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COMMUNICATION

A Rare Olefin 1,1-Carboration Reaction Opens a Synthetic Pathway to an Unusually Structured Frustrated Lewis Pair

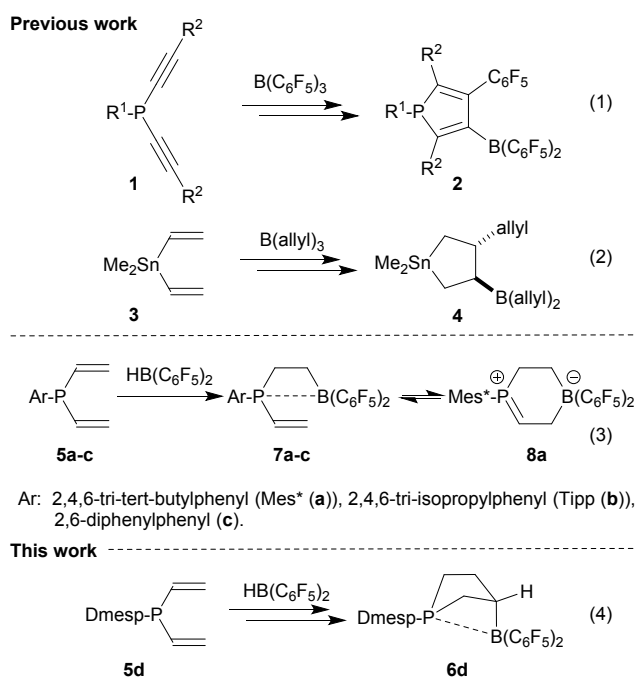
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Accepted 00th January 20xxChaohuang Chen,^a Constantin G. Daniliuc,^a Christian Mück-Lichtenfeld,^a Gerald Kehr,^a and Gerhard Erker^{*a}

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(2,6-Dimesitylphenyl)P(vinyl)₂ **5d** reacts with HB(C₆F₅)₂ in a sequence involving a rare example of a 1,1-carboration of an olefin to give the borylated tetrahydrophosphole derivative **6d**. Compound **6d** is an active frustrated Lewis pair that splits dihydrogen under mild conditions and serves as a metal-free hydrogenation catalyst. It also adds to carbon dioxide. Compound **6d** serves as an intermediate in the HB(C₆F₅)₂ catalyzed aryl(divinyl)phosphane (**5d**) to dihydrophosphole conversion.

The 1,1-carboration reaction of alkynes ('Wrackmeyer Reaction') is becoming a more and more useful method for the synthesis of alkenylboranes.¹⁻⁴ The use of various R-BAr₂ reagents featuring the strongly Lewis acidic boranes bearing activating fluorinated aryl substituents greatly facilitated the 1,1-carboration reaction and significantly extended its scope.⁵⁻⁷ This resulted in advanced procedures for the formation of e.g. -B(C₆F₅)₂ functionalized phospholes, boroles or thiophenes from the respective bis-acetylenes⁸⁻¹⁰ as well as of benzannulation reactions.¹¹ Eqn. (1) in Scheme 1 shows a typical example of such a phosphole synthesis. Even examples of alkyne 1,1-hydroboration reactions were recently reported.¹² In contrast to 1,1-carboration of acetylenes, olefin 1,1-carboration examples are rare [see eqn. (2) in Scheme 1 for an example].¹³ We have now found a 1,1-carboration reaction of a vinylphosphane system. The reaction of the bulky aryl(divinyl)phosphane **5d** with Piers borane [HB(C₆F₅)₂] proceeds readily to give the boryl substituted tetrahydrophosphole product **6d**. The reaction probably proceeds by a sequence of initial hydroboration followed by an internal olefin 1,1-carboration step. It was previously shown that HB(C₆F₅)₂ addition to the bulky Mes*-P(vinyl)₂ **5a** gave the cyclic methylene phosphonium

product **8a**.^{14,15} The reaction probably proceeds through the hydroboration product **7a** as an intermediate (Scheme 1, Eqn. (3)). It was also shown that the reaction of the corresponding Tipp-substituted divinylphosphane **5b** with HB(C₆F₅)₂ stopped at the stage of the hydroboration product **7b**. We have now found an analogous behavior of the bulkier 2,6-diphenylphenyl-substituted -P(vinyl)₂ system **5c** towards Piers borane to give **7c**. Subsequent heating was inconclusive; it gave a complicated mixture of as yet unidentified products.



Scheme 1. (1, 2) 1,1-carboration reactions of alkynes and alkenes; and (3, 4) reactions of bulky arylP(vinyl)₂ phosphanes with HB(C₆F₅)₂.

The reaction of the related Dmesp-P(vinyl)₂ starting material **5d**¹⁶ (Dmesp: 2,6-dimesitylphenyl) with HB(C₆F₅)₂ resulted in a markedly different outcome. Treatment of **5d** with HB(C₆F₅)₂¹⁷ (toluene, at 80 °C, 2h) gave the product **6d** that we isolated in

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60% yield. The ^1H NMR spectrum shows the typical signals of the Dmesp ligand [e.g. δ 6.98, 6.58 (C_6H_3), δ 6.77, 6.43 (Mes CH), δ 2.12, 1.91, 1.80, (each 6H, *p*, *o*, *o*- CH_3 of Mes)]. Due to its chirality features compound **6d** shows diastereotopic pairs of methylene hydrogens of the core. The *tert.* $\text{CH}[\text{B}]$ hydrogen atom resonance occurs at δ 2.33 with a characteristically large $^3J_{\text{PH}}$ coupling constant of 103 Hz. The heteronuclear resonances (^{31}P : δ 8.8, ^{11}B : δ 5.5) indicate the presence of a $\text{P}\cdots\text{B}$ interaction in **6d** (see the ESI for further details).

The composition of the framework of compound **6d** was confirmed by an X-ray crystal structure analysis of its derivative **12**, formed by addition of the 2,6-dimethylphenylisocyanide (Xyl-NC) donor (for details see the ESI and Fig. 1).

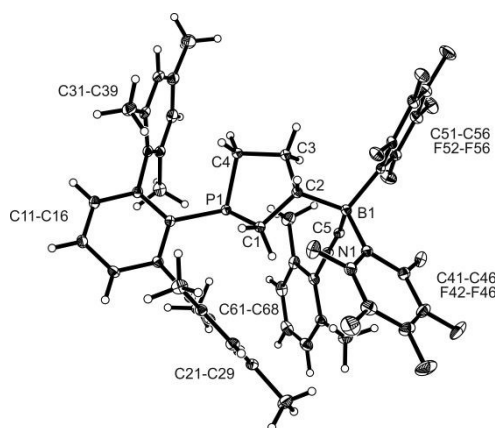


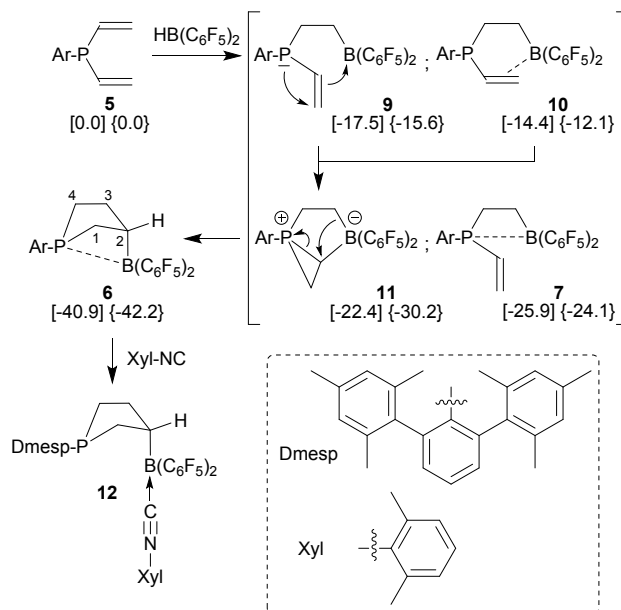
Figure 1. A view of the molecular structure of compound **12**. Selected bond lengths (Å) and angles (°). P1-C1 1.861(3), P1-C4 1.855(3), C1-C2 1.561(4), C2-C3 1.548(5), C3-C4 1.528(5), C2-B1 1.631(5), C5-B1 1.620(5), C5-N1 1.147(4); ZP1^{ccc} 303.8, ZB1^{ccc} 331.7.

Phosphanyl migration is a favoured feature in the 1,1-carboboration reaction of alkynes. The reaction may proceed through three-membered phosphirenium/borate betaine intermediates.¹⁸ We assume that the unusual olefin 1,1-carboboration reaction of the alleged P/B intermediate **7d** (Scheme 2) involves phosphanyl migration as well, and might actually proceed through the respective phosphiranium/borate betaine intermediate **11** (Scheme 2).

This reaction pathway was supported by the results of a DFT analysis.¹⁹ We first investigated computationally the reaction course to the virtual model system **6e**, which features a “small” phenyl substituent at phosphorus. The DFT calculation confirmed that the hypothetical overall reaction from **5e** plus $\text{HB}(\text{C}_6\text{F}_5)_2$ is markedly exergonic. The hydroboration intermediate **7e** is a major local minimum. The potential intermediates **9e** and **10e** were located at somewhat higher energies; these systems might be involved on the way to the P-migration product **11e** in the subsequent alkene 1,1-carboboration step (Scheme 2).

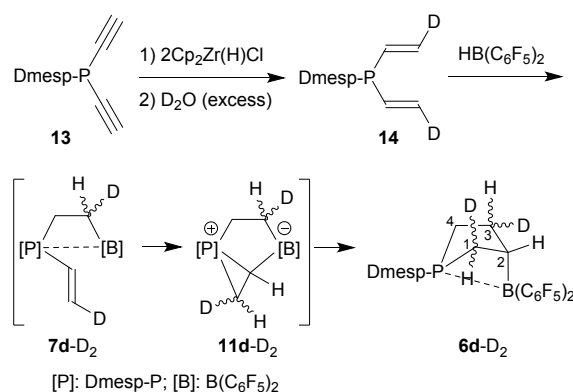
The DFT calculation of the “real” system $\text{Dmesp-P}(\text{vinyl})_2$ **7d** plus $\text{HB}(\text{C}_6\text{F}_5)_2$ revealed some remarkable differences. We note that the assumed intermediate stages **9d**, **10d** and the “resting stage” **7d** are each getting destabilized by ca. 2 kcal mol⁻¹ in the Dmesp-P system relative to the Ph-P model, whereas the attachment of the Dmesp substituent leads to a substantial energetic stabilization of the phosphiranium/borate betaine

11d. It is now energetically preferred over **7d**. In contrast, the overall formation of the final product **6d** is only marginally more exergonic (Scheme 2).



Scheme 2. Reaction of compound **5d** (Ar = Dmesp) and **5e** (Ar = Ph) with Piers' borane $\text{HB}(\text{C}_6\text{F}_5)_2$ [with DFT calculated relative Gibbs energies ΔG (in kcal mol⁻¹, 299 K, in dichloromethane) for Ar: phenyl as model system in [] and for Ar: Dmesp in { }].

The final olefin 1,1-carboboration step of the sequence results in an “inverted” bonding situation of the remaining P-vinyl group with phosphorus migrating to the former = CH_2 terminus. This was confirmed by a deuterium labelling experiment (Scheme 3). Twofold hydrozirconation of the bis(ethynyl) phosphane **13** with “Schwartz’ reagent”²⁰ followed by hydrolysis with excess D_2O gave the selectively deuterated starting material **14**. Treatment with $\text{HB}(\text{C}_6\text{F}_5)_2$ under our typical

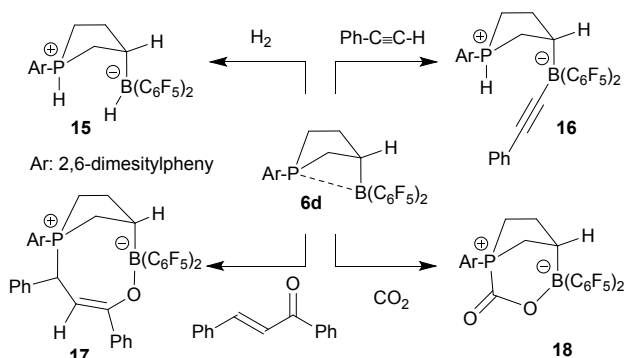


Scheme 3. Deuterium labelling experiment.

conditions led to the formation of **6d-D₂**, which we isolated in 60% yield. The NMR analysis by ^1H and ^2H NMR spectroscopy showed that carbon atoms C1 and C3 exclusively had the deuterium label bonded, carbon atoms C2 and C4 showed only the ^1H isotopes. The detailed spectroscopic analysis revealed the presence of a mixture of stereo-isotopomers. The

diastereotopic hydrogen positions at C1 are each ca. 50% occupied by deuterium. It seems that the olefin 1,1-carboration is not stereoselective, similar as it is often observed for the more frequent alkyne 1,1-carboration reactions.

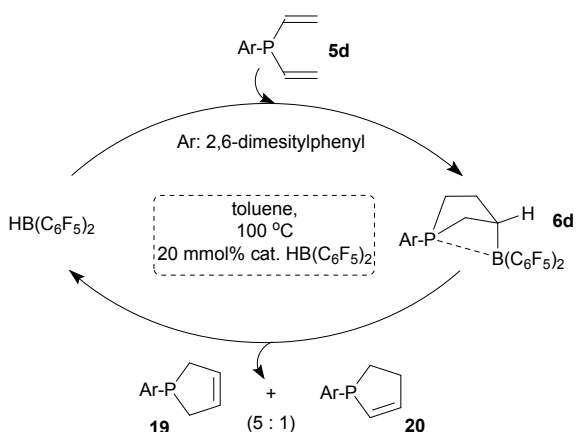
Compound **6d** undergoes a variety of typical frustrated Lewis pair reactions²¹ under mild conditions. It splits dihydrogen to give compound **15**. It served as an active metal-free hydrogenation catalyst of the bulky imine N-tert.butyl-1-phenylmethanimine to benzyl(tert.butyl)amine (see the ESI for details). The active P/B Lewis pair **6d** cleaves the C-H bond of phenylacetylene to form the $\text{PH}^+/\text{B-acetylenide}^-$ product **16**. With chalcone compound **6d** reacts by conjugate P/B addition to give **17** (Scheme 4).²²



Scheme 4. FLP reactions of compound **6d**.

Compound **6d** reacts with carbon dioxide.²³ The reaction is reversible, similar to the formation of a variety of other FLP CO_2 addition products. Removal of the solvent led to the reverse reaction; therefore, we have so far not isolated the P/B CO_2 adduct **18**. In CD_2Cl_2 solution it shows a ^{13}C NMR carbonyl signal at δ 161.1 (d, $^1J_{\text{PC}} = 91.4$ Hz).

The FLP products were characterized by C,H elemental analysis, by spectroscopy and by X-ray diffraction, except **18** (see the ESI for details)



Scheme 5. Catalytic dihydrophosphole formation.

The cyclic phosphane **6d** is prone for retro-hydroboration. We used this feature for an efficient catalytic conversion of the divinylphosphane **5d** to the dihydrophosphole isomers **19** (major) and **20** (minor).²³ For this purpose we generated 20

mmol% of the P/B FLP **6d** *in-situ* in the presence of an excess of $\text{Dmesp-P}(\text{vinyl})_2$ in toluene- d_8 solution and kept the mixture for 14 h at 100 °C. The NMR analysis revealed a complete conversion of **5d** to a mixture of the cyclic isomers **19** and **20**. Workup involving flash chromatography over silica gel (pentane/dichloromethane) gave the **19/20** mixture (ca. 5:1 ratio) as a white solid in 63% yield (Scheme 5). Single crystals suited for the X-ray crystal structure analysis of compound **19** (major isomer) were obtained from dichloromethane/heptane at r.t. (see the ESI for details of the characterization of the compounds **19** and **20**).

We conclude that treatment of aryl(divinyl)phosphanes with the $\text{HB}(\text{C}_6\text{F}_5)_2$ hydroboration reagent can have different outcomes depending on the steric bulk of the aryl substituent at phosphorus. With Tipp-[P] the reaction stops at the simple hydroboration product **7b**. A similar behavior is found for the (2,6-diphenylphenyl)-[P] system, although here unspecific decomposition is followed at elevated temperature. The $\text{Mes}^*[\text{P}]$ -system **5a** undergoes zwitterionic methylene phosphonium/borate product formation. Our DFT study indicated that the attachment of the Dmesp substituent resulted in a marked thermodynamic stabilization of the probably essential phosphiranium type intermediate **11d** (Scheme 2). It may be assumed that this pronounced influence of the Dmesp ligand at phosphorus caused the unique observed olefin 1,1-carboration pathway to prevail over a variety of alternative reaction pathways possible for these types of systems. It seems that the favored pathway in these systems can be controlled by the choice of the specific aryl ligand at the phosphorus atom. Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. C. C. thanks the Alexander von Humboldt foundation for a postdoctoral stipend.

Conflicts of interest

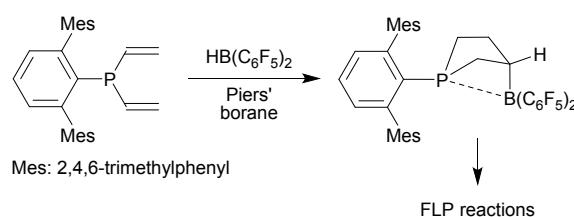
There are no conflicts to declare.

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Graphical Abstract



The bulky aryl(divinyl)phosphane reacts with Piers' borane by a sequence involving a rare olefinic 1,1-carboboration to give the active phosphane/borane Lewis pair.