A Zwitterionic Chelating Ligand

Phenyl{bis(triphenylphosphanemethylenido)}borane: A Zwitterionic Chelating Ligand Exhibiting Allyl-Type Coordination**

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The ability of phosphorus ylides to form stable organometallic complexes with both main-group metal atoms and transition-metal atoms has been known for some time.[1] The dipolar resonance form available to these molecules, by placing a formal negative charge on the carbon, makes them very effective Lewis bases that in some cases have been substituted for phosphane ligands to form even more active transition-metal organometallic catalysts.[2]

Recent work in our group employing Ph_3PCH_2 as a Lewis base adduct for the boron in borylidene bridged ansa-zirconocene complexes[3] led to the serendipitous discovery of an unusual bonding motif between a boron-bridged bis(ylide) ligand and zirconium tetrachloride. Complex **1** (Figure 1)[4] was isolated reproducibly with a yield of 14 % as a product from the reaction intended to bond Ph_3PCH_2 to a borylidene bridged bis(indenyl)zirconium species similar to the ones reported by Reetz et al.[5] The unusual allyl-type coordination between the boron-bridged diylide ligand and zirconium prompted us to pursue the synthesis of the ligand by a more direct route to determine if additional coordination chemistry with this novel, zwitterionic, chelating ligand might be accessed.

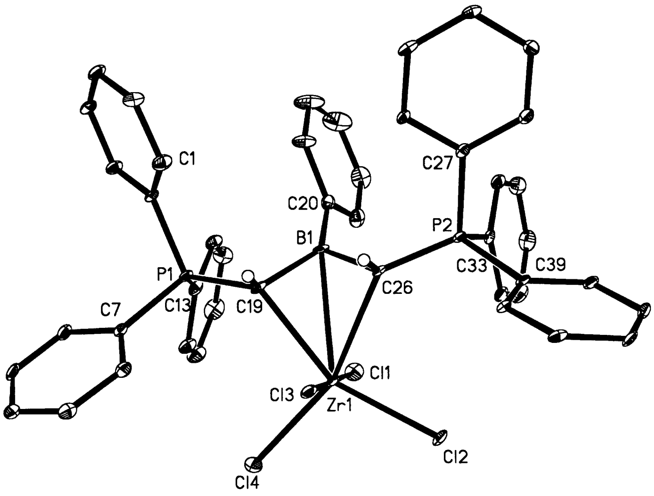
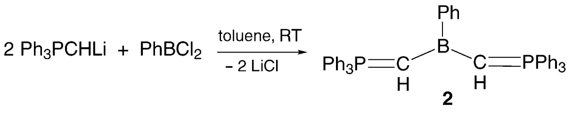


Figure 1. ORTEP drawing of complex **1** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: Zr1–B1 2.754(4), Zr1–C19 2.434(3), Zr1–C26 2.469(3), Zr–Cl1 2.4068(11), Zr1–Cl2 2.4360(11), Zr1–Cl3 2.4980(11), Zr1–Cl4 2.4076(12), B1–C19 1.544(6), B1–C26 1.532(5), B1–C20 1.587(5), P1–C19 1.748(3), P2–C26 1.734(4), C26-B1-C19 110.0(3), C26-Zr-C19 61.83(12), Cl1-Zr-Cl3 179.23(4), Cl2-Zr-Cl4 106.64(4).

Boron-bridged diylide compounds similar to the ligand in **1** were reported in 1986 by Bestmann and Arenz,[6] who prepared the compounds by treating alkyldichloroboranes with four equivalents of phosphonium ylide. Related triphenyl- and tri-*tert*-butyl-phosphiniminatoborane derivatives were reported by Dehnicke and co-workers[7] and by Stephan and co-workers.[8] Until now, however, the coordination of these molecules to metal atoms has not been reported.

Initial efforts to prepare the ligand in complex **1** by treating $PhBCl_2$ with either four equivalents of Ph_3PCH_2 or with two equivalents of the ylide in the presence of triethylamine were unsuccessful and afforded only the ylide adduct $PhCl_2B(CH_2PPh_3)$. Therefore, we used the lithium salt of the ylide[9] to prepare the desired ligand **2** as a benzene-soluble yellow powder in 68 % yield [Eq. (1)].



$$2\,\mathrm{Ph_3PCHLi} + \mathrm{PhBCl_2} \xrightarrow[-2\,\mathrm{LiCl}]{\text{toluene, RT}} \mathrm{Ph_3P{=}\underset{H}{C}{-}\overset{Ph}{B}{-}\underset{H}{C}{=}PPh_3} \qquad (1)$$

2

Two independent but structurally similar molecules were found in the asymmetric unit of the crystal (Figure 2).[4] In both molecules of **2** one triphenylphosphane group adopts a *syn* orientation and the other an *anti* orientation relative to the boron-diylide backbone instead of the double *syn* arrangement that they exhibit in the zirconium complex. The B–C(ylide) bond lengths (av. 1.521(7) Å) are at the low end of the 1.50–1.64 Å range for B–C single bonds in the Cambridge Crystallographic Database[10] and noticeably shorter than the B–C(phenyl) bond in each molecule (av. 1.598(2) Å). The P–C(ylide) bond lengths (av. 1.689(2) Å) are

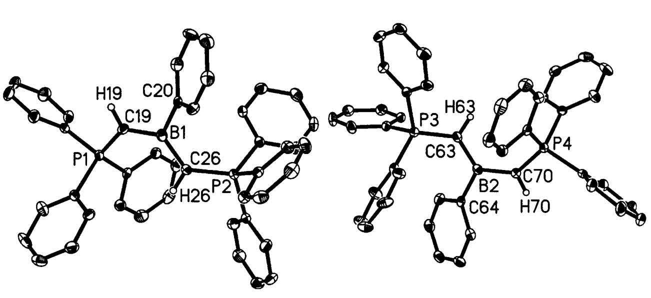


Figure 2. ORTEP drawings of two independent molecules of **2**. Thermal ellipsoids are at the 30% probability level. Selected bond lengths [Å] and angles [°]: B1–C19 1.513(5), B1–C26 1.530(5), B1–C20 1.595(5), B2–C63 1.522(5), B2–C70 1.518(5), B2–C64 1.600(5), P1–C19 1.691(3), P2–C26 1.689(3), P3–C63 1.693(3), P4–C70 1.682(3), C19-B1-C26 124.1(3), C63-B2-C70 122.9(3).

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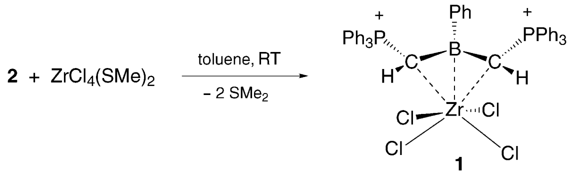
longer than the P–C bond of free Ph_3PCH_2 (1.661(8) Å), consistent with a reduction in P–C(ylide) π-bonding. These bonds are still substantially shorter than the P–C(ylide) bond length of 1.7919(14) Å in the donor–acceptor complex $Ph_3PCH_2B(C_6F_5)_3$.[11] A PM3 calculation on the molecule gave an energy optimized conformation with both phosphonium moieties in *syn* positions. The HOMO of the molecule consists almost entirely of nonbonding p-orbital density on the ylide carbons, which should be conducive to their coordination to metals. The HOMO-1 is π-bonding between the boron and these two carbons, with no contribution from either phosphorus atom. Significantly, the HOMO and HOMO-1 orbitals for the ligand are essentially identical in appearance to the corresponding molecular orbitals of an allyl ligand.[12]

Complex **1** was prepared directly by reacting **2** with $ZrCl_4(SMe_2)_2$ in toluene [Eq. (2)]. The complex is exceptionally sensitive to protonolysis, forming $[Ph_3PCH_3]Cl$, and must be stored at low temperature (−30 °C) under N_2. Another X-ray crystallographic analysis of the complex was undertaken to confirm that the structure of this complex was identical to that of the species obtained earlier by an indirect route.



1

(2)

The structure of **1** (Figure 1) can be regarded as pseudo-octahedral, with the ylide carbons occupying two sites of an equatorial plane, Cl2 and Cl4 at the other two equatorial positions, and Cl1 and Cl3 at *trans* axial positions. Although the Zr–B distance of 2.754(4) Å is significantly longer than distances between the zirconium and the ylide carbon atoms (av. 2.45(2) Å), it is well within the sum of the van der Waals radii of the two atoms.[13] Ab initio calculations at the 3-21G* level on the model complex $[(H_3PCH)_2BH]ZrCl_4$ affords an energy optimized geometry that is remarkably close to that of **2**. When an initial geometry that places the Zr, B, and ylide carbon atoms in the same plane is used, the final optimized geometry bends the boron toward zirconium with a Zr–B distance of 2.754 Å and Zr–C(ylide) distances of 2.453 Å.

To determine if ligand **2** and its allyl-type binding mode could be extended to other metal atoms, **2** was reacted with *trans*-$[PdCl_2(SMe_2)_2]$ to give **3** (Figure 3). An allyl-type bonding motif between the ligand and the palladium is again observed. In this case, however, one phosphonium group is *anti* and the other is *syn*, making the complex asymmetric. The presence of two different, weakly coupled phosphorus signals in the ^{31}P NMR spectrum, and the presence of two different methine proton signals with different couplings to phosphorus in the ^1H NMR spectrum indicate that the asymmetric geometry of the complex is retained in solution. The boron atom approaches the metal center more closely relative to the ylide carbons in **3** than it does in the zirconium complex (0.08 Å av. difference in **3** versus 0.3 Å av. difference in **1**). The Pd^{II} complex is also considerably more stable than the Zr^{IV} complex both in solution and upon storage as a solid under N_2 at ambient temperature.

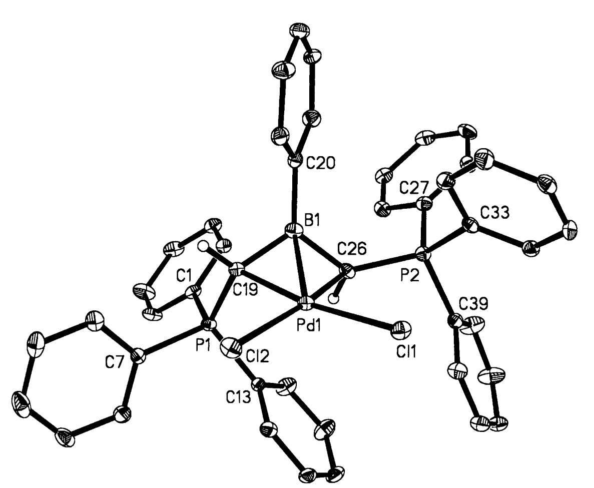


Figure 3. ORTEP drawing of complex **3** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: Pd1–C26 2.140(4), Pd1–C19 2.094(4), Pd1–B1 2.200(5), Pd1–Cl1 2.3705(11), Pd1–Cl2 2.3604, Cl1-Pd1-Cl2 93.45(4), P1-C19-Pd 112.8(2), P2-C26-Pd 128.8(2).

In summary, ligand **2** behaves like a boron-containing analogue of a η^3-allyl ligand when attached to both early and late transition-metal systems. As a neutral, zwitterionic ligand, **2** offers an interesting alternative to other neutral bidentate ligands containing phosphanes,[14] imines,[15] and nucleophilic carbenes[16] that are currently popular in transition-metal-mediated catalysis. Furthermore, it should be possible to fine-tune the electronic and steric properties of the ligand by varying the substituent on boron and the phosphonium ylide components.

Experimental Section

All manipulations were carried out under an argon or nitrogen atmosphere. NMR spectra were recorded on Bruker AMX 300 and Bruker AVANCE 500 spectrometers. H_3PO_4(aq, 80 %) and $BF_3{\cdot}Et_2O$ were used as external references for ^{31}P and ^{11}B NMR assignments, respectively. ^1H chemical shifts were referenced to residual proton signals from the deuterated solvent. ^{13}C NMR chemical shifts were also referenced to the solvent peaks. Ph_3PCH_2[17] and $Zr(SMe_2)_2Cl_4$[18] were prepared as described in the literature. Elemental analyses were determined by Desert Analytics (Tuscon, AZ). Theoretical calculations were performed with the MacSpartan Plus program (**1996**, Wavefunction, Inc., Irvine CA).

1: A solution of $Zr(SMe_2)_2Cl_4$ (373 mg, 1.04 mmol) in 30 mL toluene was added to a stirring solution of **2** (667 mg, 1.04 mmol) in toluene (150 mL) at −78 °C. The reaction was allowed to warm to room temperature and a light yellow precipitate began to form. After 18 h, the precipitate was isolated by filtration and dried in vacuo (yield: 736 mg, 74 %). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 7.60$–7.54 (m, 12H; PC_6H_5), 7.51–7.45 (m, 6H; PC_6H_5), 7.38–7.33 (m, 12H; PC_6H_5), 6.63 (tt, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 1.5$ Hz, 1H; BC_6H_5) 6.42 (dd,, $^3J(H,H) = 6.8$ Hz, $^4J(H,H) = 1.5$ Hz, 2H; BC_6H_5), 6.30 (t, $^3J(H,H) = 7.4$ Hz, 2H; BC_6H_5) 4.23 ppm (d, $^2J(P,H) = 7.9$ Hz, 2H; BCHP);

$^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 25 °C): $\delta = 134.5$ (pseudo t, $J(C,P) = 4.9$ Hz; $P(C_6H_5)_3$), 134.1 (d, $J(C,P) = 10.4$ Hz; $P(C_6H_5)_3$), 133.0 (s, $B(C_6H_5)$), 131.2 (d, $J(P,C) = 12.5$ Hz; $P(C_6H_5)_3$), 129.3 (pseudo t, $J(C,P) = 6.0$ Hz; $P(C_6H_5)_3$), 126.5 (s; $B(C_6H_5)$), 125.8 ppm (s; $B(C_6H_5)$). No ^{13}C resonance was observed for the ylide methine carbons although a cross peak at $\delta = 51$ ppm with the ylide methine hydrogens was observed in a heteronuclear multiple-quantum coherence (HMQC) experiment. $^{31}P\{^1H\}$ (121.4 MHz, CD_2Cl_2, 25 °C): $\delta = 27.0$ ppm; ^{11}B NMR (160.4 MHz, CD_2Cl_2, 25 °C): $\delta = 33$ ppm. X-ray quality crystals of **1** were grown from a concentrated CH_2Cl_2 solution cooled at −30 °C for several days. Elemental analysis calcd (%) for $C_{44}H_{37}BCl_4P_2Zr \cdot CH_2Cl_2$: C 55.97 , H 4.07; found C 56.03, H 4.12.

2: $PhBCl_2$ (635 mg, 4.00 mmol) was injected by syringe into a stirring solution of Ph_3PCHLi (2.26 g, 8.02 mmol) in toluene (120 mL) at −78 °C. The reaction mixture was stirred for 8 h at room temperature affording an orange suspension that was isolated by filtration, washed with pentane (2 × 30 mL) and dried in vacuo (yield: 1.74 g, 68 %). ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 7.7$–7.6 (br m,14 H; C_6H_5), 7.0–6.9 (m, 21 H; C_6H_5), 1.50 ppm (d, 2 H, $^2J(P,H) = 13.8$ Hz; PCH); $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6, 25 °C): 134.9 (d, $J(C,P) = 9.5$ Hz), 133.3 (s), 131.3 (d, $J(C,P) = 2.8$ Hz), 130.7 (d, $J(C,P) = 2.5$ Hz) 129.0 (d, $J(C,P) = 12$ Hz), 127.0 (s), 124.9 ppm (s). A very broad ^{13}C signal at $\delta = 34$ ppm is attributed to the ylide methine carbons. $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6, 25 °C): $\delta = 18.2$ ppm; ^{11}B NMR (160.4 MHz, C_6D_6, 25 °C): $\delta = 50$ ppm. X-ray quality crystals of **2** were obtained by layering pentane over a concentrated benzene solution of the ligand and storing the mixture at 4 °C for several days. Elemental analysis calcd (%) for $C_{44}H_{37}BP_2$: C 82.76, H 5.84; found: C 2.70, H 5.88.

3: Toluene (120 mL) was added to a mixture of $Pd(SMe_2)_2Cl_2$ (483 mg, 1.60 mmol) and **2** (1.02 g, 1.60 mmol) and the reaction mixture was stirred for 36 h at room temperature. A dark-orange slurry formed, and the precipitate was isolated by filtration, washed with toluene (30 mL), and dried under vacuum to afford a light brown solid (yield: 758 mg, 58 %): ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): $\delta = 8.0$–7.8 (m, 5 H; C_6H_5), 7.7–7.3 (m, 28 H; C_6H_5), 6.99–6.91 (m, 2 H; C_6H_5), 3.10 (d, $^2J(P,H) = 13.3$ Hz, 1 H; PCH), 3.05 ppm (d, $^2J(P,H) = 4.2$ Hz, 1 H; PC*H*). $^{13}C\{^1H\}$ (125.7 MHz, CD_2Cl_2, 25 °C): $\delta = 135.94$ (d, $J(C,P) = 3.0$ Hz), 135.15 (d, $J(C,P) = 9.8$ Hz), 134.63 (d, $J(C,P) = 11$ Hz), 133.98 (d, $J(C,P) = 2.9$ Hz), 133.21 (d, $J(C,P) = 2.6$ Hz), 133.0, 131.2 (d, $J(C,P) = 13$ Hz), 129.85 (d, $J(C,P) = 12$ Hz), 129.2 (br d, $J(C,P) = 11$ Hz) 128.0 (s), 126.9 (s), 126.5 (s), 125.8 ppm (s). No ^{13}C resonance was observed for the ylide methine carbons although a cross peak at $\delta = 31$ ppm with the ylide methine hydrogens was observed in an HMQC experiment. $^{31}P\{^1H\}$ NMR: (121.4 MHz, CD_2Cl_2, 25 °C): $\delta = 29.0$ (d, $^4J(P,P) = 3.1$ Hz), 26.0 ppm (d, $^4J(P,P) = 3.3$ Hz). ^{11}B NMR (160.4 MHz, CD_2Cl_2, 25 °C): $\delta = 35$ ppm. X-ray quality crystals of **3** were grown from a CH_2Cl_2 solution cooled at −30 °C for several days. Elemental analysis calcd (%) for $C_{44}H_{37}BCl_2P_2Pd \cdot CH_2Cl_2$: C 60.00, H 4.33; found: C 58.01, H 4.46.

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Keywords: allyl ligands · boranes · palladium · ylides · zirconium

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[4] Crystal data for **1**·CH_2Cl_2 and **2** and **3**·CH_2Cl_2 was collected by using a Bruker SMART APEX diffractometer with monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å): **1**·CH_2Cl_2: 81 K, triclinic, $P\bar{1}$, $a = 11.199(2)$, $b = 12.298(3)$, $c = 17.622(4)$ Å, $\alpha = 85.84(3)$, $\beta = 84.40(3)$, $\gamma = 68.07(3)°$, $V = 2238.8(10)$, $Z = 2$, $\rho_{calc} = 1.419\ \mathrm{mg\,m^{-3}}$, $2\theta_{max} = 56.8°$, $\mu = 0.706\ \mathrm{mm^{-1}}$, 496 parameters, 11106 independent reflections ($R_{int} = 0.0669$), 7779 with $I > 2(\sigma)I$, $R1 = 0.0597$, $wR2 = 0.1276$. **2**: 203 K, triclinic, $\bar{P}1$, $a = 9.925(2)$, $b = 19.215(4)$, $c = 19.233(4)$ Å, $\alpha = 102.03(3)$, $\beta = 92.66(3)$, $\gamma = 103.61(3)°$, $V = 3469.0(14)$, $Z = 4$, $\rho_{calc} = 1.223\ \mathrm{mg\,m^{-3}}$, $2\theta_{max} = 50°$, $\mu = 0.156\ \mathrm{mm^{-1}}$, 847 parameters, 12207 independent reflections ($R_{int} = 0.0819$), 6826 with $I > 2(\sigma)I$, $R1 = 0.0629$, $wR2 = 0.1174$. **3**·CH_2Cl_2: 82 K, monoclinic, $P2_1/n$, $a = 11.479(2)$, $b = 17.301(4)$, $c = 20.108(4)$ Å, $\beta = 91.64(3)°$, $V = 3992.1(14)$, $Z = 4$, $\rho_{calc} = 1.499\ \mathrm{mg\,m^{-3}}$, $2\theta_{max} = 55.2°$, $\mu = 0.846\ \mathrm{mm^{-1}}$, 478 parameters, 9215 independent reflections ($R_{int} = 0.0939$), 6758 with $I > 2(\sigma)I$, $R1 = 0.0560$, $wR2 = 0.1110$. Hydrogen atoms on C19, C26 (**1, 2**) and C63 and C70 (**2**) were located on the difference map and then added geometrically using a riding model. There are residuals of 1.68 and 1.03 $e\,Å^{-3}$ ca. 1 Å from the Zr center in **1**·CH_2Cl_2. CCDC 202606–202608 (**1**–**3**, respectively) 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 CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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