Formation of B−P Bonds through the Reaction of *nido*-Monophosphinocarboranes with Palladium(II) Complexes. The First Example of a Chelating $R_2P-C-B-PR_2$ Diphosphine

C. Viñas,*,[†] R. Núñez,[†] F. Teixidor,[†] R. Sillanpää,[‡] and R. Kivekäs[§]

Institut de Ciència de Materials, CSIC, Campus UAB, 08193 Bellaterra, Spain,
Department of Chemistry, University of Turku, FIN 20500 Turku, Finland, and
Department of Chemistry, University of Helsinki, Box 55, FIN 00014 Helsinki, Finland

Received July 29, 1999

Reaction of $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]$ (R = Me, H, Ph) with *cis*-$[PdCl_2(PPh_3)_2]$ in ethanol yielded $[PdCl(7\text{-}PPh_2\text{-}8\text{-}R\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$ (R = Me, H, Ph). The Pd(II) is in a square-planar arrangement. The carborane ligand chelates the Pd through two phosphorus atoms, one from $C-PPh_2$ and the second from the generated $B(11)-PPh_2$. The remaining two positions are filled by a PPh_3 and one chloride. In the complexation process, a previously nonexistent B(11)−P bond is generated in the ligand. This is unambiguously demonstrated by a doublet in the $^{11}B\{^1H\}$ NMR spectrum and a 1:1:1:1 quartet in the $^{31}P\{^1H\}$ spectrum. The structure was fully elucidated by a crystal diffraction analysis of $[PdCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]\cdot C_7H_8$. By this reaction the hitherto unknown $R_2P-C-B-PPh_2$ chelating unit has been formed.

Introduction

The influence of 7,8-dicarba-*nido*-undecaborate(1−) on the coordinating behavior of electron-rich elements such as sulfur[1] and phosphorus[2] has been reported. Previously, we have described the syntheses of metallacarboranes based on *nido*-monothiocarboranes $[7\text{-}SR\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]^-$ with Ru(II),[3] Rh(I),[4] and Pd(II)[5] and *nido*-monophosphinocarboranes $[7\text{-}PR_2\text{-}8\text{-}R'\text{-}7,8\text{-}C_2B_9H_{10}]^-$, as special tertiary phosphines, with Ru(II)[6] and Rh(I).[4b,7] These monosubstituted ligands provide one strong coordinating element, either SR or PR_2, and require one or two B−H groups, depending on the coordinating metal's demand. Although *nido*-monothio- and *nido*-monophosphinocarboranes have shown similar reactivities toward Rh(I),[4b] some differences have been found for Ru(II).[6a] Tertiary phosphines and polyphosphines are excellent ligating agents for transition-metal ions[8] and are important for catalysis,[9] organic synthesis,[10] and solid-state materials.[11] Bidentate phosphine complexes and structural aspects of polydentate compounds have been extensively reported.[12] The importance of phosphorus ligands has been extended due to their compatibility with other organic functional groups, and new technologies have emerged from the use of complexes with chelating phosphine ligands.[8] In this paper, we report on the reactivity of *nido*-monophosphinocarborane ligands toward Pd(II). With the monodentate monophosphine $[7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Me, H, Ph) ligands as starting materials, by reaction with *cis*-$[PdCl_2(PPh_3)_2]$, novel anionic bidentate chelating diphosphines $[7\text{-}PPh_2\text{-}8\text{-}R\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9]$ are obtained. These contain the new $PPh_2-P-B-PPh_2$ entity. The crystal structure of $[PdCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]\cdot C_7H_8$ proves unambiguously the formation of the chelating group $PPh_2-C-B-PPh_2$. This represents the first example of bidentate chelation of this unit toward any metal reported to date.

Results and Characterization

The reaction of $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10})]$ (R = Me, H, Ph) with *cis*-$[PdCl_2(PPh_3)_2]$ in degassed

---

[†] CSIC.
[‡] University of Turku.
[§] University of Helsinki.

(1) Teixidor, F.; Ayllón, J. A.; Viñas, C.; Sillanpää, R.; Kivekäs, R. Casabó, J. *Inorg. Chem.* **1994**, *33*, 4815 and references therein.

(2) (a) Teixidor, F.; Viñas, C.; Abad, M. M.; Núñez, R.; Kivekäs, R.; Sillanpää, R. *J. Organomet. Chem.* **1995**, *503*, 193. (b) Zakharkin, L. I.; Zhubekova, M. N.; Kazantsev, A. V. *Zh. Obshch. Khim.* **1972**, *42*, 1024. (c) Hill, W. E.; Silva-Triviño, L. M. *Inorg. Chem.* **1979**, *18*, 361.

(3) (a) Teixidor, F.; Viñas, C.; Casabó, J.; Romerosa, A. M.; Rius, J.; Miravitlles, C. *Organometallics* **1994**, *13*, 914. (b) Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1998**, *17*, 4675.

(4) (a) Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 19. (b) Viñas, C.; Flores, M. A.; Núñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1998**, *17*, 2278.

(5) Teixidor, F.; Romerosa, A. M.; Viñas, C.; Rius, J.; Miravitlles, C. *J. Am. Chem. Soc.* **1991**, *113*, 9895.

(6) (a) Viñas, C.; Núñez, R.; Flores, M. A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1995**, *14*, 3952. (b) Viñas, C.; Núñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1996**, *15*, 3850.

(7) Viñas, C.; Núñez, R.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Organometallics* **1998**, *17*, 2376.

(8) Mayer, H. A.; Kaska, W. C. *Chem. Rev.* **1994**, *94*, 1239.

(9) Bianchi, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Coord. Chem. Rev.* **1992**, *120*, 193.

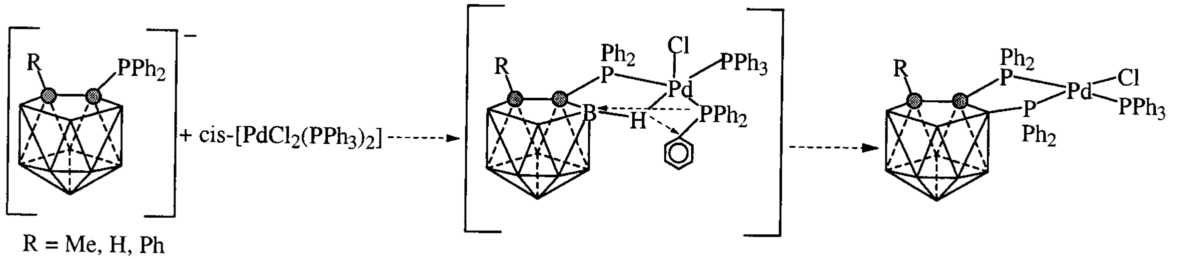
(10) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327.

(11) Hudson, S. A.; Maitlis, P. M. *Chem. Rev.* **1993**, *93*, 861.

(12) (a) Levason, W. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1992; Vol. 1, p 617. (b) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, *40*, 179. (c) Stzelzer, O.; Langhans, K. P. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1990; Vol. 1, p 191.

10.1021/om990599f CCC: $18.00

Scheme 1. Formation of [PdCl(7-PPh$_2$-8-R-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)] Complexes: Proposed Intermediate in the Reaction



ethanol resulted in the formation of yellow solids of general formula [PdCl(7-PPh$_2$-8-R-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)] (R = Me (**1**), H (**2**), Ph (**3**)). The reaction is shown in Scheme 1, where a proposed intermediate is also indicated. The spectroscopic data and elemental analyses are consistent with the proposed formula. The IR spectra of these complexes display ν(B−H) absorptions which are characteristic, between 2537 and 2551 cm^{-1}, of *nido*-[7,8-C$_2$B$_9$H$_{12}$]$^-$ derivatives. The absorptions at 1433, 1096, 744, and 695 cm^{-1} are typical of PPh$_3$-containing compounds. The ^{1}H NMR spectra displayed broad resonances in the negative region at −2.6, −2.9, and −2.1 ppm for **1**−**3**, respectively, corresponding to the bridge B−H−B bond, and evidenced the *exo-nido* coordination of the metal as opposed to a possible open face to Pd coordination. These resonances are shifted from those in the free ligands at −2.2 (R = H, Me) and −2.3 ppm (R = Ph). No resonances were found at field higher than −2.9 ppm, which would have been indicative of B−H→M interactions. Typical resonances in the aromatic region 6.71−7.95 ppm corroborated the presence of the phenyl groups. The ^{11}B{^{1}H} spectral pattern 1:1:3:1:1:1:1 was similar for all complexes. The absorptions at −2.6 ppm for **1** and **3** and at −2.2 ppm for **2** were split in two equal absorptions in the ^{11}B NMR and ^{11}B{^{1}H} NMR spectra, with J = 129, 132, and 131 Hz, respectively. This implied the substitution of a boron terminal hydrogen by an atom with nuclear spin $^1/_2$.[13] The ^{31}P{^{1}H} NMR spectra of the three complexes displayed three sets of signals, indicating three different phosphorus atoms in the molecules. Figure 1 shows a schematic representation of the ^{31}P{^{1}H} NMR spectrum of **1** as an example. The highest field resonance is a 1:1:1:1 quartet centered at 20.9 ppm with coupling constant J = 129 Hz, which parallels what is observed in the ^{11}B{^{1}H} NMR, and it was attributed to a phosphorus atom bonded to a boron atom from the cluster. This supports the formation of a new B−P bond in the complexes. The two other sets of resonances correspond to two doublets centered at 29.9 and 74.4 ppm, which can be assigned to C−PPh$_2$ and PPh$_3$, mutually *trans* in the molecule. This would indicate that the carborane ligand is chelating the metal via the PPh$_2$ bonded to the carbon cluster and one B−PPh$_2$. The remaining positions should be occupied by a Cl and a PPh$_3$ ancillary ligand. Assignment of the ^{31}P{^{1}H} NMR resonances to specific phosphorus atoms in the new complexes has been carried out by comparing the spectrum of complex **1** to that of the rhodacarborane [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$][4b] (**4**) and to the spectrum of the similar Pd(II) complex [PdCl(7-SMe-8-Me-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)][5] (**5**). A graphical representation of the three complex structures is shown in Figure 1. The ^{31}P{^{1}H} NMR spectrum of **5** displays a 1:1:1:1 quartet centered at 21.5 ppm and a singlet at 30.2 ppm that are attributed to the B(11)−PPh$_2$ and the PPh$_3$ moieties, respectively. In compound **1**, a 1:1:1:1 quartet at 20.9 ppm and two doublets at 29.9 and 74.4 ppm are observed. Considering that both compounds have similar structures, and considering the similar chemical shifts, the resonance at 29.9 ppm is assigned to the PPh$_3$ group, the

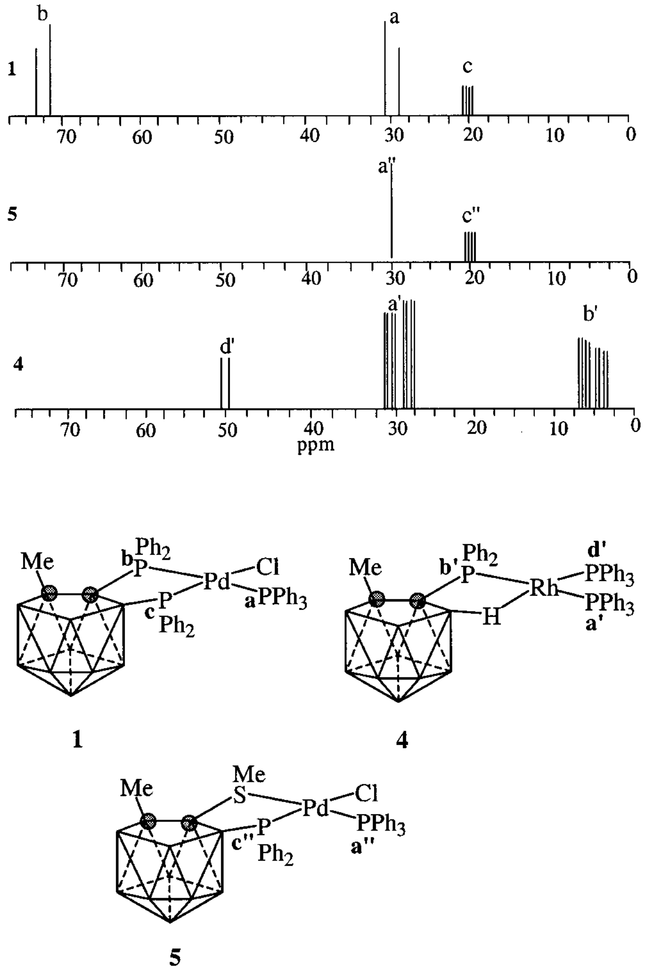


Figure 1. Schematic representation of the ^{31}P{^{1}H} NMR spectra of [PdCl(7-PPh$_2$-8-Me-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)] (**1**), [Rh(7-PPh$_2$-8-Me-7,8-C$_2$B$_9$H$_{10}$)(PPh$_3$)$_2$] (**4**), and [PdCl(7-SMe-8-Me-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)] (**5**).

---

[13] (a) Baker, R. T.; Delaney, M. S.; King, R. E., II; Knobler, C. B.; Long, J. A.; Marder, T. B.; Paxson, E.; Teller, R. G.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 2965. (b) Jung, C. W.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1980**, *102*, 3024. (c) Barker, G. K.; Grenn, M.; Stone, F. G. A.; Welch, A. J.; Wolsey, W. C. *J. Chem. Soc., Chem. Commun.* **1980**, 627.

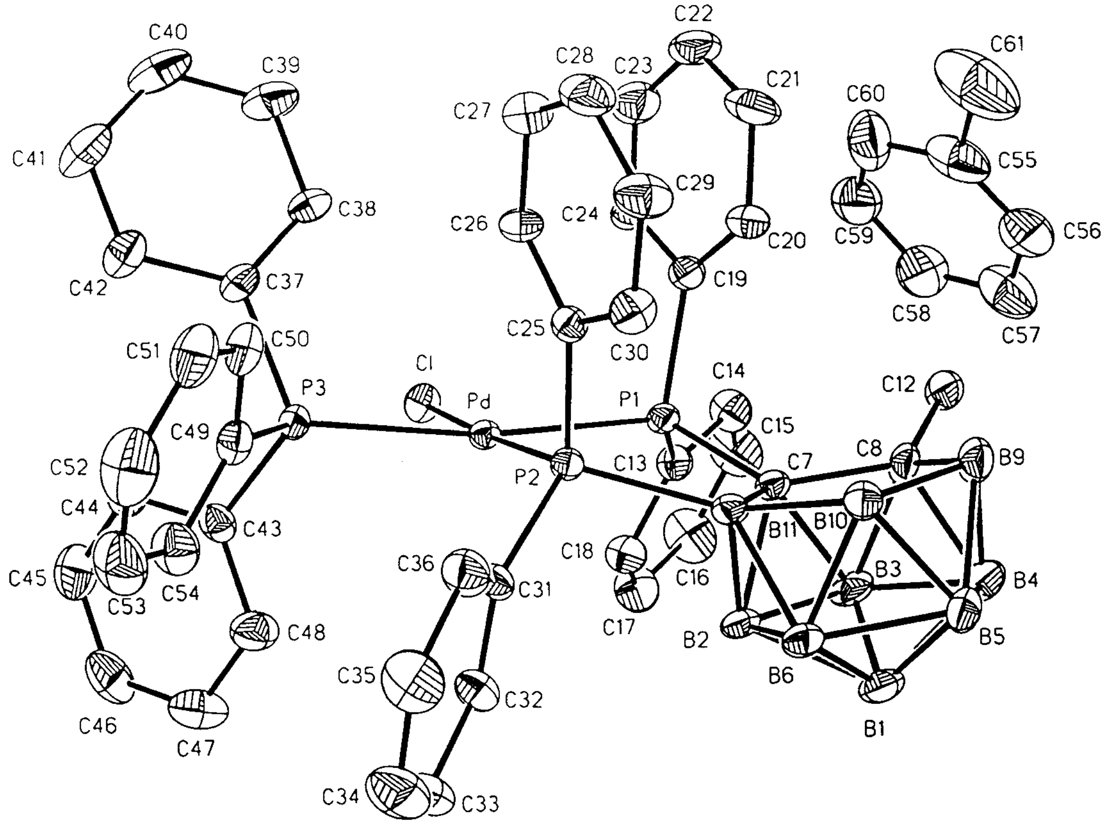


Figure 2. Simplified drawing of the complex unit of [PdCl(7-PPh$_2$-8-Me-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)]·C$_7$H$_8$. Phenyl groups and noncoordinated hydrogen atoms are omitted for clarity. Thermal displacement ellipsoids are drawn at the 20% probability level.

1:1:1:1 quartet at 20.95 ppm to the B(11)−PPh$_2$ moiety, and the lower field chemical shift at 74.4 ppm to the C−PPh$_2$ group. The ^{31}P{^{1}H} NMR spectra of **1** and **5**, having very similar chemical shifts, permit us to deduce that the C−PPh$_2$ and C−SR moieties display very similar electronic characteristics. Comparison of the ^{31}P{^{1}H} NMR spectra of **1** and **4** permits us to draw some conclusions on the capacity of a neighboring group to influence C−PPh$_2$. **1** and **4** differ in the chelating entity, Ph$_2$P−C−B−PPh$_2$ and Ph$_2$P−C−B−H, respectively. Due to the charge difference of Pd(II) and Rh(I), the ancillary ligands are also modified, and distinct *trans* influences are expected. In both cases, however, the C−PPh$_2$ and PPh$_3$ are mutually *trans*; thus, no such effect is expected on the chemical shift of C−PPh$_2$. The spectrum of **4** displays a broad doublet at 50.1 ppm and two sets of sharp doublet of doublets of doublets centered at 30.2 and 4.6 ppm. These are attributed to the two phosphorus atoms in a *trans* disposition (**a′** and **b′**). In compound **1** the corresponding resonances are at 29.9 and 74.4 ppm. Resonances corresponding to **a** (in **1**) and **a′** (in **4**) should be less influenced since both are *trans* to C−PPh$_2$; thus, it is expected that both should appear at similar chemical shifts, 29.9 ppm (**a**) and 30.2 ppm (**a′**), respectively. This implies that the C−PPh$_2$ resonance that was at 74.4 ppm in **1** is dramatically modified to 4.6 ppm in **4**. This enormous difference can be attributed to the electron-withdrawing effect induced by the B−PPh$_2$ group in **1**, which depletes C−PPh$_2$ of electron density; this cause a shift in its position to lower field and in turn converts the B−PPh$_2$ into a strong coordinating group. This will later be corroborated by the bond distances in the crystal structure, which indicates that the Pd−PPh$_2$B distance is the shortest. Following the same reasoning for all the complexes, the ^{31}P{^{1}H} NMR resonances observed in the 27−30 ppm region were attributed to the PPh$_3$ ancillary ligands and the resonance near 74 ppm to the C−PPh$_2$ group.

Molecular Structure of [PdCl(7-PPh$_2$-8-Me-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)]·C$_7$H$_8$. Complex **1** crystallized from toluene to give yellow crystals adequate for X-ray diffraction analysis. A simplified drawing of the complex unit is shown in Figure 2. The X-ray analysis confirmed the square-planar environment of the Pd(II) ion, the bidentate nature of the carborane cage, and the formation of the B(11)−P bond. The two bonds from the cage are formed by the phosphorus atoms of two diphenylphosphino groups, one being connected to C(7) and the other to B(11). This crystal structure presents the first example where the chelating group PC−BP has been observed. The chloride ion and the phosphorus atom of the ancillary PPh$_3$ ligand fulfill the coordination surroundings of the metal. As expected, orientation of the metal is *anti* with respect to the C$_2$B$_3$ open face and the atom groups P(1)−C(7)−B(11)−P(2) and P(1)−C(7)−C(8)−C(12) do not deviate much from planarity, the corresponding torsion angle values being 2.2(5) and −4.5(8)°, respectively.

Bond parameters of the coordination plane indicate distortions from regular square-planar coordination geometry. The P(2)−Pd−P(3) angle of 99.40(5)° is considerably opened, and the Cl−Pd−P(3) angle of 84.70(6)° is closed compared to the ideal value of 90°. These deviations from the ideal value are consequences of mutual steric crowding of PPh_2 and PPh_3 groups. Also, the three Pd−P bonds are dissimilar. P(2), being *trans* to Cl, forms the shortest bond (2.274(2) Å) to the metal, and P(3), being *trans* to P(1), forms the longest bond (2.346(2) Å) to the metal. The dissimilarity of the Pd−P bonds can be explained by *trans* influence. The corresponding bond parameters of **1** agree very well with those of the closely related Pd−monothiocarborane complex $[PdCl(7\text{-}SMe\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$[5] (**5**). In this complex the shortest Pd−P distance is also *trans* to the Cl atom (2.266(1) Å), being slightly shorter than that in **1**. Also the Pd−P *trans* to the S atom (2.309(1) Å) in **5** is shorter than the Pd−P bond *trans* to PPh_3 in **1**. The relatively minor differences between **1** and **5** arise from the different bulks of the −SMe and $-PPh_2$ groups along with the difference in *trans* influence of the S and P atoms, although as we have earlier indicated this should be very small.

Discussion

As is evidenced by the $^{31}P\{^1H\}$ and the $^{11}B\{^1H\}$ NMR spectra of **1**−**3**, a $B-PPh_2$ bond has been created upon the reaction of $[7\text{-}PPh_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and *cis*-$[PdCl_2(PPh_3)_2]$. The source of the $-PPh_2$ moiety can be associated with the PPh_3 ligands in the *cis*-$[PdCl_2(PPh_3)_2]$ starting complex. Furthermore, the X-ray analysis has proven that the generated $B-PPh_2$ bond corresponds to B(11), the open-face boron atom adjacent to $C-PPh_2$. By formation of this $B-PPh_2$ bond the initial ligand has modified itself to a chelating one via a $Ph_2P-C-B-PPh_2$ moiety. This may be the necessary result to complex Pd(II). In effect, as we have indicated earlier, either the mono- or disubstituted derivatives of $[C_2B_9H_{12}]^-$ with electron-rich elements are always di- or tricoordinating, depending on the geometrical requirements of the transition-metal ion.[3−7] If only one lone-pair-containing group (e.g. −SR or $-PR_2$) is available, the carborane cluster provides one or two extra B−H's to coordinate the metal. The first B−H involved is the one corresponding to B(11),[3−7] the same boron atom that has formed the B(11)−P bond. Thus, it was not necessary to form a B−P bond to render the $[C_2B_9H_{12}]^-$ derivatives chelating; they already had this possibility via the $Ph_2P-C-B-H$ moiety. If the original ligand has modified itself to produce the B−P bond, this has to do with the nature of the transition metal, Pd(II), facilitated by the R group in the PR_3 ligand, as we will see next.

It is our hypothesis that PPh_3 is dissociated from *cis*-$[PdCl_2(PPh_3)_2]$. To fulfill the vacancy, the Pd forms a Pd−H−B bond. The dissociated Lewis base PPh_3 interacts with the boron, generating $B-PPh_3$ and Pd−H bonds. The formation of both B−H−M[3−7,14] interactions and $B-PPh_3$ bonds[15] are well-documented in borane chemistry. The $B-PPh_3$ bond formation is always catalyzed by metals, and examples with Pd, Ni, and Pt have been reported.[15] The final step under these conditions is P−Ph bond cleavage from the PPh_3 group, in the synthesis of **1**−**3**. Finally, benzene is liberated concomitant with the formation of the B(11)−P−Pd bond. This reaction had never been reported previously, except for the formation of **5**.[5] This is because the geometrical requirements and *exo-nido* coordinating tendency of carbon-monosubstituted $[7,8\text{-}\ C_2B_9H_{12}]^-$ derivatives leading to chelating ligands had never been exploited before.

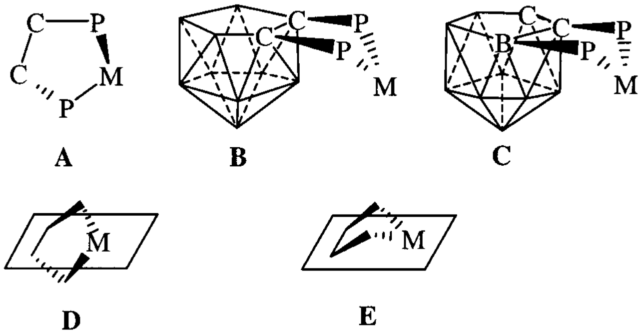


Figure 3. Geometric characteristics of diphos represented by A and D as compared to $[7,8\text{-}(PR_2)_2\text{-}7,8C_2B_9H_{10}]^-$ and the new ligand $[7\text{-}PPh_2\text{-}8\text{-}R\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9]^-$ (R = Me, H, Ph) represented by B, C, and E.

Complexes of Pd(II) and Pd(0) have been used extensively as catalysts in coupling reactions.[16] Compounds **1**−**3** can be viewed as particular examples of these sorts of reactions, where the stability of the coupled product motivated a succeeding reaction, P−C bond cleavage, to yield a chelating $PPh_2-C-B-PPh_2$ entity.

In $[PdCl(7\text{-}PPh_2\text{-}8\text{-}R\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$ (R = H, Me, Ph) complexes, the moiety $PPh_2-C-B-Ph_2P$ has been formed, acting as a bidentate ligand. A comparison between the basic geometries of diphos and $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$, when they are coordinated to metals, is shown in Figure 3. In the case of diphos, the P atoms are in above-the-plane and below-the-plane dispositions (Figure 3D) but are only in an above-the-plane disposition in the case of $[7,8\text{-}(PR_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (Figure 3E), where the torsion angle is 1.4(7)°.[17] This is due to the resticted mobility of the $PPh_2-C-C-Ph_2P$ moiety. In our complexes, we found a similar geometry in the $PPh_2-C-B-Ph_2P$ moiety, which presents a slightly higher torsion angle of 2.2(5)°. In this fragment a carbon atom from the cluster has been substituted for the B(11) atom on coordination to the metal (Figure 3C).

Once the importance of Pd(II) in this reaction was known, it remained to be disclosed if the original $C-PPh_2$ bond did play a role in the process. To learn about this, the monophosphines $[7\text{-}\ PR'_2\text{-}8\text{-}R\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Me, Ph; R′ = iPr, Et) were tested with *cis*-$[PdCl_2(PPh_3)_2]$ under the same conditions. No reaction was observed in any case, as the ligand was

---

[14] (a) Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A.; Woollam, S. F. *Organometallics* **1994**, *13*, 157. (b) Park, Y. W.; Kim, J.; Do, Y. *Inorg. Chem.* **1994**, 33, 1. (c) Carr, N.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Inorg. Chem.* **1994**, *33*, 1666.

[15] (a) King, R. E.; Miller, S. B.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1983**, *22*, 3548. (b) Boyter, H. A., Jr.; Swisher, R. G.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1985**, *24*, 3810. (c) Michaelidou, D. M.; Mingos, D. M. P.; Williams, D. J.; White, A. J. P. *J. Organomet. Chem.* **1997**, *528*, 135 and references therein.

[16] (a) Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1998**, *37*, 1544. (b) Schoberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X. S.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 3907. (c) Suzuki, M.; Doi, H.; Bjorkman, M.; Andersson, Y.; Langstom, B.; Watanabe, Y.; Noyori, R. *Chem. Eur. J.* **1997**, *3*, 2039. (d) Zakharkin, L. I.; Olshevskaya, V. A.; Guseva, V. V. *Russ. Chem. Bull. (Engl. Transl.)* **1998**, *47*, 524. (e) Grüner, B.; Janousek, Z.; King, B. T.; Woodford, J. N.; Wang, C. H.; Vsetecka, V.; Michl, J. *J. Am. Chem. Soc.* **1999**, *121*, 3122.

[17] Teixidor, F.; Viñas, C.; Abad, M. M.; Kivekäs, R.; Sillanpää. R. *J. Organomet. Chem.* **1996**, *509*, 139.

Table 1. Crystallographic Data for $[PdCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]\cdot C_7H_8$

chem formula	$C_{52}H_{55}B_9ClP_3Pd$
fw	1012.01
T (°C)	−80
λ (Å)	0.710 69
cryst syst	monoclinic
space group	$P2_1/n$ (No. 14)
a (Å)	19.007(6)
b (Å)	10.863(5)
c (Å)	25.454(7)
β (deg)	96.15(2)
V (Å^3)	5225(3)
Z	4
D_{calcd} (g cm^{-3})	1.286
μ (cm^{-1})	5.33
no. of unique rflns	9249
no. of params	606
goodness of fit on F^2	1.050
R1(F_o)^a ($I > 2\sigma(I)$)	0.0688
wR2(F_o^2)^b ($I > 2\sigma(I)$)	0.1309

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) (Esd's in Parentheses) for $[PdCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]\cdot C_7H_8$

Pd−P(2)	2.274(2)	C(7)−C(8)	1.579(8)
Pd−P(1)	2.318(2)	C(7)−B(11)	1.627(8)
Pd−P(3)	2.346(2)	C(8)−C(12)	1.526(8)
Pd−Cl	2.350(2)	P(2)−Pd−P(1)	86.22(5)
P1−C(7)	1.831(5)	P(2)−Pd−P(3)	99.40(5)
P(2)−B(11)	1.928(7)		
P(1)−Pd−P(3)	170.39(5)	C(8)−C(7)−P(1)	124.2(4)
P(2)−Pd−Cl	175.59(6)	B(11)−C(7)−P(1)	111.5(4)
P(1)−Pd−Cl	89.50(6)	C(12)−C(8)−C(7)	122.0(5)
P(3)−Pd−Cl	84.70(6)	C(7)−B(11)−P(2)	115.8(4)
C(7)−P(1)−Pd	112.3(2)	B(10)−B(11)−P(2)	128.8(4)
B(11)−P(2)−Pd	108.5(2)		

recovered unaltered. This was unexpected, and we probably require more data before providing an explanation. This result is in contrast with that found for the reaction of $[7\text{-}SR\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}]^-$ (R = Et, iPr, nBu, Ph) and *cis*-$[PdCl_2(PPh_3)_2]$. Although no complexes were detected, B−P formation occurs to produce zwitterionic species through B(10)−PPh_3 bonds. As mentioned, these were never found on starting from the *nido*-monophosphinocarboranes reported here.

The new chelating entity Ph_2P−C−B−PPh_2 is part of the anionic ligand $[7\text{-}PPh_2\text{-}8\text{-}R\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9]^-$, which in turn is bonded to Pd. Research is currently being done to liberate the ligand while preserving the new chelating entity to make it usable for metal ions other than Pd.

Conclusions

A chelating ligand with the hitherto unknown R_2P−C−B−PR_2 coordinating moiety has been generated from the R_2P−C−B−H fragment. The unique coupling capacity of Pd, its square-planar stereochemistry facilitating five-membered chelating rings, and the enhanced hydride character of the B−H group once it is bonded to the metal, is due to the achievement of this unprecedented coordinating entity, R_2P−C−B−PR_2.

Experimental Section

All reactions were performed under dinitrogen atmosphere using Schlenk techniques. Solvents were purified by distillation from appropriate drying agents before use. $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}H\text{-}7,8\text{-}C_2B_9H_{10}]$, $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}]$, and $[NBu_4][7\text{-}PPh_2\text{-}8\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{10}]$ were synthesized as described in the literature.[18] *cis*-$[PdCl_2(PPh_3)_2]$ was synthesized according to the literature.[19] Elemental analyses were performed using a Carlo Erba EA1108 microanalyzer. IR spectra were obtained with KBr pellets on a Nicolet 710-FT spectrophotometer. The ^1H, ^{11}B, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AM 400WB and a Bruker ARX 300 instruments. ^1H spectra were referenced to an internal standard of $SiMe_4$ and the $^{31}P\{^1H\}$ and ^{11}B NMR spectra to external standards 85% H_3PO_4 and $BF_3\cdot EtO_2$, respectively.

Preparation of $[PdCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$ (1). To a deoxygenated solution of ethanol (60 mL) containing $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}]$ (100 mg, 0.246 mmol) was added *cis*-$[PdCl_2(PPh_3)_2]$ (173 mg, 0.246 mmol), and the mixture was refluxed for 3 h. After this time, a yellow solid precipitated. The mixture was cooled at room temperature and filtered. Purification by thin-layer chromatography (silica gel, hexane/dichoromethane (1:1)) gave analytically pure **1** (90 mg, 40%). When the same reaction was carried out using a 2:1 ratio of $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}Me\text{-}7,8\text{-}C_2B_9H_{10}]$ to $[PdCl_2(PPh_3)_2]$, the same compound **1** was obtained, in a yield of 27%. ^1H NMR ($CDCl_3$): δ −2.6 (br s, 1H, B−*H*−B), 1.3 (s, 3H, C−CH_3), 6.9−7.9 (m, 35H, C_6H_5). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 20.9 (q, ^1J(P,B) = 129 Hz), 29.9 (d, $^{trans}J$(P,P) = 444 Hz), 74.4 (d, $^{trans}J$(P,P) = 444 Hz). ^{11}B NMR ($(CD_3)_2CO$): δ −0.8 (1B), −2.6 (d, ^1J(P,B) = 129 Hz, 1B), −9.5 (d, ^1J(B,H) = 131 Hz, 3B), −22.3 (1B), −25.2 (d, ^1J(B,H) = 131 Hz, 1B), −30.6 (1B), −35.0 (d, ^1J(B,H) = 135 Hz, 1B). FTIR (KBr; ν (cm^{-1})): 2551 (B−H). Anal. Calcd for $C_{45}H_{47}B_9ClP_3Pd$: C, 58.60; H, 5.22. Found: C, 58.95; H, 5.14.

Preparation of $[PdCl(7\text{-}PPh_2\text{-}8\text{-}H\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$ (2). The process was the same as for compound **1**, using 50 mg (0.128 mmol) of $[NMe_4][7\text{-}PPh_2\text{-}8\text{-}H\text{-}7,8\text{-}C_2B_9H_{10}]$ and 90 mg (0.128 mmol) of *cis*-$[PdCl_2(PPh_3)_2]$ in 15 mL of deoxygenated ethanol. The yellow solid was filtered and washed with ethanol (10 mL) and diethyl ether (5 mL) to give the analytically pure solid $[PdCl(7\text{-}PPh_2\text{-}8\text{-}H\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$ (**2**; yield 50 mg, 43%). ^1H NMR ($CDCl_3$): δ −2.9 (br s, 1H, B−*H*−B); 6.9−7.5 (m, 35H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.6 (q, ^1J(P,B) = 131 Hz), 27.4 (d, $^{trans}J$(P,P) = 433 Hz), 74.0 (d, $^{trans}J$(P,P) = 433 Hz). ^{11}B NMR ($CDCl_3$): δ 2.5 (1B), −2.2 (d, ^1J(P,B) = 131 Hz, 1B), −11.6 (3B), −22.2 (1B), −24.9 (1B), −27.2 (1B), −33.2 (d, ^1J(B,H) = 122 Hz, 1B). FTIR (KBr; ν (cm^{-1})): 2537 (B−H). Anal. Calcd for $C_{44}H_{46}B_9ClP_3Pd$: C, 58.34; H, 5.01. Found: C, 57.98; H, 4.62.

Preparation of $[PdCl(7\text{-}PPh_2\text{-}8\text{-}Ph\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$ (3). The process was the same as for compound **1**, using 80 mg (0.126 mmol) of $[NBu_4][7\text{-}PPh_2\text{-}8\text{-}Ph\text{-}7,8\text{-}C_2B_9H_{10}]$ and 88 mg (0.126 mmol) of *cis*-$[PdCl_2(PPh_3)_2]$ in 15 mL of deoxygenated ethanol. The mixture was refluxed for 6 h, giving a yellow solid. The solid was filtered and washed with ethanol. After recrystallization in acetone the pure compound $[PdCl(7\text{-}PPh_2\text{-}8\text{-}H\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]$ (**3**; yield 20 mg, 16%) was obtained. ^1H NMR (CD_2Cl_2): δ −2.1 (br s, 1H, B−*H*−B); 6.71−7.95 (m, 40H, C_6H_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 18.8 (q, ^1J(P,B) = 132 Hz), 29.1 (d, $^{trans}J$(P,P) = 446 Hz), 76.0 (d, $^{trans}J$(P,P) = 446 Hz). ^{11}B NMR (CD_2Cl_2): δ 1.2 (1B), −2.6 (d, ^1J(P,B) = 132 Hz, 1B), −8.8 (3B), −22.4 (1B), −24.3 (d, ^1J(B,H) = 144 Hz, 1B), −29.2 (1B), −34.1 (d, ^1J(B,H) = 134 Hz, 1B). FTIR (KBr; ν(cm^{-1})): 2537 (B−H). Anal. Calcd for $C_{50}H_{49}B_9ClP_3Pd$: C, 61.16; H, 5.53. Found: C, 61.00; H, 5.06.

X-ray Data Collection, Structure Determination, and Refinement for $[PdCl(7\text{-}PPh_2\text{-}8\text{-}Me\text{-}11\text{-}PPh_2\text{-}7,8\text{-}C_2B_9H_9)(PPh_3)]\cdot C_7H_8$. Yellow crystals were grown from toluene by

---

[18] Teixidor, F.; Viñas, C.; Abad, M. M.; Núñez, R.; Kivekäs, R.; Sillanpää, R. *J. Organomet. Chem.* **1995**, *503*, 193.

[19] Blackburn, J. R.; Nordberg, R.; Stevie, F.; Albrigde, R. G.; Jones, M. M. *Inorg. Chem.* **1970**, *9*, 2374.

slow evaporation. Single-crystal data collection was performed at −80 °C on a Rigaku AFC7S diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters were determined by least-squares refinement of 25 carefully centered reflections. A total of 9249 independent reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max} = 52°$). The data obtained were corrected for Lorentz and polarization effects. Correction for empirical absorption (ψ scan) was also applied.

The structure was solved by direct methods by using the SHELXS-86 program,[20] and least-squares refinements were performed using the SHELXL-97 program.[21] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were included in the calculations at fixed distances from their host atoms and treated as riding atoms using the SHELXL-97 default parameters. Crystallographic data are presented in Table 1 and selected bond lengths and angles in Table 2.

Acknowledgment. This work was supported by CIRIT (Projects QFN95-4721 and PB94-0226). The Academy of Finland is acknowledged by R.K.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal displacement parameters, bond distances and angles for [PdCl(7-PPh$_2$-8-Me-11-PPh$_2$-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)]·C$_7$H$_8$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

OM990599F

---

[20] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[21] Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.