DOI: 10.1002/ejic.200800024

A Phosphanyl-Substituted Benzo-1,3,2-Dioxaborol as Ambiphilic Bifunctional Lewis Donor–Acceptor Unit

Samir Chikkali,[a] Silja Magens,[b] Dietrich Gudat,*[a] Martin Nieger,[c] Ingo Hartenbach,[a] and Thomas Schleid[a]

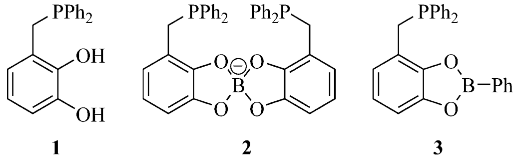
Keywords: Phosphanes / Boranes / Lewis acids / Lewis bases / Donor–acceptor systems

Condensation of 3-[(diphenylphosphanyl)methyl]benzene-1,2-diol (**1**) with phenyl boronic acid gave a phosphane-functionalised benzo-1,3,2-dioxaborol **3**. The ability of this species to act as a Lewis base through the P-centered donor and as a Lewis acid through the B-centered acceptor sites was demonstrated by the reactions with (cod)PdCl$_2$ and some nitrogen donors (4-dimethylaminopyridine, diaza-[2.2.2]-bicyclooctane, pyridine). These reactions yielded either palladium–phosphane complexes or amine–borane adducts that were characterised by spectroscopic data and, in some cases, by single-crystal X-ray diffraction studies. Reactions of a Pd complex of the phosphane-functionalised benzo-1,3,2-dioxaborol **3** with dabco, or of the dmap adduct of **3** with (cod)-PdCl$_2$, gave materials that were characterised by analytical data and solid-state NMR spectroscopic data as triple Lewis acid/base complexes and that contain both P→Pd and B←N dative bonds. Even though these adducts were unstable in solution, the results of these experiments demonstrate the ability of **3** to act as a bifunctional donor/acceptor ligand, which is of potential use as a building block for main chain organometallic polymers or multimetallic complexes.

Introduction

Tertiary phosphanes that carry additional Lewis acid functionalities are receiving increasing interest as ambiphilic bifunctional ligands. The reaction behaviour of these species has been found to depend significantly on the Lewis acidity of the acceptor moiety: ligands for which the acceptor is a strong Lewis acid form stable metal complexes through P→M–Cl→B or P→M→B interactions[1] or undergo unusual reactions such as the activation of dihydrogen.[2] In contrast, species featuring Lewis acid sites of moderate acceptor power may serve as templates for directing catalytic reactions by precoordination of substrates with complementary donor functionalities.[3,4]

Having recently begun to explore the chemistry of the catechol phosphane **1**,[5] we have demonstrated that its reaction with boric acid B(OH)$_3$ proceeds selectively at the diol unit to give the borate-templated anionic diphosphane **2**, which may bind as a *trans*-spanning bidentate ligand to a univalent metal ion such as Ag$^+$.[6] With regard to this behaviour, it was anticipated that reaction of **1** with phenyl boronic acid PhB(OH)$_2$ might give rise to an ambiphilic phosphane-functionalised dioxaborol **3**, which may then be able to act as a bifunctional ambiphilic ligand through the *P*-centred donor and *B*-centred acceptor sites. We describe here the synthesis of ambiphilic ligands of this type and present a first investigation of their reaction behaviour towards Lewis acids and bases. The results of these studies may open a new avenue towards the construction of metallopolymers and multimetallic complexes (Scheme 1).[7]



Scheme 1.

Results and Discussion

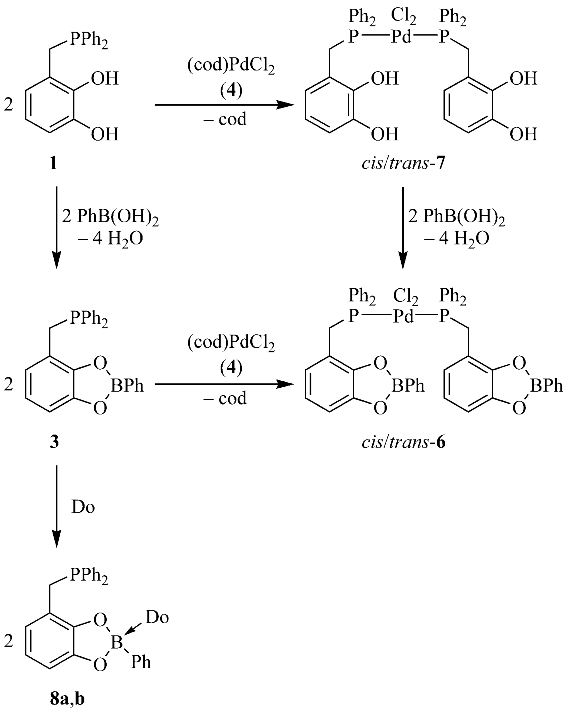
Catechol phosphane **1** was synthesised as previously reported[5] by hydrophosphanation of dihydroxy benzaldehyde with diphenylphosphane, followed by reduction of the resulting phosphane oxide with LiAlH$_4$. Reaction of **1** with 1 equiv. phenyl boronic acid in CH$_2$Cl$_2$ for 1 h at room temperature and subsequent evaporation of volatiles gave a quantitative yield of a white solid which was identified as analytically pure dioxaborol **3** by elemental analysis and spectroscopic (NMR, MS) data. The broad ^{11}B NMR signal [$\delta(^{11}B)$ = 31.7 ppm] and the sharp ^{31}P{^{1}H} NMR signal [$\delta(^{31}P)$ = –11 ppm] are found in regions that are characteris-

---

[a] Institut für Anorganische Chemie, Universität Stuttgart,
Pfaffenwaldring 55, 70550 Stuttgart, Germany
E-mail: gudat@iac.uni-stuttgart.de
[b] Institut für Organische Chemie, Universität Stuttgart,
Pfaffenwaldring 55, 70550 Stuttgart, Germany
[c] Laboratory of Inorganic Chemistry, University of Helsinki,
A. I. Virtasen aukio 1, Helsinki, Finland

tic for tricoordinate boronic esters[8] and free phosphanes, respectively, and indicate the absence of any inter- or intramolecular phosphorus/boron donor–acceptor interactions. The ability of **3** to act as a bifunctional ligand was nonetheless demonstrated by the outcome of its reactions with cyclooctadiene palladium dichloride (**4**) and dimethylaminopyridine (dmap, **5a**) or diazabicyclo-[2.2.2]-octane (dabco, **5b**).

Reaction of 0.5 equiv. **4** with **3** in thf produced a yellow solution. The formation of two reaction products that were later identified as *cis*- and *trans* isomers of complex **6** (Scheme 2) by ^{31}P NMR spectroscopy was established. The same product mixture was alternatively accessible from reaction of the complexes *cis*/*trans*-**7**, which were easily obtained from an analogous reaction of **1** and **4** with 2 equiv. phenyl boronic acid. Isolation of the pure complexes *trans*-**6** and *trans*-**7** was accomplished by recrystallisation of the crude products remaining after evaporation of all volatiles from the reaction mixtures from thf at +4 °C. The composition and identity of both products was established by analytical and spectroscopic studies and confirmed by single-crystal X-ray diffraction studies.



Scheme 2. Synthesis of the palladium complexes **6**, **7** and the N-donor complexes **8a**,**b** [cod = 1,5-cyclooctadiene, Do = 4-dimethylaminopyridine (in **8a**) or diazabicyclo-(2.2.2)-octane (in **8b**)].

The ^{31}P NMR spectra of freshly prepared solutions of crystalline samples of **6** and **7** display single sharp lines at very similar chemical shifts [$\delta(^{31}P)$ = 20.5 (*trans*-**6**), 19.1 ppm (*trans*-**7**)] that are characteristic of similar *trans*-configured palladium diphosphane complexes.[9] The onset of *trans*-/*cis* isomerisation leads to the appearance of additional signals attributable to the *cis* isomers [$\delta(^{31}P)$ = 30.6 (*cis*-**6**), 31.2 ppm (*cis*-**7**)] and produces within several hours an equilibrium mixture that contains approximately 20–25% (by integration of suitable NMR signals) of the *cis* isomers. The ^{11}B NMR spectrum of **6** contains a single broad line [$\delta(^{11}B)$ = 29 ppm], which does not change with time. This suggests that $\delta(^{11}B)$ of both isomers does not differ significantly. The signal is slightly more shielded than that of **3**, but still remains in the characteristic region of boronic esters with a trigonal-planar coordinated boron atom.[8] The proton NMR spectra of both complexes display the expected signals for the phenyl and catechol protons. The signals for the aliphatic CH$_2$ protons are clearly distinguishable and appear as doublets [δ = 4.34, J = 11.6 Hz (**6**); δ = 4.23, J = 11.6 Hz (**7**); $J = |^2J_{PH} + {}^4J_{P'H}|$] for the *cis* isomers and as slightly more shielded pseudotriplets [δ = 4.20, J = 7.5 Hz (**6**); δ = 4.13, J = 8.4 Hz (**7**)] for the *trans* isomers.

Suitable crystals for a single-crystal X-ray diffraction study of **7** were grown from a concentrated thf solution at +4 °C. The complex crystallises as a thf solvate with two solvent molecules per unit of **7** in a monoclinic unit cell (space group $P2_1$). Each molecule of **7** displays two strong OH···O hydrogen bonds (O4···O7 2.69 Å, O2···O5 2.70 Å) with the oxygen atoms of two solvent molecules (see Figure 1), whereas the remaining solvent molecules are trapped in the periphery of the complex and display no significant intermolecular interactions. A further pair of hydrogen bonds (O2···O3#/O2#···O3 2.71 Å) connects two OH groups of adjacent molecules and leads to the formation of zig-zag chains of complexes connected by hydrogen bonds. The palladium atom in each complex displays a square-planar coordination geometry and is surrounded by two mutually *trans*-positioned chlorine and phosphorus atoms [P2–Pd1–P1 178.0(1)°, Cl1–Pd1–Cl2 178.6(1)°]. The distances between the metal and the phosphorus [Pd1–P1 2.337(1) Å, Pd1–P2 2.331(1) Å] and chlorine atoms [Pd1–

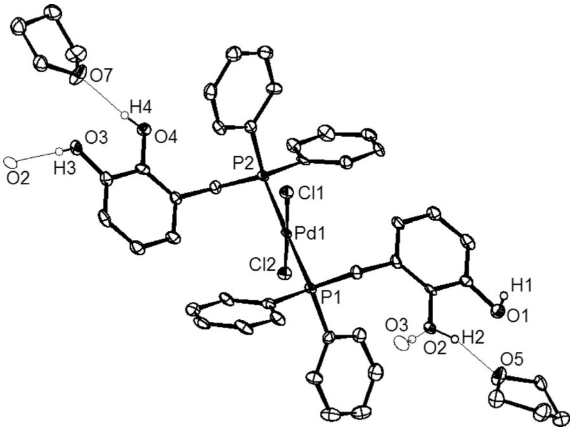


Figure 1. Molecular structure of *trans*-**7** with two out of four solvent molecules. O2# and O3# denote oxygen atoms of adjacent molecules. Thermal ellipsoids are drawn at the 50% probability level and H atoms except those of the OH groups have been omitted for clarity. Hydrogen bonds are drawn as thin lines. Selected bond lengths [Å] and bond angles [°]: Pd1–Cl1 2.299(1), Pd1–Cl2 2.306(1), Pd1–P1 2.337(1), Pd1–P2 2.331(1), Cl1–Pd1–P2 93.2(1), Cl2–Pd1–P2 86.5(1), Cl1–Pd1–P1 85.1(1), Cl2–Pd1–P1 95.3(1), P2–Pd1–P1 178.0(1), Cl1–Pd1–Cl2 178.6(1). Intermolecular distances [Å]: O2···O5 2.695(6), O2···O3# 2.713(6), O4···O7 2.693(6).

Cl1 2.299(1) Å, Pd1–Cl2 2.306(1) Å] are normal and match commonly found bond lengths[10] in *trans*-diphosphane palladium dihalides (Pd–P 2.34 ± 0.03 Å, Pd–Cl 2.30 ± 0.02 Å).

The complex **6** crystallises as a solvate with four molecules of thf in a monoclinic unit cell in the space group $P2_1/c$ (Figure 2). The discrete complexes have a crystallographic *Ci* symmetry and show no significant intermolecular interactions. The palladium atom lies on a crystallographic centre of symmetry and displays, as in **7**, a square-planar coordination geometry with the phosphorus and chlorine atoms in a *trans* arrangement. The Pd–Cl [2.298(1) Å] and Pd–P distances [2.332(1) Å] are identical to those in **7** within experimental error. The benzodioxaborol units display the same arrangement as that of the catechol rings in **7** and point away from each other. The boron atom displays a trigonal-planar geometry in which the endocyclic O1–B–O2 angle [110.9(5)°] is reduced and the C20–B–O1/O2 angles [125.2(5)/123.8(5)°] are appropriately enlarged with respect to the ideal angle of 120°. The B1–O1/O2 [1.395(6)/1.402(6) Å] and B1–C20 [1.543(8) Å] distances are in close agreement with the corresponding bond lengths in 2-phenyl-1,3,2-benzodioxaborol.[11]

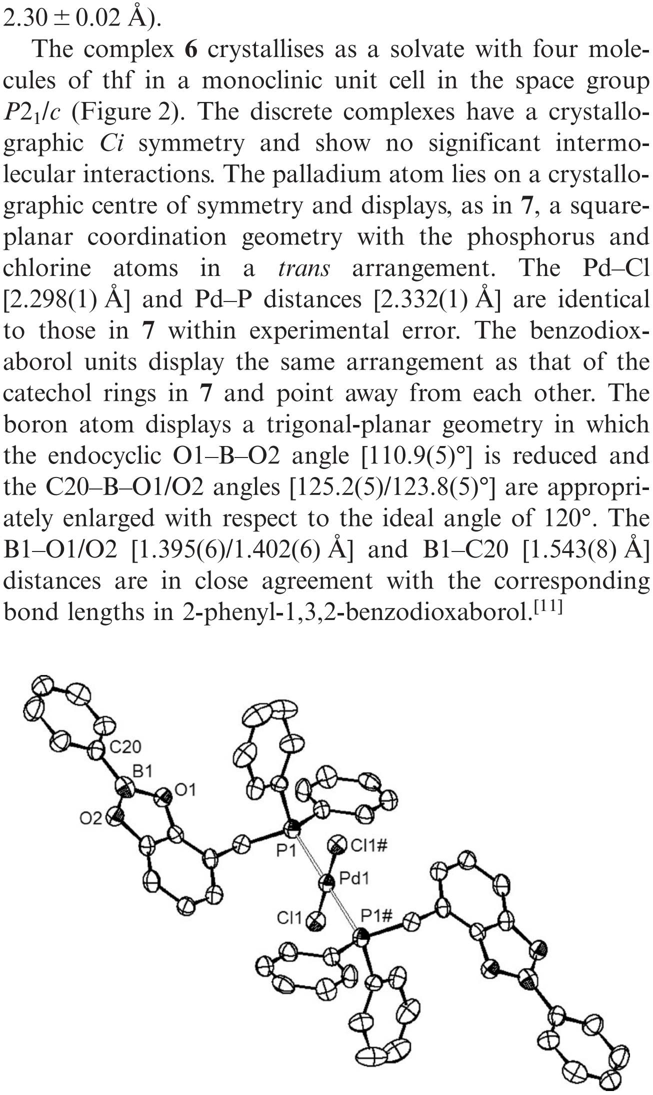


Figure 2. Molecular structure of *trans*-**6**. Thermal ellipsoids are drawn at the 50 % probability level and the H atoms and solvent molecules (thf) have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Pd1–Cl1 2.298(1), Pd1–P1 2.332(1), B1–O1 1.395(6), B1–O2 1.402(6), B1–C20 1.543(8), Cl1–Pd1–P1 86.3(1), Cl1–Pd1–P1# 93.7(1), P1–Pd1–P1# 180.0, Cl1–Pd–Cl1# 180.0, C20–B1–O1 125.2(5), C20–B1–O2 123.8(5), O1–B–O2 110.9(5).

The Lewis base complexes **8a**,**b** were prepared by treating a thf solution of **3** with 1 equiv. of the appropriate donor and isolated in a quantitative yield after evaporation of the solvent. Both species were characterised by analytical and spectroscopic data, and the identity of **8a** was further confirmed by a single-crystal X-ray diffraction study. The attachment of the donor to the boron atom was indicated by a pronounced upfield shift of the ^{11}B NMR signals [$\delta(^{11}\mathrm{B})$ = 11 (**8a**), 15 ppm (**8b**)], which appear now in a spectral region characteristic for tetracoordinate boron atoms;[8] the ^{31}P NMR chemical shifts remain similar to that of free **3**. The ^{1}H NMR spectra of **8a**,**b** show, beside the signals for the phenyl and catechol protons, further resonances that are attributable to the donor moieties. For **8a**, the number and multiplicity of these signals is as expected (AA′XX′ spin system and intense singlet for the aromatic and *N*-methyl protons, respectively), whereas **8b** displays only a single resonance accounting for all twelve protons of the donor moiety. The same effect is also observable in the ^{13}C spectrum and indicates that the adduct exhibits a fluxional structure in solution, which arises from chemical exchange between the coordinating and non-coordinating nitrogen donor sites in the dabco unit. Even though the available spectroscopic data provide no further information, it appears most likely that the exchange follows a dissociative mechanism and involves intermediate cleavage of the donor–acceptor bond. Formation of a thermodynamically and kinetically labile donor–acceptor adduct was also observed upon treatment of **3** with the weaker Lewis base pyridine. Quantitative transformation of the free dioxaborol into the pyridine complex (as judged from the upfield shift of the ^{11}B NMR signal) required, in this case, the addition of a large excess of the Lewis base (approximately 6 equiv.), and the resulting complex could not be isolated.

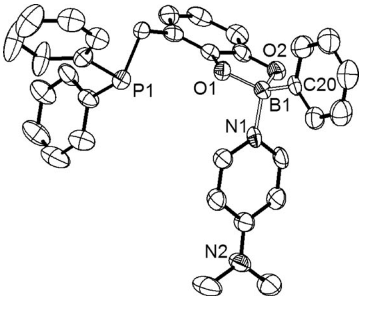


Figure 3. Molecular structure of **8a**. Thermal ellipsoids are drawn at the 50 % probability level and the H atoms and solvent molecules (thf) have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: B1–O1 1.475(8), B1–O2 1.498(8), B1–N1 1.609(9), B1–C20 1.614(10), C7–P1 1.859(7), P1–C8 1.814(7), P1–C14 1.846(6), O1–B1–O2 105.2(5), O1–B1–N1 107.9(5), O2–B1–N1 105.2(5), O1–B1–C20 111.9(5), O2–B1–C20 114.7(6), N1–B1–C20 111.5(5), C8–P1–C14 101.5(3), C8–P1–C7 104.1(3), C14–P1–C7 96.7(3).

Recrystallisation of **8a** from a concentrated dichloromethane solution to which a few drops of thf had been added produced colourless single crystals (space group $P2_1/c$) of a solvate containing one molecule of thf per formula unit. The crystal contains discrete molecules of **8a** (Figure 3) without significant intermolecular interactions. The boron atom displays a distorted tetrahedral coordination geometry, which is characterised by a reduction in the O1–B–O2 [105.2(5)°] and O1/O2–B–N1 angles [107.9(5)/105.2(5)°] and a widening of the O1/O2–B–C20 [111.9(5)/114.7(6)°] and C20–B–N1 [111.5(5)°] angles relative to the tetrahedral angle of 109.4°.[12] The increase in the boron coordination number relative to that of **3** induces a marked lengthening of the B–O1/O2 and B–C20 bonds by some 8–9 and 6 pm, respectively, which is in good agreement with literature data.[11] The length of the formal donor–acceptor bond [B–N1 1.609(9) Å] and the coplanar arrangement of the Me_2N group and the pyridine ring of the donor moiety are similar as in other known dmap–borane complexes (average B–N bond length 1.62 ± 0.03 Å[12]). The P–C bond lengths and the pyramidal coordination geometry [sum of C–P–C angle 303(1)°] are normal.

The findings described above stimulated us to investigate whether **3** is also capable of forming two complementary donor–acceptor interactions at the same time and can thus act as a μ_2-bridging ligand that can connect to a Lewis acid and a Lewis base. The controlled synthesis of such a species featuring multiple donor–acceptor bonds between *different* Lewis acid/base pairs represents a challenge as it requires the fine-tuning of the functionalities involved in order to select the desired and to suppress the undesired Lewis acid/base pairings. Since self complexation of **3** seems to be unfavourable and Pd^{II} (even if it can form stable complexes with nitrogen donors) normally has a preference to bind phosphorus donor ligands, it appears that pairing of Pd–P/B–N donor/acceptor sites is on the whole preferable, and selective simultaneous coordination of a nitrogen donor and a transition-metal (Pd) acceptor fragment to **3** should thus be feasible.

The synthesis of the targeted adducts was attempted by two different ways. In one approach, a thf solution of the dioxaborol–amine adduct **8a** was treated with 0.5 equiv. (cod)$PdCl_2$ in order to accomplish the formation of additional Pd–P dative bonds. The reaction produced a yellow precipitate, which was isolated by filtration and gave analytical data that are compatible with the expected composition [$PdCl_2$(**8a**)$_2$]. The product failed to redissolve without decomposing in organic solvents (see below) and was therefore further characterised by solid-state NMR spectroscopy. The ^{11}B MAS-NMR spectrum consists of a single, relatively narrow ($\Delta\nu_{1/2}$ = 500 Hz) line, which is centred at 6 ppm and displays the shape of a quadrupolar powder pattern (Figure 4 top). The position of this line provides clear evidence that the tetrahedral coordination at boron is retained. The $^{31}P\{^1H\}$ CP/MAS-NMR spectrum displays a complex pattern of several superimposed lines (Figure 4 middle), which indicates that the solid contains chemically nonequivalent phosphane units in several distinguishable local environments. Analysis of the isotropic chemical shifts – all lines are in the range between 31 and 43 ppm – confirms that all signals are attributable to metal-coordinated phosphane ligands and that free phosphane moieties are absent. The ^{11}B and ^{31}P NMR spectroscopic data, in combination, further support the assignment of the product as complex [$PdCl_2$(**8a**)$_2$]. The observed complexity of the ^{31}P NMR spectrum is readily accounted for if one considers that a complex of this type may exist as a mixture of *cis*- and *trans* isomers, each of which may form two diastereomers (owing to the chiral nature of the tetracoordinate boron atoms) and a variety of distinguishable rotamers.

In a second approach, complex **6** was treated with 2 equiv. dabco. This reaction likewise produced a yellow solid, which was isolated in the same manner as before and may be formulated according to analytical and ^1H NMR spectroscopic data as an adduct containing approx. 1.2 equiv. dabco per molecule of **6**. The ^{11}B MAS-NMR spectrum gave a signal that is centred at 5 ppm and displays a similar lineshape as that of the previously mentioned dmap complex, thus disclosing that the tetracoordinate environment at boron persists. Furthermore, the $^{31}P\{^1H\}$ CP/MAS-NMR spectrum shows a broad, unstructured line which extends over the region between 20 and 40 ppm (Figure 4 bottom) and indicates that the phosphorus coordination to palladium likewise remains intact. On the basis of these data, we formulated the product as a chainlike,[13] oligomeric array of alternating $PdCl_2$ and dabco units that are bridged by the ambiphilic bidentate donor **3**. The chain structures are held together by dative P→Pd and B←N interactions and are presumably terminated by dabco fragments.

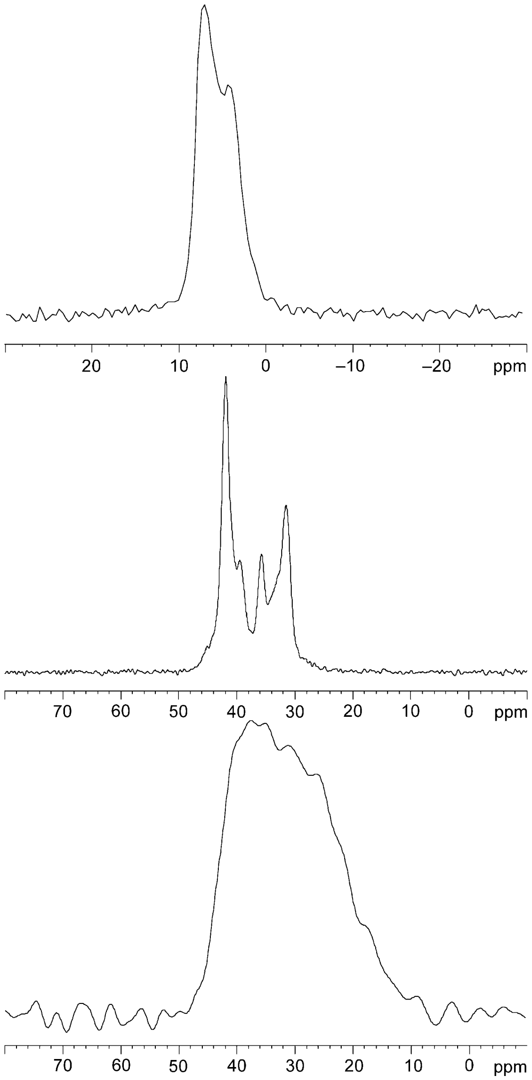


Figure 4. ^{11}B MAS NMR (top) and $^{31}P\{^1H\}$ CP/MAS-NMR (middle) spectrum of the solid adduct [$PdCl_2$(**8a**)$_2$] (middle). $^{31}P\{^1H\}$ CP/MAS-NMR spectrum of the adduct **6**·–1.2dabco (bottom).

Attempts aiming at recrystallisation of the crude products remained unsuccessful. Both materials were found to dissolve only in strongly donating solvents such as dmf or dmso, and NMR spectra of these solutions gave evidence for the occurrence of decomposition processes. Thus, whereas the ^{11}B NMR spectrum of a freshly prepared dmf solution of the dmap adduct [$PdCl_2$(**8a**)$_2$] still displays a single resonance with a similar chemical shift as that in the solid state [$\delta(^{11}B) = 10.6$ ppm], the $^{31}P\{^1H\}$ NMR spectrum shows, in addition to two signals at $\delta = 18.4$ and 37.9 ppm, which can be assigned to the phosphane ligands in the *trans*- and *cis*-P_2PdCl_2 fragments, resonances that can be assigned to the free phosphane **3** and a new product with an AX-type spin system. The se signals at $\delta(^{31}P) = 80.6$ and 27.9 ppm ($J_{PP} = 30.7$ Hz) are assigned to a *cis*-configured palladium complex with two different phosphane ligands.[14] The same signals (except that for **3**) were also visible in the $^{31}P\{^1H\}$ NMR spectrum of the dabco adduct. In this case, however, the ^{11}B NMR spectrum differed from the spectrum of the solid in that a signal at much lower field is observed [$\delta(^{11}B) = 21–29$ ppm, depending on the age of the solution), the position of which clearly indicates the presence of a three-coordinate boron atom. The ^{1}H NMR spectrum displays signals attributable to the free amine (integration of suitable resonances allowed the confirmation of a ratio of 1:1.2 for catechol phosphane/amine). The observed spectroscopic data indicate that in solution extensive dissociation of the solid adduct into **6** and dabco occurs; direct evidence of the formation of a bifunctional adduct of the ambiphile **3** is, however, provided by an ESI-MS analysis, which displays, among several other signals, a low intensity peak at $m/z = 1211$ with an isotope pattern indicative of the composition [(dabco→**3**→)$_2PdCl_2$ + H^+]. Whereas the dabco adduct is thus considered to dissociate in solution primarily through cleavage of the dative B–N bond, the data of the dmap complex suggest that in this case decomplexation of the phosphane (presumably accompanied by the formation of halide bridges or coordination of dmap) occurs. The formation of an unsymmetrical phosphane in both cases suggests that additional processes, which presumably include cleavage of the dioxaborol ring,[14] also take place.

Conclusions

It was shown that the phosphanyl-substituted benzodioxaborol **3** may react both as a Lewis base and as a Lewis acid by forming stable adducts through dative P→Pd and B←N bonds, respectively. Even bifunctional coordination with simultaneous formation of both types of donor–acceptor interactions is, in principle, feasible, although the resulting complexes could only be characterised by spectroscopic data in the solid state and were found to dissociate or decompose in solution. Provided that the interplay between donor and acceptor centres is further optimised and the stability of the donor–acceptor interaction increased, the extension of this chemistry may allow the rational design of metallopolymers[15] or multimetallic complexes with a wide structural complexity and diversity. Investigations to accomplish these goals are currently under way.

Experimental Section

General Remarks: All manipulations were carried out under a dry argon atmosphere, and solvents were dried by standard procedures unless otherwise mentioned. The catechol phosphane **1** was prepared as reported earlier.[5] Cyclooctadiene palladium dichloride was prepared according to the literature,[16] and phenyl boronic acid, 1,4-diazabicyclo-[2.2.2]-octane and dimethylaminopyridine were commercially available and were used without further purification. Solution NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H: 400.1 MHz, ^{11}B: 128.4 MHz, ^{13}C: 100.5 MHz, ^{31}P: 161.9 MHz) at 303 K unless mentioned otherwise; chemical shifts were referenced to external tms (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), or $BF_3.OEt_2$ (Ξ = 32.083974 MHz, ^{11}B). Solid-state MAS-NMR spectra were recorded on a Bruker Avance 400 MHz NMR instrument with spinning speeds between 3 and 14 kHz. Cross-polarisation with a ramp-shaped contact pulse and mixing time between 3 and 5 ms was used for signal enhancement in the CP/MAS experiments. ^{11}B NMR spectra were recorded without CP by using a Hahn-echo pulse sequence. Coupling constants are given as absolute values; prefixes *i, o, m, p* denote phenyl ring positions of P-C_6H_5 substituents, C_6H_3 represents the catechol ring protons. EI-MS: Varian MAT 711, 70 eV. ESI-MS: Bruker Daltonics micrOTOF-Q. Elemental analyses: Perkin–Elmer 2400CHSN/O Analyser; deviations from calculated values are, in the case of solvates, attributable to nonstiochiometric amounts of solvent. Melting points were determined in sealed capillaries.

Diphenyl-(2-phenylbenzo[1,3,2]dioxaborol-4-ylmethyl)phosphane (3): Phenyl boronic acid (245 mg, 2 mmol) was added to a solution of **1** (620 mg, 2 mmol) in CH_2Cl_2 (20 mL), and the reaction mixture was stirred for 1 h. The volatiles were evaporated in vacuo to give a quantitative yield of spectroscopically pure **3** as a colourless solid. $C_{25}H_{20}BO_2P$ (394.22): calcd. C 76.12, H 5.11; found C 75.50, H 5.11. ^{1}H NMR ($CDCl_3$): δ = 8.00 (m, 2 H, BC_6H_5), 7.57 (m, 1 H, BC_6H_5), 7.45 (m, 6 H, PC_6H_5), 7.35–7.25 (m, 6 H, BC_6H_5, PC_6H_5), 7.07 (ddd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, J_{PH} = 1.3 Hz, 1 H, C_6H_3), 6.93 (t, $^3J_{HH}$ = 7.9 Hz, 1 H, C_6H_3), 6.82 (ddd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, J_{PH} = 1.3 Hz, 1 H, C_6H_3), 3.62 (s, 2 H, CH_2) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 148.0 (d, J_{PC} = 1.7 Hz, C_6H_3), 146.9 (d, J_{PC} = 4.0 Hz, C_6H_3), 138.1 (s, Ph), 137.8 (s, Ph), 134.9 (s, Ph), 133.0 (s, Ph), 132.7 (s, Ph), 132.1 (s, Ph), 128.7 (s, Ph), 128.3 (d, J_{PC} = 6.5 Hz, *o*-C), 128.0 (s, Ph), 123.8 (d, J_{PC} = 7.5 Hz, *m*-C), 122.7 (d, J_{PC} = 8.3 Hz, *i*-C), 122.4 (d, J_{PC} = 1.4 Hz, *p*-C), 110.1 (d, J_{PC} = 2.5 Hz, *p*-C), 28.7 (d, $^1J_{PC}$ = 16.5 Hz, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –11.1 (s) ppm. ^{11}B NMR ($CDCl_3$): δ = 31.7 (br.) ppm. MS (EI, 70 eV): m/z (%) = 394.1 (100) [M^+], 185.0 [Ph_2P^+].

Palladium Bis[diphenyl-(2-phenylbenzo-1,3,2-dioxaborol-4-ylmethyl)phosphane] Dichloride (6): (a) Phenyl boronic acid (122 mg, 1 mmol) was added to a solution of **7** (397 mg, 0.5 mmol) in thf. The reaction mixture was stirred for 2 h at room temperature. The volatiles were then evaporated in vacuo to produce a yellow powder of spectroscopically pure **6** in quantitative yield. Suitable crystals for a single-crystal X-ray diffraction study were obtained by recrystallisation from a minimum amount of thf at +4 °C. Yield: 333 mg (69%). M.p. 240 °C (dec.). (b) (cod)$PdCl_2$ (32.5 mg, 0.11 mmol) was added to solution of **3** (90 mg, 0.22 mmol) in thf. The mixture was stirred for 2 h at room temperature. The volatiles were then evaporated under reduced pressure to produce a yellow powder, which was recrystallised from thf. The crystalline product was collected by filtration and dried in vacuo. Yield: 83 mg (75%). M.p. 240 °C (dec.). $C_{50}H_{40}B_2Cl_2O_4P_2Pd$ (965.76): calcd. C 62.19, H 4.18; found C 61.2, H 4.68. ^{1}H NMR ($CDCl_3$): δ = 7.8–7.3 (m, C_6H_5), 7.1–6.7 (m, C_6H_3), 4.3 (d, $^2J_{PH}$ = 11.5 Hz, CH_2 of *cis* isomer), 4.2 (t, ΣJ_{PH} = 7.8 Hz, CH_2 of *trans* isomer) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, only data of *trans* isomer given): δ = 147.9 (t, ΣJ_{CP} = 5.0 Hz, C_6H_3), 147.7 (t, J_{PC} = 1.2 Hz, C_6H_3), 135.0 (s, Ph), 133.9 (t, $^3J_{PC}$ = 6 Hz, *m*-C), 132.2 (s, Ph), 130.8 (s, Ph), 128.0 (s, Ph), 127.9 (t, J_{PC} = 5 Hz, *i*-C), 125.3 (br., B–C), 124.8 (t, J_{PC} = 2.4 Hz, C_6H_3), 122.4 (s, C_6H_3), 119.0 (t, J_{PC} = 2.0 Hz, C_6H_3), 110.8 (t, J_{PC} = 1.6 Hz, C_6H_3), 25.0 (t, $^1J_{PC}$ = 13 Hz, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 30.6 (*cis* isomer), 20.4 (*trans* isomer) ppm. ^{11}B NMR ($CDCl_3$): δ = 29.1 (br.) ppm.

Palladium Bis[diphenyl-(2,3-dihydroxyphenylmethyl)phosphane] Dichloride (7): To a solution of **1** (200 mg, 0.64 mmol) in thf (20 mL) was added (cod)$PdCl_2$ (93 mg, 0.32 mmol). The reaction mixture was stirred for 2 h at room temperature and then concentrated under reduced pressure to half the total volume. Shiny yellow needle-like crystals were obtained on stirring this solution overnight at +4 °C. The crystals were isolated by filtration and dried in vacuo. Yield: 240 mg (95%). M.p. 176 °C. $C_{38}H_{34}Cl_2O_4P_2Pd$·thf (866.07): calcd. C 58.25, H 4.89; found C 58.06, H 5.27. ^{1}H NMR (CD_3CN): δ = 7.8–7.1 (m, Ph), 7.0–7.65 (m, C_6H_3), 4.23 (d, $^2J_{PH}$ = 11.6 Hz, CH_2 of *cis* isomer), 4.13 (t, Σ^2J_{PH} = 8.0 Hz, CH_2 of *trans* isomer); 3.77 (m, 4 H, thf), 1.93 (m, 4 H, thf) ppm. $^{13}C\{^1H\}$ NMR (CD_3CN, only data of *trans* isomer given): δ = 145.3 (t, ΣJ_{CP} = 2.1 Hz, C_6H_3), 144.6 (t, ΣJ_{CP} = 5.8 Hz, C_6H_3), 134.8 (t, J_{PC} = 6.1 Hz, *i*-C), 131.7 (s, Ph), 130.3 (m, ΣJ_{PC} = 45.9 Hz, C_6H_3), 128.9 (t, ΣJ_{PC} = 10.2 Hz, Ph), 123.8 (t, ΣJ_{PC} = 5.8 Hz, C_6H_3), 120.9 (t, ΣJ_{PC} = 2.6 Hz, C_6H_3), 120.4 (s, C_6H_3), 114.7 (t, ΣJ_{CP} = 2.8 Hz, C_6H_3), 68.3 (s, thf), 26.2 (s, thf), 25.3 (t, J_{PC} = 13.9 Hz, CH_2) ppm. $^{31}P\{^1H\}$ NMR (CD_3CN): δ = 32.2 (*cis* isomer), 18.7 (*trans* isomer) ppm.

Diphenyl-(2-phenylbenzo[1,3,2]dioxaborol-4-ylmethyl)phosphane-3-(dimethylaminopyridine) (8a): The donor dmap (244 mg, 2 mmol) was added to a solution of **3** (790 mg, 2 mmol) in CH_2Cl_2. The reaction mixture was stirred for 1 h. Evaporation of the solvent under reduced pressure and drying of the colourless residue in vacuo gave 980 mg of **8a** (yield 95%). M.p. 167 °C. $C_{32}H_{30}BN_2O_2P$ (516.39): calcd. C 74.43, H 5.86, N 5.43; found C 74.20, H 5.93, N 5.41. ^{1}H NMR ($CDCl_3$): δ = 8.25 (m, 2 H, dmap), 7.55–7.40 (m, 6 H, C_6H_5), 7.40–7.20 (m, 9 H, C_6H_5), 6.62 (ddd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, J_{PH} = 1.3 Hz, 1 H, C_6H_3), 6.50 (m, 2 H, dmap), 6.48 (dd, $^3J_{HH}$ = 7.6 Hz, 7.8 Hz, 1 H, C_6H_3), 6.39 (ddd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, J_{PH} = 1.3 Hz, 1 H, C_6H_3), 3.5 (s, 2 H, CH_2), 3.01 (s, 6 H, dmap) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –17.2 ppm. ^{11}B NMR ($CDCl_3$): δ = 11.1 (br.) ppm.

Diphenyl-(2-phenylbenzo[1,3,2]dioxaborol-4-ylmethyl)phosphane-3-[1,4-azabicyclo(2.2.2)octane] (8b): The donor dabco (160 mg, 1.4 mmol) was added to a solution of **3** (550 mg, 1.4 mmol) in thf. The reaction mixture was stirred for 1 h. Evaporation of the solvent under reduced pressure and drying of the colourless residue in vacuo gave 664 mg of **8b** (yield 92%). M.p. 132 °C. $C_{31}H_{32}BN_2O_2P$·thf (578.50): calcd. C 72.67, H 6.97, N 4.84; found C 71.97, H 6.76, N 4.49. ^{1}H NMR ($CDCl_3$): δ = 7.66 (m, 2 H, BC_6H_5), 7.48 (m, 4 H, PC_6H_5), 7.36–7.21 (m, 9 H, BC_6H_5, PC_6H_5), 6.68–6.51 (m, 3 H, C_6H_3), 3.73 (m, thf), 3.51 (d, $^2J_{PH}$ = 1 Hz, 1 H, CH_2), 2.80 (s, 12 H, dabco), 1.83 (m, thf) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 150.9 (d, J_{PC} = 1.7 Hz, C_6H_3), 149.6 (d, J_{PC} = 4.3 Hz, C_6H_3), 139.2 (d, $^1J_{PC}$ = 16 Hz, *i*-C), 133.5 (s, Ph), 133.0 (d, J_{PC} = 18.6 Hz, *m*-C), 128.4 (s, *p*-C), 128.3 (d, J_{PC} = 6.4 Hz, *o*-C), 128.1 (s, Ph), 127.3 (s, Ph), 121.2 (d, J_{PC} = 8.0 Hz, C_6H_3), 119.5 (d, J_{PC} = 9.2 Hz, C_6H_3), 119.3 (d, J_{PC} = 1.5 Hz, C_6H_3), 107.7 (d, J_{PC} = 2.5 Hz, C_6H_3), 44.8 (s, dabco), 28.8 (d, $^1J_{PC}$ = 14.8 Hz, CH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –12.0 ppm. ^{11}B NMR ($CDCl_3$): δ = 14.9 (br.) ppm.

Reaction of 6 with dabco: The donor dabco (16 mg, 0.14 mmol) was added to a solution of **6** (70 mg, 0.07 mmol) in thf (6 mL). The resulting mixture was stirred for 1 h during which a yellow precipitate was formed. The volatiles were evaporated under reduced pressure. The residue was suspended in thf (5 mL), and diethyl ether (20 mL) was added. The supernatant liquid was decanted off, and the remaining precipitate dried in vacuo to give 56 mg of a yellow–orange powder. M.p. 167 °C. $C_{50}H_{40}B_2Cl_2O_4P_2Pd$·1.2dabco: calcd. C 62.44, H 4.98, N 3.05; found C 61.39, H 5.14, N 2.92. ^{11}B MAS NMR (solid): δ_{iso} = 5 ppm. $^{31}P\{^1H\}$ CP/MAS NMR (solid): see Figure 4 bottom.

[$PdCl_2$(8a)$_2$]: (cod)$PdCl_2$ (110 mg, 0.39 mmol) was added to a stirred solution of **8a** (400 mg, 0.78 mmol) in thf (20 mL). A yellow precipitate began to separate after 5 min, and stirring was continued for 1 h. Diethyl ether (40 mL) was then added, and the yellow precipitate was filtered off. Drying in vacuo for 3 h gave 352 mg (yield 75%) of product. M.p. 191 °C. $C_{64}H_{60}B_2Cl_2N_4O_4P_2Pd$ (1210.10): calcd. C 63.53, H 5.00, N 4.63; found C 63.00, H 4.92, N 4.64. ^{11}B MAS- and $^{31}P\{^1H\}$ CP/MAS-NMR spectra are displayed in Figure 4 top and middle. The solution NMR spectra of freshly prepared samples showed signals attributable to a mixture of *cis*/*trans* isomers of [$PdCl_2$(**8a**)$_2$] [^{11}B NMR: δ = 10.6 ppm; $^{31}P(^1H)$ NMR: δ = 37.9 (*cis* isomer), 18.4 (*trans* isomer) ppm] in addition to signals for decomposition products. The intensity of the signal for the decomposition products increased upon standing.

Crystal Structure Study: The single-crystal X-ray diffraction studies of *trans*-**6**, *trans*-**7** and **8a** were carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using Mo-K_α radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97[17]) were used for structure solution, and full-matrix least-squares refinement on F^2 (SHELXL-97[17]). H atoms were localised by difference Fourier synthesis and refined by using a riding model.

6: Yellow-orange crystals, $C_{50}H_{40}B_2Cl_2O_4P_2Pd$·2thf, M = 1109.89, crystal size 0.20 × 0.10 × 0.05 mm, monoclinic, space group $P2_1/c$ (No. 14): a = 11.7333(7) Å, b = 22.9485(17) Å, c = 10.3897(5) Å, β = 111.424(4) °, V = 2604.2(3) Å^3, Z = 2, ρ(calcd.) = 1.415 Mg m^{-3}, $F(000)$ = 1144, μ = 0.572 mm^{-1}, 22106 reflections ($2\theta_{max}$ = 50°), 4480 unique [R_{int} = 0.102], 322 parameters, 66 restraints, R_1 [$I > 2\sigma(I)$] = 0.048, wR_2 (*all data*) = 0.088, GooF = 0.862, largest diff. peak and hole 0.672 and –0.429 e Å^{-3}.

7: Yellow–orange crystals, $C_{38}H_{34}Cl_2O_4P_2Pd$·4thf, M = 1082.31, crystal size 0.5 × 0.3 × 0.1 mm, monoclinic, space group $P2_1$: a = 10.2633(2) Å, b = 22.7369(4) Å, c = 11.6400(2) Å, β = 112.586(1)°, V = 2507.93(8) Å^3, Z = 2, ρ(calcd.) = 1.433 Mg m^{-3}, $F(000)$ = 1128, μ = 0.595 mm^{-1}, 42973 reflections ($2\theta_{max}$ = 56.54°), 12092 unique [R_{int} = 0.113, R_σ = 0.087], 749 parameters, 1 restraint to fix the origin, flack parameter x = 0.51(2), therefore refined as inversion twin, R_1 [$I > 2\sigma(I)$] = 0.053, wR_2 (*all data*) = 0.126, GooF = 1.032, largest diff. peak and hole 1.27 and –1.46 e Å^{-3}.

8a: Colourless crystals, $C_{32}H_{30}BN_2O_2P$·thf, M = 588.46, crystal size 0.12 × 0.06 × 0.03 mm, monoclinic, space group $P2_1/c$ (No. 14): a = 14.7942(4) Å, b = 9.5746(4) Å, c = 22.8934(7) Å, β = 93.558(2) °, V = 3236.57(19) Å^3, Z = 4, ρ(calcd.) = 1.208 Mg m^{-3}, $F(000)$ = 1248, μ = 0.122 mm^{-1}, 10492 reflexes ($2\theta_{max}$ = 50°), 5703 unique [R_{int} = 0.145], 390 parameters, 96 restraints, R_1 [$I > 2\sigma(I)$] = 0.120, wR_2 (*all data*) = 0.227, GooF = 1.103, largest diff. peak and hole 0.385 and –0.335 e Å^{-3}.

CCDC-672200 (**6**), CCDC-672366 (**7**), CCDC-672201 (**8a**) 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.

Acknowledgments

We thank Dr. J. Opitz, J. Trinkner and K. Wohlbold (Institut für Organische Chemie, Universität Stuttgart) for recording the mass spectra. M. N. thanks the DAAD for financial support. This work was financially supported by the Deutsche Forschungsgemeinschaft.

---

[1] J. Grobe, R. Martin, *Z. Anorg. Allg. Chem.* **1992**, *607*, 146–152; S. Bontemps, G. Bouhadir, K. Miqueu, D. Bourissou, *J. Am. Chem. Soc.* **2006**, *128*, 12056–12057; S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem.* **2006**, *118*, 1641–1644; *Angew. Chem. Int. Ed.* **2006**, *45*, 1611–1614.

[2] G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.

[3] A. Börner, J. Ward, K. Kortus, H. B. Kagan, *Tetrahedron: Asymmetry* **1993**, *4*, 2219–2228; L. B. Fields, E. N. Jacobsen, *Tetrahedron: Asymmetry* **1993**, *4*, 2229–2236.

[4] D. J. Brauer, M. Hingst, K. W. Kottsieper, C. Liek, T. Nickel, M. Tepper, O. Stelzer, W. S. Sheldrick, *J. Organomet. Chem.* **2002**, *645*, 14–26.

[5] S. Chikkali, D. Gudat, *Eur. J. Inorg. Chem.* **2006**, 3005–3009.

[6] S. Chikkali, D. Gudat, F. Lissner, M. Nieger, T. Schleid, *Dalton Trans.* **2007**, 3906–3913.

[7] M. O. Wolf, *J. Inorg. Orgnomet. Polymer Materials* **2006**, *16*, 189–199; P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515; K. A. Williams, A. J. Boydston, C. W. Bielawski, *Chem. Soc. Rev.* **2007**, *36*, 729–744.

[8] P. Diehl, E. Fluck, R. Kosfeld, *Nuclear Magnetic Spectroscopy of Boron Compounds*, Springer Verlag, Berlin, **1978**, p. 144.

[9] D. J. Brauer, P. Machnitzki, T. Nickel, O. Stelzer, *Eur. J. Inorg. Chem.* **2000**, 65–73.

[10] Result of a query in the CSD for complexes *trans*-[Pd-$(PR_3)_2X_2$].

[11] F. Zettler, H. D. Hausen, H. Hess, *Acta Crystallogr.* **1974**, *3*, 1876–1878.

[12] W. Clegg, A. J. Scott, F. E. S. Souza, T. B. Marder, *Acta Crystallogr.* **1999**, *5*, 1885–1888. Result of a query in the CSD for compounds dmap$\rightarrow$$BX_3$.

[13] A mixture of chainlike and cyclic structures cannot be ruled out.

[14] In view of the fact that chelate complexes of P,O-chelating phosphanes normally display a strong deshielding of $\delta(^{31}P)$ (see ref.[9]), it appears likely that cleavage of the dioxaborol ring and additional coordination of a phenolate moiety of one phosphane ligand to Pd has occurred.

[15] The synthesis of a related P–M/B–N coordination polymer arising from interaction of a phosphaazaadamantane ruthenium complex and phenyl boroxine was recently reported: B. J. Frost, C. A. Mebi, P. W. Gingrich, *Eur. J. Inorg. Chem.* **2006**, 1182–1189.

[16] P. M. Maitlis, *The Organic Chemistry of Palladium Metal Complexes, V.1*, Academic Press, New York, **1971**, and references therein.

[17] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *6*, 112–122.

Received: January 9, 2008