CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201001575

C–C Coupling by Thermolysis of Alkynyl Phosphonium Borates

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Dedicated to the memory of Professor Pascal LeFloch

Compounds containing both phosphine and borane fragments have attracted increasing attention over the past several years. Perhaps the most widely studied use of such molecules has been as ligands for transition metals. Indeed systems that incorporate both P and B centers have been shown to be quite versatile for the coordination chemistry[1] of transition metals. Moreover the resulting complexes give rise to unusual reactivity[2] and have furnished new organometallic catalysts.[3] While the impact on the reactivity of such ancillary P/B ligands is interesting, materials containing P and B centers also exhibit interesting properties. For example, phosphorus ylide–borane adducts have been employed as latent catalysts for thermosetting resins.[4] In addition, more elaborate molecules containing P and B centers have been prepared to exploit the combination of such electron-donor and -acceptor capabilities. Together with highly conjugated organic π systems, such materials exhibit intriguing electronic and optical properties and have found applications as fluorescent and nonlinear optical[5] materials.[6] In another application, Gabbai et al have pioneered combinations of the Lewis acidity of boranes with the electron-withdrawing abilities of phosphonium groups to effect enhanced Lewis acidity at the B center for use as fluoride sensors.[7]

In a somewhat more fundamental context, we have recently described "frustrated Lewis pairs" comprising P and B centers in which steric demands preclude classical Lewis acid–base adduct formation. Such systems retain Lewis acidity and basicity that can be exploited to activate a variety of small molecules including olefins,[8] dienes,[9] THF, BH bonds,[10] terminal alkynes,[11] CO_2,[12] and N_2O.[13] Most notably these systems effect the heterolytic activation of H_2 and can be subsequently employed in metal-free hydrogenation catalysis of imines, aziridines, nitriles, enamines, and silylenolethers.[10,14,19] More recently, Bercaw et al[15] have used related phosphine-borane systems to effect H_2 activation and reduce metal-bound carbonyl fragments, while Bourissou and co-workers have exploited donor/acceptor properties of phosphine-boranes to effectively trap reactive intermediates such as singlet O_2.[16]

The nature of the organic links between the P and B centers in the above systems are frequently arene-based[17] although two-carbon alkyl[18] or alkenyl[19] chains have also been examined. Alkynyl-bridged systems bearing P and B centers were prepared some years ago by Marder[20] and others.[21] and shown to exhibit nonlinear optical properties.[20,22] More recently, Yamaguchi and co-workers have described an ingenious synthetic pathway for phosphonium borate linked stilbene derivatives formed by intramolecular nucleophilic addition of phosphine and borane across a C≡C unit in efforts to develop new organic materials.[23] Despite the interest in the electronic properties, little attention has focused on the reactivity of such alkynyl-bridged P/B systems. In a recent report, we described the unconventional binding mode of the alkynyl phosphine-borane, $t\mathrm{Bu}_2\mathrm{PC{\equiv}CB(C_6F_5)_2}$, to Ni^0.[24] Herein, the thermal reactivity of alkynyl phosphonium borates is examined. In two such systems the strongly polarized alkynyl group is shown to react via group migration and C–C coupling to give rise to unusual C4 olefinic and cumulenic fragments. The mechanism of these unusual rearrangements is probed computationally.

Thermolysis of the phosphonium borate $t\mathrm{Bu}_2\mathrm{PHC{\equiv}CBH(C_6F_5)_2}$ (**1**)[24] was performed in [D$_5$]bromobenzene at 150 °C for 12 h. The solution became yellow and subsequently orange after about 5 min. Following completion of the thermolysis, the solution was allowed to cool and a product (**2**) crystallized from the solution (Scheme 1). The crystals were isolated and washed with benzene affording **2** in 40 % yield. The ^{1}H NMR spectrum of **2** showed broad multiplets at $\delta = 5.90$ and 3.01 ppm as well as doublets at $\delta = 1.46$ and

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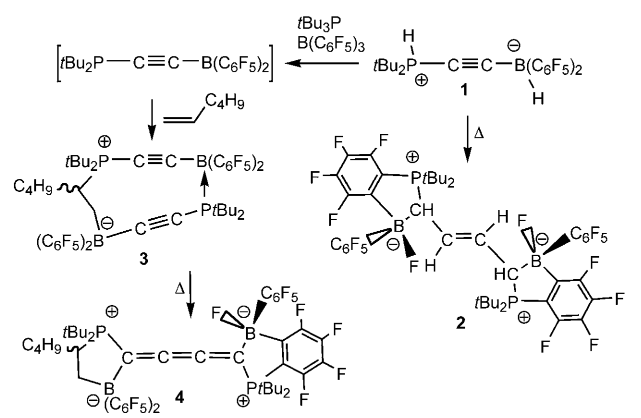
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001575.



Scheme 1. Synthesis of **2**–**4**.

1.18 ppm. The latter resonances correspond to inequivalent tertiary butyl groups. The broad ^{11}B {^{1}H} signal was observed at $\delta = 3.09$ ppm, while the ^{19}F NMR spectrum exhibited a signal at $\delta = -185.99$ ppm consistent with the presence of B*F* fragments. In addition the ^{19}F NMR resonance patterns were consistent with the presence of C_6F_5 and *ortho*-substituted C_6F_4 fragments. A singlet was observed in the ^{31}P NMR spectrum at $\delta = 75.24$ ppm. EI-mass spectral data revealed a molecular ion with an *m*/*z* ratio of 1032.2. While this mass corresponds to dimerization of the phosphonium borate, the spectral data were inconsistent with a simple dimerization process, suggesting a chemical transformation. Unambiguous confirmation of the nature of **2** was obtained by X-ray crystallography (Figure 1).[25] This species is a *trans*-disubstituted olefin in which the two equivalent substituents are five-membered rings derived from boron and phosphorus atoms linked by a fluoroarene ring and a methine carbon. The methine carbon atoms are bound to the olefin-linking fragment. Each of the P centers are cationic as they are also bound to two *tert*-butyl groups, whereas the B centers are anionic being quaternized by an additional C_6F_5 ring and a fluoride ion. The metric parameters are unexceptional, with B−F distance of 1.758(6) Å and the olefinic C=C bond length of 1.331(4) Å. It is noteworthy that the molecule sits on a crystallographically imposed center of symmetry and thus is the *meso* isomer for the chiral carbon and boron centers.

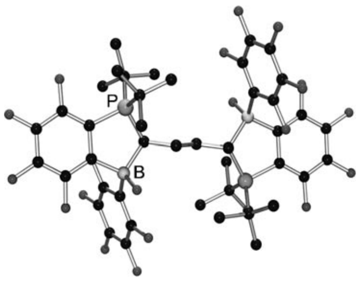


Figure 1. POV-ray drawing of **2**, H atoms have been deleted for clarity.

In targeting related thermolysis reactions, we prepared a second phosphonium borate in the following fashion. Compound **1** was treated with one equivalent each of $B(C_6F_5)_3$ and P*t*Bu$_3$ generating the salt [HP*t*Bu$_3$][HB(C_6F_5)$_3$] and *t*Bu$_2$PC≡CB(C_6F_5)$_2$ via proton and hydride transfer. Although this latter species was not isolated, subsequent addition of one equivalent of 1-hexene afforded the new species **3**, which was isolated as a fluffy white solid in 74 % yield. The ^{1}H and ^{13}C{^{1}H} NMR spectra were consistent with the incorporation of hexene and the alkyne-linked phosphine-borane in a 1:2 ratio and formulation of **3** as (*t*Bu$_2$PC≡CB(C_6F_5)$_2$)$_2$(BuCH$_2$CH). ^{31}P{^{1}H} and ^{11}B data are consistent with inequivalent quaternary P and B centers. The ^{19}F spectrum showed broad signals at room temperature and 20 resonances at −50 °C, suggesting inhibited rotation about the B−C bonds. These data collectively are consistent with addition of P and B to hexene generating phosphonium and borate centers. The presence of the ions enhances the Lewis acidity and basicity of the pendant P and B centers and promotes dative bond formation. The steric congestion resulting from this coordination presumably generates the observed rotational restriction. This reaction is analogous to the addition of simpler frustrated Lewis pairs to olefins that we have previously reported.[8]

Thermolysis of **3** in [D$_8$]toluene at 80 °C for 10 h converted the initially white suspension into a yellow solution. Following workup, a new air- and moisture-stable compound (**4**), consisting of two diastereomers in a 1:1.6 ratio, was isolated in 52 % yield. Although it was impossible to resolve the diastereomers in quantitative yields, single crystals of both diastereomers **4a** and **4b** were obtained on a few crystallization attempts. The ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR data for **4a** were consistent with the presence of two types of phosphonium and borate fragments, while the ^{19}F NMR spectrum revealed the presence of a B−F unit as well as an *o*-substituted C_6F_4 fragment and three inequivalent C_6F_5 rings. Although it was not possible to unambiguously determine the backbone structure of **4a** from the spectroscopic data, X-ray methods confirmed its formulation as (*t*Bu$_2$P)C_6F_4BF(C_6F_5)C_4B(C_6F_5)$_2$(BuCH$_2$CH)(P*t*Bu$_2$) (Figure 2),[25] which is a di-zwitterion with two discrete phosphonium-borate fragments linked through a chain of four carbons forming a bu-

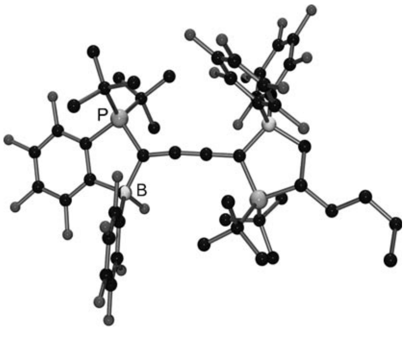


Figure 2. POV-ray drawing of **4a**, All H atoms have been deleted for clarity.

tatriene fragment. It is noteworthy that the overall geometry is one in which the two B centers and the two P centers adopt *trans* dispositions. The molecule contains two chiral centers, one on the carbon derived from hexene and the second on the B center which is chiral as a result of *o*-substitution of one of the fluoroarene rings. The relative chirality of these two centers is *RR*, however, the molecule is isolated as a racemic mixture of the *RR* and *SS* enantiomers, consistent with the crystallization of the species in a centrosymmetric space group. The metric parameters within **4** are not exceptional. The cumulene linkage is essentially linear with C-C-C angles of 172.0(2)° and 178.3(3)° and C–C distances of 1.323(3), 1.265(3), and 1.330(3) Å. ^1H, $^{11}B\{^1H\}$, ^{19}F, and $^{31}P\{^1H\}$ NMR and IR data of **4a** and **4b** revealed these species to be structurally similar. Indeed, X-ray data confirmed **4b** is the *RS*/*SR* diastereomer of **4**.

The reactions that form **2** and **4** have some common features. To probe the mechanism for the formation of **2**, particularly the C–C coupling reaction that leads to the C4 chain, DFT calculations were performed. These suggest that the rate-determining step involves the nearly isoenergetic rearrangement of **1** to boratacyclopropene **1a** through the transition state **1aTS** akin to that for hydroboration of the alkyne fragment, with a barrier of about 40 kcal mol^{-1} (Figure 3). Dimerization of the resulting boratacyclopropene ring by C–C coupling involves passage through transition state **1bTS** and its smaller barrier of about 30 kcal mol^{-1}. The product of bond rearrangement and dimerization is a symmetrical *trans*-alkene with a borataalkene substituent on each side (**1b**) that lies about 65 kcal mol^{-1} below **1**. Compound **1b** undergoes a slightly endothermic proton migration from P to the adjacent C to form monoene **1c**. Subsequent P attack at *ortho* positions of the fluoroarene rings with concurrent F transfer to B are collectively exothermic by nearly 200 kcal mol^{-1} (Figure 3).

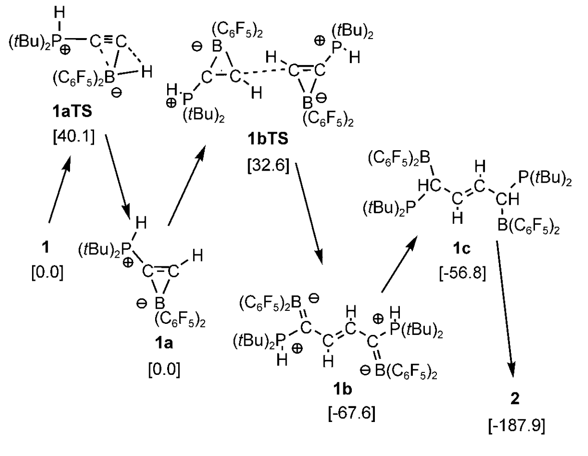
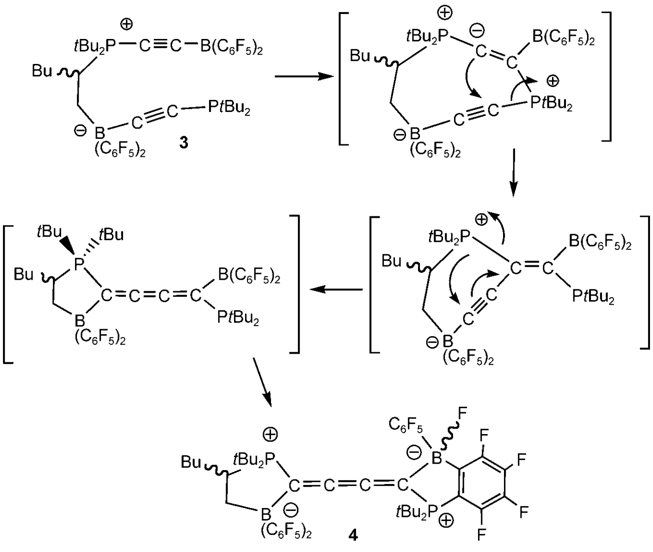


Figure 3. Energy diagram of proposed mechanism of formation of **2** based on DFT calculations; energies [M06-2x/6-311G(d,p)//oniMPW1K/6-31+G(d)] are given in kcal mol^{-1}.

Scans of the potential energy surfaces associated with these peripheral group processes suggest that the surfaces are rather flat, and that formation of the PC_6F_4B "caps" proceeds with barriers below that required in the initial step. These latter steps are not rate-determining, and so have not been studied in detail. This proposed pathway (Figure 3) is reasonable as cyclic structures related to boratacyclopropene **1a** have been reported in literature.[26] The inability to observe the formation of **1a** spectroscopically is consistent with the slow first step. As this boratacycle is expected to be a powerful reductant,[26] the presence of a reducible moiety within the molecule presumably prompts the facile dimerization. It is also noteworthy that other possible mechanisms are not supported by experimental evidence. Radical pathways are eliminated as both a radical scavenger (TEMPO) and a radical initiator (AIBN) did not substantially affect the reaction. A process involving rapid H_2 evolution and re-uptake is dismissed as there is no deuterium incorporation in the presence of D_2.

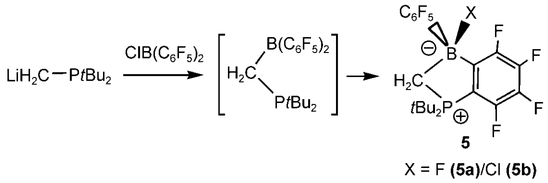
In the case of the thermolysis of **3**, the absence of B–H fragments precludes boracyclopropene intermediates. However, the strong polarization of the alkyne fragment resulting from the phosphonium, phosphine, borane, and borate fragments in **3** suggests the possibility of thermally induced intramolecular attack and rearrangements to give the resulting cumulene unit. Similar P attack at the *ortho* positions of one of the fluoroarene rings with concurrent F transfer to B completes the transformation to **4** (see Scheme 2).



Scheme 2. One proposed mechanism for formation of **4**.

In the generation of both **2** and **4**, a major driving force is believed to be the formation of five-membered cycles via *ortho*-F activation of C_6F_5 groups by the "frustrated" P and B bound to the same carbon atom. As indicated in Figure 3, one cyclization provides about 65 kcal mol^{-1} of thermodynamic stabilization. In agreement with the facile nature of this cyclization process, an attempt to synthesize a CH_2-

bridged phosphine-borane from $ClB(C_6F_5)_2$[27] and tBu$_2$PCH$_2$Li[28] led to the isolation of the cyclic product **5** (Scheme 3). Compound **5** was isolated as a mixture of the fluoro- and chloroborate compounds and X-ray data confirmed the structure to be $(C_6F_5)(C_6F_4)XBCH_2PtBu_2$ (X=F **5a**/Cl **5b**, ratio: 50:50) (Figure 4).



Scheme 3. Synthesis of **5**.

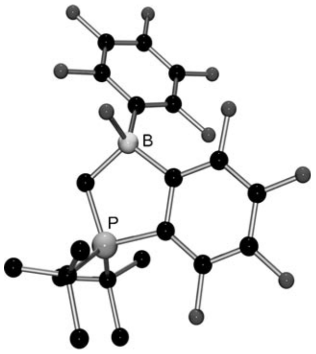


Figure 4. POV-ray drawing of **5a**. H atoms have been deleted for clarity.

In conclusion, herein we have shown that alkynyl phosphonium borates undergo unusual thermolysis to afford C$_4$ derivatives, providing a new strategy to extended and conjugated systems with electron-rich and -deficient centers. Further studies of the reactivity, properties and utility of alkynylphosphonium borate species are the subjects of current investigations.

Experimental Section

General considerations: NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer and spectra were referenced to residual solvent (^{1}H, ^{13}C) or externally (^{11}B; BF$_3$OEt$_2$, ^{19}F; CFCl$_3$, ^{31}P; 85% H$_3$PO$_4$). IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer. Combustion analysis was performed in house on a Perkin–Elmer CHN Analyzer. $(C_6F_5)_2HBCCPHtBu_2$ (**1**) was prepared as previously reported.

(tBu$_2$PCHBF(C$_6$F$_4$)(C$_6$F$_5$)CH)$_2$ (2): A J-Young NMR tube charged with **1** (84 mg, 0.163 mmol) dissolved in [D$_5$]bromobenzene (1 mL) was heated at 150 °C for 12 h. The color of the solution started turning yellow after a few minutes, and then started turning orange after about 5 min. After the heat source was removed, the product was allowed to precipitate out of the orange solution by layering benzene (1 mL) overnight. The crystalline solid was filtered out and washed with benzene, and was dried in vacuo to give a yellow powder. Yield: 34 mg, 40%. Single crystals suitable for X-ray diffraction were obtained from a reaction mixture. ^{1}H NMR: δ= 5.90 (m, 2H, =CH), 3.01 (m, 2H, P(B)CH), 1.46 (d, 18H, $^{3}J_{HP}$=16.0 Hz, tBu), 1.18 ppm (d, 18H, $^{3}J_{HP}$=15.6 Hz, tBu); ^{11}B {^{1}H} NMR: δ=3.09 ppm (br); ^{31}P {^{1}H} NMR: δ=75.24 ppm (s).

(tBu$_2$PC≡CB(C$_6$F$_5$)$_2$)(BuCH$_2$CH)(tBu$_2$PC≡CB(C$_6$F$_5$)$_2$) (3): A mixture of B(C$_6$F$_5$)$_3$ (86 mg, 0.17 mmol) and PtBu$_3$ (34 mg, 0.17 mmol) dissolved in toluene (1.0 mL) was added to a solution of **1** (88 mg, 0.17 mmol) in toluene (1.5 mL). The reaction mixture immediately turned orange-yellow, and became cloudy upon stirring for 1 h. Hexanes (8 mL) were added, and the reaction was left standing at −35 °C for 2 h. The mixture was then filtered through Celite and washed with cold hexanes. After addition of 1-hexene (2.3 mL) to the combined filtrate, the yellow solution was left standing at 25 °C without stirring until a white fluffy solid precipitated out (typically 1–2 days). The product was washed with pentane and dried in vacuo. Yield: 70 mg, 74%. ^{1}H NMR: δ=2.71 (m, 1H, PCH), 2.61 (m, 2H, PCHCH_2), 1.83 (m, 2H, BCH$_2$), 1.60 (d, 9H, $^{3}J_{HP}$= 15.4 Hz, tBu), 1.56 (m, 2H, PCHCH$_2$CH_2) 1.49 (d, 9H, $^{3}J_{HP}$=14.9 Hz, tBu), 1.43 (d, 9H, $^{3}J_{HP}$=14.7 Hz, tBu), 1.07 (d, 9H, $^{3}J_{HP}$=14.9 Hz, tBu), 1.02 (m, 2H, CH_2CH$_3$), 0.68 ppm (t, 3H, $^{3}J_{HH}$=7.3 Hz, CH$_2$CH_3);^{1}B{^{1}H} NMR: δ=−16.50 (br s), −18.02 ppm (s); ^{31}P{^{1}H} NMR: δ=41.47 (s), 25.45 ppm (br s). IR (thin film from CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$=2124 (ν(C≡C)).

(tBu$_2$P)C$_6$F$_4$BF(C$_6$F$_5$)C$_4$B(C$_6$F$_5$)$_2$(BuCH$_2$CH)(PtBu$_2$) (4): A suspension of (**3**: 21 mg, 0.02 mmol) in [D$_8$]toluene (0.5 mL) was heated at 80 °C in a J-Young NMR tube for 10 h, during which time the reaction mixture turned yellow. After confirming the full conversion of the product by NMR spectroscopy, the solvent was pumped off completely from the mixture. The product was then purified on a flash column of neutral alumina (initial wash with hexane followed by elution of the yellow band with hexane/ethyl acetate=9:1). The eluent was dried under vacuum to afford a yellow product. The product was further recrystallized from CH$_2$Cl$_2$/diethyl ether/hexane when necessary. Yield: 11 mg, 52%. Slow evaporation of toluene from a product solution gave single crystals of **4a**, and another setup afforded single crystals of **4b**, both of which were suitable for X-ray diffraction. **4a**: ^{1}H NMR: δ=3.01 (m, 1H, PCH), 2.42 (m, 2H, BCH$_2$), 2.07 (m, 1H, PCHCH_2), 1.86 (m, 1H, PCHCH_2), 1.80 (m, 2H, PCHCH$_2$CH_2), 1.51 (d, 9H, $^{3}J_{HP}$=14.6 Hz, tBu), 1.48 (d, 9H, $^{3}J_{HP}$= 15.0 Hz, tBu), 1.46 (m, 2H, CH_2CH$_3$), 1.44 (d, 9H, $^{3}J_{HP}$=14.6 Hz, tBu), 0.97 (d, 9H, $^{3}J_{HP}$=14.4 Hz, tBu), 0.96 ppm (t, 3H, $^{3}J_{HH}$=7 Hz, CH$_3$); ^{11}B{^{1}H}: δ=3.50 (br), −9.76 ppm (br). ^{31}P{^{1}H}: δ=59.10 (m), 55.56 ppm (dm, $^{5}J_{PP}$=29 Hz). **4b**: ^{1}H NMR: δ=3.08 (m, 1H, PCH), 2.42 (m, 2H, BCH$_2$), 2.07 (m, 1H, PCHCH_2), 1.84 (m, 1H, PCHCH_2), 1.80 (m, 2H, PCHCH$_2$CH_2), 1.58 (d, 9H, $^{3}J_{HP}$=16.7 Hz, tBu), 1.46 (m, 2H, CH_2CH$_3$), 1.31 (d, 9H, $^{3}J_{HP}$=16.5 Hz, tBu), 1.29 (d, 9H, $^{3}J_{HP}$=14.7 Hz, tBu), 1.17 (d, 9H, $^{3}J_{HP}$=14.5 Hz, tBu), 0.99 ppm (t, 3H, $^{3}J_{HH}$=7 Hz, CH$_3$); ^{11}B{^{1}H}: δ=3.50 (br), −9.76 ppm (br); ^{31}P{^{1}H}: δ=59.13 (m), 56.70 ppm (dm, $^{5}J_{PP}$=32 Hz); IR (thin film from CH$_2$Cl$_2$, cm^{-1}): $\tilde{\nu}$=1734 (υ(=C=C=)).

(C$_6$F$_5$)(C$_6$F$_4$)XBCH$_2$PtBu$_2$ (X=F 5a/Cl 5b=3.2/1): A solution of ClB(C$_6$F$_5$)$_2$ (400 mg, 1.05 mmol) in hexanes (10 mL) was added to a suspension of tBu$_2$PCH$_2$Li (182 mg, 1.10 mmol) in hexanes (8 mL) at room temperature. The reaction was stirred overnight and the solvents were pumped off completely. The resulting solid residue was redissolved in benzene (10 mL) and the insoluble lithium salts were filtered out using Celite. The filtrate was passed through a column of neutral alumina to eliminate the brown-colored impurities. Benzene was pumped down from the filtrate, and the concentrated solution (0.5 mL) was layered with hexanes (10 mL). After two days of standing at 25 °C, a colorless microcrystalline solid was isolated, washed with pentane, and dried in vacuo. Yield: 196 mg, 38%. Single crystals suitable for X-ray diffraction were grown by layering a CH$_2$Cl$_2$ solution of the product with pentane at 25 °C. **5a**: ^{1}H NMR: δ=1.53 (m, 1H, CH$_2$), 1.44 (d, 9H, $^{3}J_{HP}$=16.0 Hz, tBu), 1.38 (d, 9H, $^{3}J_{HP}$=15.6 Hz, tBu), 1.29 ppm (m, 1H, CH$_2$); ^{11}B NMR: δ=4.63 ppm (d, $^{2}J_{BF}$=74 Hz); ^{31}P{^{1}H} NMR: δ=87.13 ppm (m). **5b**: ^{1}H NMR: δ=1.99 (dd, 1H, $^{2}J_{HH}$=16.5 Hz, $^{2}J_{HP}$=12.8 Hz, CH$_2$), 1.65 (dd, 1H, $^{2}J_{HH}$=16.5 Hz, $^{2}J_{HP}$=8.8 Hz, CH$_2$), 1.50 (d, 9H, $^{3}J_{HP}$=16.0 Hz, tBu), 1.25 ppm (d, 9H, $^{3}J_{HP}$=15.6 Hz, tBu); ^{11}B NMR: δ=−2.02 ppm (br); ^{31}P{^{1}H} NMR: δ=88.76 ppm (m).

Acknowledgements

D.W.S. gratefully acknowledges financial support of NSERC of Canada. D.W.S. is grateful for the support of a Canada Research Chair and a Killam Research Fellowship from the Killam Foundation. X.Z. thanks the Province of Ontario and Digital Specialty Chemicals for an Ontario Graduate Scholarship (OGSST).

Keywords: alkyne complexes · boron · C–C coupling · frustrated Lewis pairs · phosphorus

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Received: June 5, 2010