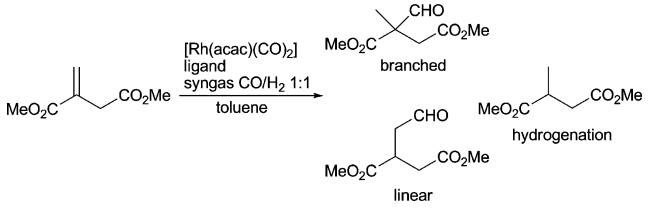
Figure 6. Molecular structure of **9** (top), (S_P,S_P,S_P,S_P)-**10** (middle) and (R_P,S_P,R_P,S_P)-**10** (bottom) with thermal ellipsoids at 50% probability level. H atoms and solvent molecules have been omitted for clarity. Only one molecule of **9** in the asymmetric unit is shown.

plexes with different steric and electronic properties have been used in technical processes.[27] In general, the majority of the most active Rh hydroformylation catalysts are derived from electron-poor and sterically demanding phosphanes,[28–31] making ligands **4**–**6** interesting candidates for study in Rh-catalysed hydroformylation.

Table 3. Selected bond lengths [pm] and angles [°] for **9** and **10**.

	9	(S_P,S_P,S_P,S_P)-**10**	(R_P,S_P,R_P,S_P)-**10**
Rh1–Cl1	241.87(5)	246.33(6)	243.35(8)
Rh1–Cl2	240.28(4)	242.83(7)	244.81(8)
Rh1–P1	213.53(5)	216.30(7)	215.77(9)
Rh1–P2	213.15(5)	217.11(6)	216.29(9)
P1–C1	185.7(2)	187.5(2)	185.1(3)
P1–O1	158.9(1)	157.7(2)	159.5(2)
P1–O2	160.6(1)	158.8(2)	158.1(2)
P2–C2	185.8(2)	187.4(3)	186.3(3)
P2–O3	160.8(1)	158.1(2)	157.6(3)
P2–O4	160.0(1)	160.1(2)	158.3(3)
C1–C2	164.6(2)	163.4(4)	164.5(4)
P1···P2	297.91(7)	297.54(8)	300.1(1)
P1–Rh1–P2	88.57(2)	86.71(3)	88.00(3)
Cl1–Rh1–Cl2	83.80(2)	79.36(2)	81.84(3)
P1–Rh1–Cl1	93.17(2)	94.70(2)	94.57(3)
P2–Rh1–Cl2	94.19(2)	99.47(2)	95.55(3)
C1–P1–Rh1	113.37(6)	112.03(9)	113.9(1)
C1–P1–O1	99.37(8)	96.6(1)	100.7(2)
C1–P1–O2	100.05(8)	101.4(1)	94.4(1)
O1–P1–O2	101.50(7)	102.9(1)	100.7(1)
Cl–Rh–Cl planes angles	134.2–138.5	172.7	176.4

The performance of ligands **4**–**6** in Rh-catalysed hydroformylation of dimethyl itaconate was investigated (Scheme 5). The catalytically active complex was produced in situ by the reaction of [Rh(acac)(CO)$_2$] (acac = acetylacetonate) as catalyst precursor and the corresponding ligand. The yields were determined by ^{1}H NMR spectroscopy against an internal standard.



Scheme 5. Hydroformylation of dimethyl itaconate.

Unfortunately, complexes of the chiral ligands **4** and both enantiomers of **6** showed a maximum conversion of only 11% (with 38% hydrogenation) over 48 h (100 °C, 50 bar). Better results were obtained with 1,2-bis[bis(4-*tert*-butylphenyloxy)phosphanyl]-*closo*-dicarbaborane(12) (**5**) (Table 4). Good regioselectivities for the linear aldehyde and full conversion were achieved by increasing the temperature to 100 °C. High temperatures are required for commercial hydroformylation reactions, as these processes proceed at a slower rate than hydrogenation reactions.[30] Unfortunately, the hydrogenation by-products make the procedure impractical for organic synthesis. In comparison to the ligands tested, dppe [1,2-bis(diphenylphosphanyl)ethane] shows inverse behaviour, with full conversion to the branched aldehyde. This shows that hydroformylation reactions are highly ligand dependent and that the use of a bidentate ligand influences the formation of the different regioisomers. Clarke et al. reported the hydroformylation of

dimethyl itaconate with high conversion to the branched isomer and minimal hydrogenation by-products by using a monodentate phosphorus cage ligand.[31a]

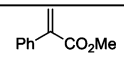
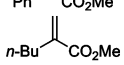
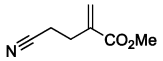
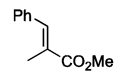
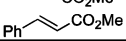
Table 4. Hydroformylation of dimethyl itaconate with **5** and dppe.

Conditions[a]	Ligand	Conversion (hydrogenation)	Branched/linear ratio
50 °C, 15 bar, 24 h	**5**	54% (20%)	1:1.6
	dppe	49% (25%)	50:2
50 °C, 50 bar, 24 h	**5**	82% (18%)	1:1.7
100 °C, 15 bar, 24 h	**5**	100% (34%)	1:18
	dppe	100% (37%)	11:2
100 °C, 50 bar, 24 h	**5**	100% (29%)	1:10

[a] 0.2% [Rh(acac)(CO)$_2$], 0.25% ligand, toluene, syngas CO/H$_2$ (1:1).

We performed hydroformylation reactions with the most active ligand **5** and optimised conditions on a series of other 1,1-disubstituted alkenes with various functional groups and side-chain lengths (Table 5). Hydrogenated by-products, as in the hydroformylation of dimethyl itaconate, are also a problem in these reactions and always arise in the range of 20–30%. All substrates with phenyl groups next to the double bond gave 100% conversions to the linear isomer. Methyl α-butylacrylate (**S2**) showed a different behaviour in its inverted branched/linear ratio. Clarke et al. also reported isomerisation/hydroformylation to the more stable trisubstituted alkene and further reaction to the quaternary product.[31a] We obtained the best results with the hydroformylation of methyl 5-cyano-2-methylenepentanoate (**S3**) to the resulting linear product. A reason for this could be coordination of the cyano group to the metal centre, to form a moderately stable intermediate, which directs the reaction to the linear product. Another explanation for the good regioselectivities of **5** could be the orientation of the 4-*tert*-butyl groups, which shield one of the coordination sides at the rhodium atom. The hydroformylation of 1,2-disubstituted unsaturated esters is one of the cleanest and easiest routes to fundamental building blocks and was previously investigated by several groups.[32] We, therefore, investigated the hydroformylation of methyl α-methylcinnamate (**S4**) and methyl cinnamate (**S5**), which both were converted into the β-form in good regioselectivity.

Table 5. Hydroformylation reactions of various olefins with ligand **5**.

	Substrate	Conversion (hydrogenation)[a,b]	Branched/linear ratio[b]
S1		100% (29%)	1:5
S2		98% (22%)	3:1
S3		92% (26%)	1:100
S4		100% (28%)	1:27[c]
S5		100% (21%)	1:25[c]

[a] Reaction conditions: 0.2% [Rh(acac)(CO)$_2$], 0.25% **5**, toluene, 100 °C, 50 bar, 24 h, syngas CO/H$_2$ (1:1). [b] Determined by ^{1}H NMR spectroscopy. [c] α/β ratio.

Summary

Chiral chlorophosphites were employed as enantiomeric mixtures for the synthesis of the first enantiomerically pure chiral phosphanyl-*ortho*-carbaborane(12) compounds. To determine the absolute configuration of the stereocentres, single-crystal X-ray diffraction was used. P···P through-space coupling in *ortho*-carbaboranes was investigated, and the coupling constants were determined by NMR spectral simulation and are in the range of 105 Hz. Several complexes were prepared, e.g., tetracarbonylmolybdenum(0) complexes with ligands **4** and **5** and chloro-bridged rhodium complexes of **4**, **5** and the (R_P,R_P)- and (R_P,S_P)-enantiomer of **6**. All compounds are configurationally stable. Rhodium complexes of the achiral ligand **5** were shown to be rather promising in homogeneous catalytic hydroformylation reactions.

Experimental Section

General Methods: All reactions were carried out under dry high-purity nitrogen using standard Schlenk techniques. Solvents were purified and degassed with an MBRAUN Solvent Purification System SPS-800. [Mo(CO)$_4$(nbd)], [{Rh(μ-Cl)(cod)}$_2$] and **S1**–**S5** were prepared by literature methods.[31a,33] PCl_3, (–)-menthol, 1-adamantanol, 4-*tert*-butylphenol and 1,2-dicarba-*closo*-dodecaborane(12), [Rh(acac)(CO)$_2$] and dppe are commercially available. The NMR spectra were recorded with a Bruker Avance DRX 400 spectrometer (^{1}H NMR 400.132 MHz, ^{11}B NMR 128.377 MHz, ^{13}C NMR 100.625 MHz, ^{31}P NMR 161.977 MHz). TMS was used as the internal standard in the ^{1}H NMR spectra and all other nuclei spectra were referenced to TMS using the Ξ scale.[34] ^{13}C{^{1}H} spectra were recorded as APT spectra and the assignment was made by 2D NMR experiments. Mass spectra were recorded with a VG Analytics ZAB-HSQ spectrometer (FAB), a Bruker Daltonics 7 Tesla APEX II (ESI), or a Finnigan MAT MAT8200 (EI). FTIR spectra were recorded with a Perkin–Elmer Spectrum 2000 FTIR spectrometer in the range of 400–4000 cm^{-1} in KBr. Elemental analysis was performed with a Heraeus VARIO EL instrument CHN-O-S Analyzer. The melting points were determined in glass capillaries sealed under nitrogen using a Gallenkamp apparatus and are uncorrected.

Hydroformylation Experiments: Hydroformylation experiments were carried out in small glass vessels under inert conditions. These vessels were placed inside stainless steel autoclaves, heated in temperature controlled oil baths or heating jackets and stirred magnetically. The air inside the autoclave was displaced by threefold flushing with syngas (CO/H$_2$, 1:1). The conversion was measured by ^{1}H NMR spectroscopy against internal standard and the spectral properties of the products were compared with authentic samples from previous work.[31]

Computational Calculations: All geometry optimisations were carried out with the programme Turbomole.[35] Density-functional theory (DFT)[36] calculations employing the BP86 functional were applied for the sake of low computational costs. The TZVPP basis

set and RI approximation[37] for all atoms were used throughout. The natural *J* coupling (NJC) analysis[38] was done with the Gaussian03[39] program in combination with the NBO 5.0 program.[40] The analysis was carried out by employing UHF calculations with a 3-21 G basis[41] set at an SCF convergence criterion of 10^{-6} Hartree. All molecular structures were fully optimised until the length of the gradient vector had approached about 10^{-4} au and the energy difference of the last twenty structures in the optimisation procedure was below 1 kJ· mol^{-1}.

X-ray Crystallography: Crystallographic measurements were made with a Stoe-IPDS imaging plate diffractometer for compound **4**, a Siemens SMART CCD diffractometer for compound **8** and an Oxford Diffraction Xcalibur S diffractometer for compounds **5**, **7**, **9** and both enantiomers of **6** and **10**. Suitable crystals were mounted in perfluoroalkyl ether. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELX97.[42] All non hydrogen atoms, except for some poorly localised solvent molecules, were refined anisotropically, and hydrogen atoms were either located and refined isotropically or included in a riding mode. Crystal data and details of data collection and refinement are given in Table 6 and Table 7. Molecular structure representations were created with ORTEP.[43]

CCDC-719517 (for **4**), CCDC-719518 (for **5**), CCDC-719519 [for (R_P,R_P)-**6**], CCDC-719520 [for (R_P,S_P)-**6**], CCDC-719521 (for **7**), CCDC-719522 (for **8**), CCDC-719523 (for **9**), CCDC-719524 [for (S_P,S_P,S_P,S_P)-**10**] and CCDC-719525 [for (R_P,S_P,R_P,S_P)-**10**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Synthesis of Dichlorophosphites:[10] One equivalent of the alcohol was slowly added to 5 equiv. of PCl_3. The

Table 6. Crystal data for compounds **4**, **5**, (R_P,R_P)-**6** and (R_P,S_P)-**6** and the metal complexes **7**.

Compound	**4**	**5**	(R_P,R_P)-**6**	(R_P,S_P)-**6**	**7**
Empirical formula	$C_{42}H_{86}B_{10}O_4P_2{\cdot}C_7H_8$	$C_{42}H_{62}B_{10}O_4P_2{\cdot}C_7H_8$	$C_{42}H_{78}B_{10}O_4P_2$	$C_{42}H_{78}B_{10}O_4P_2$	$C_{46}H_{62}B_{10}MoO_8P_2$
Formula weight	825.19	800.00	817.08	817.08	1008.94
T [K]	213(2)	180(2)	130(2)	130(2)	130(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*C*2	$P2_1/n$	$P2_1$	$P2_1$	$P2_1/m$
a [pm]	2069.2(1)	1458.48(2)	958.6(5)	1027.02(2)	953.65(1)
b [pm]	1376.74(8)	1997.75(3)	1991.6(5)	2522.42(4)	2639.23(3)
c [pm]	2301.7(1)	1814.72(3)	1252.6(5)	1029.62(2)	1073.04(1)
α [°]	90	90	90	90	90
β [°]	116.203(6)	98.183(2)	92.263(5)	115.460(2)	105.388(1)
γ [°]	90	90	90	90	90
V [nm^3]	5.8831(6)	5.2337(1)	2.3895(17)	2.40827(8)	2.60392(5)
Z	4	4	2	2	2
$\rho_{calcd.}$ [Mgm^{-3}]	1.036	1.133	1.136	1.127	1.287
$\mu_{Mo-K\alpha}$ [mm^{-1}]	0.111	0.124	0.130	0.129	0.362
F(000)	2000	1904	884	884	1048
Refl. collected	24480	85578	53521	32490	80943
Independent refl.	11895	12258	14493	14174	8110
*R*1/*wR*2 [$I>2\sigma(I)$]	0.0390/0.0885	0.0966/0.1694	0.0424/0.0638	0.0516/0.0988	0.0431/0.0811
*R*1/*wR*2 (all data)	0.0546/0.0919	0.1489/0.1910	0.0753/0.0719	0.0787/0.1150	0.0488/0.0829
Flack parameter *x*	0.03(6)	–	0.02(4)	0.00(6)	–

Table 7. Crystal data for the metal complexes **8**, **9**, (S_P,S_P,S_P,S_P)-**10** and (R_P,S_P,R_P,S_P)-**10**.

Compound	**8**	**9**	(S_P,S_P,S_P,S_P)-**10**	(R_P,S_P,R_P,S_P)-**10**
Empirical formula	$C_{46}H_{86}B_{10}MoO_8P_2$	$C_{84}H_{124}B_{20}Cl_2O_8P_4Rh_2{\cdot}3C_7H_8$	$C_{84}H_{156}B_{20}Cl_2O_8P_4Rh_2{\cdot}4CH_2Cl_2$	$C_{84}H_{156}B_{20}Cl_2O_8P_4Rh_2{\cdot}2CH_2Cl_2$
Formula weight	1033.13	1880.76	1910.96	1910.96
T [K]	213(2)	100(2)	130(2)	130(2)
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_12_12_1$	$P2_1$
a [pm]	1033.24(7)	1944.57(4)	1661.90(1)	1321.43(1)
b [pm]	1920.6(1)	2800.21(6)	2407.52(2)	2683.13(2)
c [pm]	1467.60(9)	3244.74(6)	2738.83(3)	1568.59(1)
α [°]	90	84.748(2)	90	90
β [°]	96.969(1)	80.746(2)	90	110.953(1)
γ [°]	90	74.502(2)	90	90
V [nm^3]	2.8909(3)	16.7823(6)	10.9582(2)	5.19378(6)
Z	2	6	4	2
$\rho_{calcd.}$ [Mgm^{-3}]	1.187	1.279	1.364	1.330
$\mu_{Mo-K\alpha}$ [mm^{-1}]	0.327	0.453	0.654	0.584
F(000)	1096	6756	4704	2184
Refl. collected	27443	427498	199608	25592
Independent refl.	13338	102102	33340	31698
*R*1/*wR*2 [$I>2\sigma(I)$]	0.0291/0.0648	0.0365/0.0785	0.0447/0.1072	0.0331/0.0782
*R*1/*wR*2 (all data)	0.0304/0.0653	0.0649/0.0898	0.0747/0.1318	0.0460/0.0904
Flack parameter *x*	–0.01(2)	–	–0.06(2)	–0.05(1)

reaction mixture was stirred for an additional 3 h. The HCl gas formed was neutralised with aqueous NaOH. The reaction mixture was distilled under vacuum to obtain the pure dichlorophosphite. The redistilled PCl_3 can be recycled for further use.

General Procedure for the Synthesis of Symmetric Chlorophosphites:[44] Two equivalents of the alcohol and 2.5 equiv. of triethylamine in diethyl ether were added to one equivalent of PCl_3 dropwise in diethyl ether. A white precipitate formed. The reaction mixture was stirred for 3 h at r. t. The solvent was filtered off and the solid was washed twice with diethyl ether. The solvent was removed under vacuum. The obtained oil was distilled under vacuum.

Procedure for the Synthesis of Asymmetric 1-Adamantyl (–)-Menthyl Chlorophosphite: One equivalent of (–)-menthyl dichlorophosphite in diethyl ether was added dropwise to one equivalent of 1-adamantanol and 1.5 equiv. of triethylamine in diethyl ether. A white precipitate formed. The reaction mixture was stirred for 3 h at r. t. The solvent was filtered off and the solid was washed twice with diethyl ether. The solvent was removed under vacuum. A white solid of 1-adamantyl-(–) menthyl chlorophosphite was formed.

General Procedure for the Synthesis of 1,2-Bis[alkyl/aryloxy)phosphanyl]-*closo*-dicarbaborane(12) Compounds: One equivalent of 1,2-dicarba-*closo*-dodecaborane(12) was dissolved in diethyl ether and cooled to 0 °C. Two equivalents of *n*BuLi in *n*-hexane were added via syringe and the reaction mixture was warmed to room temp. The mixture was stirred for 2 h and 1,2-dilithio-1,2-dicarba-*closo*-dodecaborane(12) formed as a white solid. This was added via a cannula to a solution of 2.1 equiv. of the chlorophosphite in diethyl ether cooled to 0 °C. The mixture was stirred overnight at room temp. and LiCl was filtered off. The solvent was evaporated under vacuum. Crystallisation leads to the desired product.

General Procedure for the Synthesis of Tetracarbonylmolybdenum(0) Complexes: One equivalent of the ligand was dissolved in *n*-hexane. A solution of one equivalent of $[Mo(CO)_4(nbd)]$ in *n*-hexane was added via syringe. The reaction mixture was heated to reflux for 2 h (**7**) or stirred at room temp. for 2 h (**8**). The mixture was filtered and concentrated under vacuum. Crystallisation leads to the colourless complexes.

General Procedure for the Synthesis of Dimeric Chloro-Bridged Rhodium(I) Complexes: Two equivalents of the ligand were dissolved in dichloromethane. A solution of one equivalent of $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ in dichloromethane was added via syringe. The reaction mixture was shortly heated to reflux and stirred for 30 min. The mixture was filtered and concentrated under vacuum. Crystallisation leads to the orange-red complexes.

General Procedure for the Hydroformylation of Alkenes: $[Rh(acac)(CO)_2]$ (2.0 mg, $7.75\cdot10^{-3}$ mmol; 0.2%) and the ligand ($9.30\cdot10^{-3}$ mmol, 0.25%) were dissolved in 2 mL toluene under inert atmosphere. substrate (3.88 mmol) was added, the mixture was transferred into the glass vessel and placed in the autoclave. Substrate-specific reaction times and conditions are given in the footnote under Table 4 and Table 5. The mixture was filtered through silica, concentrated and analysed (Figure 7).

(–)-Menthyl Dichlorphosphite: (–)-menthol (7.8 g, 0.05 mol), PCl_3 (34.3 g, 0.25 mol); yield 12.59 g (98%). B.p. 110–112 °C (260 Pa). ^{1}H NMR (C_6D_6): δ = 0.64 (m, 1 H, H^4), 0.77 (m, 10 H, H^3, H^8, H^9, H^{10}), 1.15 (m, 3 H, H^2, H^5, H^6), 1.44 (m, 2 H, H^3, H^4), 1.98 (m, 1 H, H^7), 2.30 (m, 1 H, H^6), 4.40 (m, 1 H, H^1) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 16.1 (s, C^8), 21.2 (s, C^9), 22.0 (s, C^{10}), 22.8 (s, C^3), 25.1 (s, C^7), 31.4 (s, C^5), 33.8 (s, C^4), 43.3 (s, C^6), 48.7 (s, C^2), 83.5 (d, $^2J_{PC}$ = 9.8 Hz, C^1) ppm. ^{31}P NMR (C_6D_6): δ = 176.1 (d, $^3J_{PH}$ = 13.5 Hz) ppm.

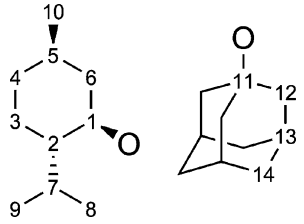


Figure 7. Assignment scheme for (–)-menthyl and 1-adamantyl groups.

Bis(–)-menthyl Chlorophosphite (1): (–)-Menthol (15.6 g, 0.1 mol) and triethylamine (12.6 g, 0.125 mol) in 100 mL of diethyl ether, PCl_3 (6.8 g, 0.05 mol) in 300 mL of diethyl ether; yield 12.22 g (65%); m.p. 53–55 °C. B.p. 130 °C (0.4 Pa). ^{1}H NMR (C_6D_6): δ = 0.67 (m, 2 H, H^4), 0.85 (m, 20 H, H^3, H^8, H^9, H^{10}), 1.33 (m, 10 H, H^2, H^3, H^4, H^5, H^6), 2.42 (m, 4 H, H^6, H^7), 4.31 (m, 2 H, H^1) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 16.0/16.2 (s, C^8, C$^{8'}$), 21.3 (s, C^9, C$^{9'}$), 22.1/22.2 (s, C^{10}, C$^{10'}$), 23.0/23.1 (s, C^3, C$^{3'}$), 25.5/25.7 (s, C^7, C$^{7'}$), 31.6/31.8 (s, C^5, C$^{5'}$), 34.2/34.3 (s, C^4, C$^{4'}$), 43.6/43.8 (s, C^6, C$^{6'}$), 49.1/49.2 (s, C^2, C$^{2'}$), 77.2/77.3 (s, C^1, C$^{1'}$) ppm. ^{31}P NMR (C_6D_6): δ = 167.8 (t, $^3J_{PH}$ = 10.3 Hz) ppm.

Bis(4-*tert*-butylphenyl) Chlorophosphite (2): 4-*tert*-Butylphenol (15.2 g, 0.1 mol) and triethylamine (12.6 g, 0.125 mol) in 100 mL of diethyl ether, PCl_3 (6.8 g, 0.05 mol) in 300 mL of diethyl ether; yield 13.29 g (73%); m.p. 49–51 °C. ^{1}H NMR ($CDCl_3$): δ = 1.31 (s, 18 H, CH_3), 7.11 (d, $^3J_{HH}$ = 8.4 Hz, 4 H, CH), 7.35 (d, $^3J_{HH}$ = 8.4 Hz, 4 H, CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 31.4 (s, C-(CH_3)$_3$), 34.4 (s, *C*-(CH_3)$_3$), 120.4 (d, $^3J_{CP}$ = 6.4 Hz, C^{ortho}), 126.6 (s, C^{meta}), 148.0 (t, $^2J_{CP}$ = 1.0 Hz, C^{ipso}), 148.7 (s, C^{para}) ppm. ^{31}P NMR ($CDCl_3$): δ = 158.7 (s) ppm.

1-Adamantyl (–)-Menthyl Chlorophosphite (3): 1-Adamantanol (3.0 g, 0.02 mol) and triethylamine (3.0 g, 0.03 mol) in 150 mL of diethyl ether, (–)-menthyl dichlorophosphite (5.1 g, 0.02 mol) in 200 mL of diethyl ether; yield 6.49 g (87%); m.p. 93–96 °C. ^{1}H NMR ($CDCl_3$): δ = 0.92 (m, 10 H, H^4, H^8, H^9, H^{10}), 1.04 (m, 1 H, H^3), 1.16 (m, 1 H, H^6), 1.19 (m, 1 H, H^2), 1.42 (m, 1 H, H^5), 1.65 (m, 8 H, H^3, H^4, H^{14}), 2.15 (m, 11 H, H^6, H^7, H^{11}, H^{12}), 4.25 (m, 1 H, H^1) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 16.4 (s, C^8, C$^{8'}$), 21.2/21.3 (s, C^9, C$^{9'}$), 22.1/22.2 (s, C^{10}, C$^{10'}$), 22.9 (s, C^3, C$^{3'}$), 25.1/25.2 (s, C^7, C$^{7'}$), 31.0 (s, C^{13}, C$^{13'}$), 31.6/31.7 (s, C^5, C$^{5'}$), 34.2 (s, C^4, C$^{4'}$), 35.7/35.8 (s, C^{14}, C$^{14'}$), 43.6/43.7 (d, $^3J_{PC}$ = 2.0 Hz, C^6, C$^{6'}$), 44.4/44.5 (d, $^3J_{PC}$ = 1.9 Hz, C^{12}, C$^{12'}$), 48.7/48.8 (d, $^3J_{PC}$ = 3.7 Hz, C^2, C$^{2'}$), 77.7/77.8 (d, $^2J_{PC}$ = 3.7 Hz, C^1, C$^{1'}$), 80.3/80.5 (d, $^2J_{PC}$ = 5.9 Hz, C^{11}, C$^{11'}$) ppm. ^{31}P NMR (C_6D_6): δ = 167.3 and 173.7 (d, $^3J_{PH}$ = 8.9 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2921, 2854, 1456, 1386, 1368, 1355, 1257, 1183, 1105, 1056, 998, 969, 951, 932, 875, 833, 812, 797, 589, 490, 432 cm^{-1}.

1,2-Bis[bis(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) (4): 1,2-Dicarba-*closo*-dodecaborane(12) (0.29 g, 2 mmol) in 30 mL of diethyl ether, *n*BuLi (1.7 mL) in *n*-hexane (2.4 M), **1** (1.6 g, 4.2 mmol) in 50 mL of diethyl ether. Crystallisation from *n*-hexane/toluene; yield 1.30 g (79%); m.p. 111–113 °C. ^{1}H NMR (C_6D_6): δ = 0.74 (m, 4 H, H^4), 0.92 (m, 40 H, H^3, H^8, H^9, H^{10}), 1.41 (m, 20 H, H^2, H^3, H^4, H^5, H^6), 2.20–3.90 (br. m, 10 H, H^B), 2.41 (m, 4 H, H^6), 2.64 (m, 4 H, H^7), 3.84 (m, 4 H, H^1) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ = –0.1 (br. s, 2 B), –6.7 (br. s, 2 B), –10.4 (br. s, 6 B) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 16.2/16.5 (C^8, C$^{8'}$), 21.2/21.4 (C^9, C$^{9'}$), 22.2 (C^{10}, C$^{10'}$), 23.1/23.3 (C^3, C$^{3'}$), 25.2/25.3 (C^7, C$^{7'}$), 32.1/

32.3 (C^5, $C^{5'}$), 34.2/34.3 (C^4, $C^{4'}$), 44.0/44.1 (C^6, $C^{6'}$), 49.2/49.9 (C^2, $C^{2'}$), 78.9/79.4 (t, $^2J_{CP}$ = 7.0 Hz, C^1, $C^{1'}$), 84.8 (m, $^1J_{CP}$ + $^2J_{CP}$ = 71.6 Hz, C^{CB}) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 143.4 ppm. IR (KBr): $\tilde{\nu}$ = 2957, 2929, 2872 (st, CH_2, CH), 2627, 2566 (st, BH), 1454 (st, CH), 1371 (m, CH_3), 1179 (w, BC), 1013, 993, 973 (st, POC), 864 (st, PO); not assigned: 3417 (w, br), 1943, 1857, 1737, 1605 (w), 1496, 1343 (m); 1295, 1269, 1238, 1155 (w), 1077 (m), 924, 818, 802 (st), 730 (m), 695, 677, 628, 596, 551, 528, 484, 465, 425 (w). MS (DEI pos.): *m/z* (%) = 824.7 (1.7) [M^+], 550.1 (1.2) [$M^+ - 2\ C_{10}H_{19}$], 410.2 (28.4) [$M^+ - 3\ C_{10}H_{19}$], 273.1 (100) [$M^+ - 4\ C_{10}H_{19}$]. $C_{42}H_{86}B_{10}O_4P_2$ (825.19): calcd. C 61.5, H 10.30; found C 62.5, H 10.50.

1,2-Bis[bis(4-*tert*-butylphenyloxy)phosphanyl]-*closo*-dicarbaborane(12) (5): 1,2-Dicarba-*closo*-doedcaborane(12) (0.44 g, 3 mmol) in 30 mL of diethyl ether, *n*BuLi (2.6 mL) in *n*-hexane (2.4 M), **2** (2.3 g, 0.63 mmol) in 60 mL of diethyl ether. Crystallisation from *n*-hexane/toluene; yield 1.85 g (77%); m.p. 119–121 °C. ^1H NMR (C_6D_6): δ = 1.07 (s, 36 H, CH_3), 2.20–3.90 (br. m, 10 H, H^B), 6.93 (m, 16 H, CH) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = 1.4 (br. s, 2 B), –6.4 (br. s, 2 B), –9.5 (br. s, 4 B) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.1 (C-(*C*H_3)$_3$), 34.0 (*C*-(CH_3)$_3$), 82.2 (m, $^1J_{CP}$ + $^2J_{CP}$ = 69.0 Hz, C^{CB}), 119.2 (t, $^3J_{CP}$ = 4.0 Hz, C^{ortho}), 126.8 (C^{meta}), 147.2 (C^{para}), 151.7 (t, $^2J_{CP}$ = 5.8 Hz, C^{ipso}) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 161.2 ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2905, 2869, 2615, 2572, 1602, 1508, 1463, 1365, 1267, 1227, 1203, 1170, 1111, 1079, 1014, 894, 843, 833, 761, 731, 552 cm^{-1}. MS (EI pos., 40 eV): *m/z* (%) = 800 (1.0) [M^+], 743 (1.2) [$M^+ - C_4H_9$], 651 (100) [$M^+ - C_{10}H_{13}O$], 502 (14.4) [$M^+ - 2\ C_{10}H_{13}O$]. $C_{42}H_{62}B_{10}O_4P_2$ (801.00): calcd. C 65.4, H 8.10; found C 65.3, H 8.06.

(R_P,R_P)-1,2-Bis[1-adamantyloxy-(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) [(R_P,R_P)-6]: 1,2-Dicarba-*closo*-dodecaborane(12) (0.29 g, 2 mmol) in 30 mL of diethyl ether, *n*BuLi (1.7 mL) in *n*-hexane (2.4 M), **3** (1.6 g, 0.42 mmol) in 50 mL of diethyl ether. The diastereomers could be separated by fractional crystallisation from *n*-hexane; yield 0.48 g (31%); m.p. 234–236 °C. ^1H NMR (C_6D_6): δ = 0.76 (m, 4 H, H^3, H^4), 0.91 (m, 18 H, H^8, H^9, H^{10}), 1.25 (m, 4 H, H^5, H^6), 1.47 (m, 18 H, H^2,H^3, H^4, H^{14}), 2.05 (m, 18 H, H^{12}, H^{13}), 2.20–4.20 (br. m, 10 B, H^B), 2.40 (m, 2 H, H^6), 2.55 (m, 2 H, H^7), 3.71 (m, 2 H, H^1) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = –0.5 (br. s, 2 B), –6.5 (br. s, 2 B), –10.3 (br. s, 6 B) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 16.5 (C^8), 21.0 (C^9), 22.1 (C^{10}), 23.1 (C^3), 25.0 (C^7), 31.1 (3·C^{13} in ada), 31.5 (C^5), 34.1 (C^4), 35.7 (3·C^{14} in ada), 43.9 (t, $^3J_{CP}$ = 3.8 Hz, C^6), 45.0 (t, $^3J_{CP}$ = 4.4 Hz, 3·C^{12} in ada), 49.0 (C^2), 77.1 (t, $^2J_{CP}$ = 7.4 Hz, C^1), 77.2 (t, $^2J_{CP}$ = 6.7 Hz, C^{11} in ada), 85.1 (m, $^1J_{CP}$ + $^2J_{CP}$ = 67.2 Hz, C^{CB}) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 130.7 ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2882, 2623, 2579, 1474, 1454, 1391, 1364, 1306, 1262, 1229, 1112, 1074, 1007, 990, 976, 942, 923, 900, 804, 742, 724, 626, 478 cm^{-1}. MS (ESI pos., $CHCl_3/CH_3OH$): *m/z* (%) = 818.6 (37.3) [M^+ + H], 840.6 (100) [M^+ + Na], 856.6 (12.8) [M^+ + K]. $C_{42}H_{78}B_{10}O_4P_2$ (817.12): calcd. C 61.74, H 9.62; found C 61.54, H 9.69.

(R_P,S_P)-1,2-Bis[1-adamantyloxy-(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12) [(R_P,S_P)-6]: The diastereomers could be separated by fractional crystallisation from *n*-hexane; yield 0.52 g (33%); m.p. 241–242 °C. ^1H NMR (C_6D_6): δ = 0.85 (m, 2 H, H^4), 0.94 (m, 20 H, H^3, H^8, H^9, H^{10}), 1.30 (m, 4 H, H^5, H^6), 1.47 (m, 18 H, H^2, H^3, H^4, H^5, H^6, H^{14}), 2.04 (m, 18 H, H^{12}, H^{13}), 2.20–4.20 (br. m, 10 B, H^B), 2.56 (m, 2 H, H^6), 3.02 (m, 2 H, H^7), 3.77 (m, 2 H, H^1) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = –0.2 (br. s, 2 B), –6.8 (br. s, 2 B), –10.2 (br. s, 6 B) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 16.0/16.5 (C^8), 21.0/21.1 (C^9), 22.0/22.1 (C^{10}), 22.7/23.1 (C^3), 24.9/25.0 (C^7), 31.1 (3×C^{13}), 31.6/31.8 (C^5), 33.9 (C^4), 35.7/35.8 (3×C^{14}), 43.3/43.7 (d, $^3J_{CP}$ = 5.7 Hz, C^6), 45.1/45.2 (d, $^3J_{CP}$ = 2.6 Hz, 3×C^{12}), 48.8/49.1 (d, $^3J_{CP}$ = 4.8 Hz, C^2), 77.2/78.4 (d, $^2J_{CP}$ = 13.6 Hz, C^1), 77.5/78.0 (d, $^2J_{CP}$ = 12.3 Hz, C^{11}), 84.4/85.2 (m, $^1J_{CP}$ + $^2J_{CP}$ = 74.8 Hz, C^{CB}) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 133.1 (d, $^1J_{PP}$ = 143.5 Hz), 137.5 (d, $^1J_{PP}$ = 143.5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2919, 2853, 2623, 2595, 2567, 1455, 1369, 1352, 1301, 1238, 1184, 1104, 1058, 1012, 990, 967, 946, 860, 825, 768, 627, 583, 552, 481 cm^{-1}. MS (EI pos., 14 eV): *m/z* (%) = 816.6 (100) [M^+ + H]. $C_{42}H_{78}B_{10}O_4P_2$ (817.12): calcd. C 61.7, H 9.62; found C 61.2, H 9.57.

[1,2-Bis[bis(4-*tert*-butylphenyloxy)phosphanyl]-*closo*-dicarbaborane-(12)]tetracarbonylmolybdenum(0) (7): 5 (0.2 g, 0.3 mmol) in 10 mL *n*-hexane, $[Mo(CO)_4(nbd)]$ (0.09 g, 0.3 mmol) 10 mL *n*-hexane. Crystallisation from *n*-hexane; yield 0.43 g (85%); m.p. 262–278 °C (decomp.). ^1H NMR (C_6D_6): δ = 1.10 (s, 36 H, CH_3), 2.20–3.90 (br. m, 10 H, H^B), 7.08 (s, 16 H, CH) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = –1.5 (br. s, 2 B), –3.2 (br. s, 2 B), –10.7 (br. s, 6 B) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.0 (C-(*C*H_3)$_3$), 34.0 (*C*-(CH_3)$_3$), 89.4 (m, C^{CB}), 121.7 (d, $^3J_{CP}$ = 4.0 Hz, C^{ortho}), 126.8 (C^{meta}), 148.8 (C^{para}), 149.8 (t, $^2J_{CP}$ = 5.8 Hz, C^{ipso}), 203.9 (t, $^2J_{CP}$ = 10.8 Hz, CO^{axial}), 209.8 (dd, $^2J_{CP}$ = 12.5, $^2J_{CP}$ = 42.1 Hz, $CO^{equatorial}$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 199.7 ppm. IR (KBr): $\tilde{\nu}$ = 2965, 2907, 2871, 2619, 2578, 2054, 1983, 1958, 1601, 1507, 1464, 1397, 1365, 1265, 1216, 1204, 1170, 1109, 1079, 1016, 903, 840, 814, 753, 677, 644, 585, 560, 529, cm^{-1}. MS (EI pos., 40 eV): *m/z* (%) = 1009.4 (7.5) [M^+], 981.4 (6.3) [M^+ – CO], 925.3 (100) [M^+ – 3CO], 897.5 (25.8) [M^+ – 4CO]. $C_{46}H_{62}B_{10}MoO_8P_2$ (1008.98): calcd. C 54.8, H 6.19; found C 52.4, H 6.33.

{1,2-Bis[bis(–)-menthyloxyphosphanyl]-*closo*-dicarbaborane(12)}-tetracarbonylmolybdenum(0) (8): Compound **4** (0.25 g, 0.3 mmol) in 10 mL *n*-hexane, $[Mo(CO)_4(nbd)]$ (0.09 g, 0.3 mmol) in 10 mL *n*-hexane. Crystallisation from *n*-hexane; yield 0.44 g (87%); m.p. 236–257 °C (decomp.). ^1H NMR (C_6D_6): δ = 0.71 (m, 4 H, H^4), 0.95 (m, 40 H, H^3, H^8, H^9, H^{10}), 1.46 (m, 20 H, H^2, H^3, H^4, H^5, H^6), 2.20–3.90 (br. m, 10 H, H^B), 2.50 (m, 4 H, H^6), 2.75 (m, 4 H, H^7), 4.29 (m, 1 H, H^1) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = –1.9 (br. s, 2 B), –4.2 (br. s, 2 B), –11.0 (br. s, 4 B) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 16.7/16.8 (C^8, $C^{8'}$), 21.2/21.3 (C^9, $C^{9'}$), 21.8/22.0 (C^{10}, $C^{10'}$), 23.1/23.4 (C^3, $C^{3'}$), 24.8/24.9 (C^7, $C^{7'}$), 31.9/32.0 (C^5, $C^{5'}$), 33.6/34.0 (C^4, $C^{4'}$), 43.4/45.2 (C^6, $C^{6'}$), 49.0/49.6 (C^2, $C^{2'}$), 80.6/82.6 (C^1, $C^{1'}$), 90.9 (m, C^{CB}), 208.4 (t, $^2J_{CP}$ = 11.3 Hz, CO^{axial}), 213.3 (dd, $^2J_{CP}$ = 13.1, $^2J_{CP}$ = 39.2 Hz, $CO^{equatorial}$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 189.5 ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2930, 2870, 2628, 2573, 2037, 1952, 1925, 1457, 1371, 1077, 1008, 986, 961, 931, 864, 822, 769, 629, 599, 591, 569, 546, 435 cm^{-1}. MS (ESI neg., CH_2Cl_2/CH_3CN): *m/z* (%) = 1033.6 (100) [M^-], 1056.6 (52) [M + Na]$^-$. $C_{46}H_{86}B_{10}MoO_8P_2$ (1033.17): calcd. C 53.5, H 8.39; found C 54.8, H 8.71.

9: Compound **5** (0.08 g, 0.1 mmol) in 5 mL of CH_2Cl_2, [{Rh(μ-Cl)(cod)}$_2$] (0.025 g, 0.05 mmol) in 2 mL of CH_2Cl_2. Crystallisation from toluene; yield 0.08 g (85%); m.p. 306–308 °C (decomp.). ^1H NMR (C_6D_6): δ = 1.15 (s, 72 H, CH_3), 2.50–3.50 (br. m, 20 H, H^B), 7.09 (d, $^3J_{HH}$ = 8.4 Hz, 16 H, CH), 7.39 (d, $^3J_{HH}$ = 8.4 Hz, 16 H, CH) ppm. $^{11}B\{^1H\}$ NMR (C_6D_6): δ = –1.7 (br. s, 6 B), –9.5 (br. s, 4 B) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 31.1 [C-(*C*H_3)$_3$], 34.0 [*C*-(CH_3)$_3$], 89.4 (m, C^{CB}), 120.8 (C^{ortho}), 126.3 (C^{meta}), 147.5 (C^{para}), 149.8 (C^{ipso}) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 152.6 (d, $^1J_{RhP}$ = 284.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2964, 2905, 2869, 2614, 2578, 1601, 1507, 1463, 1394, 1364, 1265, 1205, 1169, 1110, 1082, 1015, 923, 862, 843, 832, 808, 753, 681, 649, 635, 545, 524, 488 cm^{-1}. MS (EI pos.): *m/z* (%) = 939.4 (12.7) [M^+/2], 903.4 (35.3) [M^+/2 – Cl], 770.3 (17.9) [M^+/2 – Cl – $C_{10}H_{13}$], 754.3 (100) [M^+/2 –

Cl – $C_{10}H_{13}O$]. $C_{84}H_{124}B_{20}Cl_2O_8P_4Rh_2$ (1878.71): calcd. C 53.70, H 6.65; found C 53.64, H 6.68.

(S_P,S_P,S_P,S_P)-10: Compound (R_P,R_P)-**6** (0.08 g, 0.1 mmol) in 5 mL of CH_2Cl_2, [{Rh(μ-Cl)(cod)}$_2$] (0.025 g, 0.05 mmol) in 2 mL of CH_2Cl_2. Crystallisation from dichloromethane; yield 0.07 g (72%); m.p. 173–195 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ = 0.65 (m, 12 H, H^8), 1.03 (m, 36 H, H^3, H^4, H^6, H^9, H^{10}), 1.19 (m, 4 H, H^2), 1.64 (m, 36 H, H^3, H^4, H^5, H^{14}), 2.00–3.40 (br. m, 20 H, H^B), 2.20 (m, 40 H, H^7, H^{12}, H^{13}), 3.42 (m, 4 H, H^6), 4.12 (m, 4 H, H^1) ppm. ^{11}B{^{1}H} NMR ($CDCl_3$): δ = –4.2 (br. s, 4 B), –5.9 (br. s, 4 B), –12.1 (br. s, 12 B) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 17.0 (C^8), 21.6 (C^9), 22.4 (C^{10}), 22.9 (C^3), 24.6 (C^7), 31.4 (C^5), 31.5 (3 × C^{13}), 34.1 (C^4), 35.8 (3 × C^{14}), 44.1 (C^6), 45.0 (3 × C^{12}), 48.8 (C^2), 78.2 (C^1), 78.5 (C^{11}), 83.8 (t, $^2J_{PP'}$ = 3.4 Hz, C^{CB}) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 145.2 (d, $^1J_{RhP}$ = 273.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2917, 2855, 2609, 2570, 1454, 1369, 1354, 1300, 1262, 1100, 1051, 1016, 854, 803, 741, 705, 684, 582, 531, 467 cm^{-1}. MS (ESI pos., CH_3CN/THF): *m*/*z* (%) = 1950.15 (100) [M^+ + K], 994.50 (47.6) [1/2M^+ + K]. ($C_{42}H_{78}B_{10}ClO_4RhP_2$)$_2$ (1910.96): calcd. C 52.8, H 8.23; found C 52.5, H 8.11.

(R_P,S_P,R_P,S_P)-10: Compound (R_P,S_P)-**6** (0.08 g, 0.1 mmol) in 5 mL of CH_2Cl_2, [{Rh(μ-Cl)(cod)}$_2$] (0.025 g, 0.05 mmol) in 2 mL of CH_2Cl_2. Crystallisation from dichloromethane; yield 0.06 g (68%); m.p. 187–190 °C (decomp.). ^{1}H NMR (C_6D_6): δ = 0.75 (m, 6 H, H^8), 1.08 (m, 18 H, H^3, H^4, H^6, H^9, H^{10}), 1.23 (m, 2 H, H^2), 1.68 (m, 18 H, H^3, H^4, H^5, H^{14}), 2.20–3.50 (br. m, 10 H, H^B), 2.25 (m, 20 H, H^7, H^{12}, H^{13}), 3.62 (m, 2 H, H^6), 4.25 (m, 2 H, H^1) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ = –3.9 (br. s, 4 B), –5.7 (br. s, 4 B), –12.0 (br. s, 12 B) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 16.8 (C^8), 21.5 (C^9), 22.2 (C^{10}), 22.7 (C^3), 24.8 (C^7), 31.5 (C^5), 31.7 (3 × C^{13}), 34.5 (C^4), 36.1 (3 × C^{14}), 44.2 (C^6), 45.4 (3 × C^{12}), 48.6 (C^2), 78.5 (C^1), 78.7 (C^{11}), 84.2 (t, $^2J_{PP'}$ = 3.4 Hz, C^{CB}) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 146.9 (dd, $^1J_{RhP}$ = 279.3, $^2J_{PP}$ = 56.5 Hz), 151.1 (dd, $^1J_{RhP}$ = 279.3, $^2J_{PP}$ = 56.5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2916, 2857, 2607, 2570, 1454, 1354, 1300, 1264, 1105, 1053, 1018, 801, 705, 684, 582, 531 cm^{-1}. MS (ESI pos., CH_3CN/CH_2Cl_2): *m*/*z* (%) = 918.50 (100) [1/2M^+ – HCl – H], 994.50 (87) [1/2M^+ + CH_3CN – H]. ($C_{42}H_{78}B_{10}ClO_4RhP_2$)$_2$ (1910.96): calcd. C 52.8, H 8.23; found C 51.9, H 8.07.

11: Compound **4** (0.15 g, 0.2 mmol) in 10 mL of CH_2Cl_2, [{Rh(μ-Cl)(cod)}$_2$] (0.05 g, 0.1 mmol) in 5 mL of CH_2Cl_2. Crystallisation from toluene; yield 0.1 g (52%); m.p. 190–191 °C (decomp.). ^{1}H NMR (C_6D_6): δ = 1.03 (m, 48 H, H^3, H^4, H^8, H^9, H^{10}), 1.54 (m, 16 H, H^2, H^3, H^4, H^5, H^6), 2.20–3.90 (br. m, 20 H, H^B), 2.39 (m, 4 H, H^6), 3.14 (m, 4 H, H^7), 4.48 (m, 4 H, H^1) ppm. ^{11}B{^{1}H} NMR (C_6D_6): δ = –3.3 (br. s, 8 B), –10.8 (br. s, 12 B) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 16.1 (C^8, $C^{8'}$), 21.0 (C^9, $C^{9'}$), 22.5 (C^{10}, $C^{10'}$), 23.0 (C^3, $C^{3'}$), 25.8 (C^7, $C^{7'}$), 31.7 (C^5, $C^{5'}$), 33.8 (C^4, $C^{4'}$), 43.3 (C^6, $C^{6'}$), 48.5 (C^2, $C^{2'}$), 84.5 (C^1, $C^{1'}$), 85.3 (m, C^{CB}) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 150.2 (d, $^1J_{RhP}$ = 269.2 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2958, 2929, 2870, 2615, 2575, 1455, 1370, 1262, 1239, 1179, 1094, 1012, 994, 863, 800, 725, 683, 638, 578, 524, 505, 472 cm^{-1}. MS (ESI pos. CH_3CN/THF): *m*/*z* (%) = 1966.16 (100) [M^+ + K]. ($C_{42}H_{86}B_{10}ClO_4P_2Rh$)$_2$ (1927.09): calcd. C 52.4, H 9.00; found C 52.7, H 9.30.

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