

# Intramolecular Frustrated Lewis Pairs: Formation and Chemical Features

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**Abstract** Intramolecular vicinal and geminal frustrated Lewis pairs (FLPs) featuring bulky substituents at phosphorus or nitrogen and strongly electron-withdrawing bulky pentafluorophenyl substituents at boron undergo a variety of addition and/or activation reactions with small molecules. A number of examples of such reactions are presented and discussed, among them the FLP activation of dihydrogen to give zwitterionic phosphonium (or ammonium)/hydridoborate zwitterions. Intramolecular FLPs also add to organic carbonyl compounds (including carbon dioxide), to alkenes and alkynes (including conjugated dienes, diynes or enynes), to heterocumulenes, to azides, and to nitric oxide.

**Keywords** FLP addition reactions · Small molecule activation · Synergistic reactions · Vicinal and geminal frustrated Lewis pairs

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## Abbreviations

Bu	Butyl
CP	Cross polarization
DABCO	1,4-Diazabicyclo[2.2.2]octane
DEAD	Diethyl azodicarboxylate
DFT	Density functional theory
equiv.	Equivalent(s)
Et	Ethyl
FLP	Frustrated Lewis pair
gem.	Geminal
h	Hour(s)
HAA	Hydrogen atom abstraction
<i>i</i> -Pr	<i>iso</i> -Propyl
LA	Lewis acid
LB	Lewis base
MAS	Magic angle spinning
Me	Methyl
Mes	Mesityl, 2,4,6-trimethylphenyl
min	Minute(s)
NMR	Nuclear magnetic resonance
Ph	Phenyl
Pr	Propyl
r.t.	Room temperature
<i>s</i> -Bu	<i>sec</i> -Butyl
THF	Tetrahydrofuran
<i>t</i> -Bu	<i>tert</i> -Butyl
vic.	Vicinal

## 1 Introduction

Lewis acids (LA) and Lewis bases (LB) usually undergo strong adduct formation when brought together in solution. The ubiquitous Lewis acid/base adduct formation [1] is analogous to the neutralization reaction in Brønsted acid/base chemistry [2]. The resulting LA/LB adducts may have very interesting properties in themselves, e.g., as is found in the chemistry of ammonia borane ( $\text{H}_3\text{NBH}_3$ ) [3, 4], but they have lost the typical chemical features of their original components. Lewis acid/Lewis base adduct formation can effectively be hindered or even completely suppressed by steric and/or electronic means. Placing very bulky aryl or alkyl substituents at, e.g., phosphorus or nitrogen or even carbon based Lewis bases and combining them with, e.g., strongly electrophilic  $\text{R-B}(\text{C}_6\text{F}_5)_2$  type Lewis acids has often resulted in situations of co-existent pairs of active Lewis acids and Lewis bases in solution. Sometimes they appeared to be independent of each other,

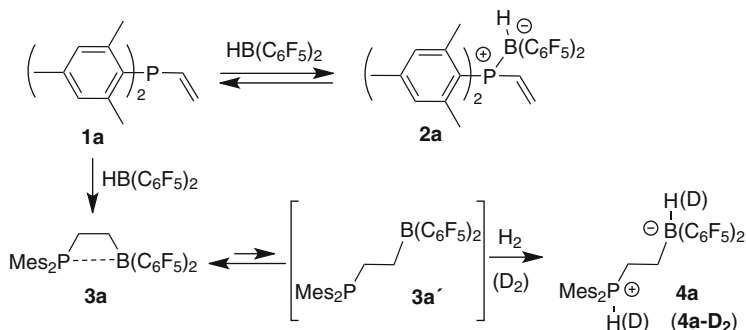
sometimes they were found to be in equilibrium with their respective LA/LB adducts, sometimes they were weakly interacting. Such frustrated Lewis pairs (FLPs) [5–16] can, of course, show reactions of their separate LA and LB components, but they are special in that they have the potential to have the Lewis acid/Lewis base components reacting synergistically with added substrates. There are indications that weak interactions between the Lewis acid/Lewis base components of a frustrated Lewis pair might favor synergistic reaction behavior, maybe it is even mandatory in some cases. Intramolecular FLPs, where active Lewis acid and Lewis base components are closely connected by sufficiently flexible bridges, may be advantageous to introduce and control typical frustrated Lewis pair behavior. Here we report about a selection of intramolecular FLPs, mostly, but not exclusively, originating from our research group in Münster and our collaborating partners, which may serve to illustrate some of the remarkable and extraordinary features that such reactive bifunctional main group element compounds may exhibit.

## 2 Vicinal Phosphorus/Boron FLPs and Their Reaction with Dihydrogen

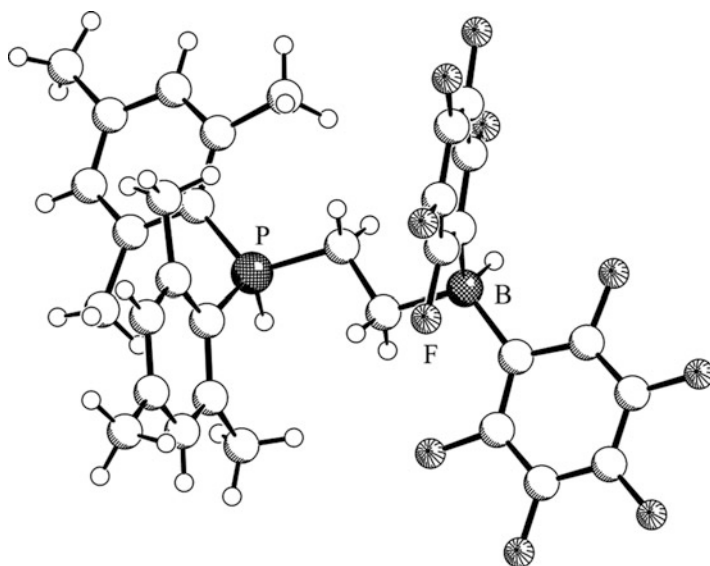
We first reacted the bulky starting material dimesitylvinylphosphane (**1a**) with Piers' borane [HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] [17–21]. The system forms a Lewis acid/Lewis base adduct (**2a**, Scheme 1) at low temperature. However, this has only a fleeting existence, since the **1a**/HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> reaction mixture undergoes a rapid hydroboration reaction of the vinyl substituent at room temperature with the usual anti-Markovnikov orientation to yield the intramolecular FLP **3a** [22].

The spectroscopic data indicate that **3a** is a weakly interacting intramolecular FLP system. In solution it features NMR shifts of the heteronuclei [<sup>31</sup>P: δ 20.6, <sup>11</sup>B: δ 8.5, <sup>19</sup>F: δ –128.8 (*o*), –157.0 (*p*), –163.6 (*m*)] that are intermediate between a phosphane/phosphonium, and borane/borate character. A detailed solid state MAS NMR analysis confirmed this [23]. Among other parameters the <sup>11</sup>B NMR quadrupolar coupling constant of **3a** pointed to a P...B interacting system with a boron center deviating only slightly from a trigonal planar BC<sub>3</sub> coordination sphere and a tentative P...B distance of ca. 2.2 Å. The DFT analysis of **3a** gave a similar result. According to this computational analysis the weak internal adduct **3a** equilibrated with a pair of open isomers **3a'** which were of slightly higher energy. One had the two functional groups oriented *gauche* to each other, whereas the other showed them in an anti-periplanar conformational arrangement [22].

Compound **3a** reacts rapidly with dihydrogen under mild conditions. It was one of the most active metal-free dihydrogen activations at the time when it was first studied. It splits dihydrogen at close to normal conditions (r.t., 1.5 bar H<sub>2</sub> pressure, pentane solution) within minutes. The pale yellow solution of **3a** turns colorless and the zwitterionic phosphonium/hydridoborate product **4a** precipitates from the solution. It was characterized by X-ray diffraction (Fig. 1) and by spectroscopy



**Scheme 1** Formation of the FLP **3a** and its reaction with dihydrogen

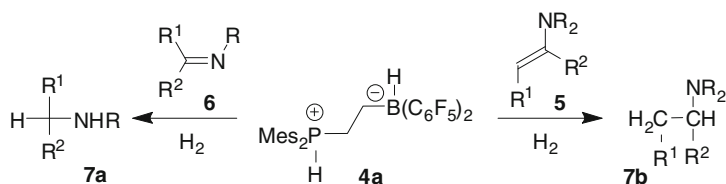
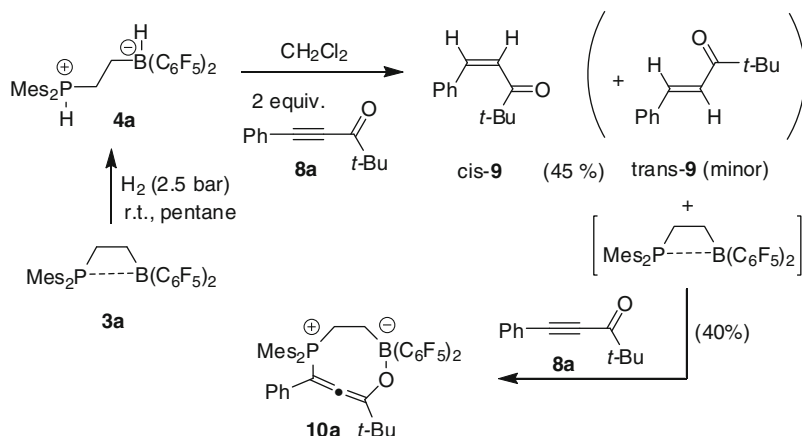


**Fig. 1** Molecular structure of the zwitterionic phosphonium/hydridoborate product **4a**

[ $^1\text{H}$  NMR:  $\delta$  7.87 ( $^1J_{\text{PH}} \sim 490$  Hz),  $^{31}\text{P}$ :  $\delta$   $-6.5$  [P–H],  $^{11}\text{B}$ :  $\delta$   $-20.1$  ( $^1J_{\text{BH}} \sim 90$  Hz) [B–H]]. The reaction was also carried out with dideuterium which confirmed the heterolytic dihydrogen splitting by observing the corresponding [B]–D and [P]–D signals in **4a-D<sub>2</sub>** (Scheme 1 and Fig. 1) [22].

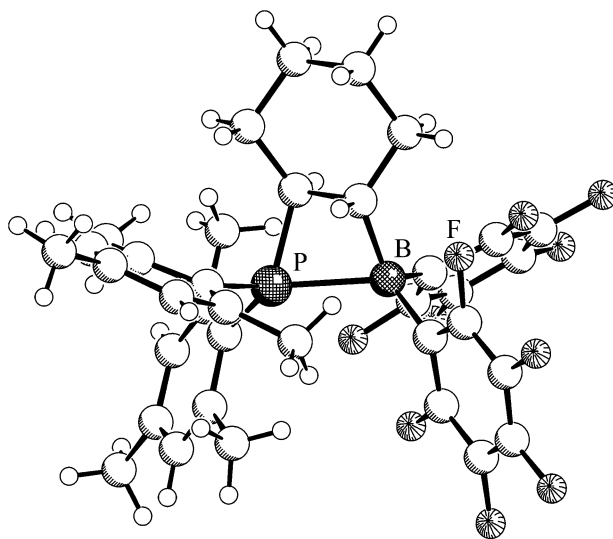
Compound **4a** is able to catalyze the hydrogenation of a variety of enamines **5** or imines **6** to the corresponding amine products **7** (Scheme 2) [24, 25] (Axenov, 2009, unpublished results).

Many FLPs have been shown to be quite reasonable catalysts for the metal-free catalytic hydrogenation of electron-rich unsaturated substrates such as enamines and dienamines (Scheme 2) [22, 24, 25] (Axenov, 2009, unpublished results), in addition to silyl enoethers [26], of a variety of imines and some aziridines [27–32].

**Scheme 2**  $\text{H}^+/\text{H}^-$  transfer from **4a****Scheme 3** Reaction of **4a** with ynone

D. W. Stephan recently showed that even the arene rings in some aniline derivatives can be hydrogenated by FLP systems to yield cyclohexylamines [33]. We showed that FLP catalyzed reactions can provide sufficiently mild conditions for reactions with rather sensitive organometallic substrates [14, 25, 34–38] (Axenov, 2009, unpublished results). All these developments posed the question of whether FLP induced hydrogenation of carbon–carbon double or triple bonds bearing strongly electron-withdrawing substituents could be achieved. For that purpose we treated the conjugated ynone **8a** with the zwitterionic  $\text{H}_2$ -activation product **4a**. We observed a rapid transfer of the  $\text{H}^+/\text{H}^-$  pair at room temperature with formation of the *cis*-enone *cis*-**9**. Unfortunately, in this case the liberated FLP **3a** reacted faster with the ynone substrate **8a** to give **10a** (Scheme 3). As a result, this FLP induced hydrogenation of the electron-poor carbon–carbon triple bond in **8a** remained stoichiometric [39].

We prepared a variety of analogs of the ethylene-bridged P/B FLP **3a** by hydroboration of a series of substituted dimesitylalkenylphosphanes with  $[\text{HB}(\text{C}_6\text{F}_5)_2]$ . The cyclohexenylphosphane derived FLP **3b** is a typical example [40]. Hydroboration of **1b** with Piers' borane gave the P/B FLP **3b** in good yield. Compound **3b** is chiral; it contains two chiral centers. Due to the fixed *cis*-[B]–H addition, the stereochemistry of the underlying hydroboration reaction, these chiral centers are dependent on each other. Only the *rac*-*trans*-diastereoisomer was formed. It is



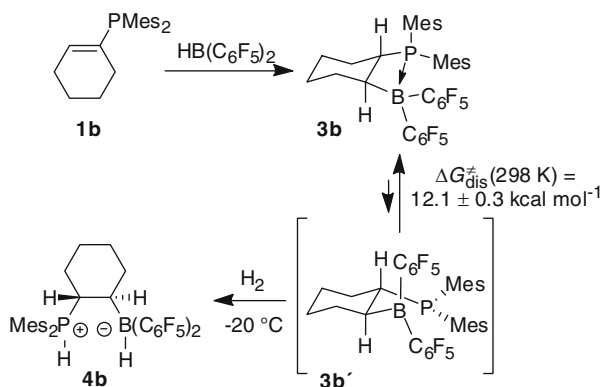
**Fig. 2** Molecular structure of the P/B FLP **3b**

characterized by having the bulky phosphanyl- and boryl-substituents *trans*-1,2-attached at the cyclohexane framework. Compound **3b** was characterized by X-ray diffraction (Fig. 2). In the crystal the cyclohexane ring of compound **3b** adopts a chair conformation with the C1-P and C2-B vectors oriented *trans*-bis-equatorially. There are two crystallographically independent molecules in the unit cell. Both show P...B interactions, although the P...B distance at 2.188(5) Å (molecule A) and 2.206(5) Å (molecule B) is at the long end of phosphane/borane interactions [41–47].

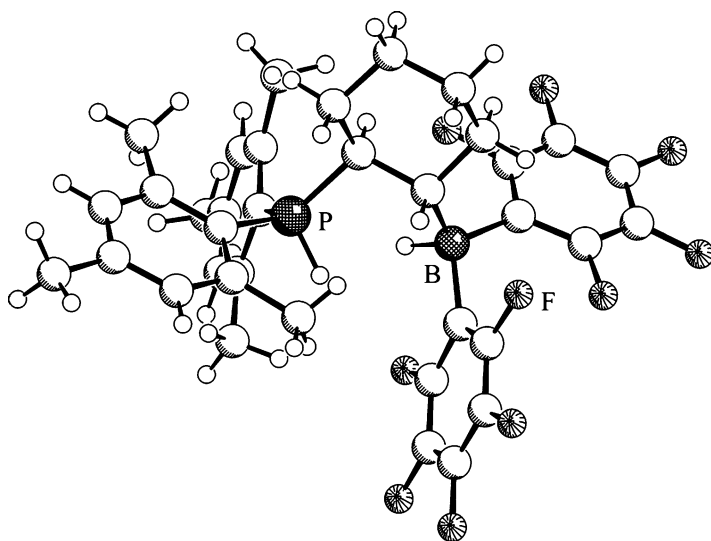
In solution we observed the  $^{19}\text{F}$  NMR signals corresponding to a pair of diastereotopic  $\text{C}_6\text{F}_5$  groups at boron at low temperatures, due to the tetracoordination at boron. Opening of the P–B linkage would result in the formation of a planar-tricoordinate boron center in the reactive intermediate **3b'**; its pair of  $\text{C}_6\text{F}_5$  substituents would, consequently, be homotopic. This feature allowed us to determine the activation energy of the reversible P–B bond cleavage in **3b** by temperature dependent dynamic  $^{19}\text{F}$  NMR spectroscopy. From the coalescence of the respective pairs of *ortho*-F resonances of the diastereotopic  $\text{C}_6\text{F}_5$  groups at boron we obtained the Gibbs activation energy of phosphane–borane dissociation in **3b** at  $\Delta G_{\text{dis}}^\ddagger$  (298 K) =  $12.1 \pm 0.3$  kcal mol $^{-1}$ . Thus, the FLP **3b** is a weak internal phosphane–borane adduct. It opens rapidly with a P–B bond dissociation energy of <12 kcal mol $^{-1}$ .

Consequently, the FLP **3b** reacts very rapidly with dihydrogen.  $\text{H}_2$  is heterolytically cleaved by **3b** at  $-20$  °C with formation of the zwitterionic  $[\text{P}]^+\text{-H}/[\text{B}]^-\text{-H}$  product **4b** (Scheme 4 and Fig. 3) [40].

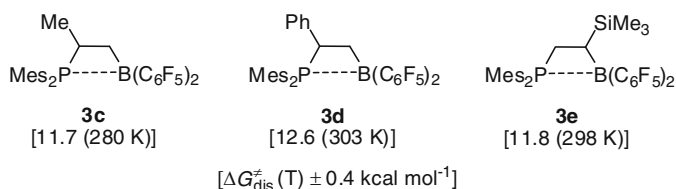
We prepared a variety of related bridge-substituted vicinal P/B FLPs analogously by hydroboration of the respective alkenyldimesitylphosphanes with Piers' borane  $[\text{HB}(\text{C}_6\text{F}_5)_2]$ , the compounds **3c–e** being typical examples (Scheme 5) [48]. Their NMR spectra indicated internal P–B coordination. Due to the presence of a chiral carbon center in the bridge, each of these compounds features pairs of



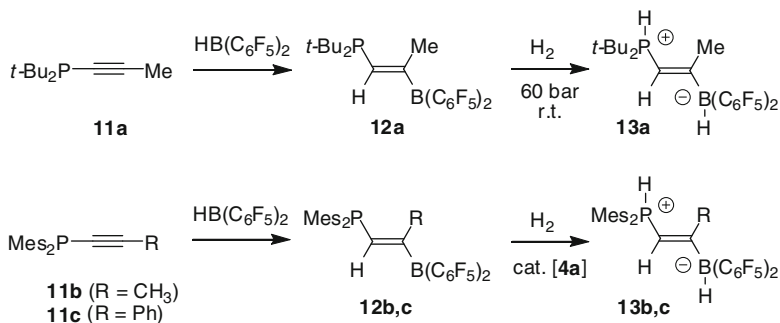
**Scheme 4** Formation of the FLP **3b** and its reaction with dihydrogen



**Fig. 3** Molecular structure of the H<sub>2</sub>-cleavage product **4b**



**Scheme 5** Examples of FLPs **3** and their activation barriers for P...B dissociation



**Scheme 6** Hydroboration of **11** with Piers' borane

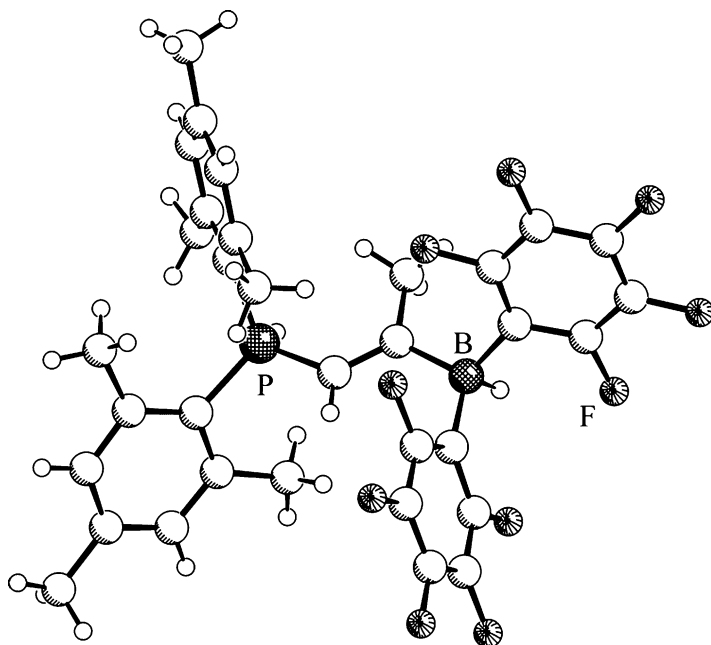
diastereotopic  $\text{C}_6\text{F}_5$  substituents at boron. From the coalescence of their respective  $^{19}\text{F}$  NMR features we have determined the activation barrier of P–B bond dissociation ( $\Delta G_{\text{dis}}^\ddagger$ ) for each of these compounds (Scheme 5). They are similar in magnitude as found for **3b** (see above). Compound **3c** splits dihydrogen under our typical mild reaction conditions (2.5 bar  $\text{H}_2$ , r.t.), whereas the more bulky compounds **3d,e** were unreactive even at 60 bar  $\text{H}_2$  pressure at r.t. [48].

Hydroboration of di-*tert*-butylphosphinopropyne (**11a**) with  $[\text{HB}(\text{C}_6\text{F}_5)_2]$  gave the unsaturated FLP **12a**. It slowly splits dihydrogen under more forcing conditions (60 bar) to give the zwitterion **13a** (Scheme 6) [24]. The dimesitylphosphino-substituted FLPs **12b,c** were prepared analogously by hydroboration of the respective  $\text{Mes}_2\text{P}$ -substituted alkynes **11b,c**. These systems were themselves inert toward  $\text{H}_2$  under our typical conditions, but they rapidly accepted the  $\text{H}^+/\text{H}^-$  pair from the saturated FLP hydrogen activation product **4a**. This hydrogen transfer reaction was developed into a protocol for the formation of the products **13b,c** with dihydrogen catalyzed by the **3a/4a** FLP/FLP- $\text{H}_2$  pairs [24]. Both the products **13b,c** were characterized by X-ray diffraction (Fig. 4 for **13b**). The FLP **13b** was used as a selective catalyst for the hydrogenation of an enamine using ammonia borane ( $\text{H}_3\text{NBH}_3$ ) as a hydrogen source [49, 50].

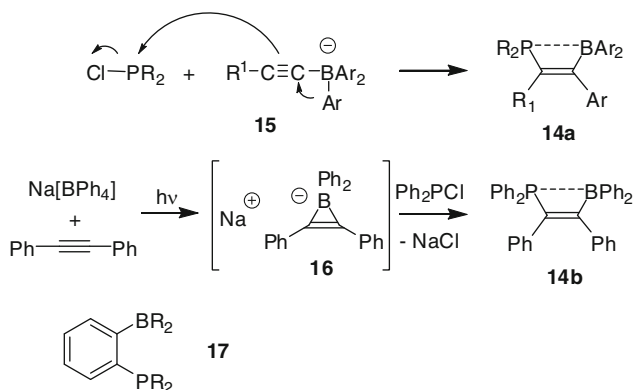
The related unsaturated vicinal *cis*-FLPs **14** were prepared in different ways. Originally, such compounds were obtained by treatment of alkynylborates (e.g., **15**) with  $\text{R}_2\text{PCl}$  reagents [51–55]. The reaction proceeds with aryl migration from boron to the adjacent carbon atom and might be regarded as an early precursor of the 1,1-carboboration reaction [56, 57]. Grobe, Würthwein et al. [58] recently reported a remarkable related formation of an example of this by means of the intermediate formation of **16**. These *cis*-**14** systems do not seem reactive towards  $\text{H}_2$  but some of these bifunctional FLP-like compounds undergo interesting reactions with a variety of metal complexes (as do D. Bourissou's related phenylene-bridged FLP derivatives **17**) [59–62] (Scheme 7).

We have developed a convenient new synthetic pathway to the unsaturated P/B systems **14** by making use of the recently discovered advanced variants of the 1,1-carboboration reaction ([63]; see also [64–68]). For this purpose we treated,



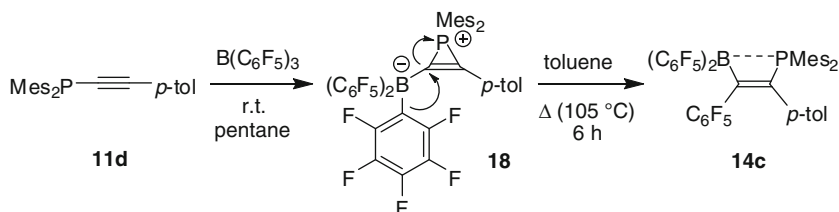


**Fig. 4** Molecular structure of compound **13b**

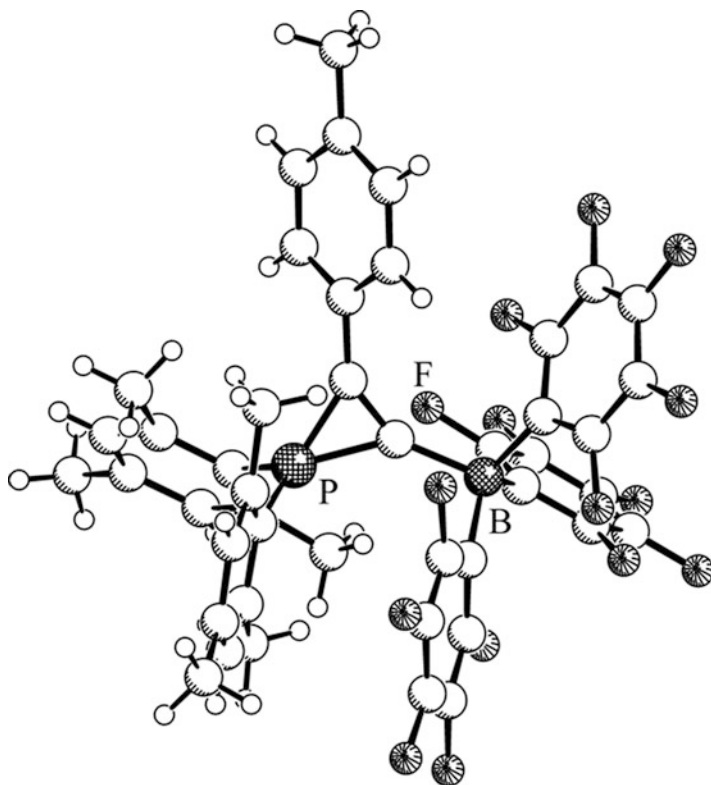


**Scheme 7** Formation of the systems **14**

e.g., the dimesitylphosphinoacetylene derivative **11d** (Scheme 8) with  $\text{B}(\text{C}_6\text{F}_5)_3$  [69, 70] at room temperature in pentane. Under these conditions  $\text{B}(\text{C}_6\text{F}_5)_3$  adds to the alkyne and initiates migration of the  $\text{Mes}_2\text{P}$  moiety along the acetylenic carbon framework. After 30 min reaction time we isolated the product **18** [71]. The X-ray crystal structure analysis of **18** revealed the presence of the unsaturated cationic three-membered heterocycle to which the borate counter anion is bonded (Fig. 5).



**Scheme 8** Pathway to compound **14c**



**Fig. 5** A view of the molecular structure of the zwitterionic phosphirenium-borate betaine **18**

This class of compounds exhibits very characteristic NMR features [71, 72]; compound **18** shows, e.g., a  $^{31}\text{P}$  NMR resonance at  $\delta -137.8$  and a  $^{11}\text{B}$  NMR signal at  $\delta -16.5$ . In the phosphirenium-borate **18** the dimesitylphosphino group had migrated about half way across the acetylenic  $\text{C}\equiv\text{C}$  bond. Heating to  $105^\circ\text{C}$  was necessary to complete the 1,1-carbaboration reaction to eventually give the product **14c**. Compound **14c** shows heteronucleic NMR resonances at  $\delta 14.6$  ( $^{31}\text{P}$ ) and  $\delta 0$  ( $^{11}\text{B}$ ), respectively. The X-ray crystal structure analysis revealed a

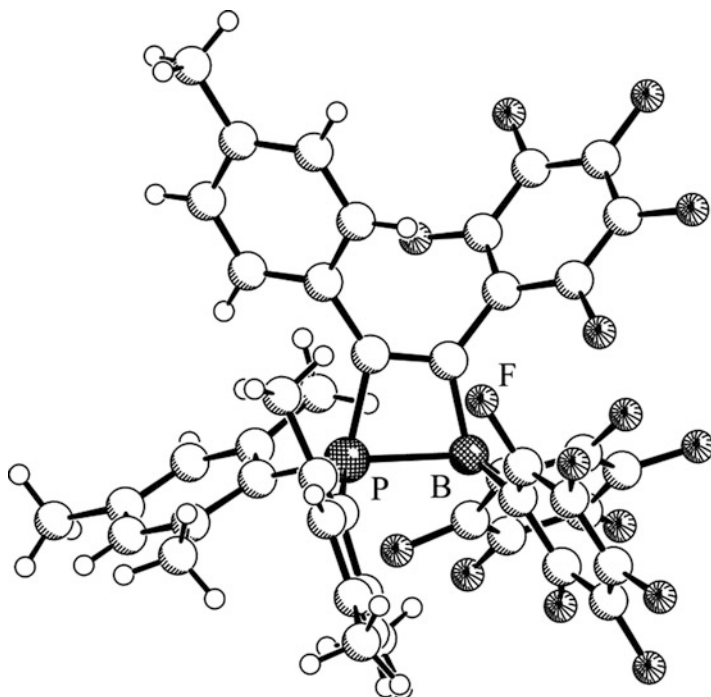


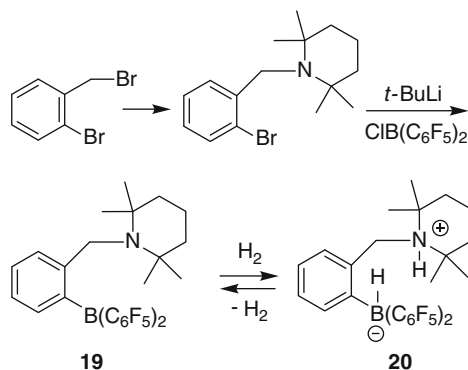
Fig. 6 Molecular structure of **14c**

pronounced B–P interaction between the  $(\text{C}_6\text{F}_5)_2\text{B}$ - and  $\text{Mes}_2\text{P}$ -substituents which are *cis*-oriented at the bridging unsaturated  $\text{C}_2$ -framework (Fig. 6).

We prepared a variety of differently substituted P/B systems **14** by this advanced 1,1-carboboration method [73] and used them for an in depth analysis of the bonding between phosphorus and boron in such systems by solid state NMR techniques [23]. Both the  $^{11}\text{B}$  NMR isotropic chemical shifts and the nuclear electric quadrupolar coupling parameters were found to serve as sensitive experimental measures. In addition the large  $^{31}\text{P}$ - $^{11}\text{B}$  scalar spin–spin coupling of  $^1J \geq 50$  Hz, obtained from the  $^{31}\text{P}\{^1\text{H}\}$ -CPMAS NMR experiments, gave further evidence for the covalent P–B bonding component in such compounds.

### 3 Intramolecular N/B FLPs

Repo, Rieger et al. prepared the  $\text{C}_3$ -bridged N/B FLP **19** by a conventional route involving metalation. The N/B system **19** is an active frustrated Lewis pair that heterolytically cleaves dihydrogen to yield **20** ([74, 75]; see also [76]). The  $[\text{N}]^+\text{-H}/[\text{B}]^-\text{-H}$  zwitterion **20** was thoroughly characterized, including a neutron diffraction



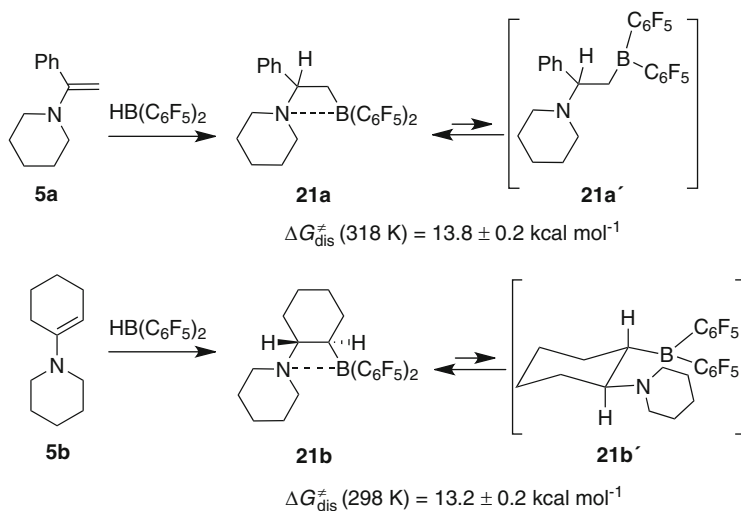
**Scheme 9** Formation of the N/B FLP **19** and its reaction with dihydrogen

study [77]. The system is special since it is one of the rare examples of reversible  $H_2$ -addition (and activation) by a frustrated Lewis pair [5, 26] (Scheme 9).

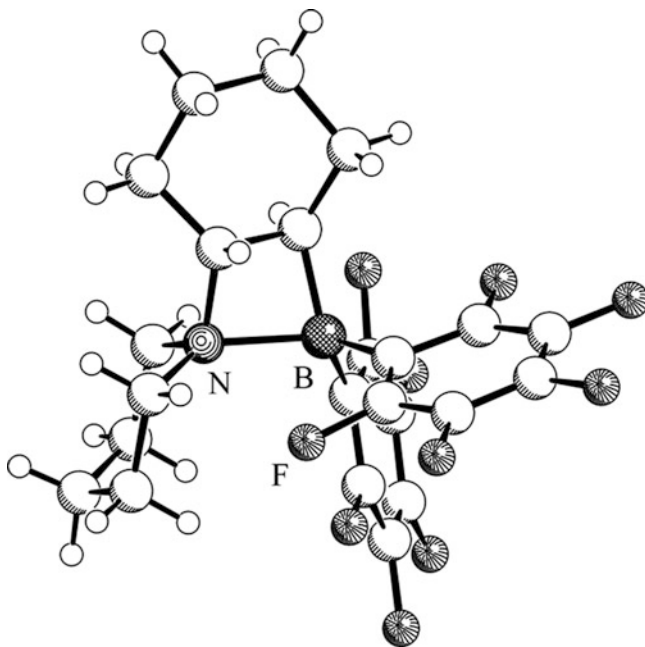
We prepared a series of vicinal N/B FLPs by enamine hydroboration [78]. A typical example is the reaction of the acetophenone derived enamine **5a** with  $[HB(C_6F_5)_2]$  which gave the phenyl substituted vicinal N/B FLP **21a** in good yield. Compound **21a** features a heterocyclic four-membered ring structure. The phenyl substituted bridge-carbon atom C1 is a chiral center. Therefore, we observed  $^1H/^{13}C$  NMR signals of the diastereotopic methylene groups of the piperidino substituent. The  $C_6F_5$  groups at boron are also diastereotopic in **21a** (at 298 K), which indicated N–B coordination. The related compound **21b** was obtained by  $[HB(C_6F_5)_2]$  hydroboration of the enamine piperidino cyclohexene (Scheme 10). The X-ray crystal structure analysis showed N–B coordination. Compound **21b** contains a heterocyclic four-membered ring structure (Fig. 7).

The N–B bond in compound **21a** is weak. This becomes evident from the dynamic  $^{19}F$  NMR spectra. The system shows signals of pairs of diastereotopic  $C_6F_5$  groups below ca. 320 K (Fig. 8). Warming leads to coalescence of both pairs of *p*- $C_6F_5$  and *m*- $C_6F_5$  signals, indicating rapid reversible N–B bond rupture and equilibration with the (invisible) reactive intermediate **21a'** on the  $^{19}F$  NMR time scale. From the dynamic  $^{19}F$  NMR spectra we estimate a barrier for the N–B opening in **21a** of  $\Delta G_{dis}^\ddagger$  (318 K) =  $13.8 \pm 0.2$  kcal mol $^{-1}$  (Fig. 8). A similar value was found for the ring opening process of the N/B FLP **21b** (Scheme 10).

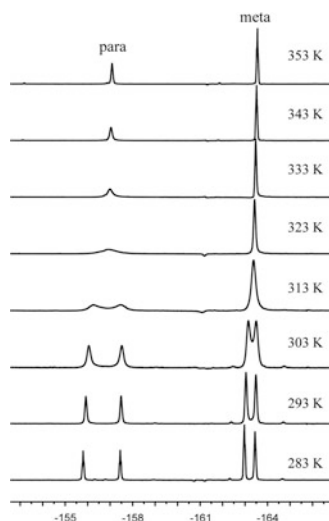
It appears that the intramolecular boron Lewis acid interaction with the *tert*-amine Lewis base in the FLPs **21** is slightly stronger than with the *tert*-phosphanes in **3**. However, the B–N bonds in the systems **21** must still be regarded as being weak (bond dissociation energies <13 kcal mol $^{-1}$ ). These LA–LB bonds open and close rapidly. Both the N/B FLPs **21a** and **21b** react readily with dihydrogen to yield the ammonium/hydridoborate zwitterions **22a** and **22b**, respectively. Both were characterized by X-ray diffraction (**22a**, Fig. 9) and by spectroscopy [**22a**:  $^{11}B$  NMR:  $\delta$  –22.8 (d,  $^1J_{BH}$  ~80 Hz),  $^1H$  NMR:  $\delta$  3.08 (br, 1:1:1:1 q, [B]–H),  $\delta$  7.46 ([N]–H)] (Scheme 11).



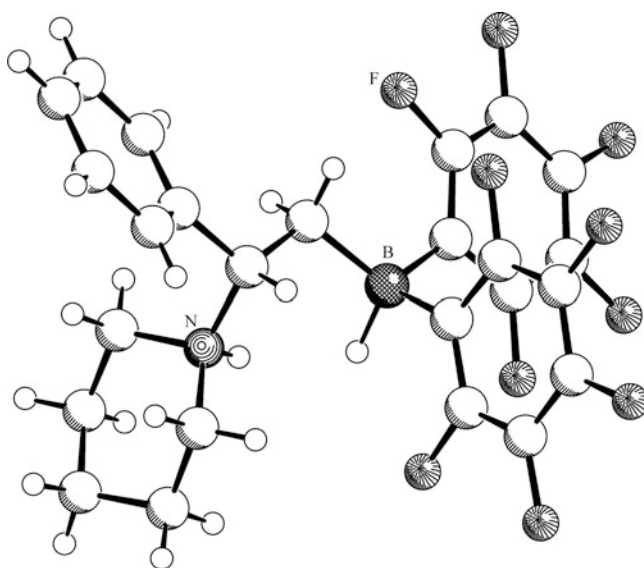
**Scheme 10** Formation and ring opening of the FLPs **21a** and **21b**



**Fig. 7** Molecular structure of the N/B FLP **21b** (N–B = 1.824(6) Å)



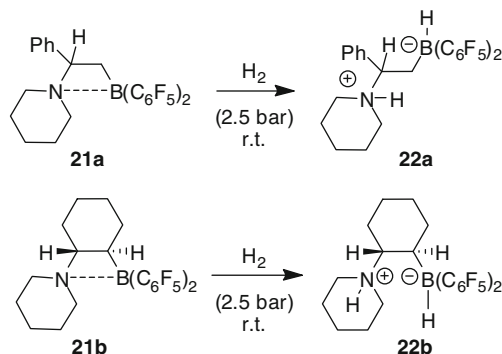
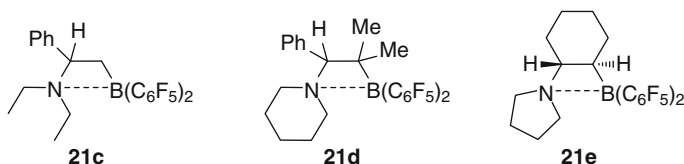
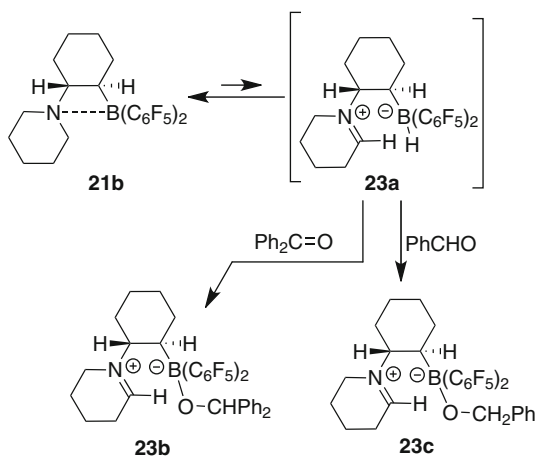
**Fig. 8** Temperature dependent dynamic  $^{19}\text{F}$  NMR spectra of the N/B FLP **21a**



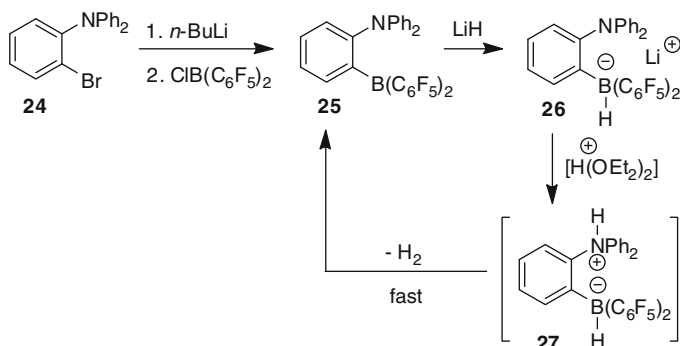
**Fig. 9** A view of the molecular structure of the ammonium/hydridoborate  $\text{H}_2$ -activation product **22a**

We prepared a variety of such vicinal N/B FLPs by means of the enamine hydroboration reaction (Scheme 12). The compounds **21c,d** did not react with dihydrogen under our typical conditions.

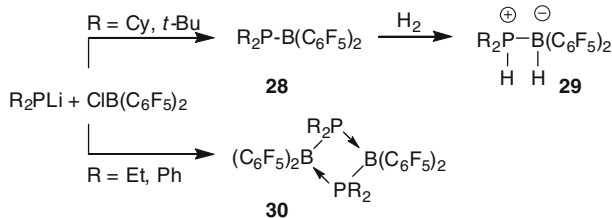
The nitrogen containing FLP **21b** shows a chemical peculiarity that appears upon its treatment with aldehydes or ketones. It is well known that  $\text{B}(\text{C}_6\text{F}_5)_3$  is able

**Scheme 11** Dihydrogen splitting with N/B FLPs **21a,b****Scheme 12** Examples of N/B FLPs **21****Scheme 13** Reactions of the FLP **21b** with organic carbonyl compounds

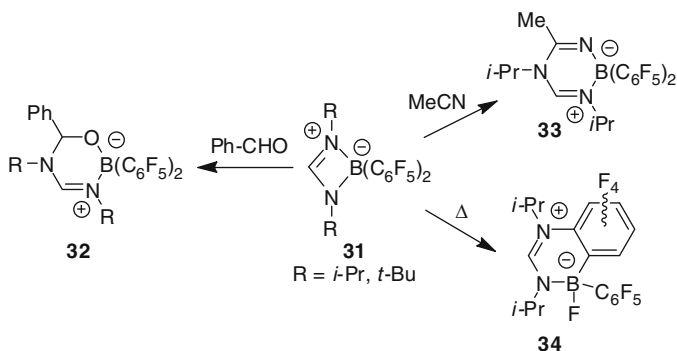
to abstract hydride anion from the  $\alpha$ -position of tertiary amines [37, 79–84]. In the case of the N/B FLP **21b** this could lead, e.g., to the formation of the iminium/hydridoborate zwitterion **23a** (Scheme 13). Without added reagents we did not observe its formation. However, added benzaldehyde or benzophenone



**Scheme 14** Generation of compound **27** and its loss of dihydrogen



**Scheme 15** Phosphidoborane FLPs

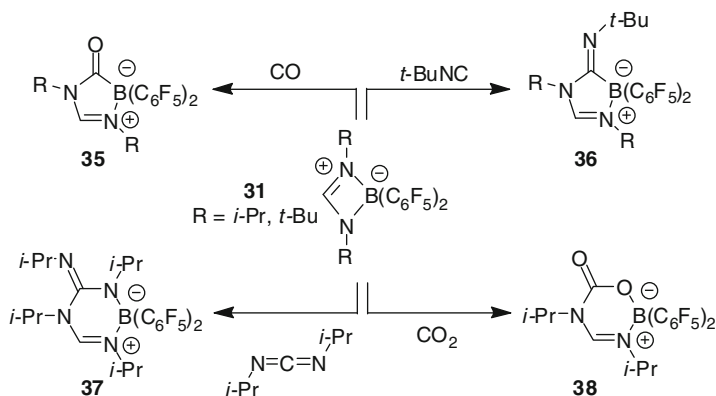


**Scheme 16** FLP behavior of a boron-amidinate

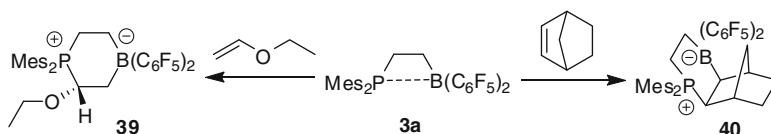
resulted in the formation of the respective trapping products, namely the zwitterionic systems **23b** and **23c**, respectively [78].

Previously, Piers reported the synthesis of a phenylene-bridged N/B system **25**. The separate addition of hydride followed by protonation may have generated the ammonium/hydridoborate system **27**, which was labile with regard to rapid  $\text{H}_2$  elimination (Scheme 14) ([85]; see also [86]).





**Scheme 17** Reactions of the boron-amidinates **31**

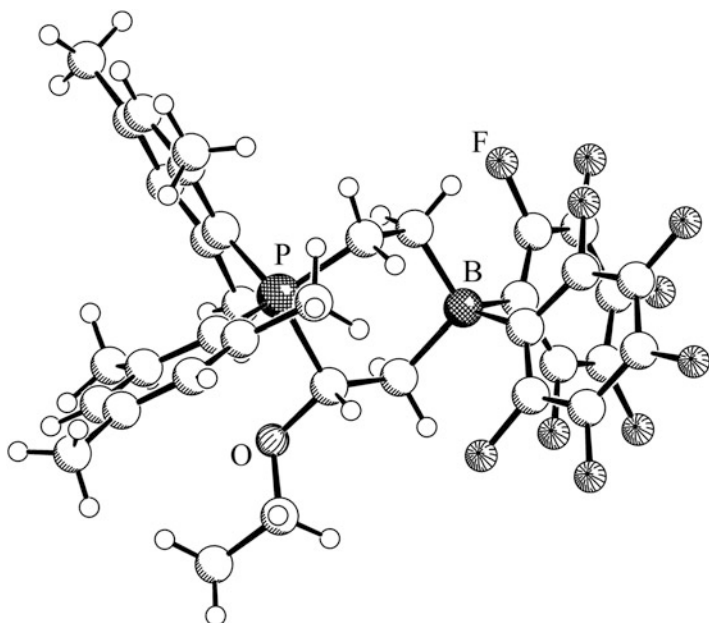


**Scheme 18** Olefin addition reactions to the FLP **3a**

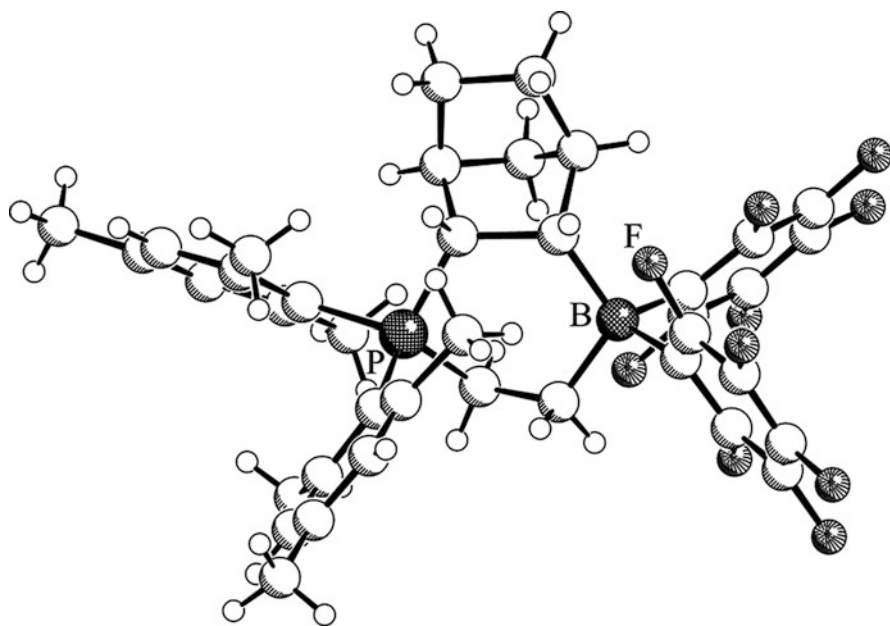
The monomeric phosphido-boranes  $\text{R}_2\text{P}-\text{B}(\text{C}_6\text{F}_5)_2$  **28** ( $\text{R}$  = cyclohexyl or *tert*-butyl) show a related FLP behavior. They react slowly at 60 °C with dihydrogen to give the phosphane–borane adducts  $\text{R}_2\text{HP}-\text{BH}(\text{C}_6\text{F}_5)_2$  **29**. In contrast, the dimeric phosphido–boranes  $[\text{R}_2\text{P}-\text{B}(\text{C}_6\text{F}_5)_2]_2$  **30** did not react with  $\text{H}_2$  under these conditions (Scheme 15) [87, 88].

Stephan and coworkers have recently shown that boron-amidinates  $\text{HC}(\text{RN})_2\text{B}(\text{C}_6\text{F}_5)_2$  **31** ( $\text{R}$  = *i*-Pr, *t*-Bu) react with benzaldehyde to give **32** ( $\text{R}$  = *i*-Pr, *t*-Bu). In addition, these species were also found to react with MeCN to give **33**. These reactions are thought to proceed via the ring opening of the boron-amidinate, although this could not be confirmed spectroscopically. However, this proposition was supported by thermolysis of the boron-amidinate which gave **34** (Scheme 16) [89].

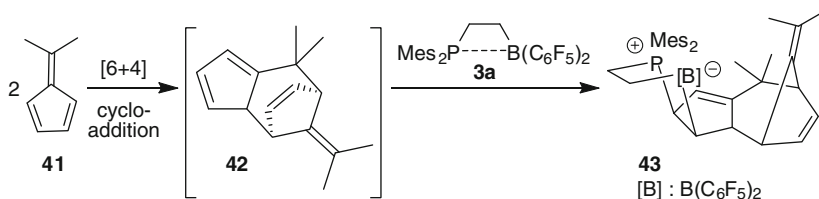
The systems **31** were also shown to insert CO and isonitriles into the B–N bond to yield the respective five-membered heterocycles **35** and **36**. Typically, **31** also reacts with a carbodiimide to give **37** and with carbon dioxide to yield the product **38** [89] (Scheme 17).



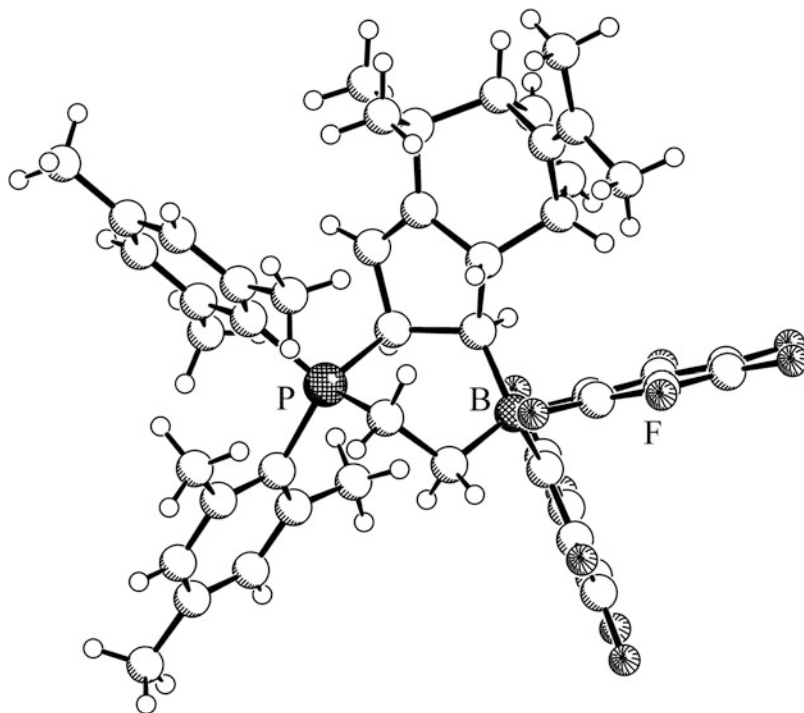
**Fig. 10** Molecular structure of compound **39**



**Fig. 11** A view of the framework of the molecular structure of **40**



**Scheme 19** Trapping of a fulvene dimer by FLP **3a**

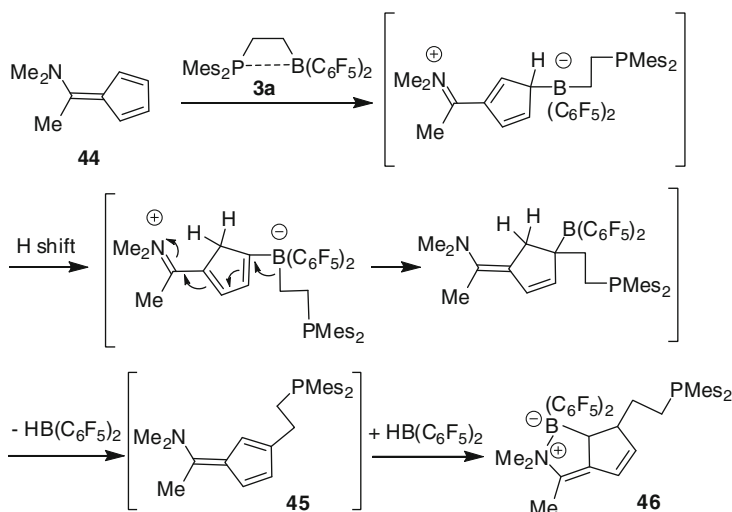


**Fig. 12** A projection of the framework structure of compound **43**

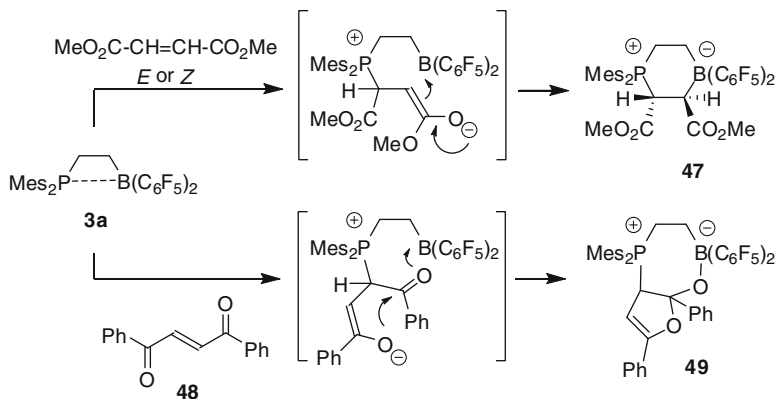
## 4 FLP Reactions with $\pi$ -Systems and More

FLPs often add to olefinic carbon–carbon  $\pi$ -systems [7, 36, 38, 90–92]. A typical example is the reaction of the intramolecular FLP **3a** with ethylvinylether. The frustrated Lewis pair adds to the electron-rich carbon–carbon double bond regioselectively to yield the six-membered heterocyclic product **39** (Scheme 18) [90]. The product was characterized by X-ray diffraction (Fig. 10) and was shown to exhibit a typical chair-like conformation of the central framework [93].

The FLP **3a** adds cleanly to the norbornene  $\text{C}=\text{C}$  double bond to give selectively the *exo*-2,3-P/B addition product **40**. Although only this product was observed,



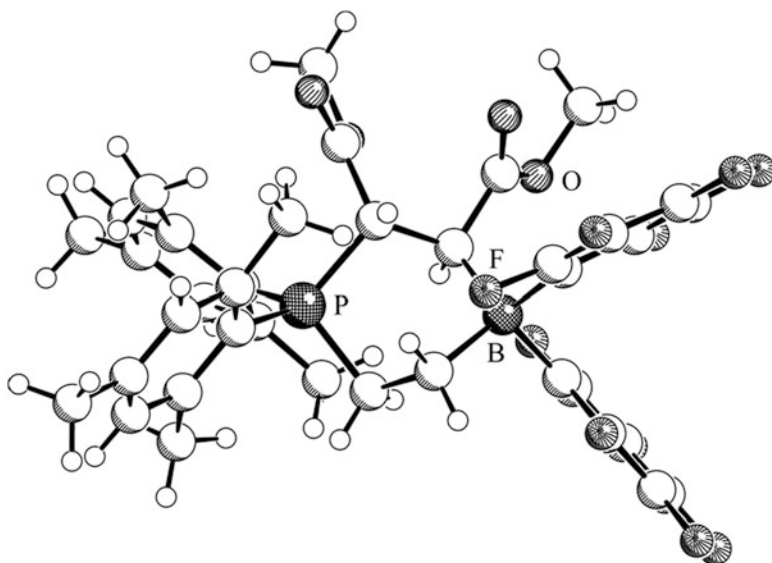
**Scheme 20** Reaction of an aminofulvene with FLP **3a**



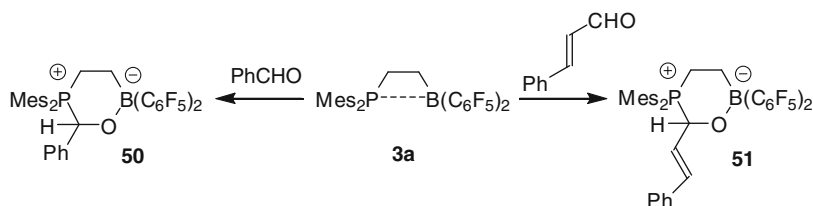
**Scheme 21** Reaction of FLP **3a** with activated alkenes

another possible rearranged product was calculated to be thermodynamically slightly favored. The selective formation of **40** without any of the typical norbornyl cation rearrangement products is in accord with the result of a computational study that indicated an asynchronous concerted 1,2-P/B FLP addition pathway of **3a** to norbornene from the *exo*-face (Fig. 11 for the structure of compound **40**) [90, 93].

A similar reaction was observed upon treatment of the FLP **3a** with 6,6-dimethylpentafulvene (**41**) in a 1:2 molar ratio. In this case the frustrated Lewis pair trapped the (otherwise unobserved) [6+4] fulvene dimer **42** by 1,2-P/B addition to one of its C=C double bonds (Scheme 19 and Fig. 12) to yield **43** [94].



**Fig. 13** A view of the molecular structure of compound **47**

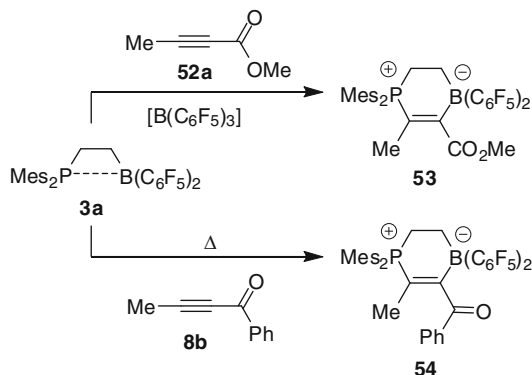


**Scheme 22** Reaction of FLP **3a** with aldehydes

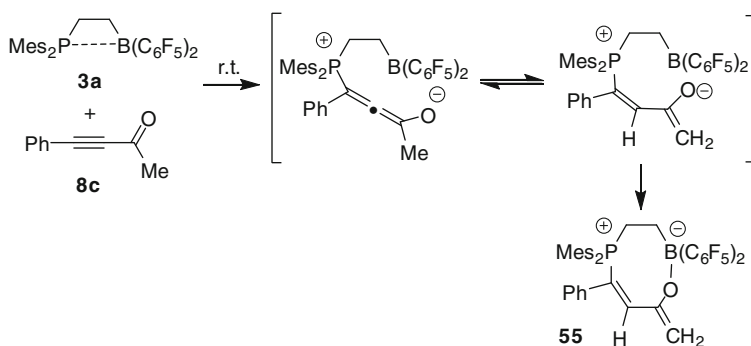
6-Dimethylamino-6-methylpentafulvene (**44**) undergoes a curious reaction with the FLP **3a** [95]. It readily forms the product **46** by a sequence that involves B–C bond cleavage. We had to assume that a retro-hydroboration reaction took place along the favored pathway (Scheme 20) that eventually was completed by addition of the in situ generated  $[\text{HB}(\text{C}_6\text{F}_5)_2]$  reagent to the substituted fulvene derivative **45**.

The FLP **3a** reacts with dimethylfumarate by 1,2-P/B addition to the activated carbon–carbon double bond to give the six-membered heterocycle **47** that features the pair of  $-\text{CO}_2\text{Me}$  substituents in *trans*-1,2-positions. The same product is obtained from the reaction of **3a** with dimethylmaleate, which indicates a conventional step-wise reaction mechanism (Scheme 21 and Fig. 13). A closely related reaction takes place upon treatment of **3a** with diphenylbutendione (**48**), only in this case O–B bond formation is favored over C–B bond formation in the second step to yield the product **49** (Scheme 21) [96].

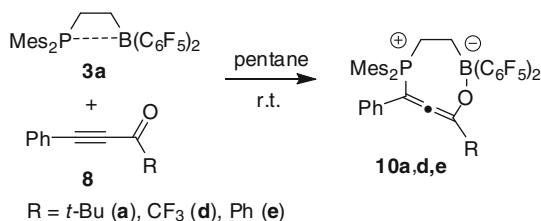
In the formation of the product **49** we see the involvement of the carbonyl functionality. This is often observed in FLP reactions. Typical examples are the 1,2-carbonyl addition reactions of **3a** to reactive aldehydes, such as benzaldehyde



**Scheme 23** Reaction of FLP **3a** with ynones



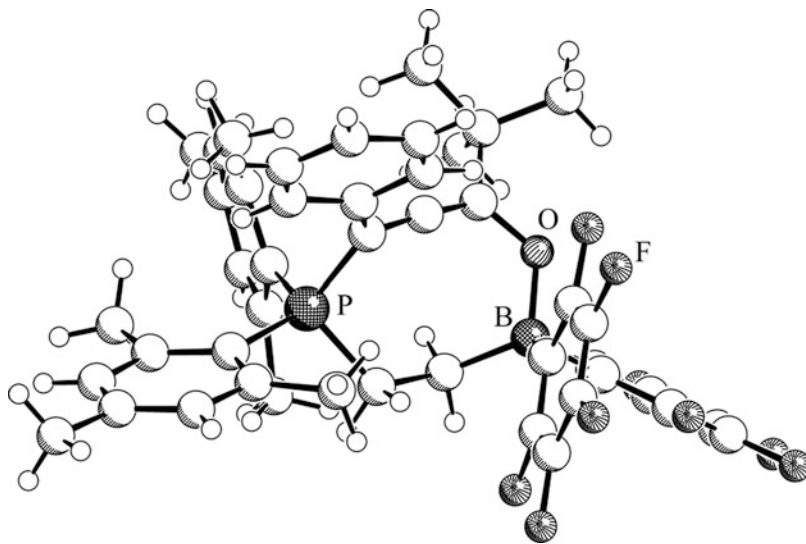
**Scheme 24** 1,4-Addition of FLP **3a** to the ynone **8c**



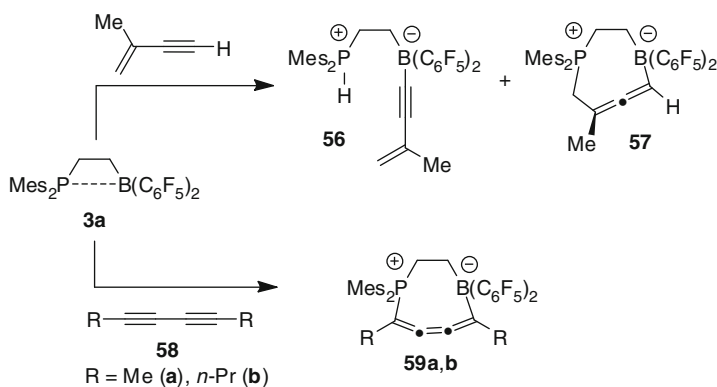
**Scheme 25** 1,4-Addition of FLP **3a** to non-enolizable conjugated ynones

(to give **50**) [97]. In a direct competition the addition of **3a** to the  $-\text{CH}=\text{O}$  group in *trans*-cinnamaldehyde forming compound **51** is strongly favored over any addition to the conjugated carbon–carbon double bond (Scheme 22) [90].

The situation which arises upon reacting the intramolecular P/B FLP **3a** with acetylenic esters **52** or conjugated ynones **8** is more subtle. The acetylenic ester **52a** itself was not reactive enough to allow for a clean product formation upon treatment with the intramolecular FLP **3a**. However, by preactivating **52a** with  $\text{B}(\text{C}_6\text{F}_5)_3$  the



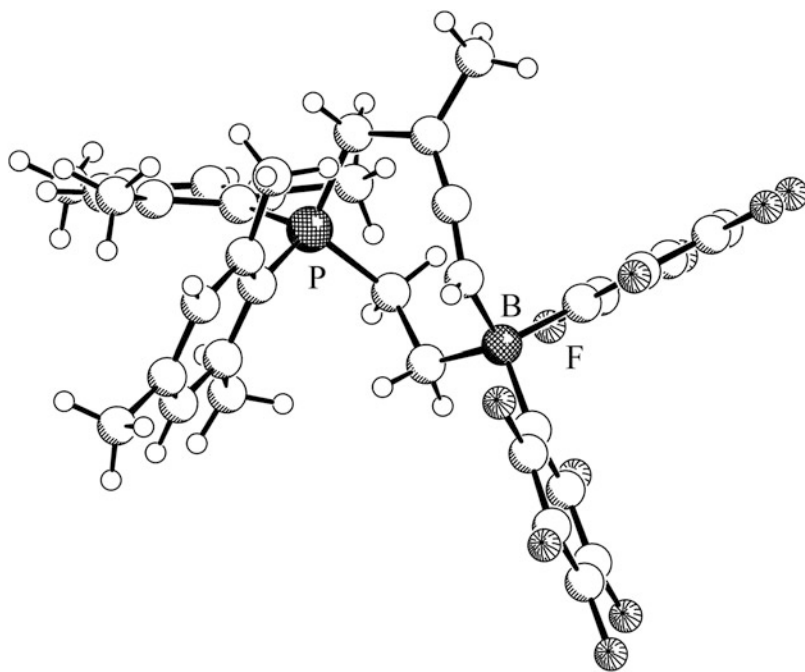
**Fig. 14** A view of the molecular structure of the product **10a** ( $R = t\text{-Bu}$ )



**Scheme 26** Cyclic cumulene formation from FLP **3a**

reaction proceeded to give the 1,2-addition product (**53**) of **3a** to the  $\text{C}\equiv\text{C}$  triple bond of the substrate **52a** [96]. The more reactive conjugated ynone **8b** did not require any extra activation to react with **3a**. It formed the six-membered addition product **54** when heated under reflux (Scheme 23) [39].

However, the formation of the six-membered products is an exception in the addition reaction of an intramolecular vicinal FLP to conjugated ynone substrates. Usually the formation of eight-membered heterocyclic compounds involving participation of the carbonyl oxygen atom is thermodynamically favored [39]. A typical example arose when the FLP **3a** was reacted at room temperature with the ynone **8c** to give the eight-membered addition product **55**. Apparently, **55** is



**Fig. 15** A view of the molecular structure of the eight-membered heterocyclic allene **57**

formed in a two step reaction sequence involving a tautomerization step before finally closing the medium sized ring by B–O bond formation (Scheme 24).

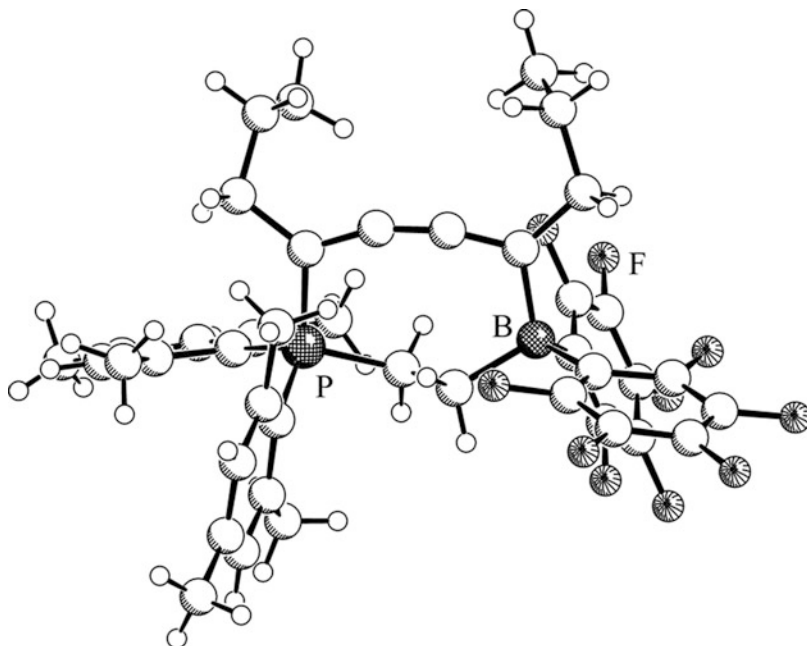
We also reacted a series of non-enolizable conjugated ynones **8a,d,e** with the intramolecular P/B FLP **3a**. They all directly gave the respective eight-membered heterocyclic allenic boron enolate products **10** (Scheme 25 and Fig. 14) [39].

The chemistry of these compounds turned out to be important for our ongoing development of FLP-derived catalysts for the metal-free hydrogenation of electron-poor alkynes and alkenes [39].

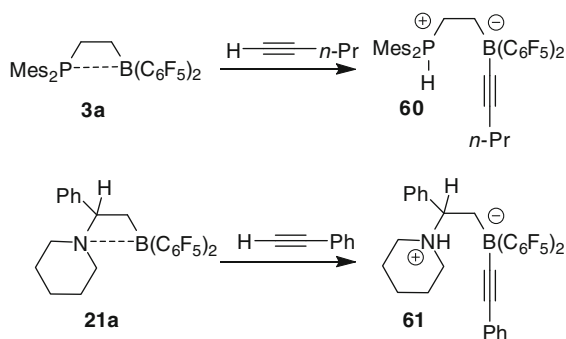
Conjugated enynes seem to react similarly with FLPs [98, 99]. Treatment of 2-methyl-1,3-butenyne with  $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$  (**3a**) at room temperature gave a ca. 1:2 mixture of the products **56** and **57** (Scheme 26). Compound **56** is a very typical reaction product of FLPs with terminal acetylenes (for further examples see below). The medium ring-sized heterocyclic allene **57** is a remarkable compound, formed by a 1,4-FLP addition reaction to the conjugated  $\pi$ -system of the enyne reagent [98]. The X-ray crystal structure analysis of **57** (Fig. 15) revealed that this compound contains an almost regular allene unit – the angle between its substituents planes at the allene termini amounts to ca.  $75^\circ$ , i.e., not too far away from the  $90^\circ$  angle of an ideal allene structure. The central carbon atom of the cumulated  $\text{C}=\text{C}=\text{C}$  unit shows a typical allene  $^{13}\text{C}$  NMR resonance ( $\delta$  204.5 ppm).

A similar reaction took place when the intramolecular FLP **3a** was reacted with conjugated diynes **58a,b** (Scheme 26). We isolated the corresponding 1,4-FLP addition products **59a,b**. The X-ray crystal structure analysis of **59b** (Fig. 16)





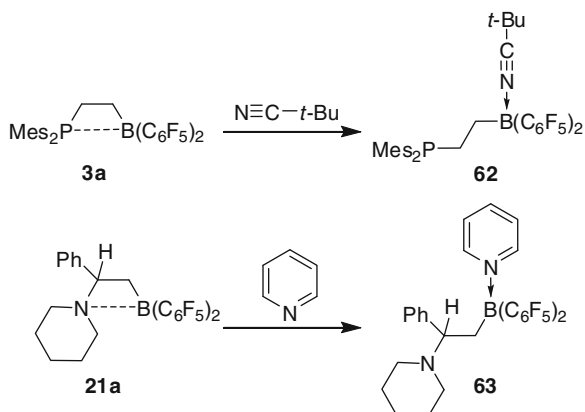
**Fig. 16** Molecular structure of the heterocyclic cumulene **59b**



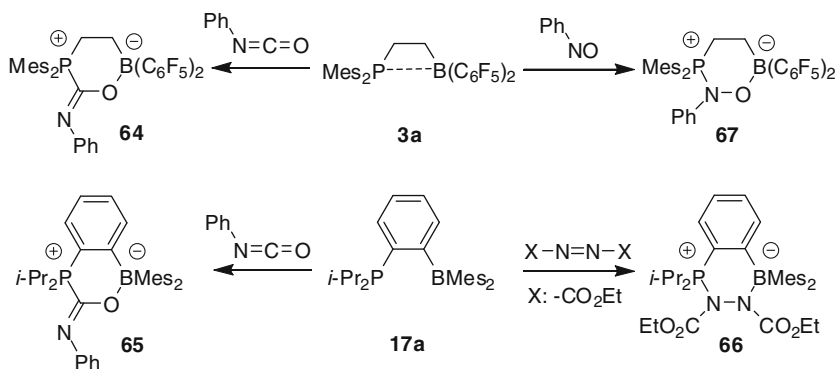
**Scheme 27** Reactions of FLPs with 1-alkynes

confirmed the formation of the substituted 1,2,3-butatriene substructure inside the strained eight-membered heterocyclic ring system. It exhibits some deviation of the  $C=C=C$  moiety from linearity featuring a pair of  $C-C-C$  angles of  $161.1(2)^\circ$  and  $165.0(2)^\circ$ . The  $P-CH_2-CH_2-B$  unit shows a dihedral angle of  $-129.8(2)^\circ$ . This unit does not conformationally equilibrate at r.t. on the NMR time scale. Consequently, we observed pairs of diastereotopic  $C_6F_5$  substituents at boron and mesityl groups at phosphorus [98].

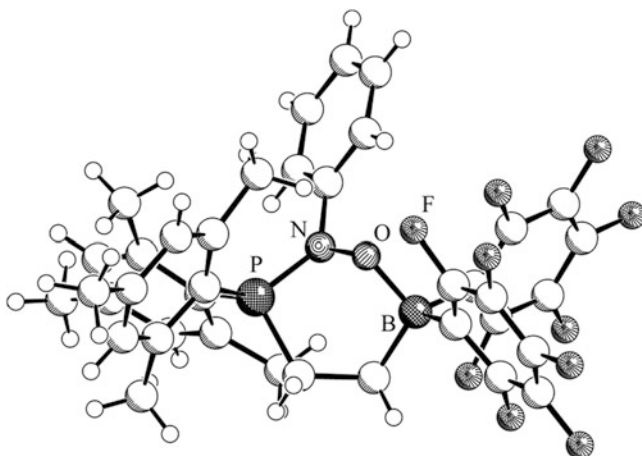
FLPs very often react with terminal acetylenes by means of deprotonation followed by boron–acetylide bond formation. The formation of compound **60** is a



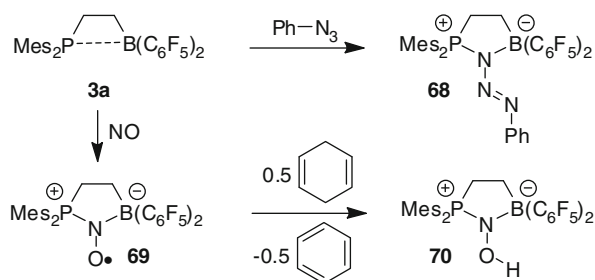
**Scheme 28** Reactions of FLPs with donor molecules



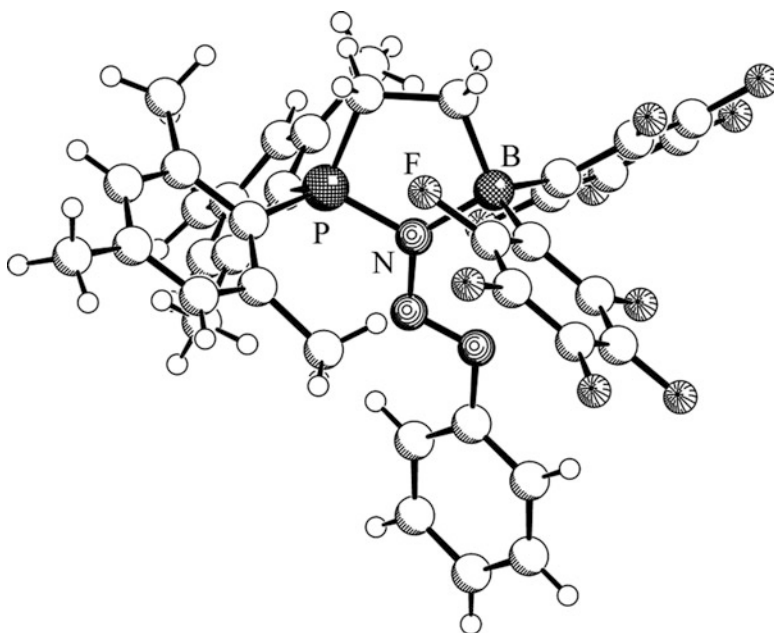
**Scheme 29** Various addition reactions to P/B FLPs



**Fig. 17** Molecular structure of the PhNO addition product **67**



**Scheme 30** Reactions of FLP **3a** with phenylazide and with nitric oxide

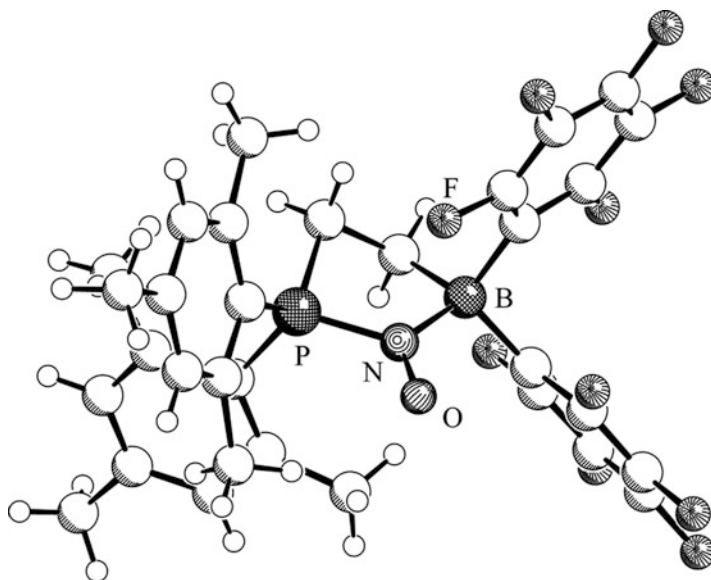


**Fig. 18** Molecular structure of compound **68**

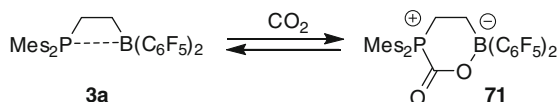
typical example [90]. The N/B FLPs often undergo analogous  $\text{H}^+$  abstraction reactions with 1-alkynes, e.g., **21a**  $\rightarrow$  **61** (Scheme 27) [78].

The FLP **3a** reacts with a variety of heteroatom containing substrates. Typical examples are the reactions with strong donor reagents such as nitriles (e.g., **62**), isonitriles, or pyridine. In all these cases the intramolecular  $\text{P} \cdots \text{B}$  interaction is lost with formation of the respective donor adducts to the borane functional group (Scheme 28) [97]. The N/B FLPs react similarly to form, e.g., **63** [78].

The heterocumulene phenylisocyanate adds to the intramolecular FLP **3a** via its reactive  $\text{C}=\text{O}$  functionality (**64**) [40, 97], as does the phenylene-bridged P/B system **17a** described by Bourissou et al. (**65**) (Scheme 29). The latter also adds to the  $-\text{N}=\text{N}-$  bond of DEAD ([59, 100]; see also [101]).



**Fig. 19** Molecular structure of the FLPNO• aminoxyl radical **69**



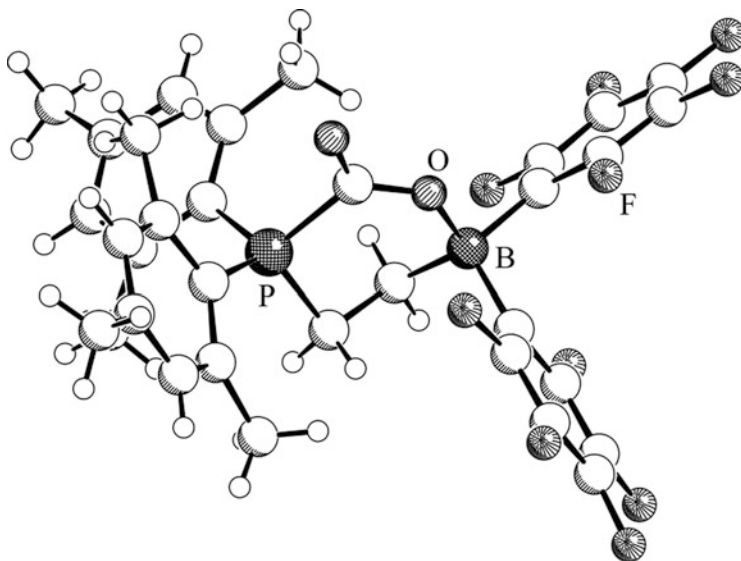
**Scheme 31** Reactions of FLP **3a** with carbon dioxide

In a related study it was shown that  $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$  (**3a**) adds to the  $-\text{N}=\text{O}$  function of nitrosobenzene to yield the six-membered heterocyclic product **67** (Scheme 29 and Fig. 17) [97].

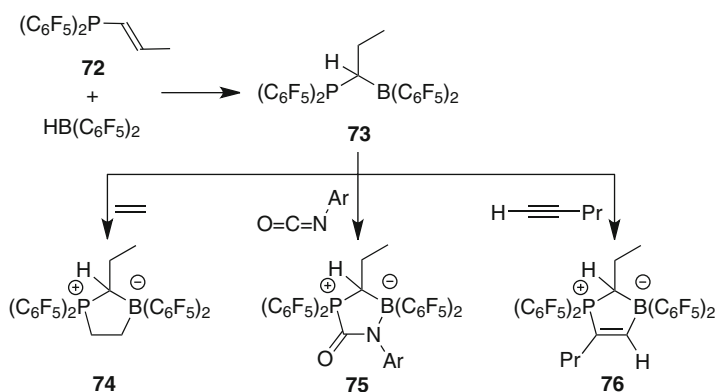
Some FLPs react cleanly with organic azides. The formation of the five-membered heterocyclic product **68** obtained by N,N-addition of **3a** to phenylazide is a typical example. In the crystal compound **68** features an alternating N–N=N bond sequence (1.374(2) Å/1.254(2) Å) (Scheme 30 and Fig. 18) [97].

The intramolecular FLP **3a** reacts readily with nitric oxide (NO) by N,N-addition to give the five-membered FLPNO• radical **69** in high yield. Compound **69** is the parent of a novel type of persistent aminoxyl radicals. It undergoes H-atom abstraction (HAA) reactions with a variety of hydrocarbon substrates to form the diamagnetic FLPNOH product **70** (Scheme 30). The FLPNO• radical **69** was characterized by X-ray diffraction (Fig. 19) [102, 103]. A detailed description of the chemistry of these new FLP derived nitroxide radicals is provided within this *Topics Curr. Chem.* volume by a separate contribution by T. W. Warren and G. Erker on “Radical Frustrated Lewis Pairs”.

There is great interest in the binding and chemical conversion of carbon dioxide. Frustrated Lewis pair chemistry has made some contributions to this field [104, 105]. We have observed that the intramolecular FLP **3a** is able to bind carbon dioxide rapidly under suitable conditions to form the 1,2-P/B addition product **71** (Scheme 31) [106].

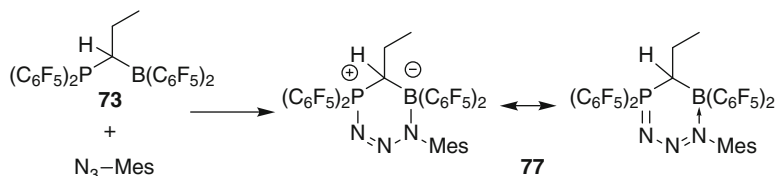


**Fig. 20** Molecular structure of the FLP- $\text{CO}_2$  addition product **71**

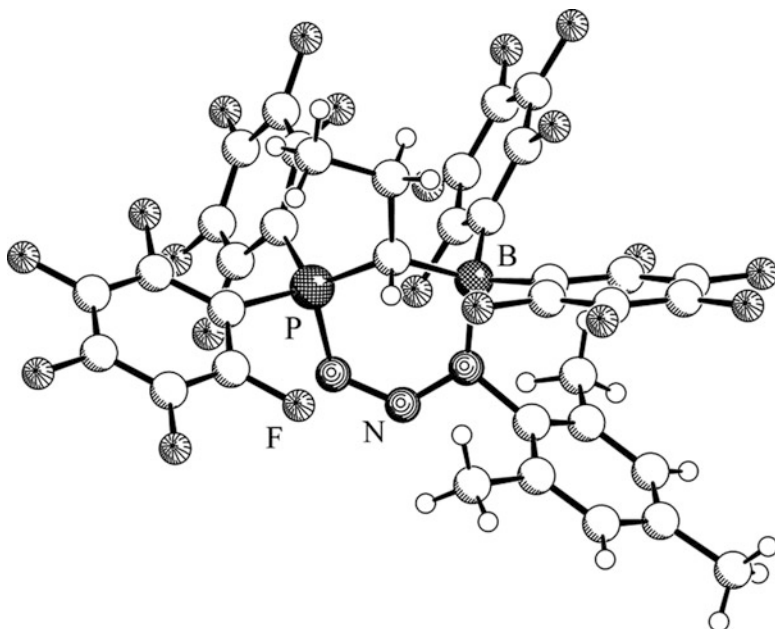


**Scheme 32** Formation and reactions of the geminal P/B FLP **73**

The compound precipitated in high yield as a white solid upon exposure of a pentane solution of **3a** to carbon dioxide at ambient temperature. When brought back into solution the adduct **71** rapidly lost  $\text{CO}_2$  at temperatures above ca.  $-20^\circ\text{C}$ . Low temperature spectroscopy characterized the new compound (e.g.,  $^{13}\text{C}(\text{C}=\text{O})$ :  $\delta$  160.5 ppm). Crystallization at  $-36^\circ\text{C}$  gave single crystals of **71** suited for the X-ray crystal structure determination (Fig. 20). A detailed DFT analysis indicated that the addition reaction of the P/B FLP **3a** to a  $\text{C}=\text{O}$  bond of carbon dioxide is probably a concerted reaction. According to this analysis both the newly formed P-C and the B-O interactions have become almost equally established in the (rather symmetrical) transition state of this reaction [106].



**Scheme 33** Addition of mesitylazide to the geminal FLP **73**

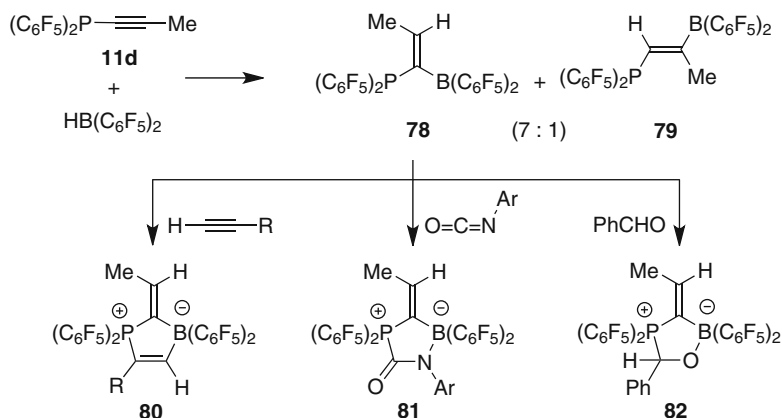


**Fig. 21** A view of the molecular structure of compound **77**

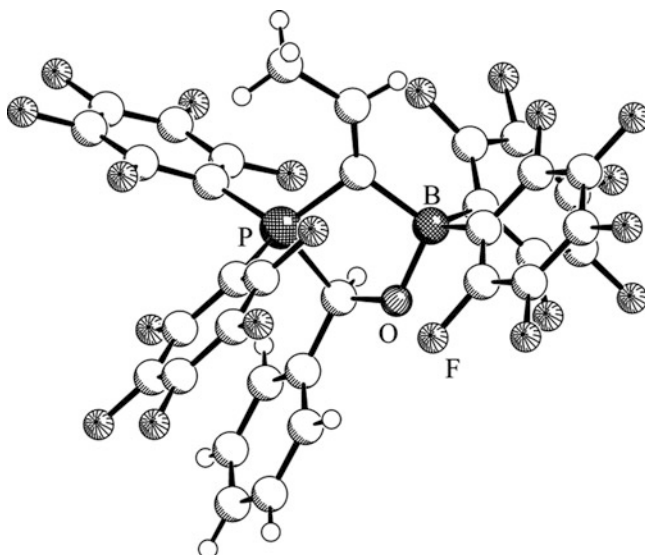
## 5 Geminal FLPs

In the literature one can find a variety of geminal P/B systems. Some of these were used as ligands in coordination chemistry (see for example [107–109]) whereas others were employed as Lewis acid catalysts [110, 111].

We have used weakly Lewis basic pentafluorophenyl substituted phosphane building blocks to construct electronically modified intramolecular FLPs. For that purpose we prepared the  $(\text{C}_6\text{F}_5)_2\text{P}$ -vinyl reagent and treated it with the  $\text{HB}(\text{C}_6\text{F}_5)_2$  hydroboration reagent. The ensuing hydroboration reaction proved to be regio-unselective, yielding a 2:1 mixture of the vicinal and geminal P/B-FLPs [112]. Introduction of a directing substituent resulted in regioselective geminal FLP formation. The  $(\text{C}_6\text{F}_5)_2\text{P}$ -propenyl (**72**) system added the  $\text{HB}(\text{C}_6\text{F}_5)_2$  reagent regioselectively to give the geminal FLP **73** in good yield (Scheme 32). NMR



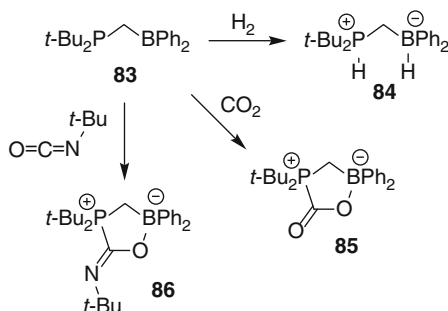
**Scheme 34** Formation and reactions of the geminal FLP **78**



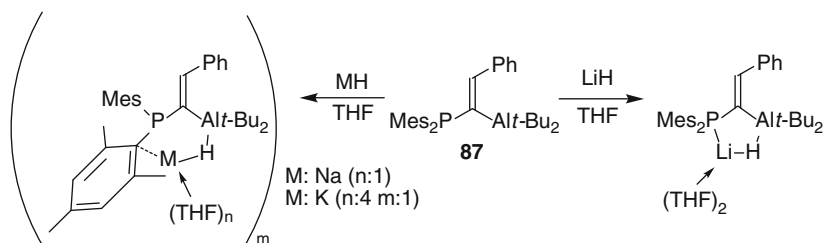
**Fig. 22** Molecular structure of compound **82**

spectroscopy indicated an open P/B FLP with no appreciable direct P...B interaction. This was evident from the  $^{11}\text{B}$  NMR resonance of **73** ( $\delta$  71) and its  $^{19}\text{F}$  NMR features ( $\Delta\delta_{\text{mp}} = 15.1$ ). Compound **73** did not activate dihydrogen under our typical conditions but reacted readily with a variety of unsaturated substrates by 1,2-addition, e.g., ethene, *p*-tolyl isocyanate, or 1-pentyne to yield **74**, **75**, and **76**, respectively [100–112].

The geminal P/B FLP **73** reacted with mesitylazide by 1,3-addition to give the six-membered heterocyclic product **77** (Scheme 33 and Fig. 21) [112]. The X-ray



**Scheme 35** Reactions of the FLP **83**



**Scheme 36** Metal hydride addition to compound **87**

crystal structure analysis revealed almost identical N1-N2 (1.304(3) Å) and N2-N3 (1.306(3) Å) bond lengths [113, 114].

Hydroboration of the electron deficient alkynyl phosphane **11d** with  $\text{HB}(\text{C}_6\text{F}_5)_2$  gave a 7:1 mixture of the products **78** and **79** [115]. The typical FLP reactivity of the non-internally coordinating major ( $\text{sp}^2$ ) $\text{C}_1$ -bridged compound **78** was probed from this mixture. It added cleanly to alkynes to give **80** and to aryl isocyanates affording **81** (Scheme 34). The addition product of, e.g., benzaldehyde **82** featured dynamic NMR spectra indicating reversible ring opening by P–C bond rupture (Scheme 34 and Fig. 22).

Lammertsma et al. prepared the  $\text{CH}_2$ -bridged P/B FLP **83** which contains phenyl substituents at boron [116]. This less Lewis acidic but markedly more Lewis basic FLP was able to activate dihydrogen affording **84**. It reacted with  $\text{CO}_2$  and added to the C=O bond of an isocyanate to give **85** and **86**, respectively (Scheme 35).

The FLP **87** even added alkali metal hydrides synergistically (Scheme 36) [117].

## 6 Conclusions

We started this work by studying P–B coordination and conformational behavior of intramolecular oligomethylene-linked phosphane/borane systems [42, 48] followed by the synthesis of the vicinal FLP  $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$  (**3a**). This system



turned out to be a very reactive frustrated Lewis pair that was able to react with a great variety of small molecules, often in a unique manner. The phosphane and the borane in this “archetypical” intramolecular FLP do interact but (as we have shown with the aid of its chiral derivatives) their interaction is weak. In addition a current DFT analysis by S. Grimme et al. has shown that the four-membered heterocyclic global minimum structure of **3a** rapidly opened to populate open local minimum structures of slightly higher energy content that have the C-P and C-B vectors either anti-periplanarly oriented or arranged in a gauche conformation. According to this calculation it is the reactive gauche type structure that undergoes the cooperative H-H activation reaction to yield the hydridoborate/phosphonium product [118–125]. This reaction has enabled us to develop protocols for metal-free FLP catalyzed hydrogenation reactions.

What is remarkable about FLP chemistry is that many such pairs of Lewis acids and Lewis bases, that have been prevented from neutralizing adduct formation by steric bulk or electronically, exhibit reactions where they act jointly with added substrates. A number of these reactions (e.g., hydrogen activation) are thermodynamically cooperative, some showing great kinetic preference by favoring concerted pathways (e.g., CO<sub>2</sub> addition and potentially FLP addition to some alkenes and to nitric oxide). This behavior, especially prone for the intramolecular FLPs, indicates that the typical FLP situation, characterized by the simultaneous presence of reactive free Lewis base and Lewis acid components in solution, bears the potential to find novel reactions in a rather simple way. From the exciting results FLP chemistry has furnished in the early stages of its development we are hopeful that this specific situation of having active non-quenched Lewis acids and bases co-existent in solution will result in discovering more such new reaction modes. We feel that intramolecular FLPs may play an important role in this forthcoming development.

**Acknowledgment** G. E. thanks his co-workers at Münster for their great contributions to this exciting field. We cordially thank the collaborating groups. For all of us it has been a pleasure to work together and discover new FLP reactions and FLP behavior. G. E. thanks the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Alexander von Humboldt-Stiftung, and the European Research Council for financial support.

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