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Platinum(II) and Palladium(II) Complexes of Chiral P−Cl Functionalized Bis-phosphino *ortho*-Carbaboranes

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Platinum(II) and palladium(II) complexes of chiral P−Cl functionalized bis-phosphino *ortho*-carbaborane are readily obtained from reactions of chiral bidentate phosphino carbaborane ligands *rac*-1,2-$(PRCl)_2(C_2B_{10}H_{10})$ with $[MCl_2(COD)]$ (M = Pd, Pt; COD = 1,5-cyclooctadiene) to give *cis-rac*-$[MCl_2\{1,2\text{-}(PRCl)_2(C_2B_{10}H_{10})\}]$ (M = Pt, Pd; R = ^{t}Bu, Ph, NEt_2, NPh_2). *cis-rac*-$[MCl_2\{1,2\text{-}(P^tBuCl)_2(C_2B_{10}H_{10})\}]$ [M = Pt (**1**), Pd (**6**)] decompose in solution in toluene or dichloromethane at room temperature over several weeks with formation of the corresponding dinuclear platinum and palladium complex with two *nido*-carbaboranyl phosphine ligands, (R_P,R_P,S_P,S_P)-$[\{M(7,8\text{-}\{P^tBuCl\}_2C_2B_9H_{10})(\mu\text{-}Cl)\}_2]$ [M = Pt (**2**), Pd (**7**)], among other decomposition products.

Introduction

Bidentate chiral phosphine ligands have received increasing attention because of their important role in the development of asymmetric catalytic applications of transition metal complexes.[1] The substituents at the two phosphorus atoms play an important role in the steric and electronic properties of the ligands.[2] Their nature determines the relative donor/acceptor ability of the phosphines.[3] Dicarba-*closo*-dodecaborane(12) is a particularly interesting substituent or backbone because of its electron-withdrawing character, electron-delocalizing ability, and large size.[4]

Derivatives of bidentate bis-phosphinodicarba-*closo*-dodecaboranes(12) can form stable complexes with platinum(II) and palladium(II) because of their ability to form five-membered chelate rings.[5] Lately, several metal complexes with five-membered chelate rings were reported to exhibit high catalytic activity.[6]

Several complexes of platinum[7] and palladium[8] with bidentate phosphine derivatives of dicarba-*closo*-dodecaborane(12) have been prepared, as well as several platinum complexes with unsymmetrical bis-phosphines, that is, *cis*-$[PtCl_2\{1\text{-}PPh_2\text{-}2\text{-}P(NMe_2)_2(C_2B_{10}H_{10})\}]$, *cis*-$[PtCl_2\{1\text{-}PPh_2\text{-}2\text{-}P(NMe_2)F(C_2B_{10}H_{10})\}]$, *cis*-$[PtCl_2\{1\text{-}P(NMe_2)F\text{-}2\text{-}P(NMe_2)_2\text{-}(C_2B_{10}H_{10})\}]$, and *cis*-$[PtCl_2\{1\text{-}PPh_2\text{-}2\text{-}PF_2(C_2B_{10}H_{10})\}]$.[9] However, only a limited number of palladium complexes with functionalized phosphine ligands having reactive phosphorus−chlorine bonds, especially those with bidentate chlorophosphine ligands, have been reported.[10] So far only one palladium complex with a chlorophosphine derivative of dicarba-*closo*-dodecaborane(12) is known,[11] whereas palladium complexes of bidentate carbaboranyl phosphine ligands without reactive phosphorus−halogen bonds have

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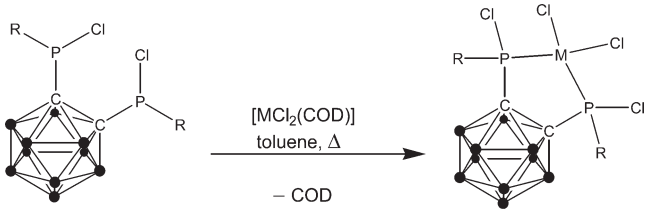
Scheme 1



M = Pt, R = ^{t}Bu (**1**), Ph (**3**), NEt_2 (**4**), NPh_2 (**5**)
M = Pd, R = ^{t}Bu (**6**), Ph,[11] NEt_2 (**8**), NPh_2 (**9**)

been extensively studied.[8,12] Only a limited number of complexes of the platinum group metals with chiral carbaboranyl phosphines have been prepared.[9,11] Chiral chlorophosphino derivatives of dicarba-*closo*-dodecaboranes(12) and transition metal complexes thereof are interesting because they are suitable starting materials for the synthesis of novel chiral phosphines by substitution of the chloro substituent[13] and might be promising catalysts in asymmetric transformation.

Coordination compounds of the platinum group metals have also received great interest for their potential application as chemotherapeutic agents, since *cis*-diammine-dichloroplatinum(II), cisplatin,[14] was reported to act as a tumor inhibitor.[15] Hence, applications can be envisioned for related carbaboranyl phosphines and transition metal complexes thereof.[16]

This report describes the preparation of some palladium and platinum complexes of P−Cl functionalized bis-phosphino *ortho*-carbaboranes having two chiral centers.

Result and Discussion

Synthesis. Platinum(II) and palladium(II) complexes with chiral bidentate phosphino carbaborane ligands were obtained by reaction of the ligands *rac*-1,2-$(PRCl)_2(C_2B_{10}H_{10})$ (R = ^{t}Bu,[17] Ph,[18] NEt_2, NPh_2[19]) with $[MCl_2(COD)]$ (COD = 1,5-cyclooctadiene) at room temperature (for palladium) or under reflux in toluene for several hours (for platinum) to give *cis-rac*-$[MCl_2\{1,2\text{-}(PRCl)_2(C_2B_{10}H_{10})\}]$ (M = Pt, Pd; R = ^{t}Bu, Ph, NEt_2, NPh_2; Scheme 1).

Except for *cis-rac*-$[PtCl_2\{1,2\text{-}\{P(NPh_2)Cl\}_2(C_2B_{10}H_{10})\}]$ (**5**), all complexes were obtained in good yield (67−93%). Complex **5** could only be obtained in 14% yield. The signal of the free ligand was observed in the ^{31}P NMR spectrum of the reaction mixture even after heating to reflux for more than 100 h, while the amount of side products increased. We assume that **5** decomposes in solution under the reaction conditions. The related palladium complex *cis-rac*-$[PdCl_2\{1,2\text{-}\{P(NPh_2)Cl\}_2(C_2B_{10}H_{10})\}]$ (**9**) was obtained in 81% yield, but also slowly decomposed at room temperature in toluene solution with formation of the dinuclear palladium complex with two *nido*-carbaboranyl phosphine ligands (R_P,R_P,S_P,S_P)-$[\{Pd(7,8\text{-}\{P(NPh_2)Cl\}_2C_2B_9H_{10})(\mu\text{-}Cl)\}_2]$, along with other decomposition products.[20]

The resulting complexes are stable as solids, but in some cases decomposition in solution was observed. Thus, the complexes *cis-rac*-$[PtCl_2\{1,2\text{-}(P^tBuCl)_2(C_2B_{10}H_{10})\}]$ (**1**) and *cis-rac*-$[PdCl_2\{1,2\text{-}(P^tBuCl)_2(C_2B_{10}H_{10})\}]$ (**6**) decomposed in toluene or in dichloromethane solution at room temperature over several weeks. The process leads to formation of dinuclear platinum or palladium complexes with two *nido*-carbaboranyl phosphine ligands, (R_P,R_P,S_P,S_P)-$[\{Pt(7,8\text{-}\{P^tBuCl\}_2C_2B_9H_{10})(\mu\text{-}Cl)\}_2]$ (**2**) and (R_P,R_P,S_P,S_P)-$[\{Pd(7,8\text{-}\{P^tBuCl\}_2C_2B_9H_{10})(\mu\text{-}Cl)\}_2]$ (**7**), along with other decomposition products (Scheme 2). Decomposition of a related palladium complex has been previously observed for *cis-rac*-$[PdCl_2\{1,2\text{-}\{PPhCl\}_2(C_2B_{10}H_{10})\}]$.[11] Here, the complex decomposed in THF, toluene, or dichloromethane solution as well as in the solid state in about 2 h, but the decomposition products could not be identified.

In complexes **2** and **7**, the positive charges on the metal atoms are compensated by a negative charge of each of the *nido*-carbaborane clusters. Their insolubility in common organic solvents (CH_2Cl_2, *n*-hexane, toluene, DMF, THF, etc.) prevented NMR spectroscopic measurements.

Partial degradation of *closo*-carbaborane clusters was observed previously for the reaction of electron-rich d^{10} metal ions (Cu^I, Ag^I, and Au^I) with 1′,2′-(1,10-dithio-4,7-dioxadecane)-1′,2′-dicarba-*closo*-dodecaborane in degassed ethanol.[21] An extended study on the partial degradation for carbaboranyl phosphine ligands with several electron-rich metals in ethanol has been reported as well.[22] It was concluded that the carbaboranyl phosphine ligands undergo structural modification upon coordination because of transfer of electron density from the metal to the cage by phosphorus−metal coordination. This causes pseudo-reduction of the cluster, and one of the boron atoms connected with the C_2 group of the carbaborane cluster becomes susceptible to nucleophilic attack, which leads to decapping of the cluster.

Ethanol is a suitable nucleophile to bring about this partial degradation. However, ethanol is not solely responsible, since partial degradation did not take place in some complexation reactions even though ethanol was present. Divalent metal cations seem to be the most

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(20) Single crystals of (R_P,R_P,S_P,S_P)-$\{Pd(7,8\text{-}\{P(NPh_2)Cl\}_2C_2B_9H_{10})(\mu\text{-}Cl)\}_2]$ were obtained from a solution of **9** in toluene after it was kept for several weeks at room temperature. The quality of the crystals was, however, too low to be able to publish the data. Empirical formula $C_{52}H_{60}B_{18}Cl_6N_4P_4Pd_2\cdot$2toluene, formula weight 1672.84, T = 213(2) K, monoclinic, space group $P2_1/c$, a = 16.970(4) Å, b = 15.218(3) Å, c = 17.041(3) Å, β = 119.274(2)°, V = 3838.7(1) Å^3, Z = 2, ρ_{calcd} = 1.447 mg/m^3, μ(Mo Kα) = 0.804 mm^{-1}, F(000) = 1691, crystal size: 0.40 × 0.20 × 0.10 mm^3, $\theta_{Min}/\theta_{Max}$: 1.92/26.39°, no. of reflns. collected 6878, no. of indep. reflns. 5114 [R(int) = 0.0721], completeness to θ_{Max} = 64.9%, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0877, wR_2 = 0.1806, R indices (all data): R_1 = 0.1110, wR_2 = 0.1901, goodness of fit on F^2 = 1.186.
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Scheme 2

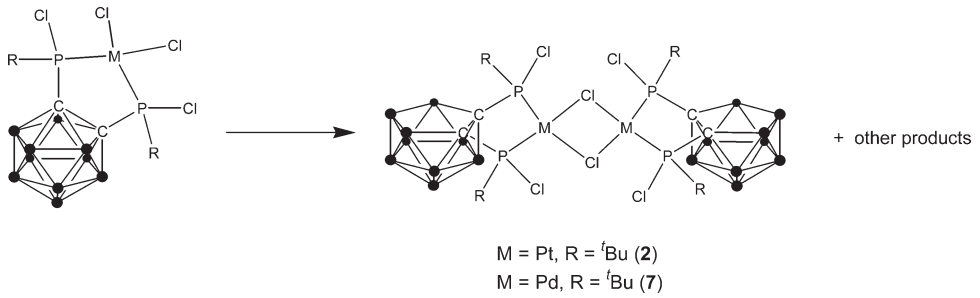

Table 1. $^{31}P\{^1H\}$ Chemical Shifts and $^1J_{PPt}$ of the Complexes and Chemical Shift Differences between the Complexes and the Free Ligand ($\Delta\delta = \delta_{complex} - \delta_{ligand}$)

complex	$^{31}P\{^1H\}$ (ppm)	$^1J_{PPt}$ (Hz)	$\Delta\delta$ (ppm)
cis-rac-[$PtCl_2$\{1,2-($P^tBuCl)_2(C_2B_{10}H_{10})$\}] (**1**)	122.6	3873	6
cis-rac-[$PtCl_2$\{1,2-(PPhCl)$_2(C_2B_{10}H_{10})$\}] (**3**)	97.8	4038	18
cis-rac-[$PtCl_2$\{1,2-(P\{NEt_2\}Cl)$_2(C_2B_{10}H_{10})$\}] (**4**)	98.2	4663	−19
cis-rac-[$PtCl_2$\{1,2-(P\{NPh_2\}Cl)$_2(C_2B_{10}H_{10})$\}] (**5**)	94.6	4895	−10
cis-rac-[$PdCl_2$\{1,2-($P^tBuCl)_2(C_2B_{10}H_{10})$\}] (**6**)	152.7		36
cis-rac-[$PdCl_2$\{1,2-(PPhCl)$_2(C_2B_{10}H_{10})$\}][11]	122.7		42
cis-rac-[$PdCl_2$\{1,2-(P\{NEt_2\}Cl)$_2(C_2B_{10}H_{10})$\}] (**8**)	122.6		6
cis-rac-[$PdCl_2$\{1,2-(P\{NPh_2\}Cl)$_2(C_2B_{10}H_{10})$\}] (**9**)	122.9		19

appropriate for the removal of a formal B^+ fragment from the *closo* species. Thus, it is believed that both the nature of the metals and that of the ligands play a major role in the degradation.[21] As compounds **2** and **7** were obtained as decomposition products of **1** and **6** in toluene or dichloromethane, the nature of the ligand and the metal are probably responsible for the decapping process.

Spectroscopic Properties. The $^{31}P\{^1H\}$ NMR spectra of all the platinum complexes distinctly show the typical platinum satellites, which are attributed to $^{31}P-^{195}Pt$ coupling, and exhibit three lines with an intensity ratio of about 1:4:1.[23] The spectroscopic data ($^{31}P\{^1H\}$ chemical shifts and $^1J_{PPt}$) for complexes **1**, **3**−**6**, **8**, **9**, and related known complexes are listed in Table 1.

Complexes **1** and **3** exhibit signals at 122.6 and 97.8 ppm in the ^{31}P NMR spectrum, respectively. These peaks are shifted by about 6 and 18 ppm to lower field relative to the signal of the free ligands, indicating P→Pt donation of the P^{t}BuCl or PPhCl group. This effect was also observed for the platinum complexes of the related compounds $^tBu_2PC_2H_4P^tBu_2$[24] and $Ph_2PC_2H_4PPh_2$.[25]

In contrast, complexes **4** and **5** have chemical shifts at higher field, by about 19 and 10 ppm, compared with the signals of the free ligands.[19] This effect reflects the increase in electron density at the phosphorus atoms, which is presumably due to the $p_\pi(N)-\sigma^*(P)$ interaction. This also affects the phosphorus−platinum donor bond as well as the platinum−phosphorus backbonding, which is expected to increase with increasing electronegativity of the substituents at phosphorus.[9] The electronegativity of the amino groups in compounds **4** and **5** is responsible for the shielding effect, which was previously observed in other platinum complexes with κP ligands bearing electronegative substituents, for example, $P(NR_2)$[9] or P(OR).[26]

The large $^1J_{PPt}$ values of the complexes (3873−4895 Hz) indicate *cis* coordination of the bidentate phosphine ligands,[22,27] as shown also by the X-ray structures, whereas the $^1J_{PPt}$ values for *trans* platinum complexes are significantly lower.[22,28] While the *tert*-butyl groups in complex **1** result in the smallest P−Pt coupling constant, the diphenylamino groups in complex **5** are responsible for the largest P−Pt coupling constant. In general, the P−Pt coupling constants of the complexes increase with increasing electronegativity of the substituents on phosphorus, which increases the π-acceptor character of the phosphines.[9,29]

The signals of the palladium complexes in the ^{31}P NMR spectrum are shifted to lower field relative to that of the free ligand. Complex **8** has a smaller difference in chemical shifts between the complex and the free ligand ($\Delta\delta$) in the ^{31}P NMR spectra. The small value of $\Delta\delta$ for **8** is presumably also due to $p_\pi(N)\rightarrow\sigma^*(P)$ interaction.

Apparently, the platinum atom provides better backbonding to the phosphine ligands with respect to palladium, as the palladium complexes have larger $\Delta\delta$ values relative to the corresponding platinum complexes. Therefore, the electron density at the phosphorus atoms of the palladium complexes is lower compared to that of the corresponding platinum complexes.

In the ^{13}C NMR spectrum, the carbaborane C atoms of complex **4** exhibit a multiplet due to a very complex ABXM spin system (P^1P^2CPt). In the center of the multiplet, the coupling pattern of an ABX spin system for the PCCP group, which appears as a pseudotriplet, can be observed.

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Table 2. Summary of Data Collection, Structure Solution, and Refinement Details for Compounds **1**−**4** and **6**−**8**

	1	**2**	**3**	**4**	**6**	**7**	**8**
empirical formula	$C_{10}H_{28}B_{10}Cl_4P_2Pt$	$C_{20}H_{56}B_{18}Cl_6P_4Pt_2$	$C_{21}H_{28}B_{10}Cl_4P_2Pt$	$C_{13.5}H_{34}B_{10}Cl_4N_2P_2Pt$	$C_{10}H_{28}B_{10}Cl_4P_2Pd$	$C_{20}H_{56}B_{18}Cl_6P_4Pd_2$	$C_{13.5}H_{34}B_{10}Cl_4N_2P_2Pd$
formula weight	655.25	1217.99	787.36	731.36	566.56	1040.61	642.67
T, K	208(2)	208(2)	217(2)	213(2)	208(2)	213(2)	210(2)
crystal system	orthorhombic	monoclinic	triclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	*Pbca*	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2_1/c$	$P\bar{1}$
a, Å	18.199(2)	8.8349(5)	11.345(2)	11.0329(9)	18.138(3)	8.814(1)	10.981(3)
b, Å	13.432(2)	17.770(1)	11.438(2)	11.886(1)	13.440(2)	17.753(2)	11.826(3)
c, Å	18.773(2)	13.9491(8)	12.091(2)	12.516(1)	18.778(3)	13.879(2)	12.433(3)
α, deg.	90	73.460(2)	112.773(9)	90	90	112.581(4)	
β, deg.	90	95.329(1)	89.131(3)	97.49(1)	90	95.212(2)	97.522(4)
γ, deg.	90	90	86.383(2)	104.01(1)	90	90	103.808(4)
vol, Å^3	4589(1)	2180.5(2)	1501.0(4)	1421.6(2)	4577(1)	2162.8(5)	1402.4(6)
Z	8	2	2	2	8	2	2
ρ_{calcd}, mg/m^3	1.897	1.855	1.742	1.709	1.644	1.598	1.522
μ (Mo Kα), mm^{-1}	6.717	6.943	5.151	5.432	1.414	1.370	1.166
F(000)	2512	1168	760	710	2256	1040	646
crystal size, mm^3	0.30 × 0.25 × 0.20	0.20 × 0.15 × 0.02	0.40 × 0.30 × 0.20	0.40 × 0.40 × 0.30	0.25 × 0.25 × 0.10	0.20 × 0.20 × 0.10	0.40 × 0.20 × 0.10
$\theta_{Min}/\theta_{Max}$, deg.	2.17/29.19	1.86/28.94	1.86/29.13	3.54/32.87	2.17/29.10	1.87/26.44	1.97/28.26
no. of reflns. collected	28068	13667	9736	37354	22461	17354	9820
no. of indep. reflns.	5819 [*R*(int) = 0.0415]	5263 [*R*(int) = 0.0584]	6907 [*R*(int) = 0.0155]	9477[*R*(int) = 0.0419]	5769[*R*(int) = 0.0382]	4432[*R*(int) = 0.0567]	6468 [*R*(int) = 0.0161]
completeness to θ_{Max}, %	93.7	91.6	85.4	89.4	93.9	99.5	93.1
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0227$, $wR_2 = 0.0543$	$R_1 = 0.0485$, $wR_2 = 0.1137$	$R_1 = 0.0289$, $wR_2 = 0.0731$	$R_1 = 0.0230$, $wR_2 = 0.0552$	$R_1 = 0.0368$, $wR_2 = 0.0637$	$R_1 = 0.0994$, $wR_2 = 0.2186$	$R_1 = 0.0306$, $wR_2 = 0.0701$
R indices (all data)	$R_1 = 0.0453$, $wR_2 = 0.0584$	$R_1 = 0.0727$, $wR_2 = 0.1200$	$R_1 = 0.0332$, $wR_2 = 0.0750$	$R_1 = 0.0290$, $wR_2 = 0.0566$	$R_1 = 0.0593$ $wR_2 = 0.0688$	$R_1 = 0.1138$, $wR_2 = 0.2249$	$R_1 = 0.0442$, $wR_2 = 0.0738$
goodness of fit on F^2	0.936	1.105	1.025	0.968	1.033	1.273	1.046
largest diff. peak and hole, e Å^{-3}	1.010 and −1.331	2.489 and −1.643	2.448 and −2.256	1.035 and −0.822	0.450 and −0.477	2.437 and −1.070	0.566 and −0.783

In the free ligand, for long measurement times, two small satellites can additionally be observed.[19] Because of the low natural abundance of ^{13}C (1.1%) the majority of the molecules which are detected by ^{13}C NMR only contain one ^{13}C atom at this special position. Therefore, these molecules are asymmetric, and the ^{13}C nucleus couples with both phosphorus nuclei ($^1J_{CP}$ and $^2J_{CP}$). This scenario results in a spin system of higher order. Both coupling constants can only be determined by simulating an ABX spin system with SpinWorks.[30] The distance between the two external signals of the triplets corresponds to the sum of $^1J_{CP}$ and $^2J_{CP}$, which is 50.6 Hz in the case of **4**. In the complex coupling to the platinum atom in form of satellites can additionally be observed. These satellites are also complex multiplets, which is why the coupling constants cannot be determined directly and must be simulated.

In contrast, complex **1** exhibits only a broad singlet with two satellites due to coupling to platinum [$^2J_{C(Carb)Pt}$ = 102.6 Hz] in the ^{13}C NMR spectra. The different behavior of complexes **4** and **1** cannot yet be explained. Complex **3** is very slightly soluble in conventional organic solvents; therefore, no ^{13}C NMR spectra could be obtained.

The signal of the quaternary carbon atom of the *tert*-butyl group in compound **1** is shifted downfield by about 10 ppm with respect to the free ligand *rac*-1,2-($P^tBuCl)_2$-($C_2B_{10}H_{10}$),[17] and is observed as a complex multiplet (ABXM spin system) due to coupling with the platinum and phosphorus atoms. In the free ligand the coupling constant is $^1J_{PC} = 17$ Hz.[17]

Molecular Structures. Single crystals of platinum and palladium complexes **1**−**4** and **6**−**8** were obtained from concentrated toluene solutions at room temperature. Platinum complexes **1**, **2**, and **4** are isostructural and isomorphous to the corresponding palladium complexes **6**, **7**, and **8**, respectively (Figures 1, 2, and 4). Because of the crystallographic center of inversion, both enantiomers (*R, R* and *S,S*) are present in the unit cell of compounds **1**, **3**, **4**, **6**, and **8**. The crystallographic data of the complexes are summarized in Table 2. Selected bond lengths and angles of the complexes are collected in Table 3.

The platinum and the palladium atoms in the mononuclear complexes are coordinated in a slightly distorted square-planar fashion by the two phosphorus atoms of the carbaboranyl phosphine ligands and two chloro ligands in *cis* positions (Figures 1, 3, and 4). Thus, the metal atom exhibits a coordination number of four, which is preferred

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Table 3. Selected Bond Lengths and Angles of Platinum and Palladium Complexes

compounds	M−P (Å)	M−Cl (Å)	P−Cl (Å)	P−$C_{cluster}$ (Å)	$C_{cluster}$−$C_{cluster}$ (Å)	P−M−P (deg)
1	2.2089(9)	2.3242(9)	2.020(1)	1.889(3)	1.710(4)	93.21(3)
	2.2166(8)	2.3341(9)	2.008(1)	1.878(3)		
2	2.215(2)	2.389(2)	2.031(4)	1.819(7)	1.59(1)	85.8(1)
	2.243(3)	2.387(2)	2.026(4)	1.815(7)		
3	2.1929(9)	2.328(1)	2.007(1)	1.861(4)	1.671(5)	92.33(3)
	2.2028(9)	2.3282(9)	2.000(1)	1.856(4)		
4	2.1919(7)	2.3424(9)	2.0096(8)	1.879(2)	1.678(3)	92.33(2)
	2.2015(6)	2.3443(6)	2.0126(8)	1.877(2)		
6	2.2309(8)	2.3186(8)	2.0160(9)	1.888(3)	1.720(3)	92.74(2)
	2.2391(8)	2.3289(8)	2.005(1)	1.883(3)		
7	2.234(4)	2.384(3)	2.010(5)	1.84(1)	1.58(2)	84.4(2)
	2.251(4)	2.385(3)	2.016(6)	1.82(1)		
8	2.2045(7)	2.3342(8)	2.002(1)	1.883(2)	1.677(3)	91.55(3)
	2.2124(8)	2.3360(8)	2.0077(9)	1.875(2)		

in platinum(II)[7,9,31] and palladium(II)[8,32] complexes. The coordination of the chelating carbaboranyl bis-phosphine ligand to the metal atom leads to the formation of a five-membered ring. The sum of the four intra- and interligand *cis* bond angles is about 360°.

According to the X-ray crystal structure determination, the molecular structures of **2** and **7** confirm the presence of dinuclear metal complexes with two bridging chloro ligands and two chelating *nido*-carbaboranyl bis-phosphine ligands, in which the four phosphorus atoms are *R, R,S,S*-configured. The positive charges on the platinum or palladium atoms are compensated by a negative charge of each of the *nido*-carbaborane clusters. These dinuclear complexes are located on a crystallographic center of symmetry and have a non-crystallographic mirror plane on which both bridging chloro ligands are located.

The P(1)−M−P(2) bond angles in mononuclear complexes **1**, **3**, **4**, **6**, and **8** are in the range of the preferred P−M−P bite angles for square-planar complexes with two carbon atoms as spacer between the two phosphorus donor atoms;[2b] that is, from 82.4[33] to 93°[7] for platinum complexes, and from 78.0[34] to 92.4°[8b] for palladium complexes. The M−P and M−Cl bond lengths are in agreement with those observed in related complexes.[11,35]

It has been reported previously, that the P−Pt coupling constants reflect the strength of the Pt−P bonds.[9] Accordingly, compound **4**, which has the largest $^1J_{PPt}$ coupling constant, displays the shortest Pt−P bonds. This trend is expected, since the electron-withdrawing substituents on the phosphorus atoms increase the $d_\pi \rightarrow \sigma^*$ interaction between the platinum and phosphorus atoms.[36] On the other hand, this so-called backbonding would also increase the σ-bond character of the Pt−P bond by a synergistic effect.[28] The backbonding effect is also revealed by the ^{31}P NMR spectra, in which the signal of platinum complex **4** is shifted to higher field relative to that of the free ligand.

The C−C distances of the carbaborane cage were found to decrease on complexation. Compound **1** shows the largest decrease, that is, 0.062 Å relative to the free ligand.[17] The diminution of the C−C distances can be rationalized by the change in electronic properties of the phosphorus atoms because of complexation. It was observed that pronounced elongation of the C−C bond occurs when the element with the lone pair of electrons is directly connected to the cluster. Transfer of the electron density from the available lone pair of electrons of the element to the cage results in an increase in the C−C distance.[37] Compounds **4** and **8**, however, have higher electron density on the phosphorus atoms because of $p_\pi \rightarrow \sigma^*$ nitrogen to phosphorus interaction, which is affected by the platinum−phosphorus σ bond. Accordingly, the nitrogen atoms in **4** and **8** are in a trigonal-planar environment (sum of bond angles at N1 359.0°, N2 359.4° (**4**), N1 358.7°, N2 359.0° (**8**)). Thus, transfer of electron density from the phosphorus atoms to the cage is facilitated. In contrast, the electron density on the phosphorus atoms in complex **1** is even lower because of the strong σ (P→Pt) donor character of the P^{t}BuCl group, which results in a larger decrease in C−C bond length relative to the free ligand. The influence of an NR_2 group on the electronic properties of the phosphorus atoms, which is reflected in changes in the P−Cl bond lengths, was also observed in the free (NEt_2 derivative) and related *ortho*-carbaborane-containing aminochlorophosphines.[19] Here, the P−Cl bonds are longer by up to 4 pm than those observed in *rac*-1,2-$(PPhCl)_2(C_2B_{10}H_{10})$ (205.1(1) pm)[18b] and *rac*- and *meso*-1,2-$(P^tBuCl)_2(C_2B_{10}H_{10})$ (207.4(9)/207.0(8) and 207.0(9)/205.8(9) pm).[17] This effect is less pronounced in the platinum and palladium complexes **1**−**4** and **6**−**8**, in which the P−Cl bond lengths range from 2.000(1) Å (in **3**) to 2.031(4) Å (in **2**).

Experimental Section

All reactions were carried out in an atmosphere of dry nitrogen. The solvents were purified and distilled under nitrogen.[38] The infrared spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer scanning

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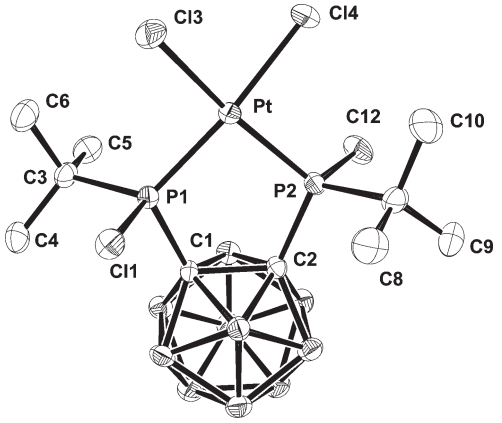

Figure 1. Molecular structure of **1** (ORTEP with atom labeling scheme, thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity, only the *R,R* enantiomer is shown). The palladium complex **6** is isotypic.

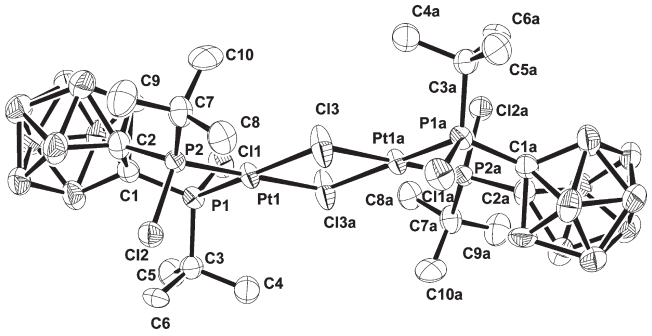

Figure 2. Molecular structure of **2** (ORTEP with atom labeling scheme, thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity). The palladium complex **7** is isotypic.

between 400 and 4000 cm^{-1} using KBr disks. The ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectra were recorded on an AVANCE DRX 400 spectrometer (Bruker). The chemical shifts for the ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) at 400.13 and 100.63 MHz, respectively, with tetramethylsilane as standard. $^{13}C\{^{1}H,^{31}P\}$, $^{13}C\{^{1}H\}$, and ^{13}C NMR spectra were recorded to determine Pt−C and, if possible, P−C coupling constants. The chemical shifts for the ^{31}P NMR spectra are reported in ppm at 161.97 MHz with 85% H_3PO_4 external standard, and chemical shifts for ^{11}B NMR spectra in ppm at 128.38 MHz with $BF_3(OEt_2)$ as external standard. The mass spectra were recorded on an Ltd. ZAB-HSQ-VG Analytical Manchester Spectrometer (FAB mass spectra). The elemental analyses were recorded on a VARIO EL (Heraeus). The melting points were determined in sealed capillaries and are uncorrected.

The crystallographic data of **1**, **2**, **3**, **6**, **7**, **8** were collected on a Siemens CCD diffractometer (SMART), empirical absorption correction with SADABS,[39] and for **4** on a Stoe image-plate diffractometer, numerical absorption correction with XRed[40] using Mo Kα radiation (λ = 71.073 pm) and ω-scan rotation. The structures were solved by direct methods or heavy atom methods (SHELXTL PLUS).[41] All H atoms were introduced at calculated positions except B−H

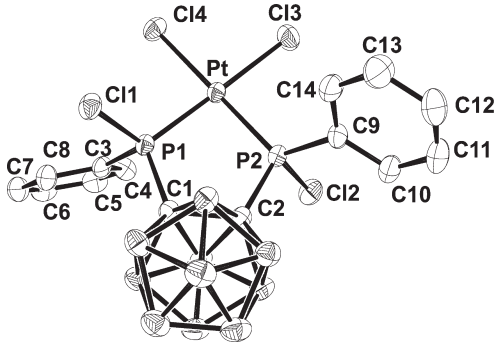

Figure 3. Molecular structure of **3** (ORTEP with atom labeling scheme, thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity, only the *R,R* enantiomer is shown).

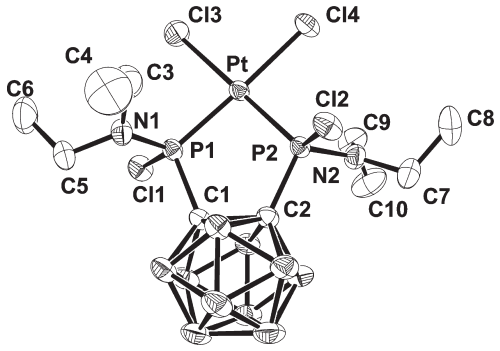

Figure 4. Molecular structure of **4** (ORTEP with atom labeling scheme, thermal ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity, only the *S,S* enantiomer is shown). The palladium complex **8** is isotypic.

hydrogen atoms for **1**, **2**, **3**, **6**, **7** which were found in a difference Fourier map calculation. Structure figures (Figures 1−4) were generated with DIAMOND-3.[42] CCDC 736027 (**1**), 736028 (**2**), 736029 (**3**), 736030 (**4**), 736031 (**6**), 736032 (**7**), and 736033 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: (+44)1223−336−033; or deposit@ccdc.cam.uk).

rac-1,2-$(P^tBuCl)_2(C_2B_{10}H_{10})$,[17] *rac*-1,2-$(PPhCl)_2(C_2B_{10}H_{10})$,[18] *rac*-1,2-$\{P(NEt_2)Cl\}_2(C_2B_{10}H_{10})$, *rac*-1,2-$\{P(NPh_2)Cl\}_2(C_2B_{10}H_{10})$,[19] and $[MCl_2(COD)]$ (M=Pd,[43] Pt[42,44]) were prepared according to the literature.

Synthesis of *cis-rac*-$[PtCl_2\{1,2\text{-}(P^tBuCl)_2(C_2B_{10}H_{10})\}]$ (1) and Formation of (R_P,R_P,S_P,S_P)-$[\{Pt(7,8\text{-}\{P^tBuCl\}_2C_2B_9H_{10})(\mu\text{-}Cl)\}_2]$ (2). A mixture of $[PtCl_2(COD)]$ (0.2 g, 0.53 mmol), *rac*-1,2-bis(*tert*-butylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (0.21 g, 0.53 mmol), and toluene (50 mL) was heated to reflux for 2 h. The mixture was then concentrated to yield a white precipitate (0.25 g). Crystallization from toluene solution gave colorless crystals of **1**. Yield: 0.25 g (73%). M.p.: 280 °C (decomposes, turns brown). Found: C 18.70; H 4.47%. Calcd for $C_{10}H_{28}B_{10}Cl_4P_2Pt$: C 18.83; H 4.31%. FAB-MS, *m*/*z*: 619 (6%, M^+− Cl), 584 (2%, M^+− 2Cl). Calcd for $C_{10}H_{28}B_{10}Cl_4P_2Pt$: M = 655.25. ^{1}H NMR ($CDCl_3$, ppm): 3.75−1.93 (m, vbr, 10H, $C_2B_{10}H_{10}$), 1.73 (d, $^{3}J_{HP}$ = 22 Hz, 18H, CH_3). ^{31}P NMR ($CDCl_3$, ppm): 122.6 ($^{1}J_{PPt}$ = 3873 Hz). $^{13}C\{^{1}H,^{31}P\}$

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NMR ($CDCl_3$, ppm): 85.1 (s with Pt satellites, $^2J_{CPt}$ = 102.6 Hz, $C_{cluster}$−P), 50.1 (s with Pt satellites, $^2J_{CPt}$ = 54.0 Hz, CMe_3), 28.5 (s, CH_3).^{11}B NMR ($CDCl_3$, ppm): 0.8 (d, $^1J_{BH}$ = 151 Hz, 2B, $C_2B_{10}H_{10}$), −3.1 (d, $^1J_{BH}$=154 Hz, 2B, $C_2B_{10}H_{10}$), −9.4 (m, vbr, 6B, $C_2B_{10}H_{10}$). IR (KBr, cm^{-1}): 3015m, 2995m, 2961m, 2926m, 2868m (CH); 2678m, 2666s, 2639s, 2595s, 2576s, 2564s (BH); 1955w, 1626w, 1471s, 1459s, 1433m, 1401s, 1368s, 1261m, 1165s, 1070s, 1017s, 976w, 930m, 902w, 884w, 835m, 797s, 772m, 749s, 733s, 682w, 665m, 629s, 570s, 542s, 495s, 458m, 448m.

Single crystals of **2** were obtained from a solution of **1** in toluene after it was kept at room temperature for several weeks. Complex **2** was characterized by X-ray crystallography. The amount of pure substance obtained was insufficient for other characterization methods.

Synthesis of *cis-rac*-[$PtCl_2${1,2-$(PPhCl)_2(C_2B_{10}H_{10})$}] (3). A mixture of [$PtCl_2$(COD)] (0.2 g, 0.53 mmol), *rac*-1,2-bis(phenylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (0.23 g, 0.53 mmol), and toluene (50 mL) was heated to reflux for 2 h. The mixture was then concentrated to yield 0.31 g of a white precipitate. Crystallization from toluene solution gave colorless crystals of **3**. Yield: 0.31 g (83%). M.p.: 320 °C (decomposes, turns brown). Found: 23.89; H 3.06%. Calcd for $C_{14}H_{20}B_{10}Cl_4P_2Pt$: C 24.19; H 2.90%. FAB-MS, *m*/*z*: 659 (100%, M^+− Cl), 624 (14%, M^+− 2Cl) 587 (11%, M^+ − 3Cl). Calcd for $C_{14}H_{20}B_{10}Cl_4P_2Pt$: M = 695.25. ^{1}H NMR (C_6D_6, ppm): 7.70−6.86 (m, 10H, Ph), 7.10−6.90 (several m, Ph and C_7H_8), 3.73−1.01 (m, vbr, 10H, $C_2B_{10}H_{10}$), 2.10 (s, 3H, CH_3 in C_7H_8). ^{31}P NMR (C_6D_6, ppm): 97.8 ($^1J_{PPt}$=4038 Hz). ^{11}B NMR (C_6D_6, ppm): −1.8 (d, $^1J_{BH}$ = 143 Hz, 4B, $C_2B_{10}H_{10}$), −10.2 (d, $^1J_{BH}$= 142 Hz, 4B, $C_2B_{10}H_{10}$), −13.6 (d, $^1J_{BH}$ = 168 Hz, 2B, $C_2B_{10}H_{10}$). IR (KBr, cm^{-1}): 3082w, 3055m, 3022m, 2959w, 2917w (CH); 2614, 2582 (BH); 2191w, 1965w, 1894w, 1809w (Ph); 1603w, 1580m, 1494m, 1475m, 1436s, 1384w, 1336w, 1310s, 1283w, 1261m, 1186m, 1160m, 1097s, 1076s, 1025m, 997m, 981m, 937m, 900m, 852s, 798s, 732s, 713s, 695s, 684s, 630s, 616s, 575s, 553s, 514s, 485s, 472s.

The low solubility of **3** prevents measurement of the ^{13}C NMR spectrum.

Synthesis of *cis-rac*-[$PtCl_2${1,2-{$P(NEt_2)Cl$}$_2(C_2B_{10}H_{10})$}] (4). A mixture of [$PtCl_2$(COD)] (0.14 g, 0.37 mmol), *rac*-1,2-{$P(NEt_2)Cl$}$_2(C_2B_{10}H_{10})$ (0.16 g, 0.37 mmol), and toluene (50 mL) was heated to reflux for 10 h. The mixture was then concentrated to obtain 0.18 g of a white precipitate. Crystallization from toluene solution gave colorless crystals of **4**. Yield: 0.18 g (70%). M.p.: 230 °C (decomposes, turns black). Found: C 17.36; H 4.39%. Calcd for $C_{10}H_{30}B_{10}Cl_4N_2P_2Pt$: C 17.53; H 4.41%. FAB-MS, *m*/*z*: 649 (100%, M^+− Cl), 614 (81%, M^+− 2Cl), 577 (12%, M^+ − 3Cl), 542 (8%, M^+ − 4Cl). Calcd for $C_{10}H_{30}B_{10}Cl_4N_2P_2Pt$: M = 685.31. ^{1}H NMR ($CDCl_3$, ppm): 3.65 and 3.42 (m, br, 8H, CH_2), 3.55−1.63 (m, vbr, 10H, $C_2B_{10}H_{10}$), 1.23 (t, $^3J_{HH}$ = 8 Hz, 12H, CH_3). ^{31}P NMR ($CDCl_3$, ppm): 98.2 ($^1J_{PPt}$=4663 Hz). ^{13}C{^{1}H,^{31}P} NMR ($CDCl_3$, ppm): 137.1, 129.0, 128.2, 125.3 (4 s, C_7H_8), 90.8 (s with Pt satellites, $^2J_{CPt}$=168.8 Hz, $C_{cluster}$−P), 44.3 (m, vbr, CH_2), 21.5 (s, CH_3 in C_7H_8), 12.8 (s, CH_3).^{11}B NMR ($CDCl_3$, ppm): −2.2 (d, $^1J_{BH}$ = 142 Hz, 4B, $C_2B_{10}H_{10}$), −10.2 (m, vbr, 4B, $C_2B_{10}H_{10}$), −14.0 (m, vbr, 2B, $C_2B_{10}H_{10}$). IR (KBr, cm^{-1}): 2981s, 2937s, 2894s (CH); 2621s, 2582s (BH); 1860w, 1706w, 1626w, 1494w, 1462m, 1444m, 1382s, 1363m, 1343m, 1289m, 1262w, 1201s, 1151s, 1100s, 1076s, 1057s, 1020s, 962s, 925w, 847s, 799s, 760w, 740m, 688m, 671m, 628s, 579s, 549s, 495s, 459m, 417w.

Synthesis of *cis-rac*-[$PtCl_2${1,2-{$P(NPh_2)Cl$}$_2(C_2B_{10}H_{10})$}] (5). A mixture of [$PtCl_2$(COD)] (0.13 g, 0.35 mmol), *rac*-{$P(NPh_2)Cl$}$_2(C_2B_{10}H_{10})$ (0.21 g, 0.35 mmol), and toluene (35 mL) was heated to reflux for 105 h. The mixture was then filtered and the filtrate concentrated to obtain a white precipitate of **5**. Yield: 0.043 g (14%). ^{1}H NMR ($CDCl_3$, ppm): 7.76−7.26 (m, br, 20H, Ph), 3.56−1.53 (m, vbr, 10H, $C_2B_{10}H_{10}$). ^{31}P NMR ($CDCl_3$, ppm): 94.6 ($^1J_{PPt}$ = 4895 Hz). ^{11}B NMR ($CDCl_3$, ppm): −2.4 (m, vbr, 4B, $C_2B_{10}H_{10}$), −11.2 (m, vbr, 6B, $C_2B_{10}H_{10}$). The amount of substance obtained was insufficient for other characterization methods.

Synthesis of *cis-rac*-[$PdCl_2${1,2-$(P^tBuCl)_2(C_2B_{10}H_{10})$}] (6) and formation of *cis*-(R_P,R_P,S_P,S_P)-[{Pd(7,8-{P^tBuCl}$_2C_2B_9H_{10}$)(μ-Cl)}$_2$] (7). A solution of [$PdCl_2$(COD)] (0.2 g, 0.70 mmol) in dichloromethane (25 mL) was added to a solution of *rac*-1,2-bis(*tert*-butylchlorophosphino)-1,2-dicarba-*closo*-dodecaborane(12) (0.27 g, 0.70 mmol) in dichloromethane (30 mL). The reaction mixture was stirred at room temperature for 5 h, and then the solvent was removed in vacuum. The product was extracted with toluene (2×30 mL), and the toluene solution was then concentrated. Yellow crystals of **6** were obtained on standing at room temperature. Yield: 0.33 g (84%). M.p.: 170 °C (decomposes, turns red), 260 °C (turns brown), 310 °C (turns black). C 21.29; H 4.93%. Calcd for $C_{10}H_{28}B_{10}Cl_4P_2Pd$: C 21.20; H 4.98%. FAB-MS, *m*/*z*: 530 (2%, M^+− Cl), 495 (6%, M^+ − 2Cl), 438 (9%, M^+ − 2Cl − ^{t}Bu). Calcd for $C_{10}H_{28}B_{10}Cl_4P_2Pd$: M = 566.56. ^{1}H NMR ($CDCl_3$, ppm): 3.65−1.83 (m, vbr, 10H, $C_2B_{10}H_{10}$), 1.77 (d, $^3J_{PH}$ = 22 Hz, 18H, CH_3). ^{31}P NMR ($CDCl_3$, ppm): 152.7. ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): 87.1 (dd, $^1J_{CP}$ = 24.8 Hz, $^2J_{CP}$ = 16.5 Hz, $C_{cluster}$−P), 51.6 (s, vbr, CMe_3), 28.6 (d, $^2J_{CP}$ = 6.0 Hz). ^{11}B NMR ($CDCl_3$, ppm): 0.9 (d, $^1J_{BH}$ = 148 Hz, 2B, $C_2B_{10}H_{10}$), −2.7 (d, $^1J_{BH}$ = 154 Hz, 4B, $C_2B_{10}H_{10}$), −9.2 (m, vbr, 4B, $C_2B_{10}H_{10}$). IR (KBr, cm^{-1}): 3028m, 3012m, 2994m, 2969m, 2926m, 2869m (CH); 2678m, 2666s, 2651m, 2639s, 2629s, 2596s, 2577s, 2565s (BH); 1955w, 1866w, 1625m, 1471s, 1459s, 1401m, 1369s, 1260w, 1160s, 1069s, 1017s, 974w, 929m, 902w, 882w, 833m, 798m, 768m, 749m, 734m, 662m, 627s, 579s, 542s, 485s, 445m, 423m, 412w.

Single crystals of **7** were obtained from a solution of **6** in dichloromethane after it was kept for several weeks at room temperature. The crystals were characterized by X-ray crystallography. The amount of pure substance obtained was insufficient for other characterization methods.

Synthesis of *cis-rac*-[$PdCl_2${1,2-{$P(NEt_2)Cl$}$_2(C_2B_{10}H_{10})$}] (8). A solution of [$PdCl_2$(COD)] (0.18 g, 0.63 mmol) in dichloromethane (25 mL) was added to a solution of *rac*-{1,2-{$P(NEt_2)Cl$}$_2(C_2B_{10}H_{10})$ (0.26 g, 0.63 mmol) in dichloromethane (35 mL). The reaction mixture was stirred at room temperature for 5 h, and then the solvent was removed in vacuum. The product was extracted with toluene (2×30 mL), and the toluene solution was concentrated. Yellow crystals of **8** were obtained on standing at room temperature. Yield: 0.30 g (80%). M.p.: 210 °C (decomposes, turns orange), 260 °C (turns brown). Found: C 23.50; H 5.34; N 4.17%. Calcd for $C_{10}H_{30}B_{10}Cl_4N_2P_2Pd\cdot0.5C_7H_8$: C 25.23; H 5.33; N 4.36%. FAB-MS, *m*/*z*: 560 (7%, M^+ − Cl), 524 (17%, M^+ − 2Cl), 488 (19%, M^+ − 3Cl), 452 (4%, M^+ − 4Cl). Calcd for $C_{10}H_{30}B_{10}Cl_4N_2P_2Pd$: M = 596.65. ^{1}H NMR ($CDCl_3$, ppm): 3.61 and 3.40 (m, br, 8H, CH_2), 3.65−1.57 (m, vbr, 10H, $C_2B_{10}H_{10}$), 1.24 (t, $^3J_{HH}$ = 8 Hz, 12H, CH_3). ^{31}P NMR ($CDCl_3$, ppm): 122.6. ^{13}C{^{1}H} NMR ($CDCl_3$, ppm): 137.9, 129.0, 128.2, 125.3 (4 s, C_7H_8), 91.5 (3 br s, $C_{cluster}$−P), 44.9 (m, vbr, CH_2), 21.4 (s, CH_3 in C_7H_8), 12.7 (s, CH_3). ^{11}B NMR ($CDCl_3$, ppm): −2.1 (d, $^1J_{BH}$ = 111 Hz, 4B, $C_2B_{10}H_{10}$), −10.1 (m, vbr, 4B, $C_2B_{10}H_{10}$), −14.4 (m, vbr, 2B, $C_2B_{10}H_{10}$). IR (KBr, cm^{-1}): 2983s, 2938m, 2892m, 2871m (CH); 2619s, 2587s (BH); 1879w, 1702w, 1626w, 1601w, 1495w, 1463s, 1441m, 1383s, 1364m, 1342w, 1289m, 1202s, 1152s, 1104s, 1074s, 1058s, 1021s, 961s, 925w, 904w, 880w, 843s, 799s, 758w, 741s, 699w, 687w, 670w, 627m, 576s, 550s, 486s, 451m, 428w, 411w.

Synthesis of *cis-rac*-[$PdCl_2${1,2-{$P(NPh_2)Cl$}$_2(C_2B_{10}H_{10})$}] (9). A solution of [$PdCl_2$(COD)] (0.16 g, 0.56 mmol) in dichloromethane (25 mL) was added to a solution of *rac*-{1,2-{$P(NPh_2)Cl$}$_2(C_2B_{10}H_{10})$ (0.34 g, 0.56 mmol) in dichloromethane (35 mL). The reaction mixture was stirred at room temperature for 6 h, and then the solvent was removed in vacuum.

The product was extracted with toluene (2 × 30 mL), the toluene solution was concentrated, and a yellow precipitate of **9** was obtained. Yield: 0.36 g (81%). M.p.: 248 °C (decomposes, turns brown), 264 °C (decomposes, turns dark red). Found: C 39.66; H 3.76; N 3.25%. Calcd for $C_{26}H_{30}B_{10}Cl_4N_2P_2Pd$: C 39.59; H 3.83; N 3.55%. FAB-MS, *m*/*z*: 753 (100%, $M^+ - Cl$), 716 (48%, $M^+ - 2Cl$), 681 (16%, $M^+ - 3Cl$), 646 (3%, $M^+ - 4Cl$). Calcd for $C_{26}H_{30}B_{10}Cl_4N_2P_2Pd$: M = 788.82. ^{1}H NMR ($CDCl_3$, ppm): 7.76−7.30 (m, 20H, Ph), 3.55−1.37 (m, vbr, 10H, $C_2B_{10}H_{10}$). ^{31}P NMR ($CDCl_3$, ppm): 122.9. $^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 142.8 (s, *ipso*-C, Ph), 129.9 (s, *o*-C, Ph), 129.4 (br s, *m*-C, Ph), 128.4 (s, *p*-C, Ph), 85.3 (t, $C_{cluster}$−P). ^{11}B NMR ($CDCl_3$, ppm): −2.1 (m, vbr, 4B, $C_2B_{10}H_{10}$), −10.9 (m, vbr, 6B, $C_2B_{10}H_{10}$). IR (KBr, cm^{-1}): 3060m (CH); 2584s (BH); 1960w, 1883w, 1802w (Ph); 1589m, 1488s, 1450m, 1314w, 1281w, 1220s, 1185s, 1070s, 1032s, 1016m, 989s, 918w, 882s, 838m, 798w, 755s, 729w, 694s, 671w, 629m, 611m, 573m, 559s, 534s, 506w, 478s, 442w, 410w, 431w.

Conclusion

Complexes of platinum(II) and palladium(II) containing chiral P−Cl functionalized bis-phosphino *ortho*-carbaborane are readily obtained from suitable chiral bidentate phosphino carbaborane ligands. The substituents at the two phosphorus atoms in the ligands play an important role in the steric and electronic properties of the phosphine ligands and the obtained complexes. Thus, *cis*-*rac*-[MCl_2{1,2-($P^tBuCl)_2(C_2B_{10}H_{10}$)}] [M = Pt (**1**), Pd (**6**)] decompose in toluene or in dichloromethane solution at room temperature over several weeks with formation of dinuclear platinum or palladium complexes with two *nido*-carbaboranylphosphine ligands, (R_P,R_P,S_P,S_P)-[{M(7,8-{P^tBuCl}$_2C_2B_9H_{10}$)-(μ-Cl)}$_2$] [M = Pt (**2**), Pd (**7**)], among other decomposition products.

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