

Reversible C-H activation, facile C-B/B-H metathesis and apparent hydroboration catalysis by a dimethylxanthene-based frustrated Lewis pair

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Abstract: A dimethylxanthene-based phosphine/borane frustrated Lewis pair (FLP) is shown to effect reversible C-H activation, cleaving phenylacetylene, PhCCH, to give an equilibrium mixture of the free FLP and phosphonium acetylide in CD₂Cl₂ solution at room temperature. This system also reacts with B-H bonds although in a different fashion: reactions with HBpin and HBcat proceed via C-B/B-H metathesis, leading to replacement of the -B(C₆F₅)₂ Lewis acid component by -Bpin/-Bcat, and transfer of HB(C₆F₅)₂ to the phosphine Lewis base. This transformation underpins the ability of the FLP to catalyze the hydroboration of alkynes by HBpin: the active species is derived from the HB(C₆F₅)₂ fragment generated in this exchange process.

Introduction

Frustrated Lewis pairs (FLPs) were first identified conceptually in 1942,¹ but it was not until a landmark 2006 report from Stephan and co-workers on the cleavage of H₂ that their use in small molecule capture/activation was established.² In the intervening 12 years, numerous examples of both inter- and intramolecular FLPs have been reported, together with their applications in the binding and/or activation of both polar and non-polar substrates.³ Although the interaction of FLPs with H₂ – and derived applications in catalytic hydrogenation – have been the focus of a significant proportion of this research,⁴ more recent reports have even seen this extended to the activation and functionalization of C-H bonds.⁵

In this FLP context we have been interested in exploiting the dimethylxanthene framework as a scaffold on which to install the Lewis acid and base components.^{6,7} This offers a degree of preorganization – based on a separation of 4.0–4.5 Å between the phosphine and borane units – which is optimal for the cleavage of H₂.⁸ Thus an FLP of this type (**1b**, Figure 1) has been shown to reversibly activate H₂ in solution under conditions

of ambient temperature and pressure,⁶ and a related system (**1a**) can catalyze dehydrogenation chemistry, including B-N dehydrocoupling processes.⁷

Recent work has shown that – in addition to shuttling dihydrogen – FLPs can also act as catalysts for various hydroelementation processes.⁹ One such process, which has widespread synthetic potential is the hydroboration of CC multiple bonds, not least because organoboron derivatives are very useful building blocks in organic chemistry.¹⁰ ‘Metal-free’ approaches to the hydroboration of alkynes in particular have attracted significant attention.^{11,12} For example, Stephan and co-workers recently showed that the hydroboration of alkynes by pinacolborane (HBpin, HBO₂C₂Me₄) could be effected by a variety of strong Lewis acids,¹² and is sensitive to the choice of catalyst. In particular, Piers’ borane, HB(C₆F₅)₂,¹³ was shown to act as an efficient and versatile pre-catalyst, generating *in situ* 1,1-diboryl species of the type RCH₂CR'(Bpin)(B(C₆F₅)₂) which were reported to act as the active catalytic species.¹²

Considering the track record of the dimethylxanthene-derived FLPs **1a** and **1b** in the activation of E-H bonds,^{6,7} and the use of other systems featuring the -B(C₆F₅)₂ function in hydroboration chemistry,^{12,13} we were interested to investigate their potential to carry out similar transformations. In this account, we describe the stoichiometric reactions of FLPs **1a/b** with both terminal and internal alkynes, together with their reactivity towards boranes and their unexpected role as pre-catalysts in the catalytic hydroboration of alkynes.

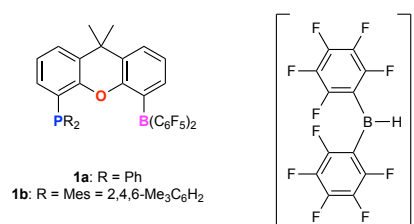


Figure 1. Key compounds relevant to the current study: (left) dimethylxanthene-based FLPs **1a/b** and (right) Piers’ borane ($n = 1, 2$).^{6,7,13}

Results and Discussion

FLP reactivity towards alkynes

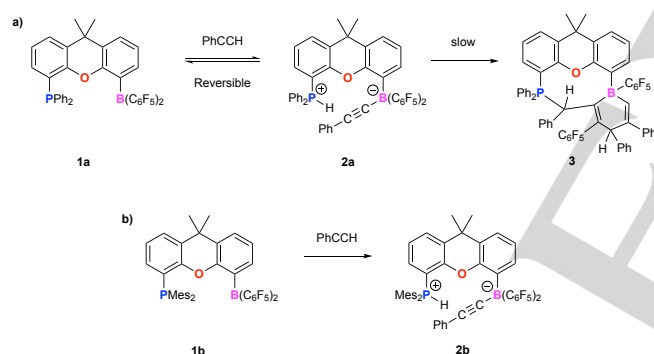
In our initial experiments we scoped out the potential for FLP **1a** to act as a catalyst for the hydroboration of alkynes using commercially available pinacolborane. Accordingly, we found that the hydroboration of PhCCMe proceeds to 95% completion

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in dichloromethane solution at room temperature over a period of 3 h at 10% catalyst loading. The reaction is shown by ^1H NMR spectroscopy to proceed with the expected *syn* stereochemistry and to be *ca.* 90% selective for the anti-Markovnikov product, PhC(H)=C(Me)Bpin . Similar chemistry carried out on PhCCPh proceeds more slowly, with the reaction taking *ca.* 12 h to achieve 50% conversion under similar conditions. While such behaviour is consistent with the more sterically hindered nature of this alkyne, more difficult to rationalize is the behaviour of the terminal alkyne PhCCH . In this case, turnover is also apparently slower than with PhCCMe , with >95% completion achieved only after *ca.* 12 h at 10 mol% loading, and 80–85% after a similar period at 5 mol%. Intrigued by this unusual difference in rate as a function of alkyne, we set out to probe the mechanism(s) of the catalysis. With this in mind, we first investigated the stoichiometric reactions involving **1a** and the respective alkynes/boranes.

FLP **1a** does not react in isolation with either of the internal alkynes PhCCMe or PhCCPh , but does react with PhCCH at room temperature in either dichloromethane or toluene. In the latter solvent, the reaction is essentially complete after 30 min, with a white solid precipitating out of solution. The product could be isolated in good yield (81%) and characterized by multinuclear NMR spectroscopy in CD_2Cl_2 solution. These data suggest the formation of the C-H activated product **2a** (Scheme 1).



Scheme 1. Stoichiometric reactions (a) between **1a** and PhCCH ; and (b) between **1b** and PhCCH .

The ^{31}P NMR spectrum of **2a** features a doublet at $\delta_{\text{P}} = -9.1$ ppm with a $^1J_{\text{P-H}}$ coupling constant of 544 Hz, and the $^{11}\text{B}\{^1\text{H}\}$ spectrum shows a sharp signal at $\delta_{\text{B}} = -18.4$ ppm, consistent with a tetra-coordinate boron atom. These NMR shifts are in good agreement with data previously published for zwitterionic phosphonium/alkynylborate compounds formed via the reactions of FLPs reactions with phenylacetylene. For example, Erker *et al.* report ^{11}B and ^{31}P NMR shifts of $\delta_{\text{B}} = -17.6$ ppm and $\delta_{\text{P}} = 1.6$ ppm ($^1J_{\text{P-H}} = 490$ Hz) for the product of C-H cleavage by an anthracene-based intramolecular FLP,¹⁴ and $\delta_{\text{B}} = -16.5$ ppm and $\delta_{\text{P}} = 0.0$ ppm ($^1J_{\text{P-H}} = 470$ Hz) for a cyclopentane-derived system.¹⁵

The ^{31}P and ^1H NMR spectra of **2a** in CD_2Cl_2 , however, also feature signals due to the FLP **1a** and free phenylacetylene, which we hypothesized might be due to the presence of an equilibrium between PhCCH and its C-H activated form at room temperature. Investigation by variable temperature NMR spectroscopy revealed that the relative proportions of **1a/2a** vary

as a function of temperature ($K = 5.4$ mM at 308 K for the loss of PhCCH ; 0.61 mM at 198 K), and a Van't Hoff analysis (see ESI) yields thermodynamic data ($\Delta H^\circ = +34$ kJ mol $^{-1}$; $\Delta S^\circ = +68$ J mol $^{-1}$ K $^{-1}$) for the loss of PhCCH from **2a**. These data can be put into context by the corresponding values of +38 kJ mol $^{-1}$ and +102 J mol $^{-1}$ K $^{-1}$ for the loss of H_2 from the phosphonium borate derived from the related FLP **1b**.⁶

Over a period of several hours at room temperature, solutions of **2a** in dichloromethane undergo a further transformation, as shown by *in situ* NMR monitoring. This instability is intrinsically linked to the reversible nature of the reaction of **1a** with PhCCH , in that the onward reactivity of **2a** is related to the presence of free alkyne in solution (vide infra). However, a consequence of this lability is that our attempts to crystallize **2a** for X-ray crystallographic analysis were inhibited. Reasoning that the use of the more strongly P-donating FLP **1b** (in which the phosphine phenyl groups are replaced by mesityl) might render the C-H activation reaction effectively irreversible, we examined its chemistry towards phenylacetylene. Accordingly, **1b** was reacted with PhCCH in dichloromethane, and the corresponding phosphonium acetylide **2b** was isolated in 44% yield. Compound **2b** can also be characterized in solution by multinuclear NMR spectroscopy, although in this case neither ^1H nor ^{31}P NMR data gave any indication of reversibility. Thus, the ^{31}P NMR spectrum shows a single resonance at $\delta_{\text{P}} = -27.3$ ppm ($^1J_{\text{P-H}} = 532$ Hz) and the $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum a singlet at $\delta_{\text{B}} = -17.9$ ppm. Moreover, in this case, X-ray quality crystals could be grown from a mixture of dichloromethane and hexane at 25 °C; **2b** crystallizes in the monoclinic $\text{P2}_1/\text{n}$ space group with a molecule of dichloromethane, and confirms the structure as resulting from cleavage of the C-H bond in phenylacetylene across FLP **1b** (Figure 2). The xanthene backbone is virtually planar with tetrahedral boron and phosphorus centres. The phosphorus-bound hydrogen was found in the electron difference map with a P(1)-H(1) distance of 1.19(4) Å, and the boron-bound phenylacetylide moiety shows an almost linear B(1)-C(46)-C(47) angle of 171.7(4)°.

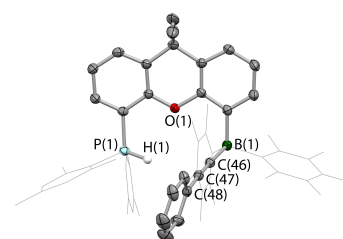


Figure 2. Molecular structure of **2b** as determined by X-ray crystallography. Most H atoms and disordered solvent molecules are omitted and Mes/C $_6\text{F}_5$ groups are shown in wireframe format for clarity; thermal ellipsoids are drawn at the 35% probability level. Key bond lengths (Å) and angles (°): B(1)-C(46) 1.604(5), C(46)-C(47) 1.190(5), P(1)-H(1) 1.19(4), B(1)-C(46)-C(47) 171.7(4).

As noted above, solutions of **2a** in dichloromethane undergo onward reactivity over a period of several hours (while similar solutions of **2b** do not). Monitoring by *in situ* NMR in CD_2Cl_2 shows that on standing at room temperature for 2 hours this process starts to give rise to two new signals at around 20 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. Specifically, these are a broad partially collapsed quartet at 19.1 ppm (with a coupling constant of *ca.* 20 Hz) and a sharp singlet at $\delta_{\text{P}} = -20.1$ ppm. The latter

signal increases in intensity at the expense of the former over time. In addition, changes in the ^1H NMR spectrum over this time period include the appearance (and then decay) of a sharp doublet at $\delta_{\text{H}} = 9.06$ ppm ($J = 38.5$ Hz). Reasoning that this further chemistry might involve the reaction of **2a** with free PhCCH present in the equilibrium mixture, we examined the reaction between **1a** and excess PhCCH. After stirring the reagents in toluene for 14 hours, the solution was concentrated and layered with pentane. Slow diffusion produced colourless crystals of the major product (**3**) suitable for single-crystal X-ray diffraction studies (Scheme 1 and Figure 3). Crystallographic analysis revealed **3** to be a multi-insertion product, in which three molecules of PhCCH have been assimilated by one molecule of the FLP **1a**. Compound **3** features an unusual boracyclohexadiene heterocycle, with one B-bound C_6F_5 group having migrated to form a new C-C bond to the terminal carbon of one of the phenylacetylene moieties. In addition, a further PhCCH molecule has undergone a 1,2-hydrogen shift and bridges between the phosphine and the heterocycle. The ^{31}P NMR spectrum of crystals of **3** in CD_2Cl_2 confirm that the signal at $\delta_{\text{P}} = 20.1$ ppm which appears in the spectrum of **2a** on aging, is due to this multi-insertion product. Moreover, the 3:1 ratio of alkyne:FLP in **3** is consistent with the idea that it is formed from **2a** by assimilation of the 'free' PhCCH liberated through the reversible nature of the C-H activation chemistry. Of additional interest is the observed migration of one of the B-bound C_6F_5 -groups: carbo-boration processes of this sort (involving formal insertion of unsaturated substrates into B-C bonds) are well known, including examples involving the migration of a fluoroaryl ring.¹⁶

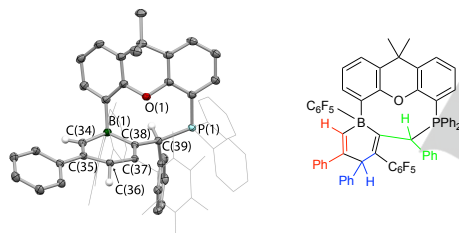
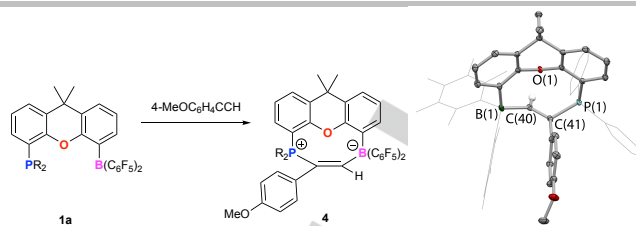


Figure 3. Molecular structure (left) and diagrammatic representation (right) of **3** as determined by X-ray crystallography. Most H atoms and disordered solvent molecules are omitted and selected Ph/ C_6F_5 groups are shown in wireframe format for clarity; thermal ellipsoids are drawn at the 35% probability level. Key bond lengths (Å): P(1)-C(39) 1.881(2), C(38)-C(39) 1.548(2), B(1)-C(34) 1.608(2), C(34)-C(35) 1.339(2), C(35)-C(36) 1.512(2), C(36)-C(37) 1.540(2), C(37)-C(38) 1.339(2), B(1)-C(38) 1.641(2).

In view of the facts (i) that the solid-state structure of **3** features a bridging unit between the phosphorus and boron atoms derived from a single molecule of PhCCH; and (ii) the 1,2-addition of phosphine/borane FLPs across alkynes has literature precedent,¹⁷ we hypothesized that the species giving rise to the signal at $\delta_{\text{P}} = 19.1$ ppm which precedes the formation of **3** might be the corresponding 1,2-alkyne addition product of **1a**. While we were unable to isolate this labile species in the case of PhCCH, the corresponding (stoichiometric) reaction of **1a** with the more electron rich alkyne, 4-MeOC $_6\text{H}_4$ CCH, did yield more promising results. The product of this reaction (**4**, Scheme 2) can be isolated in 79% yield and gives rise to two diagnostic NMR signals.



Scheme 2. (left) Stoichiometric reaction between **1a** and 4-MeOC $_6\text{H}_4$ CCH. (right) Molecular structure of **4** as determined by X-ray crystallography. Most H atoms and disordered solvent molecules are omitted and Ph/ C_6F_5 groups are shown in wireframe format for clarity; thermal ellipsoids are drawn at the 35% probability level. Key bond lengths (Å): B(1)-C(40) 1.6319(18), C(40)-C(41) 1.3480(18), C(41)-P(1) 1.8034(12).

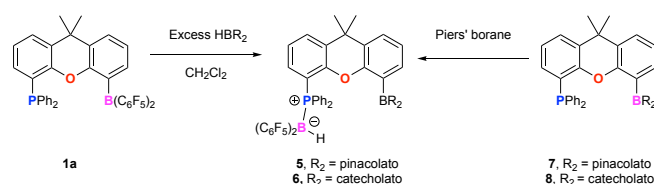
Thus, its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a broad (partially collapsed) 1:1:1:1 quartet at $\delta_{\text{P}} = 18.6$ ppm with a coupling constant of $^3J_{\text{P-B}} = 19.3$ Hz, while the alkyne CH is observed as a doublet at 9.81 ppm ($^3J_{\text{P-H}} = 38.1$ Hz). By means of comparison, the corresponding data measured for $\text{Ph}_3\text{P}(\text{Ph})\text{CC}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3$ are $\delta_{\text{P}} = 25.2$ ($^3J_{\text{P-B}} = 15$ Hz and $^3J_{\text{P-H}} = 36$ Hz).¹⁷ Confirmation that **4** is indeed the 1,2-addition product of **1a** and 4-MeOC $_6\text{H}_4$ CCH can be obtained from single-crystal X-ray diffraction studies on crystals grown from a mixture of toluene and pentane at room temperature (Scheme 2). Both B(1) and P(1) are tetrahedral with the two heteroatoms being linked via a two-carbon bridging unit. The associated bond lengths, B(1)-C(40) = 1.6319(18) Å, C(40)-C(41) = 1.3480(18) Å and C(41)-P(1) = 1.8034(12) Å, are consistent with the presence of a double bond between C(40) and C(41). Thus, these bond metrics are in good agreement with other 1,2 addition products of phenylacetylene with P/B FLPs (e.g. $d(\text{B-C}) = 1.639(2)$ Å, $d(\text{C=C}) = 1.345(5)$ Å, $d(\text{P-C}) = 1.806(1)$ Å, for $\text{Ph}_3\text{P}(\text{Ph})\text{CC}(\text{H})\text{B}(\text{C}_6\text{F}_5)_3$).¹⁷

While the reactions of PhCCH with **1a** do not, on the face of it, shed much light on the mode of action of the FLP in catalytic hydroboration, they do provide potential insight into the widely differing turnover frequencies obtained in the reactions of HBpin with (for example) PhCCH and PhCCMe. It is apparent from stoichiometric studies with the terminal alkyne, that its reactivity towards **1a** in isolation provides a potential avenue through which much of the FLP might be 'tied up' off-cycle via reversible CH activation, and even undergo irreversible catalyst decomposition through the formation of multi-insertion compound **3**. PhCCMe and PhCCPh do not appear to react with **1a** in isolation over the timeframe of the hydroboration chemistry.

FLP reactivity towards boranes

With a view to shedding light on the mechanism by which **1a** effects catalytic hydroboration, we turned our attention to its reactivity towards pinacolborane and related boranes.¹⁸ This system has previously been shown to react with tetra-coordinate systems of the type $\text{R}_3\text{N-BH}_3$ via heterolytic B-H bond cleavage,⁷ but a different mode of reactivity is revealed towards tri-coordinate boranes. Thus, the stoichiometric reaction between **1a** and HBpin can be shown by ^{11}B NMR spectroscopy to give rise to two signals (at $\delta_{\text{B}} = -21.2$ and 31.6 ppm) consistent with the formation of one tetra-coordinate and one tri-coordinate boron atom. The corresponding $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum features two broad singlets at $\delta_{\text{P}} = 14.8$ and 18.2 ppm. A preparative scale reaction carried out using excess HBpin in dichloromethane over a period of 72 h, afforded a pale-yellow

solution from which colourless crystals could be grown by concentration and layering with *n*-hexane. Single-crystal X-ray diffraction allows for structural characterization of the product, **5** (Scheme 3 and Figure 4).



Scheme 3. Formation of **5** and **6** by the reaction of **1a** with HBpin and HBcat and via the addition of Piers' borane to **7** and **8**.

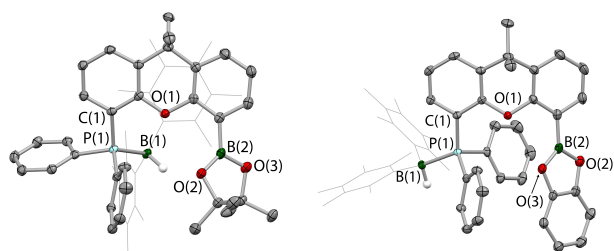


Figure 4. Molecular structures of **5** (left) and **6** (right) as determined by X-ray crystallography. Most H atoms and solvent molecules are omitted and Mes/C₆F₅ groups are shown in wireframe format for clarity; thermal ellipsoids are drawn at the 35% probability level. Key bond lengths (Å): P(1)-B(1) 2.021(3) (for **5**); 1.978(2) (for **6**).

Compound **5** crystallizes in the monoclinic C2/c space group with one molecule of **5**, and disordered hexane and dichloromethane solvent molecules in the asymmetric unit. The structural analysis shows that FLP **1a** has reacted with one molecule of HBpin via borane exchange, leading to formation of an ArBpin function with accompanying migration of the B(C₆F₅)₂ group (as HB(C₆F₅)₂) to the phosphine through construction of a P-B coordinate bond. Both P(1) and B(1) are tetrahedral with a P(1)-B(1) bond length of 2.021(3) Å, while the geometry around B(2) is trigonal planar as expected for a tri-coordinate boron atom.

The ¹H, ¹¹B, ³¹P and ¹⁹F NMR spectra measured for isolated crystalline samples of **5** are found to be identical to those obtained *in situ* for the reaction of **1a** and HBpin. The solid-state structure of **5** does not, however, explain the presence of two sets of signals in these spectra (e.g. in the ³¹P NMR spectrum at $\delta_P = 14.8$ and 18.2 ppm). Looking closely at the X-ray structure of **5** we wondered whether the origin of the two signals could be the presence of rotational isomers in solution – relating to restricted rotation about the Ar-P bond, given the large steric bulk of the P-bound HB(C₆F₅)₂ unit and the presence of the –Bpin function (with four pendant CH₃ groups) acting, in effect, as a ‘ratchet’. Two further observations are consistent with this observation: (i) VT-NMR shows that the two ³¹P signals coalesce into a singlet at 15.9 ppm at 373 K (see ESI); and (ii) the use of the less bulky borane HBcat – while bringing about similar chemistry – gives a product which is characterized by only one ³¹P signal at room temperature.

The reaction of excess catecholborane (HBcat) with **1a** yields **6**, the structure of which is superficially very similar to that

of **5** (Scheme 3 and Figure 4). As such, analogous migration of the B(C₆F₅)₂ group to the phosphine has occurred with accompanying formation of a new aromatic carbon-boron bond. Compound **6** features four coordinate P(1) and B(2) centres, with the associated P-B bond length (1.978(2) Å) being notably shorter than that found in **5** (2.021(3) Å), despite the presence of identical –Ph₂PBH(C₆F₅)₂ functions in each case. Closer inspection shows that the rotational alignment of the P- and B-bound substituents about the P-B bond in **6** is close to an ideal staggered arrangement (with torsional angles falling in the range of 50–70°), while in **5** the same substituents are much closer to being eclipsed (torsions: 10–20°). This in turn reflects the positioning of the HB(C₆F₅)₂ group itself: in **6** rotation about the P(1)-C(1) bond places it away from the ArBcat moiety in space, while in **5** it is projected towards the ArBpin unit and is presumably subject to a much more sterically crowded environment. Consistently, NMR studies carried out on **6** reveal only one ³¹P{¹H} NMR resonance at room temperature (at $\delta_P = 13.4$ ppm) in contrast to the two signals observed for **5**. The –Bcat unit offers a less demanding three-dimensional steric profile than –Bpin, which therefore presumably presents less of a barrier to rotation about the P-Ar bond.

The ‘migrated’ species **5** and **6** both feature Piers' borane,¹³ HB(C₆F₅)₂, coordinated to the phosphine moiety, and we wanted to know if the two compounds could be synthesized via a more logical approach – e.g. via the direct reaction of Piers' borane itself with the FLP analogues of **1a** featuring –Bpin or –Bcat as the Lewis acid component (**7** and **8**; Scheme 3, right). Accordingly, compounds **7** and **8** were synthesized by reacting 4-(diphenylphosphino)(5-lithio)-9,9-dimethylxanthene with ClBpin or ClBcat, respectively, in *n*-hexane, and characterized in each case by standard spectroscopic, analytical and crystallographic techniques (Figure 5). Both compounds are shown to contain unquenched (tri-coordinate) borane and phosphine components, featuring P-B separations of 4.548(2) and 4.383(3) Å, respectively. In C₆D₆ solution, **7** and **8** show signals at 31.0 and 32.0 ppm (¹¹B{¹H}) and –14.0 and –13.0 ppm (³¹P{¹H}), respectively. Moreover, as expected, the addition of one equivalent of Piers' borane to **7/8** gives identical spectra to samples of **5/6** obtained from **1a**; uptake of the HB(C₆F₅)₂ fragment at phosphorus is apparently quantitative, with no evidence being found for the existence of free borane in solution at equilibrium.

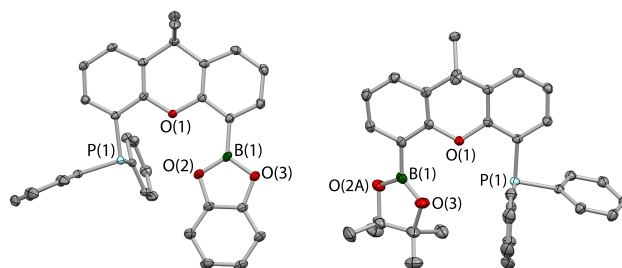


Figure 5. Molecular structures of **7** (left) and **8** (right) as determined by X-ray crystallography. H atoms are omitted for clarity; thermal ellipsoids are drawn at the 35% probability level. Key distances (Å): P(1)···B(1) 4.383(3)/4.377(2) (for **7**); 4.548(2) (for **8**).

An additional feature of interest in respect of the phosphine/borane adducts **5** and **6** is the mechanism by which

they are accessed from **1a** and HBpin/HBcat. To probe whether this rearrangement is unique to **1a** (or at least is facilitated in some way by the presence of the phosphine component), we probed the simpler reaction between $\text{PhB}(\text{C}_6\text{F}_5)_2$ and HBpin for evidence of borane exchange under ambient conditions. Thus, a mixture of $\text{PhB}(\text{C}_6\text{F}_5)_2$ and ca. 0.5 equivalents of HBpin in C_6D_6 was monitored by ^1H , ^{11}B and ^{19}F NMR, over a period of 72 h at room temperature. These studies reveal the formation of three new boron-containing species in addition to unreacted $\text{PhB}(\text{C}_6\text{F}_5)_2$. The ^1H NMR spectrum features signals for H_2 , PhBpin, and Piers' borane,¹³ with the latter two and the third new compound, $\text{B}(\text{C}_6\text{F}_5)_3$, being additionally identified via ^{11}B and ^{19}F NMR spectroscopy. Evidently substituent exchange under these conditions is facile, with the formation of $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$ and PhBpin in this simple system being consistent with the C-B/B-H exchange observed in the formation of **5/6** from **1a**.

In addition to model experimental studies, the reaction mechanism of substituent exchange between $\text{PhB}(\text{C}_6\text{F}_5)_2$ and HBpin was studied computationally by DFT calculations. All geometry optimizations were carried out using the PBE1PBE exchange-correlation functional in combination with the def-TZVP basis set. Ph/H exchange was found to be exergonic overall by 10 kJ mol^{-1} with a transition state being located at 111 kJ mol^{-1} corresponding to concerted transfer of the two fragments between the Bpin and $\text{B}(\text{C}_6\text{F}_5)_2$ centres (Figure 6). The calculated barrier is consistent with the experimental findings (exchange at room temperature and above) and implies more generally that carbon-boron bonds in systems of the type $\text{ArB}(\text{C}_6\text{F}_5)_2$ are potentially labile in the presence of boranes of this type.

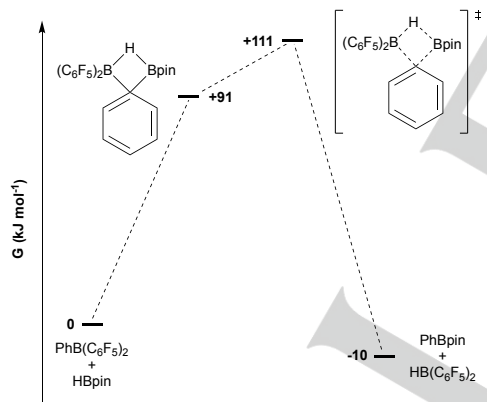


Figure 6. Calculated reaction barrier for exchange of Ph/H substituents between $\text{PhB}(\text{C}_6\text{F}_5)_2$ and HBpin.

Mode of FLP action in catalysis

With the stoichiometric reactions between **1a** with PhCCH/HBpin mapped out, the mode of action of the FLP in the catalytic hydroboration of alkynes was investigated. In particular given (i) the formation of **5** from **1a** in the presence of HBpin; and (ii) previous reports from Stephan and co-workers of alkyne hydroboration using $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$ as the pre-catalyst,¹² we hypothesized that the apparent catalytic activity of **1a** might be due to its conversion to **5** and subsequent release of Piers' borane into solution. Although NMR studies show that isolated samples of **5** do not spontaneously release the $\text{HB}(\text{C}_6\text{F}_5)_2$ fragment, Stephan has shown that catalysis of the

HBpin/PhCCH reaction by $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$ proceeds via initial hydroboration of the alkyne by the more reactive borane to give *trans*- $\text{PhC}(\text{H})=\text{C}(\text{H})\text{B}(\text{C}_6\text{F}_5)_2$ (and then to the proposed active form of the catalyst, $\text{PhCH}_2\text{CH}(\text{Bpin})\text{B}(\text{C}_6\text{F}_5)_2$).¹² With this in mind, we could show that **5** reacts with excess PhCCH to form $\text{PhC}(\text{H})=\text{C}(\text{H})\text{B}(\text{C}_6\text{F}_5)_2$ (**9**) in a timeframe consistent with the observed catalysis (in effect, faster than a ^1H NMR spectrum could be acquired). In a similar fashion, the reactions with excess PhCCMe or PhCCPh rapidly yield the corresponding hydroboration products $\text{PhC}(\text{H})=\text{C}(\text{R})\text{B}(\text{C}_6\text{F}_5)_2$ ($\text{R} = \text{Me}, \text{Ph}$), respectively.^{13b}

In the case of PhCCMe and PhCCPh, it can readily be shown that **1a** is not only chemically competent to produce the pre-catalyst $\text{PhC}(\text{H})=\text{C}(\text{R})\text{B}(\text{C}_6\text{F}_5)_2$, but kinetically competent too. Thus, the performance of **1a** in the catalytic hydroboration of both of these alkynes by HBpin (Figure 7) is very similar to the data reported by Stephan using Piers' borane as the pre-catalyst (e.g. for PhCCMe: 95% conversion in 3 h at room temperature using 10 mol% of **1a**; cf. 94% in 5 h at room temperature using 5 mol% $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$). Moreover, in the case of PhCCMe the regioselectivity of the catalytic hydroboration using **1a** (89:11 in favour of the anti-Markovnikov product) is essentially identical to that reported using $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$ (88:12).¹² These data suggested to us that it is rearrangement of **1a** to **5** and the subsequent availability of the $\text{HB}(\text{C}_6\text{F}_5)_2$ fragment which is responsible for the catalytic hydroboration of PhCCMe/PhCCPh by **1a**.

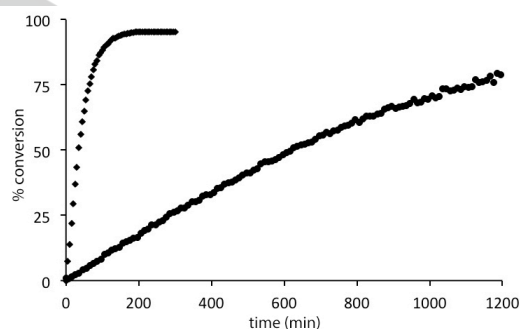


Figure 7. Plot of % conversion vs time for the hydroboration of PhCCMe (♦) and PhCCPh (●) by HBpin catalysed by **1a** (10 mol%, CD_2Cl_2 solution, room temp.).

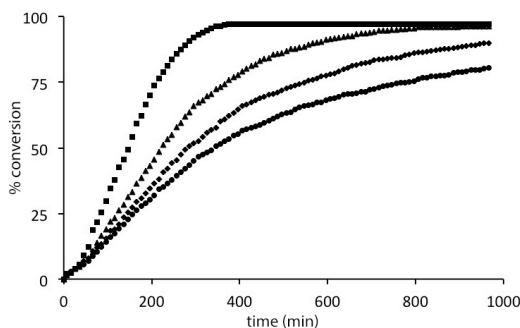
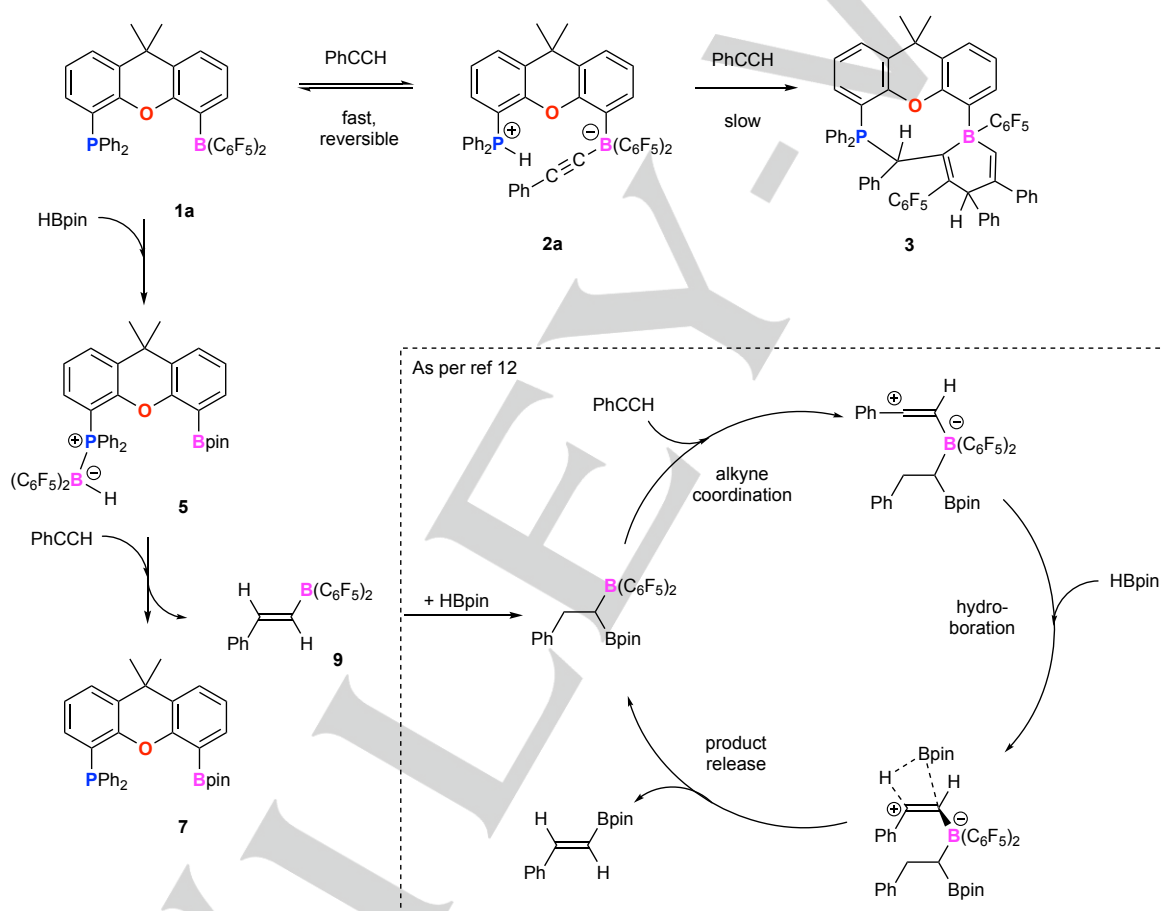


Figure 8. Plot of % conversion vs time for the hydroboration of PhCCH by HBpin catalysed by **1a** at different catalyst loadings in CD_2Cl_2 solution. Key: ■ 20 mol%; ▲ 10 mol%; ◆ 5 mol%; ● 2.5 mol%.

With this mode of operation in mind, the catalytic performance of **1a** in the hydroboration of PhCCH is apparently anomalous. The use of $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$ as the pre-catalyst in this reaction is reported to bring about 90% conversion in 5 h using 5 mol% catalyst at room temperature. In the case of reaction catalysed by **1a**, conversion is somewhat slower (Figure 8): the reaction only reaches completion in <12 h at room temperature at very high (10–20 mol%) catalyst loadings, and at 5 mol% is only 80–85% complete after 12 h. Moreover, catalytic performance at a range of loadings is characterized by a noticeable induction period which is absent in the kinetic plots for either of the internal alkynes.

The use of **5** (or **9**) as the pre-catalyst, by contrast, gives hydroboration activity which is comparable to that reported using $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$, suggesting that the poorer performance using **1a** (and the induction period seen in Figure 8) is related to the

formation of **5** from **1a** in the presence of PhCCH. Moreover, the comparable performance of **1a** to $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$ in the hydroboration of PhCCMe and PhCCPh¹² suggests that it is the presence of the terminal alkyne which is inhibiting the conversion of **1a** to **5**. This hypothesis is readily confirmed by *in situ* NMR monitoring under catalytic conditions (**1a** plus 10 equivalents of PhCCH/HBpin). ³¹P{¹H} NMR shows that at short reaction times **1a** is converted almost exclusively into the C–H activation product **2a**, together with traces of the multi-insertion compound **3**. While the formation of the former is known to be reversible, and evidence for the formation of **5** can be seen after 30 min, it is apparent that the reaction of **1a** with PhCCH is much faster than that with HBpin, such that even after 120 min, much of the FLP is 'tied up' as **2a**, and therefore not able to contribute catalytically (Scheme 3).



Scheme 3. Proposed catalytic cycle for the hydroboration of PhCCH by FLP **1a**.

Conclusions

We have shown that the xanthene-based FLP **1a** – which has previously been shown to be capable of the reversible activation of H_2 ,⁶ can also effect similar (reversible) cleavage of the C–H bond in phenylacetylene, PhCCH. FLP **1a** also reacts with B–H bonds, such as those in HBpin and HBcat, although in a different fashion, proceeding via C–B/B–H exchange. This process leads to replacement of the $-\text{B}(\text{C}_6\text{F}_5)_2$ Lewis acid component

by $-\text{Bpin}/-\text{Bcat}$ and transfer of $\text{HB}(\text{C}_6\text{F}_5)_2$ to the phosphine Lewis base. Moreover, it also proves to be at the heart of the ability of **1a** to act as a catalyst for the hydroboration of alkynes by HBpin (Scheme 3): the active species is derived from the $\text{HB}(\text{C}_6\text{F}_5)_2$ fragment generated in this exchange process. In the case of the internal alkynes PhCCMe and PhCCPh, this leads to catalytic performance which is comparable to that reported using $\{\text{HB}(\text{C}_6\text{F}_5)_2\}_n$ itself, while with PhCCH, the apparently faster rate of C–H activation chemistry means that much of the FLP is

sequestered as the phosphonium acetylide, and catalytic turnover is much slower.

Experimental Section

General methods: All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent and stored over potassium or 4 Å sieves. NMR spectra were measured in benzene- d_6 (dried over potassium), dichloromethane- d_2 (dried over CaH_2), or toluene- d_8 (dried over potassium), with the solvent then being distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. The ^1H , ^{13}C , ^{11}B , ^{31}P , and ^{19}F NMR spectra were recorded on Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer at ambient temperature and referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm), ^{31}P resonances are referenced externally to H_3PO_4 (85 %), ^{19}F chemical shifts to CF_3COOH , and ^{11}B chemical shifts to $\text{BF}_3\cdot\text{Et}_2\text{O}$. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. 4-(Diphenylphosphino)-9,9-dimethylxanthene,²⁰ FLPs **1a** and **1b**,^{6,7} ClBpin,²¹ ClBcat,²² and $\text{PhB}(\text{C}_6\text{F}_5)_2$ ²³ were prepared by literature methods. All other reagents were used as received.

Details of the X-ray diffraction measurements: Single-crystal X-ray diffraction data for **2b–8** were collected at 150 K on Oxford Diffraction/Agilent SuperNova diffractometers with $\text{Cu-K}\alpha$ ($\lambda = 1.54184$ Å) radiation equipped with nitrogen gas Oxford Cryosystems Cryostream unit.²⁴ Raw frame data were reduced using CrysAlisPro.²⁵ The structures were solved using SHELXT²⁶ and refined to convergence on R^2 and against all independent reflections by full-matrix least-squares using SHELXL²⁷ in combination with the SHELXLE²⁸ program. Distances and angles were calculated using the full covariance matrix. Selected crystallographic data are summarized in the tables S1–S2 and full details are given in the supplementary deposited CIF files (CCDC 1827962–1827968). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Computational details: All computational work reported here utilized the density functional theory (DFT) level with Gaussian09 (Revision D.01) program package.²⁹ Geometry optimizations were performed with the PBE1PBE exchange-correlation functional using def-TZVP basis sets.³⁰ The nature of all stationary points found (minimum or saddle point) was confirmed by full frequency calculations.

Synthesis of compound 2a: FLP **1a** (0.100 g, 0.14 mmol) was dissolved in toluene (1.5 mL) and phenylacetylene (16 μL , 0.14 mmol) was added at room temperature. After 30 min, a white precipitate formed and the solvent was removed by filtration. The precipitate was washed with pentane (3 x 5 mL) and dried *in vacuo* to afford **2a** as a white solid (0.075 g, 81%). The compound is stable in CD_2Cl_2 for 2 h at room temperature. Attempts to crystallize compound **2a** from various solvents were unsuccessful as it converted into multi-insertion product **3**. ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta = 1.72$ (br, 6H, XAN-C(CH_3)₂), 6.68 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 1H, ArH), 6.72–6.78 (m, 1H, ArH), 6.95 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, ArH), 7.01–7.11 (m, 8H, ArH), 7.13–7.17 (m, 2H, ArH), 7.34–7.39 (m, 4H, ArH), 7.62–7.66 (m, 2H, ArH), 7.88 (d, $^3J_{\text{H-H}} = 8.0$ Hz, 1H, ArH), and 10.50 ppm (d, $^1J_{\text{P-H}} = 544$ Hz, 1H, P-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , 258 K): $\delta = 21.3$ (XAN-C(CH_3)₂), 34.7 (XAN-C(CH_3)₂), 100.9 (PhCCB), 114.6 (PhCCB), 122.7, 123.8, 124.1 (d, $^1J_{\text{C-P}} = 19.4$ Hz), 125.2, 126.2, 126.9, 127.9, 128.2, 128.5, 129.0, 129.9 (d, $^1J_{\text{C-P}} = 13.4$ Hz), 131.7 (d, $^2J_{\text{C-P}} = 4.5$ Hz), 132.3, 133.5 (d, $^1J_{\text{C-P}} = 11.6$ Hz), 134.0 (d, $^1J_{\text{C-P}} = 5.9$ Hz), 134.9 (d, $^1J_{\text{C-P}} = 2.7$ Hz), 137.0 (dm, $^1J_{\text{C-F}} = 235$ Hz), 137.8 (dm, $^1J_{\text{C-F}} = 238$ Hz),

148.6 (d, $^1J_{\text{C-F}} = 253$ Hz) 153.6, and 155.4 ppm (ArC). ^{11}B NMR (128 MHz, CD_2Cl_2 , 298 K): $\delta = -18.4$ ppm (br). ^{31}P NMR (162 MHz, CD_2Cl_2 , 298 K): $\delta = -9.1$ ppm (d, $^1J_{\text{P-H}} = 544$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CD_2Cl_2 , 298 K): $\delta = -131.4$ (br, *o*-CF, 4F), -161.2 (t, $^3J_{\text{F-F}} = 20.7$ Hz, 2F, *p*-CF), and -166.0 ppm (m, *m*-CF, 4F). No reliable microanalysis was obtained due to the instability of the compound.

Preparation of Compound 2b: FLP **1b** (0.164 g, 0.20 mmol) was dissolved in dichloromethane (3 mL). Phenylacetylene (25 μL , 0.23 mmol) was added to the solution yielding an instant colour change from bright yellow to colourless. The solution was stirred at room temperature for 16 h, filtered, concentrated, and layered with hexane to yield colourless crystals of **2b** (0.081 g, 44%). ^1H NMR (400 MHz, CD_2Cl_2 , 298 K): $\delta = 1.73$ (br, 6H, XAN-C(CH_3)₂), 1.88 (br, 12H, *o*-CH₃ of Mes), 2.32 (s, 6H, *p*-CH₃ of Mes), 6.71 (d, $^3J_{\text{H-H}} = 6.9$ Hz, 1H, ArH), 6.83–6.91 (m, 4H, MesH), 6.96 (m, 2H, ArH), 7.11 (td, $^3J_{\text{H-H}} = 7.7$ Hz, $^3J_{\text{H-H}} = 2.7$ Hz, 1H, ArH), 7.16 (m, 3H, ArH), 7.24 (m, 2H, ArH), 7.33 (dd, $^3J_{\text{H-H}} = 7.9$ Hz, $^3J_{\text{H-H}} = 1.6$ Hz, 1H, ArH), 7.86 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 1H, ArH), and 10.18 ppm (d, $^1J_{\text{P-H}} = 532$ Hz, 1H, P-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): $\delta = 21.0$ (Mes-CH₃), 21.4 (XAN-C(CH_3)₂), 21.8 (Mes-CH₃), 21.9 (Mes-CH₃), 34.7 (XAN-C(CH_3)₂), 104.3 (PhCCB), 105.0 (PhCCB), 123.5, 124.2, 124.3, 124.4, 126.6, 127.2, 127.9, 128.4, 128.8, 131.9, 132.1 (br), 132.4, 133.3 (d, $^1J_{\text{P-C}} = 9.4$ Hz), 133.8, 134.0 (d, $^1J_{\text{P-C}} = 6.4$ Hz), 134.6 (d, $^2J_{\text{P-C}} = 1.5$ Hz), 135.8 (br), 137.5 (br), 139.3 (br), 144.2 (br), 146.3 (br), 147.8 (br), 149.7 (br), 154.0 and 155.1 ppm (d, $^2J_{\text{P-C}} = 2.4$ Hz). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CD_2Cl_2 , 298 K): $\delta = -17.9$ ppm (s). ^{31}P NMR (162 MHz, CD_2Cl_2 , 298 K): $\delta = -27.3$ ppm (dd, $^1J_{\text{P-H}} = 532$ Hz, $^3J_{\text{P-H}} = 14$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CD_2Cl_2 , 298 K): $\delta = -129.7$ (br, 2F, *o*-CF), -131.9 (br, 1F, *o*-CF), -135.3 (br, 1F, *o*-CF), -159.8 (br, 1F, *p*-CF), -162.9 (br, 1F, *p*-CF), -166.4 (br, 4F, *m*-CF). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, CD_2Cl_2 , 240 K): $\delta = -130.0$ (dd, $^3J_{\text{F-F}} = 26.0$ Hz, $^4J_{\text{F-F}} = 6.0$ Hz, 1F, *o*-CF), -130.4 (dd, $^3J_{\text{F-F}} = 25.4$ Hz, $^4J_{\text{F-F}} = 8.2$ Hz, 1F, *o*-CF), -131.9 (d, $^3J_{\text{F-F}} = 25.9$ Hz, 1F, *o*-CF), -136.2 (d, $^3J_{\text{F-F}} = 25.1$ Hz, 1F, *o*-CF), -158.8 (t, $^3J_{\text{F-F}} = 21.2$ Hz, 1F, *p*-CF), -162.3 (t, $^3J_{\text{F-F}} = 21.2$ Hz, 1F, *p*-CF), -165.4 (m, 2F, *m*-CF), -166.3 (t, $^3J_{\text{F-F}} = 23.1$ Hz, 1F, *m*-CF) and -166.6 ppm (t, $^3J_{\text{F-F}} = 23.2$ Hz, 1F, *m*-CF). Elemental anal. calc. for $\text{C}_{47}\text{H}_{30}\text{BF}_{10}\text{OP} + \text{CH}_2\text{Cl}_2$: C 64.24% and H 4.19%, found C 64.67% and H 4.66%.

Synthesis of compound 3: Phenylacetylene (0.35 mL, 3.17 mmol) was added to a stirred solution of **1a** (0.150 g, 0.32 mmol) in toluene (10 mL). The mixture was stirred for 20 h at room temperature after which the yellow solution was concentrated and layered with pentane. Multi-insertion product **3** crystallized as colourless crystals suitable for single-crystal X-ray diffraction studies. The solvent was decanted, and the crystals washed with pentane (3 x 5 mL) to yield 0.035 g (12%) of **3**. ^1H NMR (400 MHz, C_6D_6 , 298K): $\delta = 1.43$ (s, 3H, XAN-C(CH_3)₂), 1.67 (s, 3H, XAN-C(CH_3)₂), 4.79 (s, 1H, PhCCH), 6.40 (s, 1H B-Ar-CH), 6.44 (d, $^3J_{\text{H-H}} = 6.5$ Hz, 1H, XAN-ArH), 6.45–6.53 (m, 5H, ArH), 6.61–6.66 (m, 5H, ArH), 6.71–6.82 (m, 10H, P-ArH), 6.92 (t, $^3J_{\text{H-H}} = 7.08$ Hz, 1H, XAN-ArH), 7.03–7.12 (m, 5H, ArH), 7.26 (dd, $^3J_{\text{H-H}} = 7.4$ Hz, $^1J_{\text{P-H}} = 13.8$ Hz, 1H, XAN-ArH), 7.36 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 1H, ArH), 7.51 (s, 1H, ArH), 7.58 (d, $^3J_{\text{H-H}} = 7.5$ Hz, 1H, XAN-ArH), and 7.88 ppm (d, $^3J_{\text{H-H}} = 7.2$ Hz, 1H, XAN-ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 298 K): $\delta = 26.0$ (XAN-C(CH_3)₂), 33.3 (XAN-C(CH_3)₂), 58.4 (d, $^1J_{\text{P-C}} = 12.2$ Hz, Ph₂P-C-Ph), 59.6, 106.4, 107.4, 119.7, 120.3, 125.3, 125.5 (d, $^1J_{\text{P-C}} = 11.1$ Hz), 125.6, 125.8, 127.1, 127.5 (d, $^1J_{\text{P-C}} = 9.1$ Hz), 128.5, 128.8 (d, $^1J_{\text{P-C}} = 4.8$ Hz), 129.1 (d, $^1J_{\text{P-C}} = 5.6$ Hz), 129.3, 129.6, 131.6 (d, $^1J_{\text{P-C}} = 12.5$ Hz), 132.6 (d, $^1J_{\text{P-C}} = 8.6$ Hz), 133.0 (d, $^1J_{\text{P-C}} = 7.3$ Hz), 133.0, 133.3 (d, $^1J_{\text{P-C}} = 4.8$ Hz), 133.5 (d, $^1J_{\text{P-C}} = 4.2$ Hz), 134.3, 134.4 (d, $^1J_{\text{C-F}} = 235$ Hz), 134.5, 135.4, 136.5 (d, $^1J_{\text{P-C}} = 6.3$ Hz), 136.7, 136.8 (d, $^1J_{\text{C-F}} = 234$ Hz), 137.0 (d, $^1J_{\text{C-F}} = 251$ Hz), 138.7 (d, $^1J_{\text{C-F}} = 245$ Hz), 143.0 (d, $^1J_{\text{C-F}} = 234$ Hz), 144.4, 145.6, 144.4, 145.8, 146.2 (d, $^1J_{\text{C-F}} = 238$ Hz), 152.4, and 158.3 ppm (ArC). ^{11}B NMR (128 MHz, C_6D_6 , 298 K): $\delta = 11.8$ ppm (s). ^{31}P NMR (162 MHz, C_6D_6 , 298K): $\delta = 20.1$ ppm (s). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, C_6D_6 , 298 K): $\delta = -125.7$ (d, $^3J_{\text{F-F}} = 42.0$ Hz, 1F, *o*-CF), -130.6 (d, $^3J_{\text{F-F}} = 37.6$ Hz, 1F, *o*-CF), -132.2 (d, $^3J_{\text{F-F}} = 39.9$ Hz, 1F, *o*-CF), -135.1 (d, $^3J_{\text{F-F}} = 37.1$ Hz, 1F, *o*-CF), -156.7 (t, $^3J_{\text{F-F}} = 24.3$ Hz, 1F, *p*-CF), -159.2 (m, 1F, *m*-CF), -162.2 (m, 1F, *m*-CF), -163.2 (t, $^3J_{\text{F-F}} = 25.3$ Hz, 1F, *p*-CF), -166.1 (m, 1F, *m*-CF), and -167.8 ppm (m, 1F, *m*-CF). Elemental anal. calc. for $\text{C}_{63}\text{H}_{40}\text{BF}_{10}\text{OP} +$

C₇H₈ + 0.5 C₅H₁₂: C 74.24% and H 4.64%, found C 74.41% and H 4.46%.

Synthesis of compound 4: FLP **1a** (0.100 g, 0.14 mmol) was dissolved in toluene (1.5 mL). 4-MeOC₆H₄CCH (19 µL, 0.15 mmol) was then added and the mixture was stirred for 14 h at room temperature. The solvent was removed by filtration, the white precipitate washed with pentane (3 x 5 mL) and dried *in vacuo* to afford compound **4** as a white solid (0.075 g, 79%). Single crystals suitable for X-ray diffraction studies were grown by slow diffusion from a toluene/pentane mixture at room temperature. ¹H NMR (500 MHz, C₆D₆, 298 K): δ = 1.42 (s, 3H, XAN-C(CH₃)₂), 1.60 (s, 3H, XAN-C(CH₃)₂), 3.23 (s, 3H, OCH₃), 6.21 (d, ³J_{H-H} = 7.8, 2H, ArH), 6.49-6.56 (m, 4H, MeO-ArH), 6.67 (t, ³J_{H-H} = 7.8, 2H, ArH), 6.79 (dd, ¹J_{P-H} = 14.2 Hz, ³J_{H-H} = 7.5 Hz, 1H, ArH), 7.02-7.16 (m, 10H, ArH), 7.39 (d, ³J_{H-H} = 7.8 Hz, 1H, ArH), 7.56 (dd, ³J_{H-H} = 12.7, ³J_{H-H} = 7.7 Hz, 1H, ArH), 7.82 (d, ³J_{H-H} = 6.6 Hz, 1H, ArH), and 9.81 ppm (d, ¹J_{P-H} = 38.1 Hz, 1H, P-H). ¹³C{¹H} NMR (101 MHz, C₆D₆, 298 K): δ = 21.1 (XAN-C(CH₃)), 26.5 (XAN-C(CH₃)₂), 27.6 (XAN-C(CH₃)₂), 55.4 (CH₃-O-PhCC), 120.4, 121.0, 121.2, 121.8, 123.4, 123.6 (d, ¹J_{P-C} = 12.1 Hz), 125.4 (MeO-PhC=CH-B(C₆F₅)₂), 127.4, 129.0 (d, ¹J_{P-C} = 11.7 Hz), 128.4, 129.2, 130.3 (d, ¹J_{P-C} = 12.6 Hz, MeO-Ph-C-PPH₂), 131.6 (d, ¹J_{P-C} = 2.9 Hz), 132.3 (dm, ¹J_{C-F} = 237 Hz), 132.7, 132.8 (d, ¹J_{P-C} = 10.2 Hz), 132.9 (d, ¹J_{P-C} = 3.4 Hz), 135.5 (dm, ¹J_{C-F} = 257 Hz), 133.8 (d, ¹J_{P-C} = 8.7 Hz), 134.8 (d, ¹J_{P-C} = 9.9 Hz), 135.4, 138.2 (dm, ¹J_{C-F} = 236 Hz), 140.3 (d, ¹J_{P-C} = 3.1 Hz), 156.5 ppm (d, ¹J_{P-C} = 3.1 Hz) and 160.2 ppm (ArC). ¹¹B NMR (160 MHz, C₆D₆, 298 K): δ = -11.9 ppm (s). ³¹P NMR (202 MHz, C₆D₆, 298 K): δ = 18.6 ppm (q, ³J_{P-B} = 19.3 Hz). ¹⁹F{¹H} NMR (470 MHz, C₆D₆, 298 K): δ = -127.6 (br, 4F, o-CF), -162.3 (t, ³J_{F-F} = 45.7 Hz, 2F, p-CF), and -167.3 ppm (br, 4F, m-CF). Elemental anal. calc. for C₄₈H₃₀B₁₀O₂P: C 66.23% and H 3.47% found C 66.34% and H 3.60%.

Synthesis of compound 5: FLP **1a** (0.136 g, 0.18 mmol) was dissolved in dichloromethane (4 mL) and HBpin (0.1 mL, 0.69 mmol) was added dropwise at room temperature. The yellow solution was stirred at room temperature for 3 d after which the colour had faded to pale yellow. The reaction mixture was filtered, concentrated, and layered with *n*-hexane to yield colourless crystals suitable for single-crystal X-ray diffraction studies upon standing at -30 °C. Yield 0.051 g (33%). ¹¹B{¹H} NMR (128 MHz, C₇D₈, 298 K): δ = -21.2 (s, HB(C₆F₅)₂) and 31.6 ppm (s, B-O). ³¹P{¹H} NMR (162 MHz, C₇D₈, 298 K): δ = 14.8 (br s) and 18.2 ppm (br s). ¹⁹F{¹H} NMR (376 MHz, C₇D₈, 298 K): δ = -127.2 (d, ³J_{F-F} = 23.7 Hz, 4F, o-CF), -158.1 (t, ³J_{F-F} = 19.2 Hz, 2F, p-CF), and -164.2 ppm (td, ³J_{F-F} = 23.5 Hz, ⁴J_{F-F} = 8.3 Hz, 4F, m-CF). ¹H NMR (400 MHz, C₇D₈, 373 K): δ = 0.84 (s, 12H, Bpin-CH₃), 1.33 (s, 6H, XAN-C(CH₃)₂), 4.70 (br, 1H, B-H), 6.87 (t, ³J_{H-H} = 7.5 Hz, 2H, ArH), 6.95-7.04 (m, 7H, ArH), 7.18 (d, ³J_{H-H} = 7.6 Hz, 1H, ArH), 7.33 (m, 1H, ArH), 7.61 (br, 4H, ArH) and 7.75 ppm (d, ³J_{H-H} = 6.5 Hz, 1H, ArH). ¹¹B{¹H} NMR (128 MHz, C₇D₈, 373 K): δ = -20.8 (s, HB(C₆F₅)₂) and 30.2 ppm (s, B-O). ³¹P{¹H} NMR (162 MHz, C₇D₈, 373 K): δ = 15.9 ppm (br s). We were not able to obtain ¹³C{¹H} NMR spectrum due to decomposition of the compound at elevated temperatures. Elemental anal. calc. for C₄₅H₃₅B₂F₁₀O₃P: C 62.39% and H 4.07%, found C 62.31% and H 3.81%.

Synthesis of compound 6: FLP **1a** (0.127 g, 0.17 mmol) was dissolved in dichloromethane (4 mL) and HBcat (0.05 mL, 0.47 mmol) was added dropwise at room temperature. The yellow solution was stirred at room temperature for 3 d to afford a colourless solution. The reaction mixture was filtered, concentrated, and layered with *n*-hexane to yield colourless crystals suitable for single-crystal X-ray diffraction studies upon standing at -30 °C. Yield 0.075 g (51%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 1.26 (s, 6H, XAN-C(CH₃)₂), 4.60 (br, 1H, B-H) 6.69-6.74 (m, 6H, ArH), 6.80 (t, ³J_{H-H} = 7.5 Hz, 1H, ArH), 6.84-6.92 (m, 4H, catH), 6.96 (t, ³J_{H-H} = 7.8 Hz, 1H, ArH), 7.12 (d, ³J_{H-H} = 7.5 Hz, 1H, ArH), 7.25 (d, ³J_{H-H} = 7.5 Hz, 1H, ArH), 7.46 (t, ³J_{H-H} = 9.5 Hz, 4H, ArH), 7.54 (d, ³J_{H-H} = 6.9 Hz, 1H, ArH), and 8.26 ppm (br, 1H, ArH). ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 30.4 (XAN-C(CH₃)₂), 34.7 (XAN-C(CH₃)₂), 112.6, 112.7 (Bcat O-C), 115.0, 116.7 (B-C), 122.8, 123.0, 124.3, 124.4 (d, ¹J_{P-C} = 13.5 Hz), 125.9, 126.4, 128.0, 128.2, 128.3, 129.2, 130.5, 131.3, 131.3 (d, ¹J_{P-C} = 2.7 Hz), 132.8 (d, ¹J_{P-C} = 8.5 Hz), 133.3 (d, ¹J_{P-C} = 3.8 Hz), 135.7,

137.5 (dm, ¹J_{C-F} = 260 Hz), 140.0 (dm, ¹J_{C-F} = 251 Hz), 148.1, 148.5, 148.7 (dm, ¹J_{C-F} = 237 Hz), 153.7 (d, ²J_{P-C} = 2.0 Hz), and 154.6 ppm (ArC). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 298 K): δ = -21.8 (s, HB(C₆F₅)₂) and 31.8 ppm (s, B-O). ³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ = 13.4 ppm (s). ¹⁹F{¹H} NMR (376 MHz, C₆D₆, 298 K): δ = -127.4 (br, 4F, o-CF), -157.9 (t, ³J_{F-F} = 19.6 Hz, 2F, p-CF) and -164.1 ppm (m, 4F, m-CF). Elemental anal. calc. for C₄₅H₂₇B₂F₁₀O₃P: C 62.97% and H 3.17%, found C 62.90% and H 3.17%.

Synthesis of compound 7: 4-(Diphenylphosphino)-9,9-dimethylxanthene (2.138 g, 5.39 mmol) was dissolved in Et₂O (40 mL) and cooled to -78 °C. ⁿBuLi (3.6 mL, 1.6 M, 5.76 mmol) was added dropwise. The mixture was slowly warmed up to room temperature and stirred for 16 h. The resulting off-white precipitate was allowed to settle, and solution was decanted. The white powder product was washed with cold Et₂O (2 x 10 mL) and dried under vacuum to give 4-(diphenylphosphino)(5-lithio)-9,9-dimethyl-xanthene (1.160 g, 50%), which was used directly to prepare compound **7**. 4-(diphenylphosphino)(5-lithio)-9,9-dimethylxanthene (0.500 g, 0.57 mmol) was dissolved in *n*-hexane (20 mL) and ClBpin (0.170 g, 1.04 mmol) was added dropwise as an *n*-hexane solution (10 mL) at -78 °C. The white slurry was stirred at -78 °C for 15 min and then at room temperature for 16 h. The precipitate was allowed to settle and the solution filtered and concentrated to incipient crystallization. Single crystals suitable for X-ray diffraction studies were grown from *n*-hexane solution at 6 °C. Yield 0.210 g (39%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 1.17 (s, 12H, Bpin CH₃), 1.39 (s, 6H, XAN-C(CH₃)₂), 6.76 (t, ³J_{H-H} = 7.6 Hz, 1H, ArH), 6.85-6.88 (m, 1H, ArH), 6.98 (t, ³J_{H-H} = 7.5 Hz, 1H, ArH), 7.05-7.11 (m, 6H, ArH), 7.13 (d, ³J_{H-H} = 7.7 Hz, 1H, ArH), 7.25 (d, ³J_{H-H} = 7.5 Hz, 1H, ArH), 7.50 (t, ³J_{H-H} = 7.0 Hz, 4H, ArH) and 8.01 ppm (d, ³J_{H-H} = 7.3 Hz, 1H, ArH). ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 25.0 (Bpin CH₃), 31.9 (XAN-C(CH₃)₂), 34.5 (XAN-C(CH₃)₂), 83.6 (Bpin C(CH₃)₂), 118.6 (B-C), 123.2, 123.8, 125.9, 126.1, 126.9, 128.0, 128.2, 128.4, 128.6 (d, ¹J_{P-C} = 6.2 Hz), 129.0, 130.2, 130.6, 132.7, 134.4 (d, ¹J_{P-C} = 19.6 Hz), 135.8, 139.3 (d, ¹J_{P-C} = 15.7 Hz), 153.9 (d, ¹J_{P-C} = 18.2 Hz), and 155.6 ppm (ArC). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 298 K): δ = 31.0 ppm (s). ³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ = -14.0 ppm (s). Elemental anal. calc. for C₃₃H₃₄BO₃P: C 76.16% and H 6.59%, found C 76.03% and H 6.72%.

Synthesis of compound 8: 4-(diphenylphosphino)(5-lithio)-9,9-dimethylxanthene (0.400 g, 0.46 mmol) was dissolved in *n*-hexane (20 mL). An *n*-hexane solution (10 mL) of ClBcat (0.140 g, 0.91 mmol) was added dropwise at -78 °C. The white slurry was stirred at -78 °C for 15 min and then at room temperature for 16 h. The white precipitate was allowed to settle and the solution filtered and concentrated to incipient crystallization. Single crystals suitable for X-ray diffraction studies were grown from *n*-hexane solution at -30 °C. Yield 0.120 g (26%). ¹H NMR (400 MHz, C₆D₆, 298 K): δ = 1.39 (s, 6H, XAN-C(CH₃)₂), 6.81-6.98 (m, 12H, ArH), 7.20-7.24 (m, 3H, ArH), 7.33 (t, ³J_{H-H} = 7.5 Hz, 4H, ArH), and 7.77 ppm (dd, ³J_{H-H} = 7.3 Hz, ³J_{H-H} = 1.6 Hz, 1H, ArH). ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ = 30.9 (XAN-C(CH₃)₂), 34.7 (XAN-C(CH₃)₂), 113.0 (Bcat O-C), 115.2 (B-C), 122.7, 123.5, 124.1, 126.3, 126.6, 126.8, 128.0, 128.2, 128.3, 128.5 (d, ¹J_{P-C} = 6.7 Hz), 128.6, 129.5, 130.9, 130.9, 132.1, 134.3 (d, ¹J_{P-C} = 21.1 Hz), 135.1, 137.9 (d, ¹J_{P-C} = 13.6 Hz), 149.3, 153.4 (d, ¹J_{P-C} = 16.3 Hz), and 156.1 ppm (ArC). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 298 K): δ = 32.0 ppm (s). ³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ = -13.0 ppm (s). Elemental anal. calc. for C₃₃H₂₆BO₃P: C 77.36% and H 5.12%, found C 77.28% and H 5.19%.

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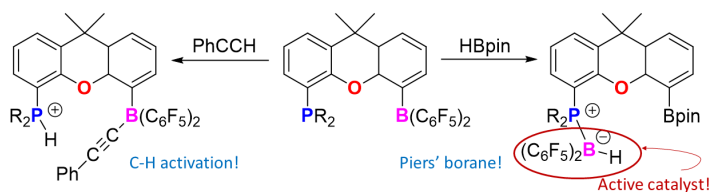
Keywords: Frustrated Lewis Pairs • Phosphine • Borane • Metal-free Catalysis • Hydroboration

- [1] H. C. Brown, H. I. Schlesinger, S. Z. Cardon, *J. Am. Chem. Soc.* **1942**, *64*, 325-329.
- [2] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124-1126.
- [3] For recent review articles see: a) D. W. Stephan, G. Erker, *Angew. Chem., Int. Ed.* **2010**, *49*, 46-76; b) D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch, M. Ullrich, *Inorg. Chem.* **2011**, *50*, 12338-12348; c) G. Erker, *Dalton Trans.* **2011**, *40*, 7475-7483; d) D. W. Stephan, *Org. Biomol. Chem.* **2012**, *10*, 5740-5746; e) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400-6441; f) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018-10032.
- [4] For initial demonstration of the use of FLPs in hydrogenation catalysis see: a) P. A. Chase, G. C. Welch, T. Jurca, D. W. Stephan, *Angew. Chem. Int. Ed.* **2007**, *46*, 8050-8053; b) P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Froehlich, G. Erker, *Angew. Chem., Int. Ed.* **2008**, *47*, 7543-7546. For a review of related hydrosilylation chemistry see: c) W. E. Piers, A. J. V. Marwitz, L. G. Mercier, *Inorg. Chem.* **2011**, *50*, 12252-12262.
- [5] M.-A. Légaré, M.-A. Courtemanche, E. Rochette, F.-G. Fontaine, *Science* **2015**, *349*, 513-516.
- [6] Z. Mo, E. L. Kolychev, A. Rit, J. Campos, H. Niu, S. Aldridge, *J. Am. Chem. Soc.* **2015**, *137*, 12227-12230.
- [7] Z. Mo, A. Rit, J. Campos, E. L. Kolychev, S. Aldridge, *J. Am. Chem. Soc.* **2016**, *138*, 3306-3309.
- [8] Quantum chemical studies of the FLP activation of H₂: a) T. A. Rokob, A. Hamza, A. Stirling, T. Soós, I. Pápai, *Angew. Chem. Int. Ed.* **2008**, *47*, 2435-2438; b) Y. Guo, S. Li, *Inorg. Chem.* **2008**, *47*, 6212-6219; c) S. Grimme, H. Kruse, L. Goerigk, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 1402-1405; d) I. Bakó, A. Stirling, S. Bálint, I. Pápai, *Dalton Trans.* **2012**, *41*, 9023-9025; e) C. Mück-Lichtenfeld, S. Grimme, *Dalton Trans.* **2012**, *41*, 9111-9118; f) T. A. Rokob, I. Bakó, A. Stirling, A. Hamza, I. Pápai, *J. Am. Chem. Soc.* **2013**, *135*, 4425-4437.
- [9] a) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306-316; b) M. Fleige, J. Möbus, T. vom Stein, F. Glorius, D. W. Stephan, *Chem. Commun.* **2016**, *52*, 10830-10833.
- [10] See, for example: a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457-2483; b) M. Vaultier, G. Alcaraz, *Science of Synthesis, Vinylboranes*, Georg Thieme Verlag KG, **2014**.
- [11] For examples of metal-free hydroboration of alkynes and related chemistry see: a) K. Shirakawa, A. Arase, M. Hoshi, *Synthesis* **2004**, 1814-1820; b) G. A. Molander, N. M. Ellis, *J. Org. Chem.* **2008**, *73*, 6841-6844; c) H. Ye, Z. Lu, D. You, Z. Chen, Z. H. Li, H. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 12047-12050; d) K. Wen, J. Chen, F. Gao, P. S. Bhadury, E. Fan, Z. Sun, *Org. Biomol. Chem.* **2013**, *11*, 6350-6356; e) A. Boussonnière, X. Pan, S. J. Geib, D. P. Curran, *Organometallics* **2013**, *32*, 7445-7450; f) H. E. Ho, N. Asao, Y. Yamamoto, T. Jin, *Org. Lett.* **2014**, *16*, 4670-4673; g) S. Hong, W. Zhang, M. Liu, Z.-J. Yao, W. Deng, *Tetrahedron Lett.* **2016**, *57*, 1-4; h) J. S. McGough, S. M. Butler, I. A. Cade, M. J. Ingleson, *Chem. Sci.* **2016**, *7*, 3384-3389; i) Q. Yin, S. Kemper, H. F. T. Klare, M. Oestreich, *Chem.-Eur. J.* **2016**, *22*, 13840-13844; j) T. Wang, X. Jentgens, C. G. Daniliuc, G. Kehr, G. Erker, *ChemCatChem* **2017**, *9*, 651-658.
- [12] M. Fleige, J. Möbus, T. vom Stein, F. Glorius, D. W. Stephan, *Chem. Commun.* **2016**, *52*, 10830-10833.
- [13] D. J. Parks, R. E. v. H. Spence, W. E. Piers, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 809-811.
- [14] K.-Y. Ye, C. G. Daniliuc, S. Dong, G. Kehr, G. Erker, *Organometallics* **2017**, *36*, 5003-5012.
- [15] L.-M. Elmer, G. Kehr, C. G. Daniliuc, M. Siedow, H. Eckert, M. Tesch, A. Studer, K. Williams, T. H. Warren, G. Erker, *Chem.-Eur. J.* **2017**, *23*, 6056-6068.
- [16] C. Chen, G. Kehr, R. Fröhlich, G. Erker, *J. Am. Chem. Soc.* **2010**, *132*, 13594-13595.
- [17] M. A. Dureen, D. W. Stephan, *J. Am. Chem. Soc.* **2009**, *131*, 8396-8397.
- [18] For examples of B-H bond activation by an FLP, see: a) M. A. Dureen, A. Lough, T. M. Gilbert, D. W. Stephan, *Chem. Commun.* **2008**, 4303-4305; b) C. J. Lata, C. M. Crudden, *J. Am. Chem. Soc.* **2010**, *132*, 131-137.
- [19] D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492-5503.
- [20] M. J.-L. Tschan, H. Launay, H. Hagen, J. Benet-Buchholz, P. W. N. M. van Leeuwen, *Chem.-Eur. J.* **2011**, *17*, 8922-8928.
- [21] H. F. Bettinger, M. Filthaus, H. Bornemann, I. M. Oppel, *Angew. Chem. Int. Ed.* **2008**, *47*, 4744-4747.
- [22] W. B. Reid, J. J. Spillane, S. B. Krause, D. A. Watson, *J. Am. Chem. Soc.* **2016**, *138*, 5539-5542.
- [23] P. A. Deck, C. L. Beswick, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1772-1784.
- [24] J. Cosier, A. M. Glazer, *J. Appl. Cryst.* **1986**, *19*, 105-107.
- [25] CrysAlisPro, Agilent Technologies, Version 1.171.35.8.
- [26] G. M. Sheldrick, *Acta Cryst. Sect. A* **2015**, *71*, 3-8.
- [27] G. M. Sheldrick, *Acta Cryst. Sect. A* **2008**, *64*, 112-122.
- [28] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, B., *J. Appl. Cryst.* **2011**, *44*, 1281-1284.
- [29] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT, **2009**.
- [30] a) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868; b) J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982-9985; c) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170; d) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396; e) A. Schaefer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829-5835.

Entry for the Table of Contents

Layout 2:

FULL PAPER



A dimethylxanthene-based FLP can effect reversible cleavage of the C-H bond in PhCCH, and can also react with B-H bonds, such as those in HBpin and HBcat via a B-C/B-H exchange. The latter reactivity gives rise to Piers' borane, $\text{HB}(\text{C}_6\text{F}_5)_2$, which acts as the active catalyst for the hydroboration of alkynes by HBpin.

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Reversible C-H activation, facile B-C/B-H metathesis and apparent hydroboration catalysis by a dimethylxanthene-based frustrated Lewis pair