# Double FLP-Alkyne Exchange Reactions: A Facile Route to Te/B Heterocycles

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**S** *Supporting Information*

**ABSTRACT:** 1-Bora-4-tellurocyclohexa-2,5-diene undergoes sequential [4 + 2] cycloadditions/alkyne-elimination reactions to incorporate 2 equiv of terminal alkyne with the loss of diarylalkyne, affording access to a series of 11 new tellurium-boron heterocycles. These alkyne exchange reactions proceed regioselectively and can tolerate a variety of functional groups, thus providing the potential for further derivatization. The mechanism of the exchange reaction is confirmed by a DFT study to involve the interaction of the Te and B with the alkyne in a frustrated Lewis pair fashion in the transition states.

The field of organochalcogen chemistry has long been centered on studies of sulfur and selenium compounds, while the reactivity of tellurium compounds was often assumed to be analogous to its lighter congeners. However, over the past decade, Te chemistry proved to be distinct, prompting Chivers and Laitinen to describe it as a "maverick among the chalcogens."[1] Specifically, the interest in Te-containing heterocycles has been spurred by their unique properties, including solid-state phosphorescence[2,3] and highly efficient photo-reductive eliminations.[4−6] Furthermore, the incorporation of tellurium into conjugated polymers results in a narrow HOMO−LUMO gaps and provides promising materials for new optoelectronic devices.[7,8] In another vein of inquiry, tellurium heterocycles have been investigated for potential applications as dyes in photodynamic therapy (PDT).[9−13] Despite these interesting applications, synthetic routes to tellurium-containing heterocycles remain scarce. The synthesis of tellurophene described by Sweat and Stephens is laborious and affords a modest yield.[14,15] Cationic telluropyrylium dyes used in PDT trials are accessible in a five-step synthetic process.[16] More recently, Rivard et al.[2] have exploited Fagan's transmetalation strategy,[17] which involves the reaction of a suitable zirconocene precursor with (bipy)TeCl$_2$ to prepare a series of substituted tellurophenes.

We have previously reported the facile synthesis of the heterocycles RB(RCCPh)$_2$Te (R = Ph, C$_6$F$_5$) via the double 1,1-carboboration of Te(CCPh)$_2$ by a variety of triarylborane.[18] The formation of the six-membered Te/B heterocycle stands in stark contrast to the thiophene derivatives obtained from the analogous reactions between dialkynylthioethers and triarylboranes.[19] In other work we have also shown that the borane and telluroether units in PhCH$_2$CH$_2$TeC(Ph) = C(C$_6$F$_5$)B(C$_6$F$_5$)$_2$

can act as an intramolecular frustrated Lewis pair (FLP) to effect *cis*-1-2-addition across an alkyne affording a zwitterionic Te/B heterocycle (Scheme 1).[20] These precedents prompted

**Scheme 1. Carboboration of Te-Alkyne To Give a Te/B FLP and Subsequent FLP-Alkyne Addition Reaction**
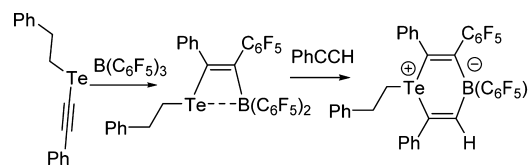


us to probe the utility of PhB(PhCCPh)$_2$Te **1** in reactions with alkynes. Herein, we report the relatively high-yielding synthesis of a series of Te/B heterocycles by an unprecedented double-alkyne exchange reaction sequence. Computational studies affirm that these reactions proceed via FLP-alkyne addition reactions followed by the extrusion of diphenylacetylene.

Noting that FLPs have been shown to react with alkynes and that the Te/B heterocycle **1** is nominally an intramolecular FLP, **1** was combined with phenylacetylene. At room temperature, there was no reaction, however upon heating above 80 °C, the liberation of diphenylacetylene was observed to be concurrent with the formation of a clean new species **2**. This species exhibited a downfield resonance at ~8.28 ppm in the ^{1}H NMR spectrum. Two equiv of phenylacetylene were required to completely convert **1** to **2**. Interestingly, compound **2** exhibits similar solubility to that of PhCCPh, but can be isolated as a yellow solid from the reaction mixture by repeated sonication of the crude mixture in hexamethyldisiloxane (63% isolate yield). The simple ^{1}H and ^{13}C{^{1}H} NMR spectra of the isolated **2** (see SI) suggests a symmetrical product. The ^{11}B NMR spectrum of **2** shows one broad resonance at 49.9 ppm, which is shifted slightly upfield in comparison to the parent compound **1** (53.3 ppm), consistent with the presence of three coordinate boron in **2**. The downfield ^{1}H resonance at 8.28 ppm is attributed to the (B)C*H* proton, while a [125]Te resonance at 659.7 ppm is consistent with the presence of the Te(II) center. This latter signal is significantly shielded relative to the signal for **1** (772.8 ppm). Collectively these data support the formulation of **2** as PhB(HCCPh)$_2$Te.

The facile and clean reaction between **1** and phenylacetylene prompted an investigation of the scope of this unique double alkyne exchange reaction. Indeed, **1** was shown to react with a series of terminal alkynes (R = 4-$C_6H_4Br$, 4-$C_6H_4OMe$, 4-$C_6H_4OtBu$, 4-$C_6H_4CF_3$, 3-$C_6H_4Cl$, 3,5-$C_6H_4F_2$, 4-$C_6H_4Ph$, $C_6H_3CH_2C_6H_4$, 3-$C_4H_3S$, ($C_5H_4$)FeCp) in nearly quantitative yields as determined by ^{1}H NMR spectroscopy in most cases, affording compounds formulated as PhB(HCCR)$_2$Te **2−12** (Figure 1). These compounds could all be isolated in moderate
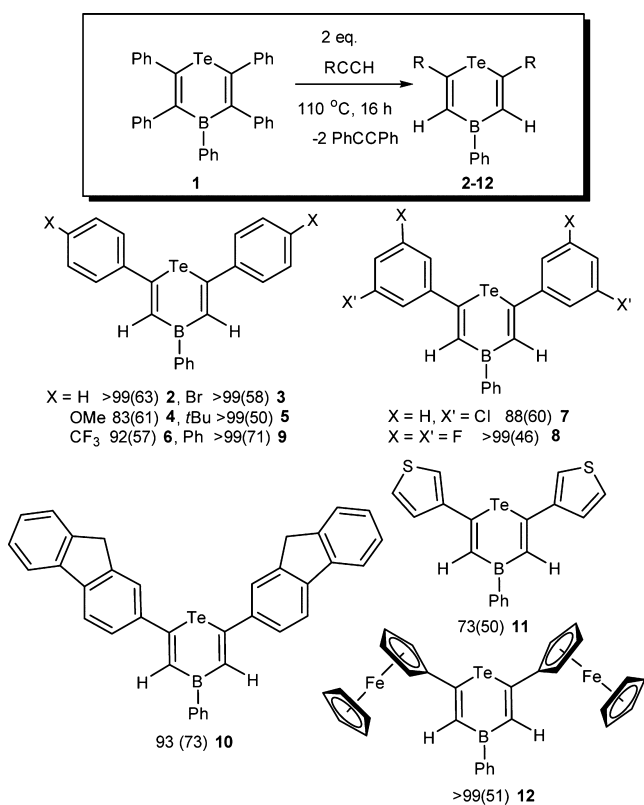


**Figure 1.** Synthesis of **2–12**. Spectroscopic conversions and (isolated yields) are shown.
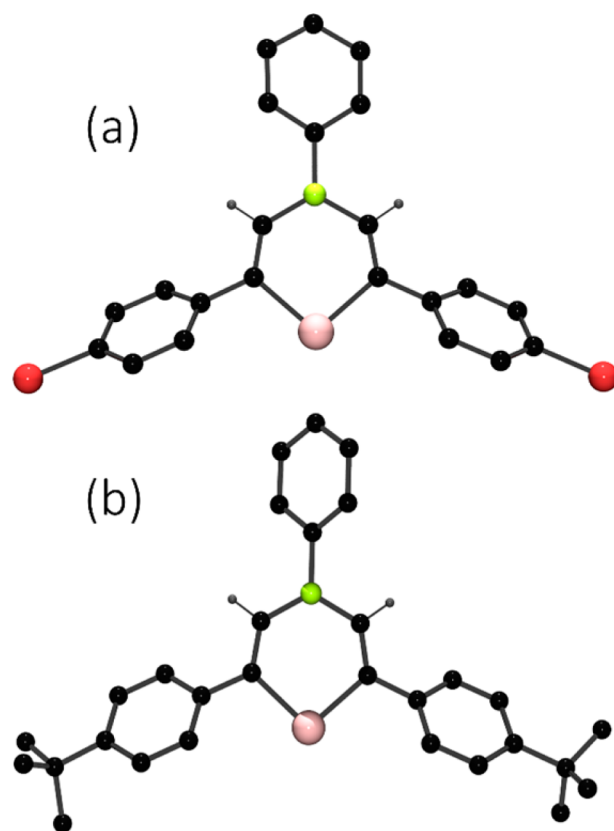


**Figure 2.** POV-ray depictions of (a) **3** and (b) **5**. C: black, B: yellow-green, Te: pink, Br: brown-red, H: gray. Hydrogen atoms except for olefinic CH are omitted for clarity. Selected bond lengths (Å) and bond angles (°): **3**: Te−C: 2.085(7); B−C: 1.577(7); C(1)−C(2): 1.344(8); C(1)−Te−C(4): 96.8(2); C(2)−B−C(3): 120.1(5). **5**: Te−C: 2.092(2); B−C: 1.534(3); C(1)−C(2): 1.356(2); C(1)−Te−C(4): 96.66(7); C(2)−B−C(3): 121.8(2).

to high yields (46−73%) as yellow or red powders. In all cases the reactions proceeded with high regioselectivity yielding only the product in which the terminal CH carbon attaches to the Lewis acidic B center. This is consistent with the appearance of the characteristic ^{1}H resonances of (B)C*H* at 8.17−8.36 ppm and the ^{13}C resonances of the TeC*R* fragment at 154−164 ppm. The [125]Te resonances for **2−12** are in the range of 626−684 ppm, providing a facile handle on the electronic structure of the central six-membered ring as upfield [125]Te shifts are observed for species with more donating R groups. Efforts to effect similar exchanges with internal alkynes led to no reaction.

Single crystals of **3** and **5** suitable for X-ray diffraction studies were grown at room temperature from saturated solutions of these compounds in pentane. The structural data (Figure 2) are consistent with the above formulation and confirm the formation of these unique Te/B heterocycles. Like **1**, species **3** and **5** feature planar central six-membered rings with the aryl substituents slightly twisted out of the plane of the central six-membered TeC$_4$B moiety. The Te−C distances are 2.085(7) and 2.092(2) Å, while the B−C bonds in **3** and **5** are 1.577(7) and 1.534(3) in **3** and **5**, respectively. These Te−C distances are only slightly shorter than typical Te−C single bonds.[21] The

corresponding C−Te−C angles are 96.8(2)° and 96.66(7)°, while the C−B−C angles are 120.1(5)° and 121.8(2)° in **3** and **5**, respectively. While the C−Te−C angles are similar to the in **1** (97.08(9)°), the angle at B is significantly smaller than that in **1** (124.3(2)°), presumably due to less steric crowding at the B centers in **3** and **5** compared to **1**. The C−C distances in the central rings are typical of C−C double bonds, and thus these data suggest a limited degree of delocalization in these heterocycles.

The mechanism of these reactions of compound **1** and alkynes was postulated to proceed through a [4 + 2] cycloaddition reaction, followed by the extrusion of PhCCPh. Repetition of this process would afford the observed hetero-cycles (Scheme 2). In this proposition the Te and B centers in **1** act as an FLP, giving *cis*-addition to the incoming alkyne to afford the intermediate. Consistent with previous observation the B adds exclusively to the less hindered C of the alkyne, providing an explanation for the observed regioselectivity.

Efforts to intercept or isolate intermediates in the above alkyne exchange reactions were unsuccessful, suggesting that the second alkyne exchange has similar energetic barrier as the first. In order to provide further support for this proposed mechanism, computational studies were undertaken at the dispersion-corrected density functional level of theory.[22,23] We apply the new composite DFT method PBEh-3c[24] for full structure optimizations and frequency calculations, while single point energies (Gibbs free energies) were obtained at the

**Scheme 2. Proposed Reaction Mechanism for the FLP-Alkyne Exchange Synthesis of 2−12**
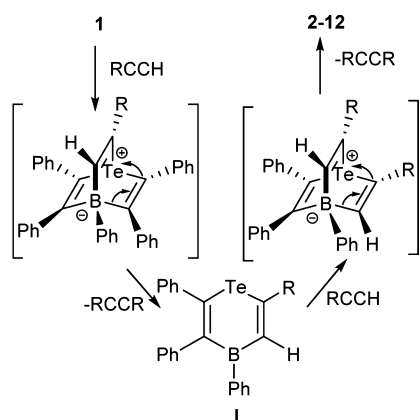


hybrid level with a large AO basis set (denoted PW6B95-D3/def2-TZVP//PBEh-3c,[25−30] for further details see SI). Both computational methods yield consistent relative energies for all structures agreeing to within 1−2 kcal/mol thus supporting the theoretical data.

Consistent with the proposition of FLP type reactivity, the addition of **1** with PhCCH yields (from a preceded van der Waals complex) a transition state (**TS1**) as shown in Figure 3.
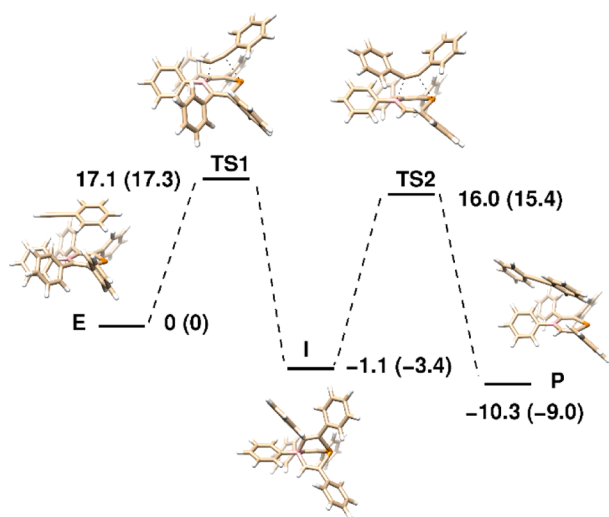


**Figure 3.** Computed (PW6B95-D3/def2-TZVP//PBEh-3c) reaction profile for the FLP-alkyne exchange reaction of **1** with PhCCH to yield **2** and PhCCPh. Gibbs free energies are given in toluene using the COSMO-RS solvation model,[25−30] numbers in parentheses are bare gas phase energies for comparison (all values in kcal/mol).

The free energy $\Delta G$ of this species is computed to be 17.1 kcal/mol above the reagents in toluene. This relatively high barrier is in agreement with the observed slow reaction at elevated temperatures. Formation of new B−C and Te−C bonds affords the intermediate species **I**, in an overall reaction that is slightly exergonic ($\Delta G$ of −1.1 kcal/mol). In a subsequent step the intermediate **I** loses a second equivalent of PhCCPh via an analogous transition state (**TS2**) to give the product **2** in an overall exergonic reaction ($\Delta G$ = −10.3 kcal/mol). The forward free energy barrier from **I** to the final product complex is smaller (17.1 kcal/mol) than for the backward step to the reactants (18.2 kcal/mol), which explains the overall observed

process. In both cases, the transition states involve a concerted interaction of the alkyne with the Lewis acidic B and Lewis basic Te centers, affording a pseudoborato-telluronium zwitterion intermediate. The reaction occurs in a more or less concerted (but asynchronous, i.e., the C−B bond forms slightly "faster" than the C−Te one) manner (see SI for computed bond orders of all species). The ejection of PhCCPh is thermodynamically favored as this diminishes the steric crowding in the respective heterocycles, **I** and **2**.

The reversible binding of an alkyne to a Ga-diamide chelate complex has been described by Fedushkin et al.[31] while more recently a recent report by Kinjo[32] has described [4 + 2] addition of alkyne to a dissymmetric diboron heterocycle. Nonetheless the formation of **2−12** is a rare example of a [4 + 2] cycloaddition−elimination reaction involving a heterocyclic compound. One notable related example involved the reaction of 2-diazaphosphinine with various alkynes to access functionalized phosphinines reported by Mathey and Le Floch.[33,34] In their report, the driving force was thought to be the increased aromaticity of the product. In the present compounds, the structural data reveal variations in the C−C, Te−C, and B−C bond distances in **1**, **3**, and **5** that is <0.02 Å.[18] Furthermore, the calculated nucleus-independent chemical shifts indices[35,36] of **2** and **1** at points 1 Å above the ring centers are −3.4 and −2.9 ppm, respectively. Collectively, the structural and computational data do not support the notion of significant aromaticity in compounds **1−12**. This is consistent with the DFT results that suggest the exchange reactions involve the cooperative action of the Lewis acidity at B and the basicity at Te, driven by the relief of steric congestion around the central TeC₄B ring. This conclusion is consistent with the observation that compound **1** is unreactive toward internal alkynes even on heating to higher temperatures (140 °C). It is interesting to note that while compound **1** readily decomposes upon exposure to air and moisture, compounds **2−12** can be stored on the bench under ambient conditions for up to a month without evidence of degradation as confirmed by ¹H NMR spectroscopy. In addition compound **3** proved to be stable in refluxing aqueous base, a feature that augurs well for further derivatization. This is consistent with the greater computed thermodynamic stability.

In conclusion, we have described a new synthetic route to a series of Te/B heterocycles via sequential alkyne exchange reactions. DFT studies confirm that the mechanism of these alkyne exchange reactions proceed via a nominal Te/B FLP addition to the incoming alkyne followed by PhCCPh elimination. Interestingly, this occurs twice to transform **1** to **2−12**. This protocol provides a comparatively high-yielding and versatile route to air stable Te-containing heterocycles. While the physical and optical properties as well as the potential applications of these new heterocycles are the subject of ongoing study, we are also examining the potential of **1** to undergo other FLP-type exchange reactions as a more general route to new inorganic heterocycles.

## ■ ASSOCIATED CONTENT

### ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09526.

Experimental procedures, spectroscopic data, computational details and computed structures (PDF)

Crystallographic data (CIF)

Crystallographic data (CIF)

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**Notes**
The authors declare no competing financial interest.

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