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Terminal Alkyne Activation by Frustrated and Classical Lewis Acid/Phosphine Pairs

Meghan A. Dureen and Douglas W. Stephan*
Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6

Received May 5, 2009; E-mail: dstephan@chem.utoronto.ca

The activation of alkynes by transition metals has resulted in a wide variety of useful synthetic strategies for organic chemists.[1] Stoichiometric metalations of terminal alkynes provide classic synthons, while use of transition metal catalysts facilitates C−C coupling reactions such as oxidative dimerizations,[2] alkyne−arene coupling reactions,[3] and alkynylations of aldehydes.[4] Whereas transition metal mediated hydroboration[5] or hydrophosphination[6−8] of alkynes has been thoroughly investigated, the direct reaction of main group species with alkynyl fragments has seen very limited study. In developing our approach to metal-free activations of small molecules, we have uncovered the concept of *frustrated Lewis pairs*,[9] which is based on the combination of unquenched Lewis acidity and basicity that results from steric congestion precluding classical Lewis acid−base adduct formation. Such systems,[10,11] including simple combinations of a sterically encumbered phosphine,[12,13] imine,[14,15] or carbene[16,17] with electron-deficient boranes, have been shown to effect the heterolytic activation of H_2. While we[14,15] and others[18−21] have exploited this chemistry for metal-free catalytic hydrogenations, we have also probed the reactivity of frustrated Lewis pairs for the activation of a variety of other small molecules including THF,[22,23] catechol borane,[24] terminal olefins,[25] and dienes.[26] In this report, we demonstrate the reactivity of alkynes with phosphine/Lewis acid combinations describing the ready formation of boron- or alane-alkyne derivatives via reactions with terminal alkynes. Depending on the nature of the phosphine, either alkynylborate(aluminate) salts or zwitterionic, olefinic phosphonium borates(aluminates) will react via terminal C−H activation or P/B(Al) addition to the alkyne. Moreover, such reactivity is not only derived frustrated Lewis pairs but also classical Lewis acid−base adducts.

Frustrated Lewis pairs were generated by the combination of $B(C_6F_5)_3$ or $(PhMe)\cdot Al(C_6F_5)_3$[27] and $t\mathrm{Bu}_3P$. These mixtures were subsequently added to PhC≡CH in toluene at −35 °C. Shaking the samples prompted a phase separation, where an oil was found to separate from the solvent. These oils were isolated and recrystallized to give the colorless, crystalline solid **1** and **2** in 82% and 91% yields, for the B and Al reactions, respectively. The ^1H NMR spectrum (CD_2Cl_2) of **1** showed a doublet at 4.80 ppm with a characteristically large P−H coupling of 428 Hz. This, together with the $^{31}P\{^1H\}$ signal at 61.5 ppm are consistent with the formation of the cation $[t\mathrm{Bu}_3PH]^+$. The ^{11}B NMR resonance was observed at −20.8 ppm, while the ^{19}F NMR showed resonances at −132.73, −163.94, and −167.45 ppm consistent with the formation of a borate anion. The corresponding data for **2** are similar, and collectively these data suggest the formulation of these products as $[t\mathrm{Bu}_3PH][PhC{\equiv}CX(C_6F_5)_3]$ (X = B (**1**), Al (**2**)) (Figure 1). These postulates were subsequently confirmed by X-ray crystallography.[28] The structural parameters for the cation within **1** and **2** are unexceptional. The B and Al centers of the anions of **1** and **2** adopt pseudotetrahedral geometry with B−C and Al−C bond lengths of 1.592(3) and 1.9478(19) Å, respectively, while the C≡C bond lengths were typical being 1.202(3) and 1.207(2) Å in **1** and **2**, respectively.

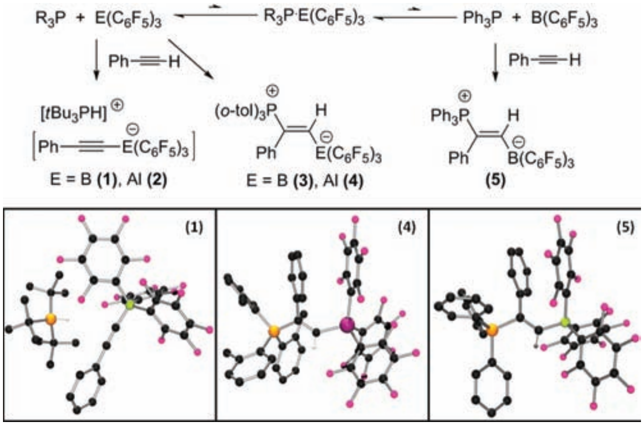

Figure 1. Reactions of Lewis acid/phosphine pairs with alkynes; molecular structures of **1**, **4**, and **5**. C: black, F: pink, P: orange, B: yellow-green, Al: fuscia.

Combinations of $B(C_6F_5)_3$ or $(PhMe)\cdot Al(C_6F_5)_3$ and $(o\text{-}C_6H_4Me)_3P$ also generated frustrated Lewis pairs which react with PhC≡CH to give white solids **3** and **4** in 75% and 84% yields, respectively. X-ray crystallographic studies revealed the formulation of **3** and **4** as the zwitterionic species with the general formula $E\text{-}(o\text{-}C_6H_4Me)_3PC(Ph){=}C(H)E(C_6F_5)_3$ (E = B, Al) (Figure 1).[28] In contrast to the formation of **1** and **2**, these products show that the phosphine and borane (or alane) added to the alkyne in *E*-fashion with the B (or Al) adding to the CH end of the alkyne. The alkenyl B−C and Al−C distances were found to be 1.642(3) Å and 2.004(2) Å in **3** and **4**, respectively. A twist of the *ipso*-C−C−P planes with respect to the H−C−B or H−C−Al plane was observed to be 10.5° in **3** and 9.7° in **4**. This feature appears to result from the steric congestion about the central double bond. These twists also accommodate the $\pi-\pi$ stacking of the electron-rich phenyl derived from the alkyne with one of the electron-poor C_6F_5 rings on B at typical distances.[29−31] Compound **3** is the four coordinate B/P relative of alkenyl-linked, three-coordinate phosphino-borane species $Ph_2PCH{=}CHB(C_6H_2Me_3)_2$, prepared by Marder et al. via a more conventional synthetic method involving hydroboration of the phosphinoalkyne.[32] The NMR spectra for **3** and **4** show temperature dependence resulting from a rotational barrier about the P−C bond for the *o*-tolyl substituents. In the case of **3**, two broad, overlapping ^{31}P NMR resonances, in addition to broad ^{11}B, ^1H, and ^{19}F spectra, were observed. Upon heating **3** to 385 K the ^{31}P signals merge and sharpen into a single peak at 31.1 ppm with a B−P coupling of 16 Hz, while the ^{11}B resonance sharpens to a single resonance at −13.55 ppm. Upon cooling to 215 K, two broad ^{31}P and ^{11}B resonances were observed. These data are attributed to major and minor rotamers in a 1.7:1 ratio. Interestingly, the ^1H NMR data are consistent with the solid state structure that reveals the three *o*-tolyl groups are in distinct environments: one being oriented away from the olefinic linkage and the other two being disposed on either side of it. Nonetheless, efforts to confirm the precise nature of the major rotamer in solution by 2D NOESY NMR techniques were not conclusive.

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In contrast to the above, the isolated classical Lewis acid−base adduct $Ph_3P{\cdot}B(C_6F_5)_3$ shows no evidence of dissociation by NMR spectroscopy. Nonetheless, this species reacts with PhC≡CH, to give a white solid **5**, isolated in 87% yield. The spectroscopic data for **5** were similar to the high temperature spectra of **3** and **4**, consistent with the absence of the rotational isomers. The formulation of **5** as $Ph_3PC(Ph){=}C(H)B(C_6F_5)_3$ was confirmed crystallographically (Figure 1).

The formation of **5** infers that an equilibrium involves some degree of dissociation of PPh_3 from the classical adduct $Ph_3P{\cdot}B(C_6F_5)_3$.[33−37] Free borane and phosphine are not discernible spectroscopically in C_6D_5Br, consistent with the calculated P−B bond dissociation energy 39 kcal mol^{-1}.[36] Nonetheless, the introduction of alkyne affords **5** by irreversibly consuming the apparently small equilibrium concentration of free borane and phosphine. In a related sense, we have recently demonstrated that reaction of lutidine and $B(C_6F_5)_3$ affords a classical Lewis acid−base adduct and yet also exhibits frustrated Lewis pair behavior in the activation of H_2, although, in the lutidine-$B(C_6F_5)_3$ case both the adduct and free Lewis acid/base were observed in solution.[38] The formation of **5** further affirms that classical and frustrated Lewis pair reactivity are not mutually exclusive. These observations also suggest the possibility that a broad new range of frustrated Lewis pair reactivity is accessible from classical Lewis adducts, previously thought to be a synthetic dead end.

The mechanism of formation of **1**−**5** is a subject of interest; however, the facile and rapid natures of these reactions complicate kinetic study. A radical mechanism seems unlikely given that solutions of phosphine and borane are EPR silent. The most reasonable mechanism is based on the initial π-interaction of the alkyne with the Lewis acidic center. This notion is consistent with the known ability of $Al(C_6F_5)_3$ to interact with arene solvents in a π-fashion[39] and the observation that terminal alkynes and $E(C_6F_5)_3$ in the absence of Lewis bases react rapidly to give multiple undetermined products. Such coordination is expected to activate the alkyne toward nucleophilic attack as well as enhance the acidity of the C−H bond. Thus it is consistent that the subsequent reactivity depends on the nature of the phosphine. For tBu$_3$P, the Brönsted basicity prompts deprotonation of the alkyne-CH affording the phosphonium salt of the alkynyl-borate. In contrast, arylphosphines, which are less basic than tBu$_3$P, act as a nucleophile, attacking the substituted carbon of the alkyne affording the zwitterionic olefinic species **3**−**5**. A mechanism where the borane or alane polarizes the alkyne prompting nucleophilic addition to the more stable carbocation is consistent with this regiochemistry. Similar reactivity has been effected in the recent report of Yamaguchi and co-workers[40] in which they describe a clever synthetic route to extended conjugated photoactive materials via an intramolecular addition of phosphine and borane fragments to an internal alkyne.

In conclusion, discrete phosphine-borane or phosphine-alane frustrated Lewis pairs react with phenylacetylene via two reaction pathways. Deprotonation affords a facile route to alkynylborates, while the addition pathway affords unique zwitterionic olefinic phosphonium borates. Together these results demonstrate two reaction pathways for Lewis acid−base pairs with terminal alkynes. Furthermore, frustrated Lewis pairs are accessible from classical Lewis acid−base adducts, thus broadly extending the potential for frustrated Lewis pair chemistry. We are currently investigating the reactivity of other classical Lewis acid−base adducts with small molecules, the subsequent reactivity and properties of both classes of alkyne derivatives described herein, and the broader implications for Lewis adducts in chemistry.

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Supporting Information Available: Experimental procedures and X-ray crystallographic details of **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) X-ray data: **1**: monoclinic, $P2_1/n$, $a = 15.330(3)$ Å, $b = 15.326(3)$ Å, $c = 15.626(3)$ Å, $\beta = 100.60(3)^o$, $V = 3608.7(13)$ Å^3. Data: 8229, var = 500, $R(>3\sigma) = 0.0439$, R_w (all) = 1181, GOF = 1.015. **2**·0.5(C_6H_5Cl): monoclinic, $P2_1/c$, $a = 12.5867(4)$ Å, $b = 16.6533(5)$ Å, $c = 19.4595(6)$ Å, $\beta = 100.5490(10)^o$, $V = 4010.0(2)$ Å^3. Data: 9205, var = 554, $R(>3\sigma) = 0.0406$, R_w (all) = 1079, GOF = 1.034. **3**·(C_6H_5Br): triclinic, $P\bar{1}$, $a = 13.0438(5)$ Å, $b = 14.3208(5)$ Å, $c = 14.5274(5)$ Å, $\alpha = 93.6020(10)^o$, $\beta = 111.4250(10)^o$, $\gamma = 111.947(2)^o$, $V = 2279.78(14)$ Å^3. Data: 11 938, var = 640, $R(>3\sigma) = 0.0422$, R_w (all) = 0.1222, GOF = 1.019. **4**·0.5(CH_2Cl_2): triclinic, $P\bar{1}$, $a = 11.7981(3)$ Å, $b = 12.7991(4)$ Å, $c = 15.8684(4)$ Å, $\alpha = 90.4970(10)^o$, $\beta = 99.7450(10)^o$, $\gamma = 115.5190(10)^o$, $V = 2122.25(10)$ Å^3. Data: 9431, var = 604, $R(>3\sigma) = 0.0431$, R_w (all) = 0.1246, GOF = 1.004. **5**: monoclinic, $P2_1/c$, $a = 17.5355(6)$ Å, $b = 11.2841(4)$ Å, $c = 19.4421(7)$ Å, $\beta = 103.055(2)^o$, $V = 3747.6(2)$ Å^3. Data: 9931, var = 551, $R(>3\sigma) = 0.0360$, R_w (all) = 0.0941, GOF = 1.037.

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