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Frustrated Lewis pairs: Reactions with dihydrogen and other “small molecules”

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ARTICLE INFO

Article history:

Received 2 May 2011

Accepted after revision 24 May 2011

Available online 13 July 2011

Keywords:

Lewis acid/Lewis base pairs

Frustrated Lewis pairs

Hydrogenation

Catalysis

1,1-carbaboration

Carbon-carbon bond activation

ABSTRACT

Frustrated Lewis pairs, comprised of combinations of sterically encumbered phosphine (or amine) Lewis bases with boron Lewis acids containing the strongly electron withdrawing bulky pentafluorophenyl substituents, show very remarkable reaction behaviour. They are able to cooperatively induce heterolytic splitting of dihydrogen under mild conditions. They cooperatively add to various unsaturated organic compounds, including carbon dioxide. With some substrates competing 1,1-carbaboration reactions become important. The latter reaction has methodically been developed into a conceptual alternative to the ubiquitous hydroboration reaction and has been used for the development of a novel way of carbon-carbon bond activation.

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1. Introduction

Lewis acids and Lewis bases usually quench each other when brought together in solution by formation of strong adducts [1]. This situation may be changed when these compounds become so sterically encumbered that their nucleophilic and electrophilic core centers can no longer come close enough to annihilate each other's characteristic properties by adduct formation. This situation had been encountered in the past by a small number of unsystematic examples [2,3], but the emerging field of frustrated Lewis pairs (FLPs) [4] has taken up pace only recently by the use of very strongly electrophilic and at the same time bulky C₆F₅ substituent containing borane Lewis acids in conjunction with rather bulky Lewis bases [5,6]. In this account we will describe a variety of examples of FLPs, mostly from my research group at Münster, and illustrate their remarkable properties by selected reactions with various small molecules.

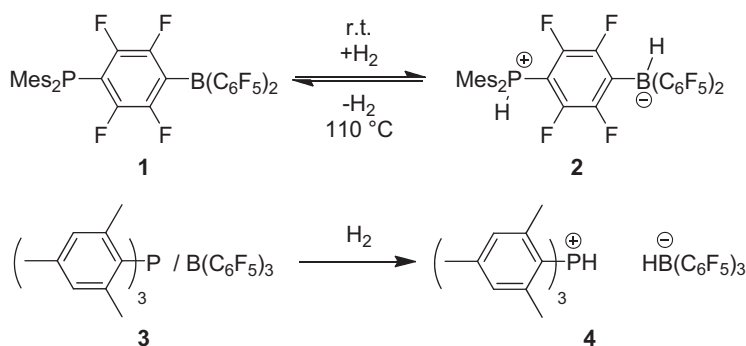
2. Results and discussion

2.1. Reactions with dihydrogen

The activation of dihydrogen is commonly carried out with the aid of metals, whether it is achieved heterogeneously at a noble metal surface or homogeneously by using suitable well defined molecular transition metal complexes [7]. Even nature usually uses metal centers in the hydrogenase enzymes to achieve heterolytic dihydrogen activation [8]. There is a small number of examples scattered unsystematically across the chemical literature describing various types of metal-free catalytic hydrogenation reactions, most taking place at rather forcing reaction conditions [9]. In addition a few specific monoaminocarbenes were recently shown to add H₂ to the carbene carbon center to form C-H bonds, as shown by Bertrand, Schöller et al. [10]. Sander et al. had shown that the strongly electrophilic carbene difluorovinylidene reacts with H₂ in a hydrogen-doped argon-matrix to form the respective alkene [11].

Stephan et al. had shown that the intramolecular frustrated P/B Lewis pair (**1**) adds dihydrogen reversibly to yield the zwitterionic phosphonium/hydridoborate product **2** [5,12,13,27]. They also showed that intermolecular

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Scheme 1.

FLPs like **3** heterolytically split dihydrogen to yield the phosphonium/hydridoborate salt **4**, but this reaction is apparently not reversible (Scheme 1).

My group had early on contributed to this interesting new development of FLP mediated metal-free dihydrogen activation. Patrick Spiess, then a member of the group at Münster, prepared the intramolecular ethylene-bridged frustrated Lewis pair (**7**) by a straightforward route [14]. This system turned out to be one of the most active dihydrogen activating systems of this type. Under ambient conditions it rapidly reacts with dihydrogen to yield the intramolecular phosphonium/hydridoborate zwitterion (**8**). The product was characterized by X-ray diffraction (Fig. 1) (Scheme 2).

We prepared the related frustrated P/B Lewis pair **10** by “Piers’ hydroboration” of dimesityl(cyclohexenyl)phosphine (**9**) [15]. The X-ray crystal structure analysis of the P/B pair **10** (Fig. 2) features a four-membered heterocyclic structure annulated with the cyclohexane ring system. The P–B bond is rather long (**10** features two independent molecules in the unit cell: mol. A: P–B: 2.188(5) Å, mol. B: 2.218(5) Å).

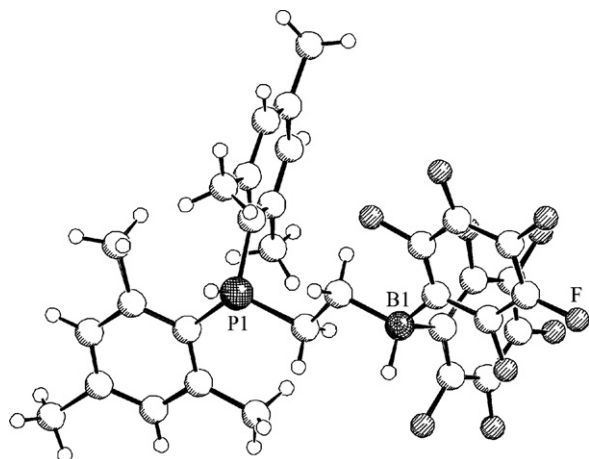
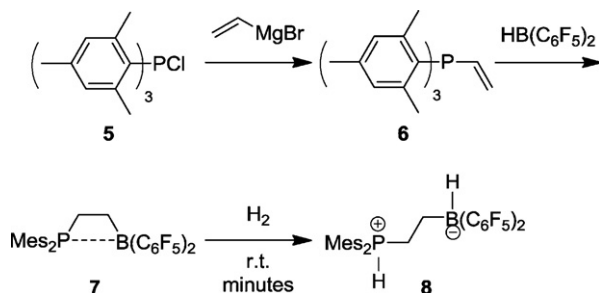
The P/B FLP **10** contains a pair of chirality centers on the bridgehead carbon atoms. Therefore, we observe the NMR features of a pair of diastereotopic mesityl substituents at phosphorus and of a pair of diastereotopic C₆F₅ rings at

boron. Reversible rupture of the P–B linkage (to generate the non-observed high lying intermediate **11**) would result in a disappearance of the B(C₆F₅)₂ diastereotopism due to the non-prochiral nature of the trigonal planar borane moiety. This equilibrium actually reveals itself in the temperature dependent ¹⁹F NMR spectra of compound **10**. From the observed coalescence of the pair of C₆F₅ rings in the temperature dependent ¹⁹F NMR spectra of **10** we have calculated a Gibbs activation energy of ΔG_{dis}[‡](283 K) = 12.1 ± 0.5 kcal mol⁻¹ [15]. Consequently, the P–B bond dissociation energy in the FLP **10** must be below this value.

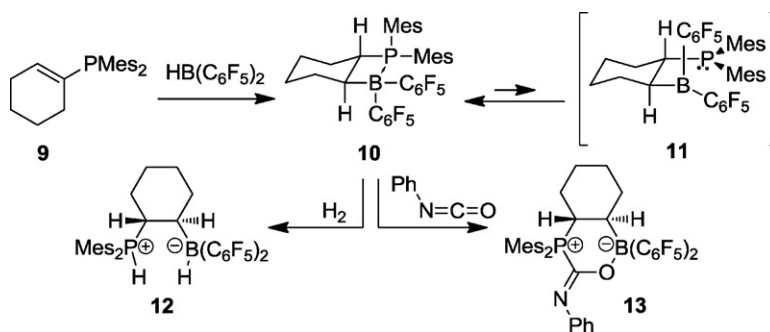
As expected for a rapidly opening P/B FLP system, we observe that **10** is a reactive activator of dihydrogen. Already at low temperature it splits dihydrogen heterolytically to yield the phosphonium/hydridoborate product **12**. With phenylisocyanate it undergoes another typical FLP reaction, namely the 1,2-addition of the P/B pair to the reactive C=O double bond of the heterocumulene reagent to yield the product **13** (Scheme 3).

The intramolecular FLPs have served as catalysts for the hydrogenation of a variety of enamines under rather mild conditions [16]. Some representative examples are depicted in Scheme 4. Simple enamines, such as the example **14**, are rapidly hydrogenated to yield the respective tert-amines. Conjugated dienamines are often fully hydrogenated. In some special cases (e.g. the [3]ferrocenophane dienamine **18**) we have observed selective 1,4-hydrogenation instead, catalyzed by the system **7/8**, to yield the respective allylamine product (**19**) [17].

The systems **7** and **10** activated dihydrogen nicely but the heterolytic dihydrogen cleavage by these systems to

Fig. 1. A view of the molecular structure of the zwitterion **8**.

Scheme 2.



Scheme 3.

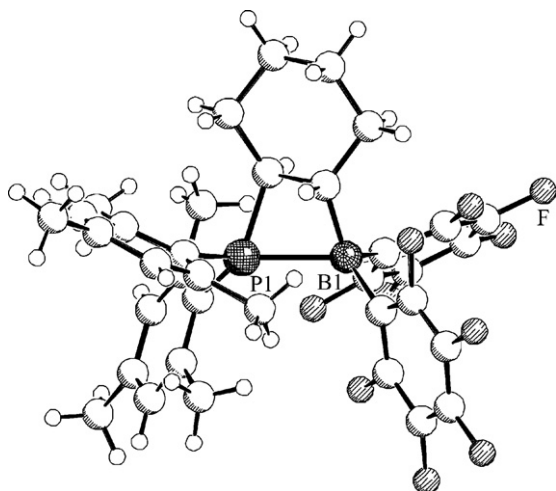
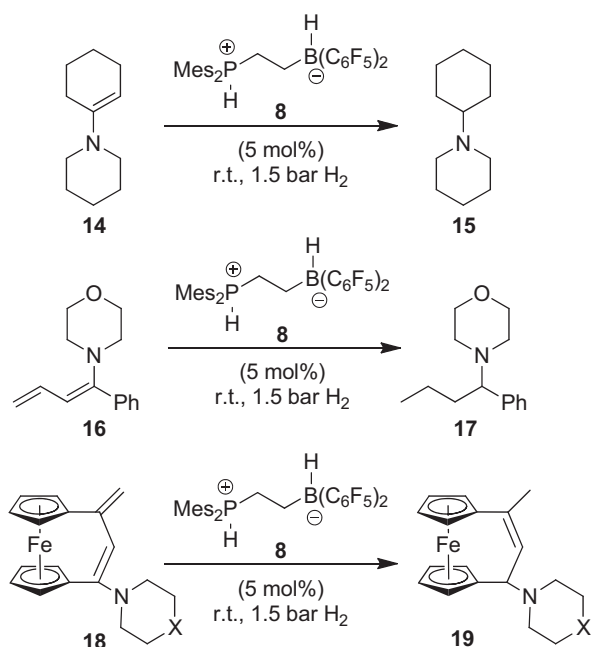


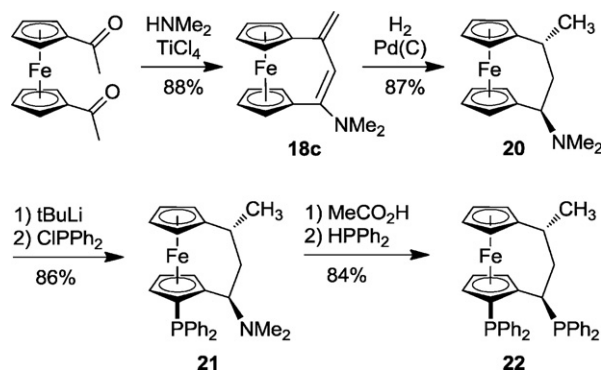
Fig. 2. A view of the molecular structure of compound 11.



Scheme 4.

yield **8** or **12**, respectively, was irreversible under the applied reaction conditions. Therefore, we searched for specific systems that might allow studying FLP/ H_2 systems that were reversible. Some $B(C_6F_5)_3$ /chelate phosphine combinations were shown to do just that. Here is a typical example (Scheme 5). It comprised a chelate [3]ferrocenophane bisphosphine (**22**) that was synthesised in the following way. Mannich coupling of 1,1'-diacetylferrocene with dimethylamine and catalytic $TiCl_4$ gave the unsaturated [3]ferrocenophane system **18c** [18] that was subsequently catalytically hydrogenated to yield **20** (as 7:1 mixture of *trans*- and *cis*-diastereoisomers). The pair of phosphinyl substituents was then introduced by directed lithiation followed by quenching with Ph_2PCl to give **21** [19]. Exchange of the $-NMe_2$ group by $-PPh_2$ was then carried out in the typical two step procedure at the carbon in α -position to the ferrocenophane to yield the system **22** with overall retention of configuration [20].

Compound **22** had been used as a chelate ligand either in its racemic or enantiomerically pure form [21]. With $B(C_6F_5)_3$ [22] it formed a frustrated Lewis pair that rapidly activated dihydrogen at ambient conditions. It turned out that only one of the P-atoms of the phosphine was used in the H_2 -activation process. The other one remained untouched. The crystalline material features the proton on the "ortho"- PPh_2 group (Fig. 3). However in solution we "see" both possible isomers **23a**, **23b** in a ratio of ca. 60:40 as judged by their typical ^{31}P NMR spectra (Fig. 4). The heterolytic splitting of dihydrogen at this system is



Scheme 5.

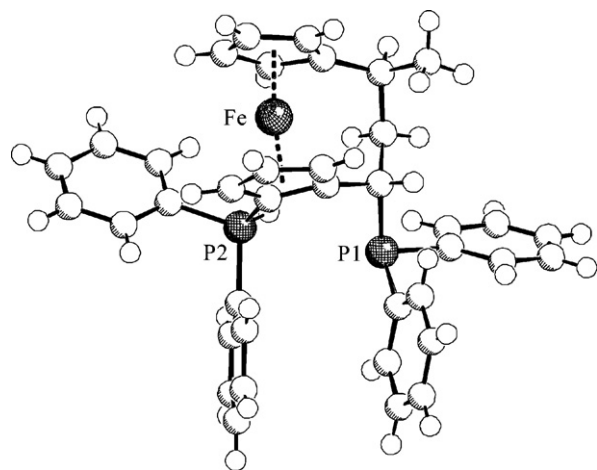


Fig. 3. A view of the molecular structure of the [3] ferrocenophane derived phosphonium cation **23a** (the $[\text{HBC}_6\text{F}_5]^-$ anion is not shown).

reversible. Heating the mixture of the mono-phosphonium/hydroborate salts **23a/23b** to 75 °C in toluene solution resulted in a rapid evolution of dihydrogen to reform the frustrated Lewis pair **22**/ $\text{B}(\text{C}_6\text{F}_5)_3$. The reaction cycle could then be closed by reacting this FLP again with dihydrogen at ambient conditions to again yield **23** [23] (Scheme 6).

The system **23** is an active catalyst for the hydrogenation of silylenoethers, similar as it had been previously

shown by us for the 1,8-bis(diphenylphosphino)naphthalene/ $\text{B}(\text{C}_6\text{F}_5)_3/\text{H}_2$ system [24].

2.2. Reactions with carbon dioxide

Many frustrated Lewis pairs react readily with carbon dioxide to yield the respective adducts. The very reactive intramolecular FLP **7** reacts with CO_2 at ambient temperature in pentane solution to yield a white precipitate of the CO_2 addition product **24**. This is a rather thermolabile substance in solution, which rapidly loses CO_2 again above -20°C . In this way the CO_2 uptake/ CO_2 elimination can be shuttled easily between the FLP **7** and the FLP- CO_2 adduct **24** [25] (Scheme 7).

At low temperature the CO_2 adduct **24** features a $\nu(\text{CO})$ IR band at 1694 cm^{-1} , a ^{13}C NMR carbonyl carbon signal at δ 168.8 ppm and ^{31}P and ^{11}B NMR resonances at δ 0.6 ppm and δ -2.5 ppm, respectively. The X-ray crystal structure analysis of **24** shows the presence of a non-planar half-chair like six-membered heterocycle with bond length of O1-C3: 1.284(4) Å, B-O1: 1.550(4) Å, a C3-O1-B angle of $130.9(3)^\circ$ and a carbonyl C=O bond length of 1.209(4) Å (C3-O2) (Fig. 5).

Many intermolecular P/B Lewis pairs also add to CO_2 . Usually these adducts are thermally more robust and split off CO_2 at higher temperatures [25]. Scheme 8 shows several examples of such systems that we have recently isolated and characterized [26].

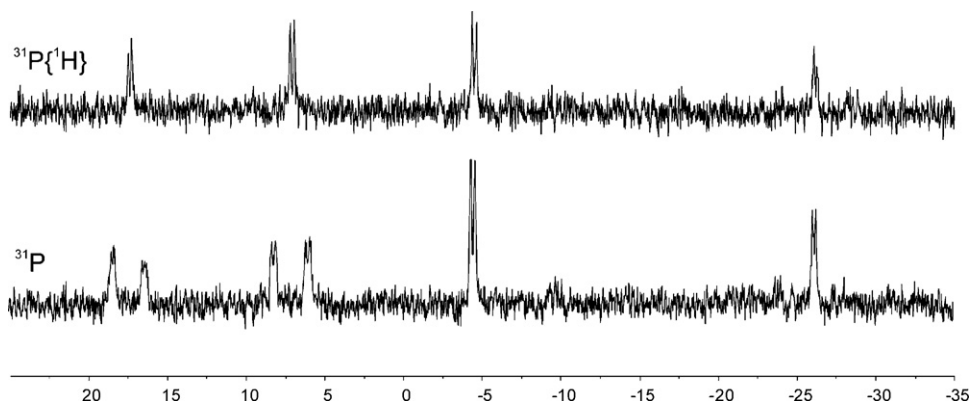
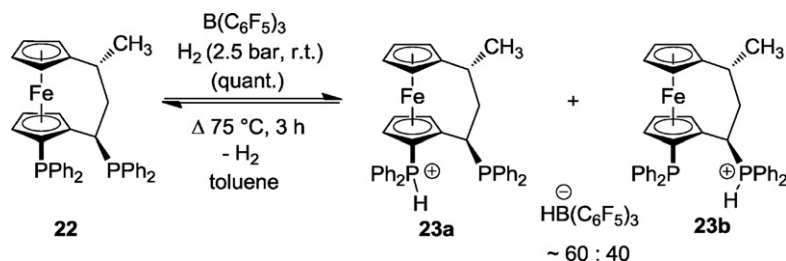
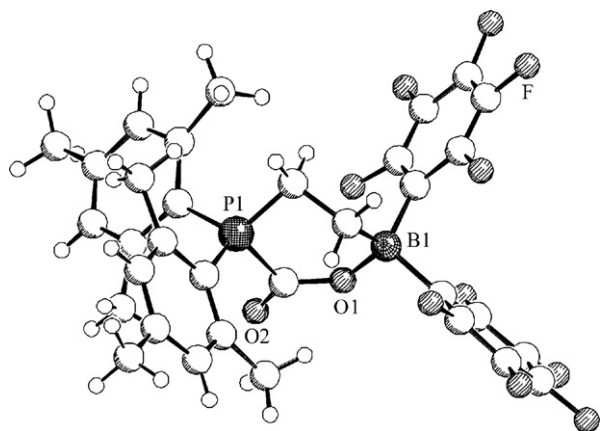
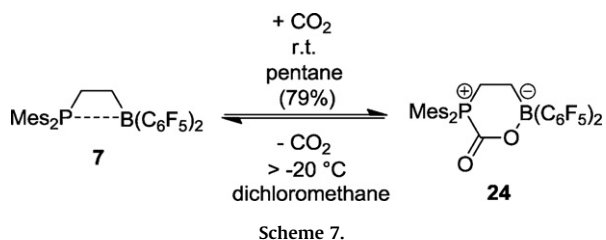


Fig. 4. ^{31}P NMR spectra (243 MHz, 248 K, d_6 -toluene) of the **23a/23b** mixture of isomers.



Scheme 6.

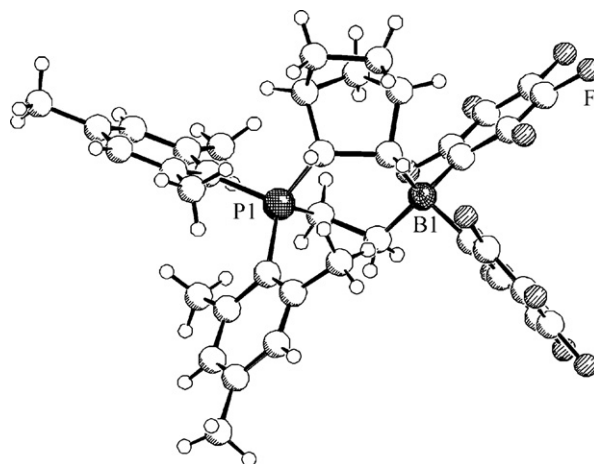
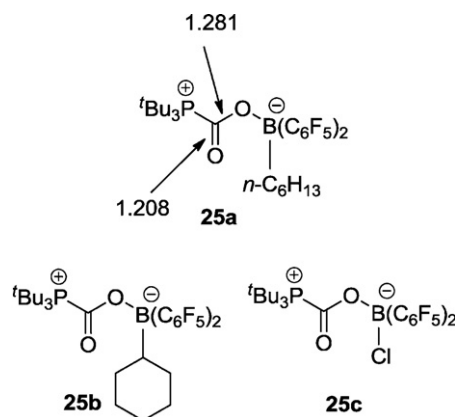
Fig. 5. Molecular structure of the FLP-CO₂ adduct **24**.

2.3. Reactions with alkenes and alkynes

Frustrated Lewis pairs react with olefins. Very early examples comprise the addition of the BPh₃/PPh₃ pair to *in situ* generated benzyne or the reaction of the Ph₃C[−]/BPh₃ pair to butadiene [3]. Stephan had shown that B(C₆F₅)₃ adds to alkenylphosphines and that the B(C₆F₅)₃/P^tBu₃ pair undergoes 1,2-addition to e.g. ethylene [27].

We have reacted the intramolecular P/B Lewis pair **7** with norbornene [28]. In this reaction the 2,3-exo-addition product **26** is formed exclusively. It was unequivocally characterized spectroscopically and by X-ray diffraction (Fig. 6).

The theoretical analysis revealed that **26** is probably formed in a concerted but highly asynchronous reaction. In

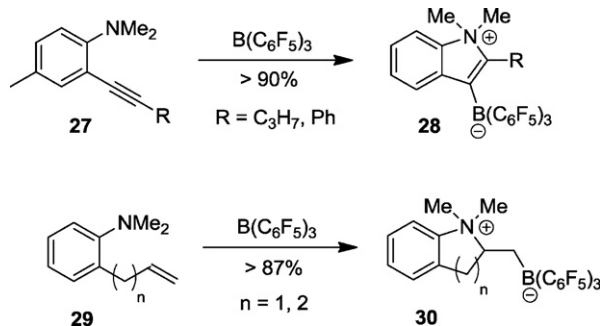
Fig. 6. A projection of the molecular geometry of compound **26**.

the transition state the C–B bond formation is more advanced than the formation of the C–P linkage (Scheme 9).

There are many variations of related 1,2-addition reactions to alkenes and alkynes. Typical examples are the intramolecular ring closure reactions by FLP addition to the pendant alkynyl or alkenyl units in the compounds **27** or **29** to yield the zwitterionic heterocyclic products **28** and **30**, respectively (Scheme 10). Fig. 7 shows the structure of an example [29].

N/B FLP systems can also add to 1-alkynes. A typical example is the addition of the N,N-dimethylaniline/B(C₆F₅)₃ pair to 1-hexyne to yield the adduct **31** (Scheme 11).

Stephan et al. had shown that intermolecular P/B pairs can either add to 1-alkynes or abstract the acidic acetylene hydrogen depending on the basicity of the phosphorus Lewis base [30]. We have found an illustrative example



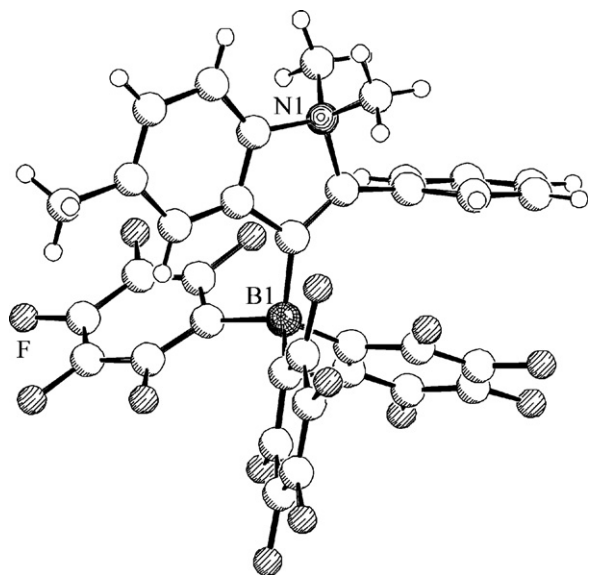
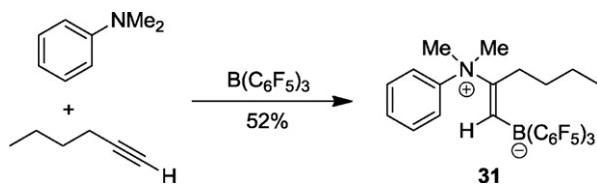


Fig. 7. Molecular structure of the zwitterionic heterocycle **28b** (R = Ph).



Scheme 11.

where these two pathways almost equally compete. The Lewis pair comprised of $B(C_6F_5)_3$ and dimesitylethylphosphine reacted with phenylacetylene to yield a 1:1 mixture of the addition product **32** and the phosphonium/borate salt **33** (Scheme 12).

With the conjugated enyne **34** the intramolecular FLP **7** also reacts by deprotonation (to yield **35**), but this is only the minor reaction pathway in this remarkable system. The major product is the eight-membered heterocyclic

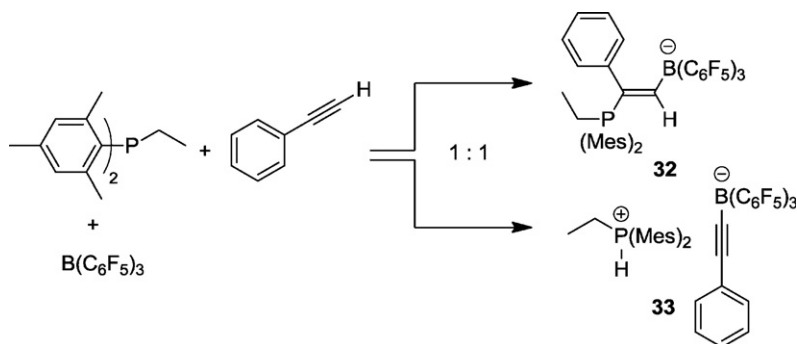
allene **36** [31]. This is the 1,4-addition product of the P/B FLP (**7**) to the conjugated enyne system **34** (Scheme 13). The product **36** is formed under kinetic control as shown by DFT. The possible six-membered heterocyclic isomer formed by alternative 1,2-P/B addition to the triple bond of **34** is thermodynamically more favourable but only the 1,4-addition to yield **36** was observed (in addition we find the acid/base reaction to occur, yielding the minor product **35**). Compound **36** was characterized by X-ray diffraction. It features an almost unstrained allene moiety inside the heterocyclic eight-membered ring structure (Fig. 8).

With a series of internal conjugated diynes the P/B pair **7** reacted selectively by 1,4-addition to yield the heterocyclic butatriene derivatives **37**. Several examples of this remarkable class of compounds were characterized by X-ray diffraction [31]. Typically, the structure of **37b** (R = *n*-propyl) shows a slightly bent central $C=C=C$ unit (angles C4–C5–C6: $165.0(2)^\circ$, C5–C4–C3: $161.2(2)^\circ$) (Fig. 9). The framework of these systems is non-planar (Scheme 14).

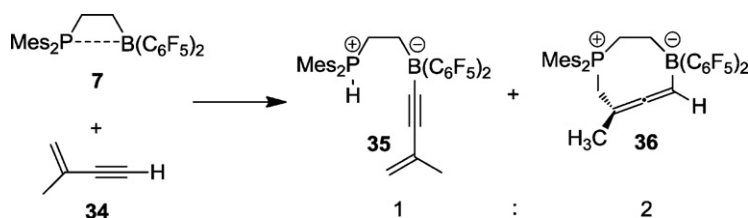
Non-conjugated diynes may undergo different types of reactions with frustrated P/B Lewis pairs. The $P(o\text{-tolyl})_3/B(C_6F_5)_3$ pair reacts readily with 1,7-octadiyne to yield the zwitterionic addition product **38** (Scheme 15 and Fig. 10) [32]. This product can be thought to be formed by addition of the strong boron Lewis acid to one of the terminal acetylene units followed by a rapid carbon-carbon coupling reaction. Eventually capture by the phosphine concluded the reaction sequence.

Treatment of 1,6-heptadiyne with the $P(o\text{-tolyl})_3/B(C_6F_5)_3$ pair gives a different type of product. We isolated in good yield the eight-membered heterocycle **39** (Scheme 15 bottom and Fig. 11) [31]. The new product features an ^{11}B -NMR signal at $\delta -13.3$ and a ^{31}P NMR resonance at $\delta 29.3$. It shows the borate type ^{19}F NMR signals of the endocyclic $B(C_6F_5)_2$ moiety and a separate set of ^{19}F NMR signal of the isolated single C_6F_5 substituent.

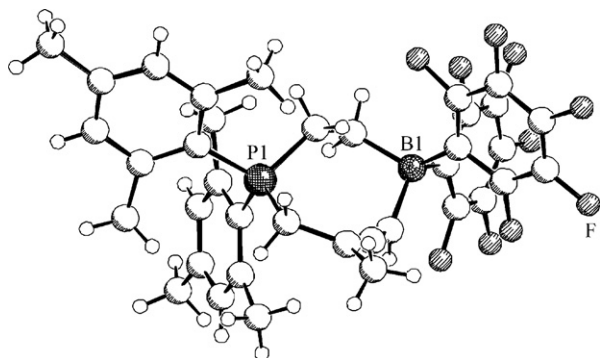
Apparently product **39** was formed by means of a two step mechanism initiated by 1,1-carboration of a terminal alkynyl unit with $B(C_6F_5)_3$. This reaction proceeds by borane addition to the terminal $C(sp)$ carbon center coupled with 1,2-migration of a C_6F_5 substituent from boron to the same carbon atom and 1,2-hydrogen



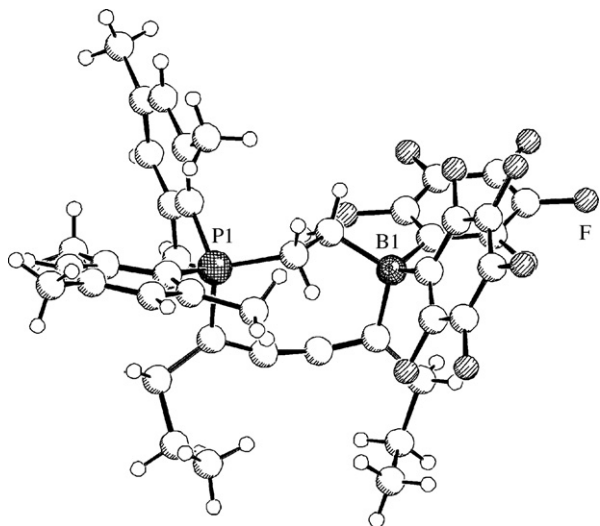
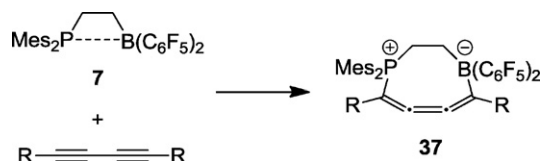
Scheme 12.



Scheme 13.

Fig. 8. Molecular geometry of the zwitterionic eight-membered heterocyclic allene **36**.

migration from C1 to C2 (Scheme 16). The intermediate **40** contains a strongly acidic boron Lewis acid. It then undergoes 1,2-addition with the $\text{P}(o\text{-tolyl})_3$ Lewis base, present in the solution, to the remaining second terminal alkynyl group of the substrate – a typical FLP reaction – to yield **39**.

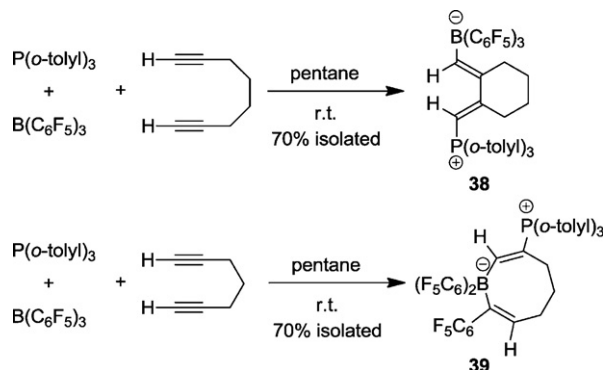
Fig. 9. A view of the molecular structure of compound **37b** (R = n-propyl).

Scheme 14.

1,1-carboration reactions have long been known for activated alkynes bearing silyl, stannyl, plumblyl or some transition metal containing substituents at the C(sp) center, i.e. groups that migrate well [33]. Our example (and a small group of other related reactions) [34] indicated that the 1,1-carboration reaction of $\text{R}-\text{B}(\text{C}_6\text{F}_5)_2$ systems with 1-alkynes might be a facile reaction in general. This turned out to be the case. This reaction type actually might be considered a conceptual synthetic alternative to the hydroboration reaction [35] of some alkynes.

2.4. 1,1-Carboration reactions of alkynes by the $\text{R}-\text{B}(\text{C}_6\text{F}_5)_2$ reagents

The 1,1-carboration reaction of terminal alkynes with $\text{B}(\text{C}_6\text{F}_5)_3$ proceeds rapidly at room temperature. Treatment of a series of 1-alkynes $\text{H}-\text{C}\equiv\text{C}-\text{R}^2$ (with $\text{R}^2 = n\text{-propyl}$, $-(\text{CH}_2)_4\text{Cl}$, $-(\text{CH}_2)_3\text{Ph}$, $-\text{Ph}$ or $-\text{CMe}_3$) rapidly gives a practically quantitative yield of the respective 1,1-carboration products. The reaction is non-stereoselec-



Scheme 15.

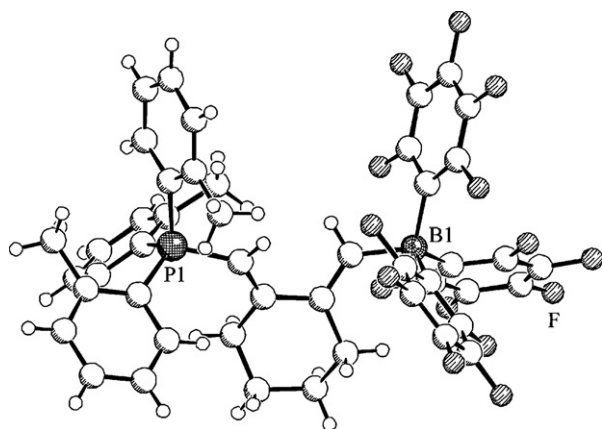


Fig. 10. Molecular structure of the zwitterionic addition/C-C coupling product **38**.

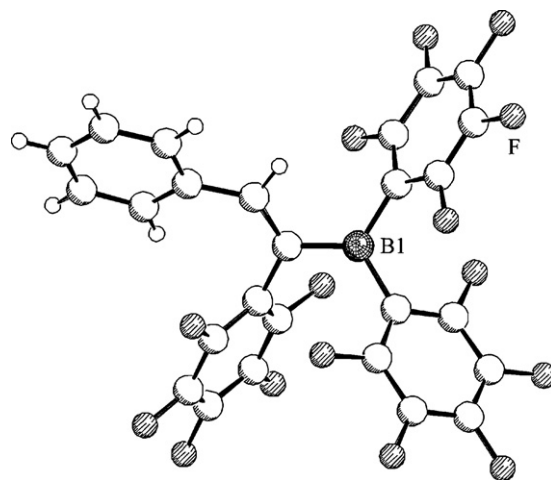


Fig. 12. Molecular structure of the 1,1-carbaboration product **Z-41d**.

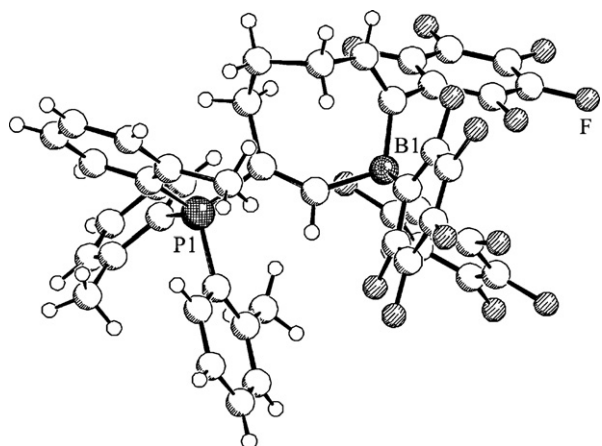


Fig. 11. Molecular structure of the eight-membered heterocycle **39**.

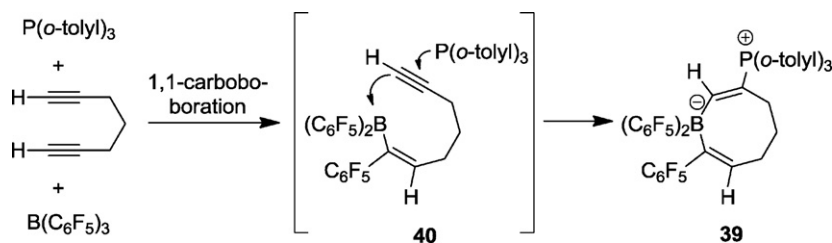
tive. We obtained mixtures of the respective **Z-41** and **E-41** isomers (Scheme 17). However, subsequent photolysis in most cases cleanly converted the **E-41** isomer to **Z-41**, so that highly enriched **Z-41** samples were obtained in high yield. One example ($R^2 = \text{Ph}$, **Z-41d**) was characterized by X-ray diffraction (Fig. 12) [35,36].

Alkyl- $\text{B}(\text{C}_6\text{F}_5)_2$ reagents (e.g. **42a**, **42b**) also undergo 1,1-carbaboration reactions with 1-alkynes. In these cases we observed only the migration of the alkyl group from boron to carbon to selectively yield the alkyl-substituted 1,1-carbaboration products **43** (Scheme 17). Again photolysis resulted in a high **E-42** to **Z-42** conversion.

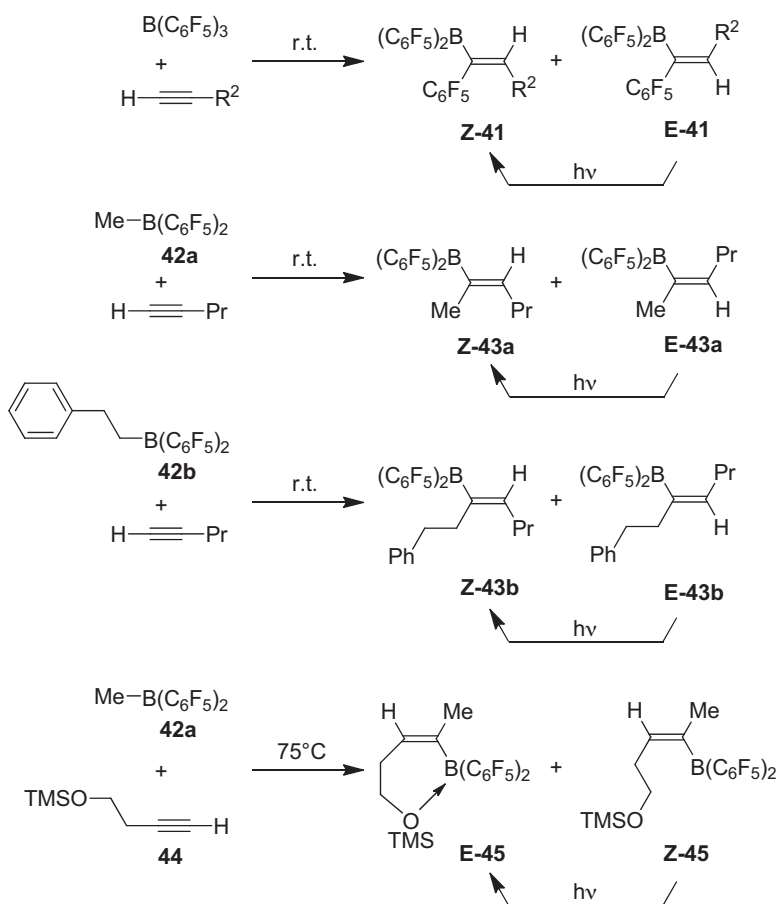
Treatment of the -OTMS substituted 1-alkyne (**43**) with the $\text{Me-B}(\text{C}_6\text{F}_5)_2$ reagent opened a selective pathway into the **E-1,1-carbaboration** series. The thermally induced carbaboration reaction again yielded a **E-Z-alkenylborane** mixture **44**. In this case the photostationary equilibrium lied on the side of the **E-44** isomer [35].

The alkenylboranes are very interesting Lewis acids but they also may serve as tricoordinated borane reagents for cross-coupling reactions. Thus treatment of the product **Z-41a** with iodobenzene under typical Suzuki-Miyaura reaction conditions (catalytic $\text{Pd}(\text{PPh}_3)_4/\text{NaOH}/\text{THF}$) resulted in an efficient formation of the C-C coupling product, here the respective trisubstituted alkene **46a** (Scheme 18). These reactions can be performed as one-pot reactions as well. Thus, the sequence starting from **42a** and 5-phenyl-1-pentyne eventually gave the olefinic product **46b** in an overall yield of 76%. The -OTMS functionalized systems undergo these reactions similarly [35,36].

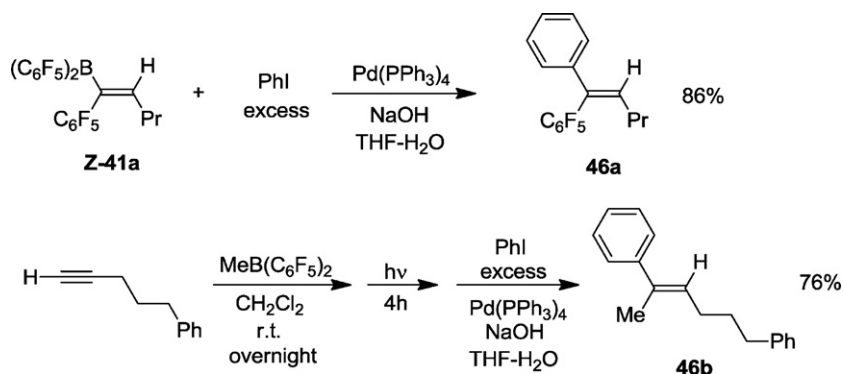
We have even achieved the 1,1-carbaboration of internal alkynes with either $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{Me-B}(\text{C}_6\text{F}_5)_2$, although this needs rather forcing conditions. 4-Octyne



Scheme 16.



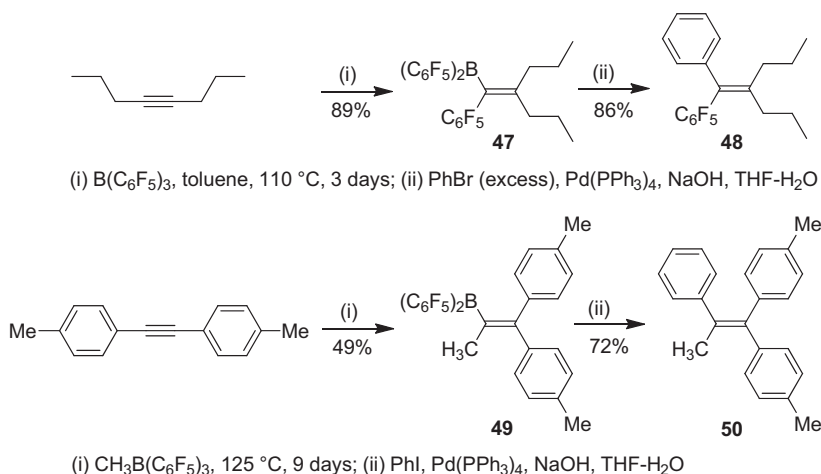
Scheme 17.



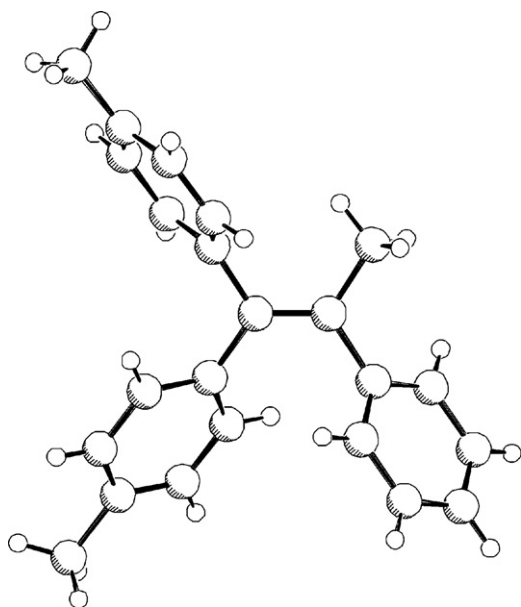
Scheme 18.

reacted with $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene at 110°C over 3 days to give the 1,1-carbaboration product **47** in good yield. This reaction represents a novel pathway for the activation of otherwise non-activated carbon-carbon σ -bonds. The product **47** of this remarkable C-C bond activation process can subsequently be utilized as a reagent for Pd-catalyzed cross-coupling (Scheme 19) [37].

$\text{MeB}(\text{C}_6\text{F}_5)_2$ (**42a**) reacts with 1,2-di-*p*-tolylacetylene during 9 days at 125°C by means of a clean C-C bond activating 1,1-carbaboration reaction to yield the product **49**. This also undergoes a Suzuki-Miyaura type cross-coupling reaction with phenyliodide to yield the tetra-substituted alkene (**50**) that was characterized by X-ray crystal structure analysis (Fig. 13) [37].



Scheme 19.

Fig. 13. A projection of the molecular structure of the product **50**.

3. Conclusion

Frustrated Lewis pair chemistry has made a rapid development during the recent years. It has led to a situation where many of these main group element systems show chemical features as they are commonly found in transition metal chemistry. Heterolytic splitting and activation of dihydrogen has certainly been one prominent feature but we are finding more and more other remarkable examples of typical FLP chemistry and characteristic FLP reactivities. These include the unusual 1,4-addition reactions to conjugated olefins and acetylenes and certainly not the least the rather common FLP addition chemistry to carbon dioxide. Although FLP chemistry still is at its early stages, it is foreseeable that we will find more

and more interesting novel reaction types of non-quenched Lewis acid/Lewis base pairs appear. Some of these reactions, as we have shown, are in a close competition with other very interesting new alternative reaction variants, such as the 1,1-carboration reactions of 1-alkynes and even of internal alkynes. All this indicates that the use of the pentafluorophenyl-derived boranes have served to open a very interesting chapter in the chemistry of reactions mediated by strongly electrophilic Lewis acidic species in a variety of reaction environments.

Acknowledgement

Our part of the work described in this account was carried out by a group of very talented coworkers whose names are listed in the respective references. I cordially thank all of them. I think we all had fun and a good time working together in this exciting new field of chemistry. The financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Alexander von Humboldt Stiftung is gratefully acknowledged.

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