Reactivity of Organoplatinum Complexes with $C_6H_4O_2B-BO_2C_6H_4$: Syntheses of a Platinum Diboryl Complex with, and without, Metathesis of Boron−Boron and Metal−Carbon Bonds[†]

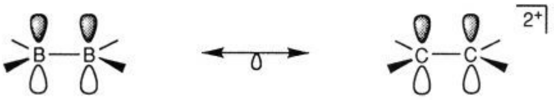
Carl N. Iverson and Milton R. Smith, III*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Received September 6, 1994

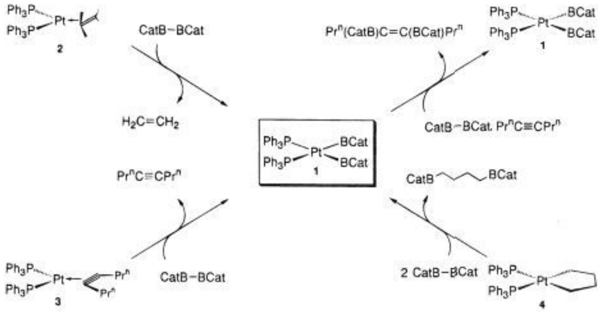
The diboron tetrahalides, X_2B-BX_2 (X = F, Cl, Br), are exceptionally reactive reagents whose reactivity with unsaturated carbon−carbon bonds is well-documented.[1] Two drawbacks that have hampered their utility as synthetic reagents are the problems associated with their preparation and the inherent instability of these compounds. In contrast to the halide species, derivatives which contain oxygen and nitrogen functionality are stable and readily prepared on multigram scales.[2,3] Unfortunately, these molecules are much less reactive than their halide cousins, and uncatalyzed additions to unsaturated carbon−carbon bonds do not occur. Suzuki has recently shown that *cis* addition of the B−B bond in pinacol ester derivatives to alkynes can be catalyzed by addition of $(Ph_3P)_4Pt$.[4] It was suggested that *cis*-$(Ph_3P)_2Pt(BPin)_2$ (Pin ≡ $(CH_3)_2CO-CO(CH_3)_2^{2-}$) is formed *in situ* and serves as the active catalyst in this system. When PinB−BPin and $(Ph_3P)_4Pt$ are heated to 100 °C, a new phosphine-containing product, tentatively assigned as *cis*-$(Ph_3P)_2Pt(BPin)_2$, is formed (^{31}P data); however, a direct synthesis of this compound was not reported, which certainly hampers attempts for definitively probing this mechanism.

We have recently been investigating reactivity of borane reagents with transition-metal olefin compounds with two main objectives. First, the rich reactivity of olefin complexes with various carborane derivatives suggests that olefin complexes are particularly attractive synthons for preparing compounds with unsupported metal−boron bonds via B−X oxidative addition.[5−7] Second, reactions of olefin and alkyl complexes with borane reagents potentially offer chemistry which is mechanistically distinct from other metal-mediated hydroboration processes.[8] In light of the isolobal relationship between boron tetrahalide complexes and olefin dications, we are particularly interested in the synthesis of boryl complexes by reaction of B−B bonded reagents with olefin complexes. This approach would complement the route to $(PPh_3)_2RhCl(BCat)_2$ (Cat ≡ $[C_6H_4O_2^{2-}]$), where HBCat serves as the boronating reagent.[9,10] Since the olefinic by-products should be readily removable, this general route avoids complications from side reactions of dissociated phosphine ligands with H−B reagents[11] and circumvents formation of hydride species *via* B−H oxidative addition.[12] With respect to the objectives outlined above, this communication describes reactivity of CatB−BCat with bis(triphenylphosphine)platinum olefin, alkyne, and dialkyl complexes. In each case a diboryl complex is formed, and the dissimilar fates of the expelled organic fragments are noteworthy in terms of reactivity of metal−carbon bonds with B−B bonds.



cis-$(Ph_3P)_2Pt(BCat)_2$ (**1**) is cleanly formed as the sole platinum-containing product (75% yield) by reacting the ethylene complex $(Ph_3P)_2Pt(\eta^2-CH_2{=}CH_2)$ (**2**)[13] with CatB−BCat (Scheme 1). The reaction is accompanied by rapid evolution of ethylene at −80 °C, and attempts to measure rates have been thwarted thus far. While ^1H and $^{31}P\{^1H\}$ NMR data were consistent with formulation as a diboryl complex, ^{11}B NMR spectra did not exhibit any well-defined features.[14] We anticipated potential complications in the boron spectrum due to coupling to platinum and phosphorus nuclei, but the failure to observe a resonance in this case is somewhat surprising.

Scheme 1



Diffraction quality crystals of **1** were grown from a concentrated toluene solution as colorless parallelepipeds.[15] The structure of **1** indicates a *cis* geometry (Figure 1), and the Pt center adopts a distored square-planar geometry where ∠P(1)−Pt−P(2) (107.4(2)°) and ∠B(1)−Pt−B(2) (77.8(7)°) are the most obtuse and acute angles reported for a *cis*-$(PPh_3)_2PtX_2$ complex.[16] As has been observed for other boryl complexes,[17−19] the metal−boron distances in **1** are shorter than would be

---

[†] This work was presented at the International Symposium on Molecular Reaction Mechanisms Involving Transition Metals: Experimental and Theoretical Aspects, Florence, Oct 25−30, 1994.

(1) For a review of boron subhalide chemistry, see: Massey, A. G. *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 1.

(2) Brotherton, R. J.; McClosky, A. L.; Petterson, L. L.; Steinberg, H. *J. Am. Chem. Soc.* **1960**, *82*, 6242.

(3) Welch, C. N.; Shore, S. G. *Inorg. Chem.* **1968**, *7*, 225.

(4) Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018.

(5) Oxidative insertions of zero-valent nickel and platinum olefin complexes into carborane frameworks have been described. For a representative example, see: Green, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1679.

(6) For a review of "ligand-free" platinum chemistry, see: Stone, F. G. A. *Acc. Chem. Res.* **1981**, *14*, 318.

(7) This strategy has proven effective for synthesis of η^2-disilene and silyl complexes: Pham, E. K.; West, R. *Organometallics* **1990**, *9*, 1517.

(8) Motry, D. H.; Smith, M. R., III. Manuscript submitted.

(9) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350.

(10) While this work was in review, oxidative addition of B−B bonds to rhodium (I) phosphine complexes was reporoted: Nguyen, P.; Lesley, G.; Taylor, N. J.; Marder, T. B.; Picket, N. L.; Clegg, W.; Elsegood, M. R. J.; Norman, N. C. *Inorg. Chem.* **1994**, *33*, 4623.

(11) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993**, *32*, 2175.

(12) Kono, H.; Ito, K.; Nagai, Y. *Chem. Lett.* **1975**, 1095.

(13) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464.

(14) The $^{31}P\{^1H\}$ resonance is relatively broad at room temperature,[4] but it sharpens on cooling (−50 °C). We are unable to detect an ^{11}B resonance at low temperature. When C_6D_6 solutions of **1** are heated to 80 °C for 1 h, weak boron resonances appear at 32.4, 28.8, 25.7, and 22.4 ppm. The resonance at 28.8 ppm corresponds to catecholborane, and the resonance at 22.4 ppm may indicate formation of $B_2(OC_6H_4)_3$.[11] The remaining resonances have not been identified. The ^{11}B resonances persist at room temperature, and ^1H and $^{31}P\{^1H\}$ spectra of the heated sample are essentially identical to those for pure **1**. Spectral data for **1**: ^1H NMR (300 MHz, C_6D_6) δ 6.54 (m, 4 H, $BO_2C_6H_4$) 6.77 (m, 4 H, $BO_2C_6H_4$) 6.80 (m, 18 H, $P(C_6H_5)_3$), 7.55 (m, 12 H, $P(C_6H_5)_3$)); $^{31}P\{^1H\}$ NMR(C_6D_6) δ 30.19 ($^1J_{Pt-P}$ = 1608 Hz).

(15) Crystal data for **1**: $a = 11.304(3)$ Å, $b = 21.248(4)$ Å, $c = 11.206(3)$, $\alpha = 103.33(2)°$, $\beta = 116.14(2)°$, $\gamma = 74.64(2)°$, $P\bar{1}$ (No. 2), $Z = 2$, 5231 unique data ($F_o \geq 2\sigma F_o$), $R_1(w/R_2) = 0.0692(0.175)$.

(16) For *cis*-$(Ph_3P)_2Pt(C(O)Ph)_2$, ∠P(1)−Pt−P(2) and ∠C(1)−Pt−C(2) are 104.44(9)° and 80.5(3)°, respectively: Chen, J.-T.; Huang, T.-M.; Cheng, M.-C.; Wang, Y. *Organometallics* **1990**, *9*, 539.

(17) Knorr, J. R.; Merola, J. S. *Organometallics* **1990**, *9*, 3008.

(18) Nguyen, P.; Blom, H. P.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 9329.

(19) Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661.

0002-7863/95/1517-4403$09.00/0 © 1995 American Chemical Society

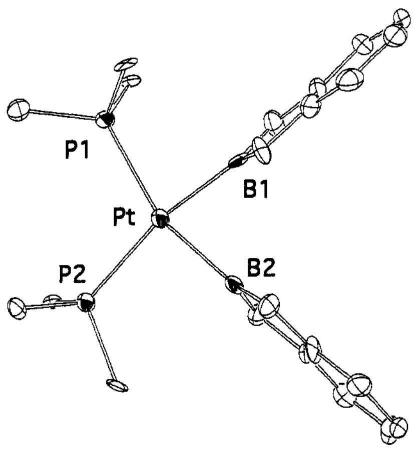


Figure 1. ORTEP drawing of **1** (25% probability ellipsoids; hydrogen atoms are omitted and only the *ipso* carbons of the phosphine ligands are shown for clarity). Selected bond distances (Å): Pt−B(2), 2.07(2); Pt−B(1), 2.08(2); Pt−P(1), 2.350(5); Pt−P(2), 2.375(5), B(1)···B(2), 2.60. Selected bond angles (deg): B(2)−Pt−B(1), 77.9(7); P(1)−Pt−P(2), 107.3(2); B(2)−Pt−P(1), 90.5(5); B(1)−Pt−P(2), 84.6(5); B(1)−Pt−P(1) 168.1(5); B(2)−Pt−P(2) 159.9(5).

expected on the basis of comparisons to related aryl complexes,[20] when differences in bond distances for sp^2-hybridized B−B and C−C bonds are considered.[21−25] Along similar lines $|^1J_{\mathrm{Pt-P}}|$ for *cis*-$(Ph_3P)_2PtX_2$ compounds has been shown to decrease with increasing *trans* influence of X for a relatively complete series of compounds.[26] Thus, the progression of $|^1J_{\mathrm{Pt-P}}|$ for X = Cl ≫ Ph > BCat supports the notion that boryl ligands are stronger field ligands than their aryl counterparts.[27]

The alkyne complex $(Ph_3P)_2Pt(\eta^2$-4-octyne) (**3**)[28] also reacts with CatB−BCat to generate **1** (62%) with loss of the alkyne. In the absence of CatB−BCat, thermolyses of **1** and alkynes give complicated mixtures; however, when **1** and 4-octyne are reacted in the presence of excess CatB−BCat (1.5 molar equiv), clean conversion to the 4,5-bis(boryl)octene product is observed (Scheme 1).[29] Presumably excess CatB−BCat prevents decomposition by trapping the transient "$(Ph_3P)_2Pt$" fragment. Since we have a clean route for preparing **1**, we should be in a good position to probe the mechanistic details of this process. Preliminary results indicate that other olefin complexes in group 10 will prove to be reactive; however, the olefin does not always serve as an innocent "mask" for the low-valent metal center as tris(bicyclo[2.2.1]heptene)platinum(0)[30] reacts with CatB−BCat instantaneously at room temperature to give a bis(boryl)bicyclo[2.2.1]heptane as the chief organic product.[31,32]

Since a wide variety of related dialkyl complexes are known and a wealth of mechanistic information concerning reactivity of these compounds exists, these systems seemed ideally suited for surveying potential metatheses between metal−carbon and boron−boron bonds. In this vein, we chose to investigate reactivity of the metallacyclopentane complex, $(Ph_3P)_2Pt(CH_2)_4$ (**4**),[33] with CatB−BCat since **4** exhibits superior stability when compared to other Pt(II)−dialkyl species, and the decomposition pathways for **4** are well documented.[34] **4** reacts cleanly with CatB−BCat (2 molar equiv, 8 h at 95 °C) to form **1** (68%, Scheme 1) and $CatB(CH_2)_4BCat$ (47%).[35] It is noteworthy that we do not observe formation of 1- or 2-butenes which are known byproducts of the thermal decomposition of **4**. This result marks the first clear demonstration of metathesis reactions of B−B bonds with M−C bonds. Considering the plethora of olefin coupling reactions reported for the group 10 metals, this finding bodes favorably for potential elaboration and functionalization of olefins.

In summary, we have demonstrated that (1) olefin and alkyne complexes can serve as synthons for a diboryl complex via oxidative addition of a B−B bond to a low-valent metal center with loss of olefin or alkyne, (2) metal−olefin complexes can rapidly mediate diboration of olefins which are otherwise unreactive with B−B bonds, and (3) B−B bonds can react cleanly with metal−carbon bonds to give metal−boryl complexes and boron-substituted organic products. We are currently investigating the mechanistic details of the preliminary results outlined herein and are exploring chemistry of boron−boron-bonded reagents in related systems.

Acknowledgment. We thank Dr. Donald L. Ward for assistance in the structural determination. We acknowledge the administrators of the ACS Petroleum Research Fund and Michigan State University (AURIG) for generous financial support of this work. The single-crystal X-ray equipment at MSU was supported by the National Science Foundation (CHE-8403823), and the NMR equipment was provided by the National Science Foundation (CHE-8800770) and the National Institutes of Health (1-S10-RR04750-01).

Supplementary Material Available: Synthetic details including ^{1}H, ^{31}P{^{1}H}, and ^{11}B NMR data and atomic coordinates, thermal parameters, and bond distances and angles for **1** (12 pages); observed and calculated structure factors (32 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9429632

---

(20) Pt−C bonds for aryl derivatives are typically 2.08 Å. For a representative structure, see: Bebaerdemaeker, T.; Berhalter, K.; Weisemann, C.; Brune, H. A. *Acta Crystallogr., Sect. C* **1987**, *43*, 1253.

(21) The predicted difference between bond distances for sp^2-hybridized M−C and M−B bonds was calculated by the following formula: $(B-B)_{av} - (C-C)_{av}/2 = 0.08$ Å. Appropriate B−B[22,23] and C−C[24,25] values from the literature were used.

(22) (a) For an excellent discussion of bond order and B−B bond distances, see: Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1992**, *114*, 2715. (b) Moezzi, A.; Olmstead, M. M.; Power, P. P. *J. Chem. Soc., Dalton Trans.* **1992**, 2429.

(23) Nöth, H. *Z. Naturforsch.* **1984**, *39b*, 1463.

(24) Trotter, J. *Acta Crystallogr.* **1961**, *14*, 1135.

(25) Gabe, E. J.; Le Page, Y.; Lee, F. L.; Barclay, L. R. *Acta Crystallog., Sect. B* **1981**, *B37*, 197.

(26) (a) Piddock, A.; Richards, R. E.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1707. (b) For a detailed listing of ^{31}P data for $PtX_2(PR_3)_2$ systems, see: Harris, R. K.; McNaught, I. J.; Reams, P.; Packer, K. J. *Magn. Reson. Chem.* **1991**, *29*, S60.

(27) A recent paper provides evidence that M−B bonds are significantly stronger than related M−C bonds: Rablen, P. R.; Hartwig, J. F.; Nolan, S. P. *J. Am. Chem. Soc.* **1994**, *116*, 4121.

(28) Wittig, G.; Fischer, S. *Chem. Ber.* **1972**, *105*, 3542.

(29) ^{1}H NMR (300 MHz, C_6D_6): δ 0.90 (tr, 6 H, $CH_2CH_2CH_3$), 1.53 (sextet, 4 H, $CH_2CH_2CH_3$), 2.49 (tr, 4 H, $CH_2CH_2CH_3$), 6.73 (m, 4 H, $BO_2C_6H_4$), 6.91 (m, 4 H, $BO_2C_6H_4$). ^{11}B NMR (C_6D_6): δ 32.7.

(30) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271.

(31) (a) The spectral data[31b] strongly suggest the formation of single isomer that contains a mirror plane. Since electrophilic additions to norbornene generally proceed by attack of the exo face, *syn-exo*-2,3-bicyclo[2.2.1]heptane is the most likely product. The details of this reaction are under investigation. (b) ^{1}H NMR (300 MHz, C_6D_6): δ 6.80 (m, 4 H), 6.67 (m, 4 H), 2.55 (m, 2 H), 1.95 (m, 1 H), 1.62 (s, 2 H), 1.43 (m, 2 H), 1.25 (m, 1 H), 1.19 (m, 2 H). ^{11}B NMR: δ 35.6. EI/MS: *m/e* = 332 (M^+), *I* = 100 (100); *m/z* = 333 ($[M + 1]^+$), *I* = 22 (21); *m/z* = 331 ($[M - 1]^+$), *I* = 53 (46). Intensities are reported relative to the most abundant isotopomer and simulated intensities based on natural isotopic abundances are given in parentheses.

(32) Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Nguyen, P.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 4367.

(33) Biefeld, C. G.; Eick, H. A.; Grubbs, R. H. *Inorg. Chem.* **1973**, *9*, 2167.

(34) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.

(35) Spectral data for CatB−$(CH_2)_4$−BCat: ^{1}H NMR(C_6D_6) δ 1.08 (m, 4 H, $(CH_2)_4$), 1.56 (m, 4 H, $(CH_2)_4$), 6.78 (m, 4 H, $BO_2C_6H_4$), 7.01 (m, 4 H, $BO_2C_6H_4$); ^{11}B (NMR (C_6D_6) δ 35.8; EI/MS, *m/e* = 294 100 (100), M^+; 295 18 (18), $(M + 1)^+$; 294 53 (46), $(M - 1)^+$. CatB−$(CH_2)_4$−BCat is also formed in the reaction of $(bpy)Ni(CH_2)_4$ with CatB−BCat: Iverson, C. N.; Smith, M. R., III. Unpublished results.