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Communications

Oxidative Addition of the B−Cl Bond with Palladium Species and Insertion of Alkynes and a Vinyl Ketone into the Resulting B−Pd Bond

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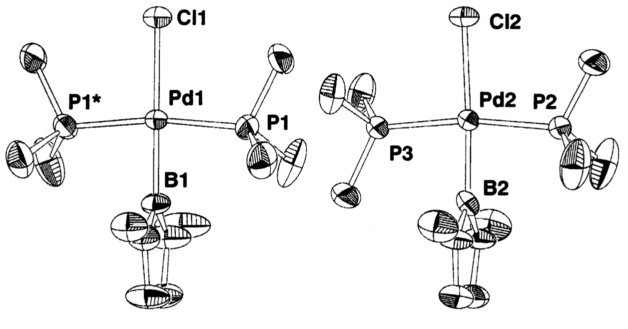
*Summary: The chloroborane ClB[NMe(CH$_2$CH$_2$)NMe] (**1**) reacts with Pd(η^3-C$_3$H$_5$)(η^5-C$_5$H$_5$) and PMe$_3$ (2 equiv) to afford trans-PdCl{B[NMe(CH$_2$CH$_2$)NMe]}(PMe$_3$)$_2$ (**2**), which was characterized by X-ray crystallography. Treatment of complex **2** with alkynes or methyl vinyl ketone gave chloro(1-boryl-1-alken-2-yl)palladium complexes or a chloro(3-boroxy-2-buten-1-yl)palladium complex, respectively.*

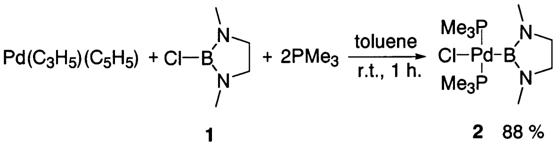
Organoboranes are useful reagents in organic synthesis, and transition-metal-catalyzed synthesis of the organoboranes is an active area of research these days.[1] The chemistry of boron−transition-metal species has also been reported in a number of papers.[2] However, oxidative addition of halogen−boron bonds with transition-metal complexes and the reactivity of the resulting species toward unsaturated carbon linkages have not been well studied.[3] There has been only one structurally characterized borylpalladium complex reported,[4] and knowledge of the chemistry of borylpalladium species is very limited, despite the rapid emergence of the use of palladium catalysts to manipulate boron compounds. We report herein (1) the first example of oxidative addition of the B−Cl bond with palladium species leading to chloro(boryl)palladium species and (2) insertion reactions of the resulting B−Pd bonds with alkynes and an α,β-unsaturated ketone.[5]



2a **2b**

Figure 1. Molecular structure of complex **2**. Selected bond lengths (Å) and bond angles (deg): Pd1−Cl1 = 2.476(2), Pd1−P1 = 2.301(1), Pd1−B1 = 2.037(9), Pd1−P1* = 2.301(1), Pd2−Cl2 = 2.491(2), Pd2−P2 = 2.296(2), Pd2−B2 = 2.006(9), Pd2−P3 = 2.292(2); Cl1−Pd1−P1 = 94.47(4), P1−Pd1−B1 = 85.54(4), B1−Pd1−P1* = 85.54(4), P1*-Pd1−Cl1 = 94.47(4), Cl2−Pd2−P2 = 97.31(7), P2−Pd2−B2 = 85.7(2), B2−Pd2−P3 = 85.3(2), P3−Pd2−Cl2 = 91.72(7).

When a mixture of Pd(η^3-C$_3$H$_5$)(η^5-C$_5$H$_5$) (0.99 mmol) and PMe$_3$ (2 equiv) in toluene (1 mL) was treated with ClB[NMe(CH$_2$CH$_2$)NMe] (**1**; 2 equiv) at room temperature, the color of the solution immediately turned from red to yellow (eq 1). Stirring for 1 h resulted in a suspension of pale yellow precipitates. Hexane (2 mL) was added, and the mixture was filtered to give pure *trans*-PdCl{B[NMe(CH$_2$CH$_2$)NMe]}(PMe$_3$)$_2$ (**2**) in 88% yield. Adduct **2** displayed satisfactory ^{1}H, ^{13}C, ^{31}P, and ^{11}B NMR spectra and analytical data.[6] The trans configuration was suggested by virtual triplets at 1.15



(1)

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[6] Chloro(boryl)palladium complex **2**: IR (KBr) 551, 736, 958, 1063, 1237, 1279, 1385, 1430, 2844 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.15 (quasi t, 18H, J_{H-P} = 3.4 Hz, PCH$_3$), 2.69 (s, 6H, NCH$_3$), 2.92 (s, 4H, NCH$_2$); ^{13}C NMR (C$_6$D$_6$) δ 15.7 (quasi t, J_{C-P} = 14.5 Hz, PCH$_3$), 36.1 (NCH$_3$), 52.6 (NCH$_2$); ^{31}P NMR (C$_6$D$_6$) δ −17.1; ^{11}B NMR (C$_6$D$_6$) δ 40.0 (broad). Anal. Calcd for C$_{10}$H$_{28}$BClN$_2$P$_2$Pd: C, 30.72; H, 7.22; N, 7.17. Found: C, 30.63; H, 7.34; N, 6.64.

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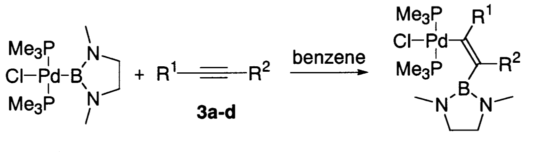
and 15.7 ppm in ^{1}H and ^{13}C NMR spectroscopy, respectively, and by the observation of only one singlet at −17.1 ppm in the ^{31}P NMR spectrum.

Slow cooling of a tetrahydrofuran solution of **2** to −30 °C resulted in the growth of colorless plates. Single-crystal X-ray diffraction has verified the square-planar trans configuration, as shown in Figure 1.[7,8] There are two crystallographically independent molecules, **2a** and **2b**, in a unit cell, which are eclipsed and staggered conformers with respect to the PMe_3 ligands (P1 and P1* in **2a** and P2 and P3 in **2b**). Molecule **2a** has a plane of symmetry comprising the diazaborolidine ring and Pd and Cl atoms. Both **2a** and **2b** have another plane of symmetry, which is the mean plane defined by B, Pd, P, and Cl atoms. The Cl2−Pd2−P3 angle (91.72°) of **2b** is smaller than the Cl2−Pd2−P2 angle (97.31°) of **2b** and the Cl1−Pd1−P1* angle (94.47°) of **2a**, due probably to steric reasons.

Boryl complex **2** was found to insert alkynes into its B−Pd bond to form the adduct **4** (eq 2). In most cases



(2)

rt, 24 h; **4a**: R^1 = *n*-Hex, R^2 = H, 66% (^{1}H NMR)
rt, 24 h; **4b**: R^1 = Me, R^2 = H, 80% (^{1}H NMR)
80 °C, 1 h; **4c**: $R^1 = R^2$ = Me, 92% (^{1}H NMR)
rt, 24 h; **4d**: $R^1 = R^2$ = COO*t*-Bu 77% (^{1}H NMR)

oily materials resulted and their purification was troublesome. However, the structure assignments could be made on the basis of spectroscopic data and their comparison with those of a successfully isolated product (**4d**; vide infra). Thus, when the reaction with 1-octyne (**3a**; 3.0 equiv) in benzene-d_6 was monitored at room temperature by ^{1}H NMR spectroscopy, the signals arising from **2** gradually diminished, while a new signal centered at 6.01 ppm (t, J_{H-P} = 6.7 Hz) assignable to a vinylic proton of **4a** emerged over a period of 24 h. A separate reaction between **2** and **3a** for 24 h using 1,4-dioxane as internal standard allowed an NMR yield estimate at 66%. Neither recrystallization to obtain **4a** as solid material nor chromatography on silica gel to purify it was successful. However, spectral data[9] support the structure; an NOE experiment,[10] virtual triplets for Me−P in ^{1}H and ^{13}C NMR spectroscopy, and only one resonance in ^{31}P NMR spectroscopy clearly indicate the *Z* configuration at the C═C double bond and a trans configuration of the palladium complex. Propyne (**3b**) reacted under the same conditions to give **4b** in 80% NMR yield (using 1,4-dioxane as internal standard). 2-Butyne (**3c**) also reacted with **2**, more sluggishly at room temperature (after 9 h, conversion <10%) but rapidly at 80 °C to provide the corresponding cis addition product **4c** (1 h, 92% NMR yield). Attempted isolation of **4b** and **4c** by recrystallization and chromatography was unsuccessful. The reaction of phenylacetylene (at 80 °C) resulted in a complicated mixture and did not allow isolation of a solid product either. However, di-*tert*-butyl acetylenedicarboxylate (**3d**), an electron-deficient internal olefinic compound, afforded a crystalline product; **3d** was much more reactive toward **2** than **3c** and formed **4d**[11] in 77% NMR yield in 24 h at room temperature. Crystallization of another sample of **4d** in a toluene solution by slow addition of hexane afforded orange crystals, which allowed X-ray diffraction to unequivocally verify the structure as shown in Figure 2.[12] The palladium atom is in a slightly distorted square planar environment; the sum of four angles about palladium is 359.6°. The mean plane is

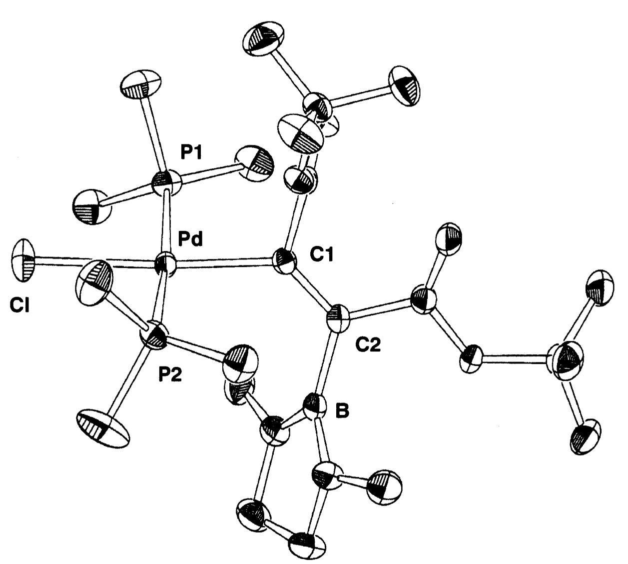


Figure 2. Molecular structure of complex **4d**. Selected bond lengths (Å) and bond angles (deg): Pd−Cl = 2.385(1), Pd−P1 = 2.331(1), Pd−C1 = 2.003(2), Pd−P2 = 2.309(1), C1−C2 = 1.353(3), C2−B = 1.584(3), Cl−Pd−P1 = 88.20(2); P1−Pd−C1 = 92.36(5), C1−Pd−P2 = 91.59(5), P2−Pd−Cl = 87.44(2), Pd−C1−C2 = 129.4(1), C1−C2−B = 123.6(2).

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(7) X-ray data for **2**: $C_{10}H_{28}BClN_2P_2Pd$, M_r = 390.96, colorless plate, crystal size 0.40 × 0.50 × 0.10 mm, orthorhombic, a = 10.314(2) Å, b = 26.296(5) Å, c = 13.396(3) Å, V = 3633(1) Å^3, space group *Pbcm* (No. 57), Z = 8, μ(Mo Kα) = 13.30 cm^{-1}, D_{calcd} = 1.429 g/cm^3. The 3580 independent reflections ($I > 3.00\sigma(I)$, $2\theta < 55°$) were measured on a Rigaku AFC7R diffractometer at −70(1) °C using Mo Kα radiation and a ω scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically by full-matrix least squares to R = 0.042, R_w = 0.088, and GOF = 2.56.

(8) Oxidative addition of the B−halogen bond with platinum(0) complexes forming trans adducts has been reported.[3c]

(9) Complex **4a**: ^{1}H NMR (C_6D_6) δ 0.93 (t, J = 7.0 Hz, 3H, $CH_2(CH_2)_4\mathit{CH_3}$), 1.21 (quasi t, J_{H-P} = 3.5 Hz, 18H, PCH_3), 1.25−1.53 (m, 8H, $CH_2\mathit{(CH_2)_4}CH_3$), 2.43 (t, J = 7.9 Hz, 2H, $\mathit{CH_2}(CH_2)_4CH_3$), 2.94 (s, 6H, NCH_3), 3.01 (s, 4H, NCH_2), 6.01 (s, 1H, J_{H-P} = 6.6 Hz, CH); ^{13}C NMR (C_6D_6) δ 14.1 (quasi t, J_{H-P} = 13.9 Hz, PCH_3), 14.4 ($CH_2(CH_2)_4\mathit{CH_3}$), 23.3, 30.6, 31.8, 32.4 ($CH_2\mathit{(CH_2)_4}CH_3$), 35.6 ($NCH_3$), 50.8 (t, J_{C-P} = 6.7 Hz, $\mathit{CH_2}(CH_2)_4CH_3$), 52.1 ($NCH_2$), 121.1 (broad, BCH), 177.8 (t, J_{C-P} = 3.6 Hz, PdC); ^{31}P NMR (C_6D_6) δ −17.2; ^{11}B NMR (C_6D_6) δ 29.9 (broad).

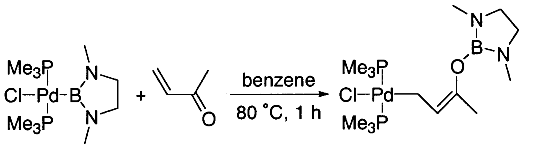
(10) Irradiation of the allylic protons at 2.43 ppm resulted in a 14% enhancement of the vinylic proton signal at 6.01 ppm.

(11) Complex **4d**: IR (KBr) 742, 855, 952, 1142, 1232, 1290, 1368, 1391, 1421, 1496, 1694, 2910, 2978 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.35 (quasi t, 18H, J_{H-P} = 3.8 Hz, PCH_3), 1.41 (s, 9H, CCH_3), 1.59 (s, 9H, CCH_3), 2.75 (s, 6H, NCH_3), 3.05 (s, 4H, NCH_2); ^{13}C NMR (C_6D_6) δ 14.5 (quasi t, J_{C-P} = 14.5 Hz, PCH_3), 28.4 ($C\mathit{CH_3}$), 28.8 ($C\mathit{CH_3}$), 36.2 (NCH_3), 52.2 (NCH_2), 78.7 ($OCMe_3$), 79.5 ($OCMe_3$), 165.2 (C═O), 173.2 (C═O), 178.5 (t, J_{C-P} = 5.7 Hz, Pd*C*═CB); ^{31}P NMR (C_6D_6) δ −13.2; ^{11}B NMR (C_6D_6) δ 30.1 (broad). Anal. Calcd for $C_{22}H_{46}BClN_2O_4P_2Pd$: C, 42.81; H, 7.51; N, 4.54. Found: C, 42.49; H, 7.49; N 4.21.

(12) X-ray data for **4d**: $C_{22}H_{46}BClN_2O_4P_2Pd$, M_r = 617.23, orange prism, crystal size 0.30 × 0.20 × 0.60 mm, monoclinic, a = 15.333(3) Å, b = 10.175(2) Å, c = 20.030(3) Å, β = 105.78(1) °, V = 3007.2(9) Å^3, space group $P2_1/n$ (No. 14), Z = 4, μ(Mo Kα) = 8.40 cm^{-1}, D_{calcd} = 1.363 g/cm^3. The 5850 independent reflections ($I > 3.00\sigma(I)$, $2\theta < 55°$) were measured on a Rigaku AFC7R diffractometer at −120(1) °C using Mo Kα radiation and a $\omega-2\theta$ scan. The structure was solved by direct methods, and all non-hydrogen atoms were refined anisotropically by full-matrix least squares to R = 0.026, R_w = 0.037, and GOF = 1.18.

near perpendicular to the plane of the olefinic double bond, the dihedral angle being 105°. The C1−C2 distance (1.353(3) Å) is in the typical range of the carbon−carbon double bond. The *Z* configuration of the double bond clearly shows that cis insertion of the triple bond into the Pd−B bond has taken place.

An α,*β*-unsaturated ketone also proved to cleanly insert into the Pd−B bond. Thus, when complex **2** was treated at 80 °C for 1 h with methyl vinyl ketone (1.1 equiv) in benzene-d_6 containing 1,4-dioxane (10 μL) as internal standard, the NMR spectrum of the reaction mixture displayed signals assignable to chloro(3-boroxy-2-buten-1-yl)palladium complex **5** (96% NMR yield; eq 3),[13] arising from 1,4-addition of the Pd−B bond. Attempts to isolate a solid material failed, but the chemical shifts in ^{11}B and ^{13}C NMR spectroscopy were in good agreement with those reported for similar compounds.[14,15] In addition, irradiation at 1.80 ppm (allylic methyl protons) exhibited a 15% enhancement of the vinylic proton signal at 4.79 ppm, suggesting the *Z* geometry at the double bond. The insertion of the α,*β*-unsaturated ketone into the Pd−B bond represents a model for platinum- and copper-catalyzed diboration of α,*β*-unsaturated carbonyl compounds.[16]



(3)

2

5 96 %

In summary, oxidative addition of the B−Cl bond has been found to smoothly take place with palladium species to form the chloro(boryl)palladium complex **2**, the Pd−B bond of which readily undergoes insertion reaction with alkynes or an α,*β*-unsaturated ketone.

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Supporting Information Available: Text giving detailed experimental procedures and characterization data for complexes **2**, **4a**−**d** and **5**, figures giving ^{1}H NMR spectra of **4a**−**c** and **5**, and text and tables giving full details of the crystal structure analyses for **2** and **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Complex **5**: ^{1}H NMR (C_6D_6) δ 1.24 (quasi t, 18H, $J_{H-P} = 3.4$ Hz, PCH_3), 1.80 (s, 3H, CCH_3), 2.37 (dt, 2H, $J = 7.8$ Hz, $J_{H-P} = 7.5$ Hz, $PdCH_2$), 2.63 (s, 6H, NCH_3), 2.91 (s, 4H, NCH_2), 4.79 (t, 1H, $J = 7.8$ Hz, C═CH); ^{13}C NMR (C_6D_6) δ 8.64 ($PdCH_2$), 13.9 (quasi t, $J_{C-P} = 13.5$ Hz, PCH_3), 23.0 ($C\mathit{CH_3}$), 33.0 (NCH_3), 50.0 (NCH_2), 113.7 (═CH), 143.2 (═CO); ^{31}P NMR (C_6D_6) δ −15.8; ^{11}B NMR (C_6D_6) δ 23.9.

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