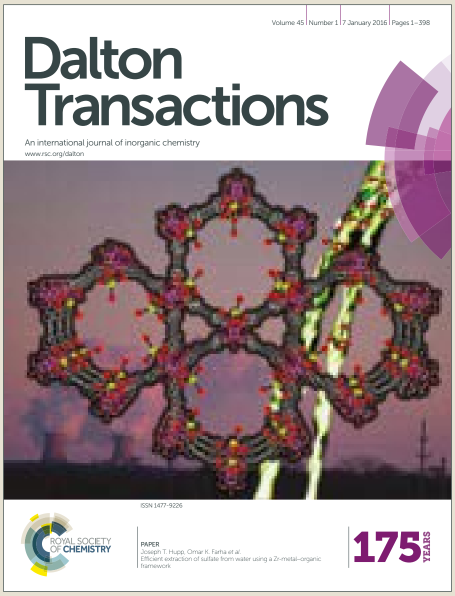
View Article Online
View Journal

Dalton Transactions

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Erker, Z. Jian, G. Kehr, C. G. Daniliuc and B. Wibbeling, *Dalton Trans.*, 2017, DOI: 10.1039/C7DT02315D.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/dalton

View Article Online
DOI: 10.1039/C7DT02315D

Journal Name

ARTICLE

Hydroboration route to geminal P/B frustrated Lewis pairs with a bulky secondary phosphane component and their reaction with carbon dioxide

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

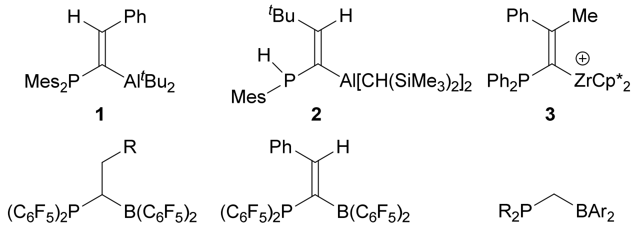
www.rsc.org/

Zhongbao Jian, Gerald Kehr, Constantin G. Daniliuc, Birgit Wibbeling and Gerhard Erker*

The secondary aryl-P(H) phosphanyl substituted *tert*-butylacetylenes **7a,b** (aryl: Mes or Mes*) undergo hydroboration with [$HB(C_6F_5)_2$] with a rarely observed regiochemistry to give the geminal vinylidene-bridged P/B Lewis pairs **8a,b**. Treatment of **8a,b** with benzonitrile, *N*-sulfinylaniline, and phenyl isothiocyanate, respectively, gives the addition products **12a,b**, **13a,b**, and **14** with proton transfer from the phosphorus to the more basic nitrogen site. The reaction of the FLPs **8a,b** with carbon dioxide yields a doubly boron bonded addition product. The reaction of **8b** with a conjugated ynone formally proceeded by *trans*-1,2-hydrophosphination of the alkyne at the geminal FLP framework to give the seven-membered heterocycle **21**.

Introduction

The combination of Lewis acids and bases with sufficiently bulky substituents to effectively hinder their neutralizing Lewis adduct formation has opened ways of cooperative binding of small molecules, often resulting in their activation. Intramolecular frustrated Lewis pairs (FLPs) have played a significant role in this current development.[1,2] Most of these intramolecular systems contain hydrocarbyl bridges that feature a separation by two or more atoms between the FLP antagonists. In contrast, geminal FLPs are less frequently encountered. There is a sizable number of alkylidene-bridged phosphane/aluminum FLPs (**1** and **2**, Scheme 1) that were mostly reported by Uhl et al.[3–5] We had communicated a related cationic P/Zr$^+$ system **3**.[6] The related C$_1$-bridged P/B FLP systems are rather rare, including our unusual $(C_6F_5)_2P/B(C_6F_5)_2$ systems **4** and **5** with a much less nucleophilic phosphane component.[7] Lammertsma, Wagner and others have described a few methylene-bridged P/B compounds **6** with various types of substituents at the heteroatoms, most of which show typical FLP reactivities.[8,9]



Scheme 1 Geminal intramolecular frustrated Lewis pairs.

We have now prepared a pair of geminal alkylidene-bridged $Ar(H)P/B(C_6F_5)_2$ FLPs by means of a simple regioselective hydroboration route and found them to show some specific reaction behavior toward CO$_2$ and some related organic reagents.

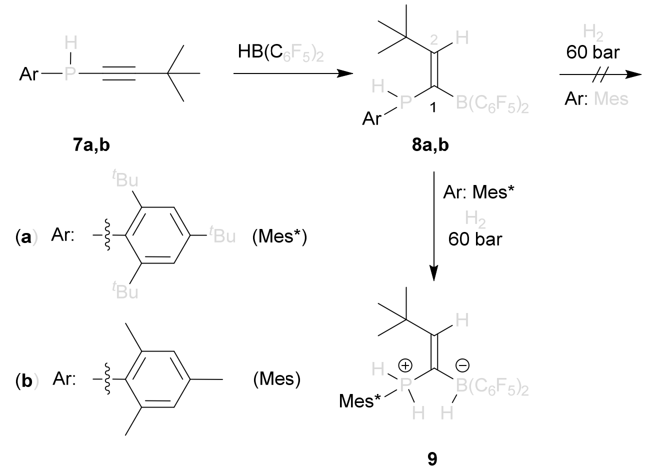
Results and discussion

The secondary aryl, alkinyl phosphanes **7a**,**b** were prepared in a two-step procedure by treatment of 2,4,6-tri-*tert*-butylphenyl (Mes*), respectively mesityl (Mes)PCl$_2$ with in situ generated lithio *tert*-butylacetylene followed by chloride exchange for hydride at phosphorus with the Li[$HBEt_3$] reagent.[4] We had previously shown that di-mesityl vinyl- or substituted alkynyl phosphanes added Piers' borane [$HB(C_6F_5)_2$][10] with anti-Markovnikov orientation, giving the respective vicinal C$_2$-bridged P/B systems.[2,11] The secondary phosphane **7a** (Ar: Mes*) reacted rapidly with the [$HB(C_6F_5)_2$] reagent (pentane, r.t., 1 h) to cleanly give the hydroboration product with the opposite regioselectivity, namely the geminal P/B system **8a**, which we isolated as an orange solid in 90% yield (Scheme 2). It was characterized by C,H elemental analysis and by NMR spectroscopy [^{1}H: δ 6.60 ($^3J_{PH}$ = 25.2 Hz, 2-H), 5.93 ($^1J_{PH}$ = 234.8 Hz, PH); ^{13}C: δ 151.9 ($^1J_{PC}$ = 37.8 Hz, C1), 170.1 ($^2J_{PC}$ = 22.0 Hz, C2); ^{31}P: δ −67.2; ^{11}B: δ 62.1; ^{19}F: $\Delta\delta^{19}F_{m,p}$ = 11.7 ppm, for further details see the Supporting Information]. Compound **7b** reacted with [$HB(C_6F_5)_2$] during a period of 12 h at r.t. to give the geminal P/B product **8b.** We isolated it from the reaction mixture in 85% yield. It shows similar spectroscopic features as **8a** (see the Supporting Information).

Organisch-Chemisches Institut, Universität Münster, Corrensstr. 40, 48149 Münster, Germany. E-mail: erker@uni-muenster.de

Electronic Supplementary Information (ESI) available: Experimental and analytical details, spectral data and crystallographic data. CCDC 1534139 to 1534147. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7DT02315D



Scheme 2 Preparation of secondary PH/B FLPs by regioselective hydroboration.

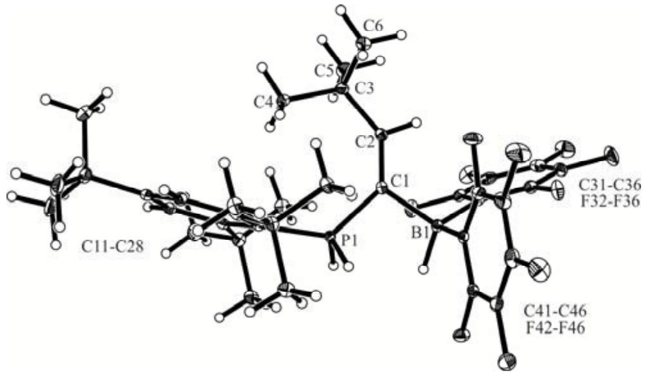
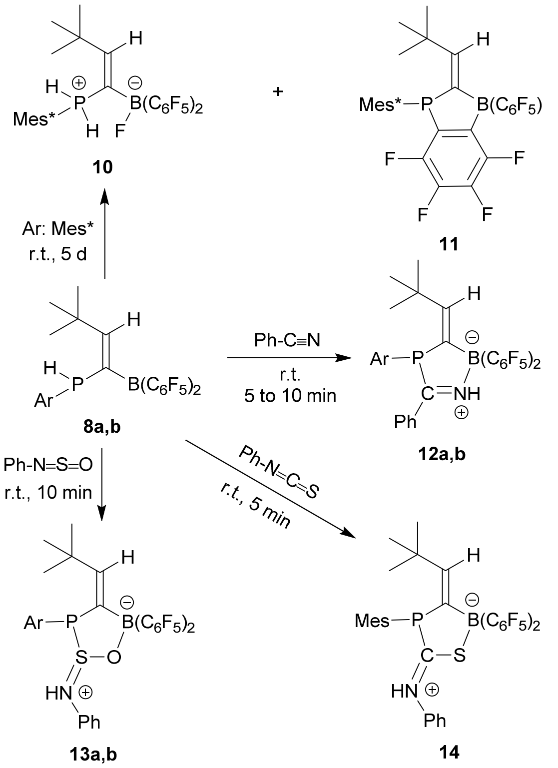


Fig. 1 A view of the molecular structure of the geminal P/B FLP dihydrogen splitting product **9** (thermal ellipsoids are shown with 30 % probability). Selected bond lengths (Å) and angles (°): P1–C1 1.789(1), C1–B1 1.667(2), C1–C2 1.335(2); C1–P1–C11 129.0(1), P1–C1–B1 102.1(1), $\Sigma B1^{CCC}$ = 335.2(1).

The mesityl P/B compound **8b** did not turn out to be reactive toward H_2 (60 bar). However, the mesityl* P/B compound **8a** showed FLP behavior and heterolytically split dihydrogen under more forcing conditions (r.t., 60 bar H_2, 7 h) to give the PH_2^+/BH^- zwitterion **9**, which we isolated as a white solid in 82% yield (Scheme 2) [^{31}P NMR: δ −41.4 (t, $^1J_{PH}$ = 486.9 Hz); ^{11}B: δ −18.7 ($^1J_{BH}$ = 85.9 Hz); ^1H: δ 7.46 (d, PH_2), δ 3.32 (BH)]. Compound **9** was characterized by X-ray diffraction (Fig. 1). The structure has confirmed the unusual regioselective outcome of the hydroboration reaction of the bulky secondary alkynyl phosphane **7a** with [$HB(C_6F_5)_2$] plus the heterolytic dihydrogen splitting reaction. The central sp²-hybridized carbon atom (C1) has the boron and the phosphorus atom attached it. The phosphorus atom P1 bears a pair of hydrogen atoms attached and the bulky Mes* substituent, the boron atom B1 has one hydrogen bonded to it in addition to the pair of C_6F_5 groups. Compound **8a** was found being a metal-free catalyst for the hydrogenation of a bulky imine and an enamine under more forcing conditions (60 bar H_2, r.t.) but it is not overly active (see the Supporting Information for details).

The geminal P/B FLP **8a** is thermally sensitive. Over a period of 5 d in cyclohexane-d_{12} solution at r.t., it was converted to a ca. 1 : 1 mixture of the products **10** and **11** (Scheme 3). This is due to the frequently observed internal nucleophilic aromatic substitution reaction of the phosphane at an adjacent C_6F_5 group.[8a,12] Capture of fluoride and H^+ transfer then resulted in the formation of the **10**/**11** product pair (see the Supporting Information for their characterization). Compound **10** was also isolated and identified by an X-ray crystal structure analysis. Both the compounds **8a** and **8b** reacted rapidly (5 to 10 min) with benzonitrile at r.t. in pentane solution to give the products **12a**,**b** which were isolated in good yield (Scheme 3). The products were probably formed by a typical P/B FLP addition reaction to the −C≡N π-system followed by proton transfer to the more basic nitrogen site. A similar rapid reaction is observed upon treatment of **8a**,**b** with *N*-sulfinylaniline.[13] We isolated the zwitterionic five-membered heterocycles **13a**,**b** (Scheme 3). Again, we note that proton transfer from phosphorus to nitrogen had occurred. Compound **8b** reacted rapidly with the heterocumulene phenyl isothiocyanate to give the similar compound product **14** (Scheme 3) (isolated in 82% yield, see the Supporting Information for the characterization of these compounds). The structures of the products **12b**, **13b** and **14** were also secured by X-ray diffraction.



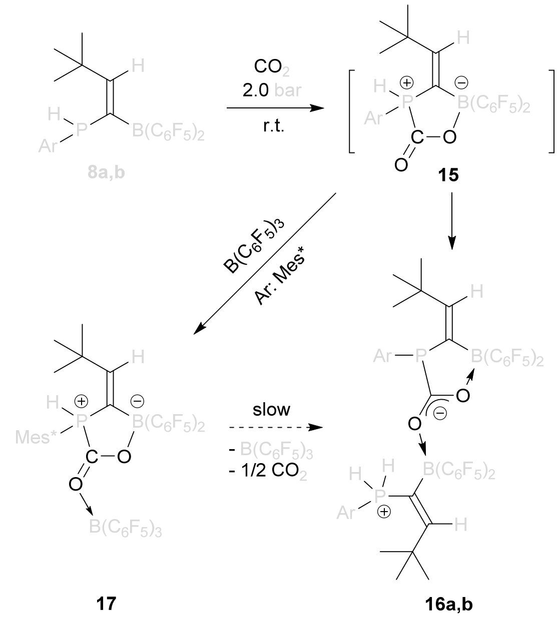
Scheme 3 FLP reactions of the geminal systems **8a**,**b**.

The geminal P/B FLP **8b** was exposed to carbon dioxide[14,15] (2 bar) in pentane at r.t. for ca. 12 h. During this time a white precipitate had formed. The product **16b** was isolated in 65% yield (Scheme 4). The X-ray crystal structure analysis revealed that CO_2 had reacted with **8b** in a 1:2 molar ratio (Fig. 2).[16]

The formation of the unusually structural product **16b** can be rationalized by P/B FLP addition to a C=O bond of carbon dioxide followed by trapping of the intermediate **15** by a second equivalent of the bifunctional starting material **8b** with the boron Lewis acid coordinating to the remaining active carbonyl

View Article Online
DOI: 10.1039/C7DT02315D

oxygen atom and the phosphorus Lewis base serving as a proton acceptor in the final stabilization step.



Scheme 4 Reaction of the geminal FLPs **8a**,**b** with carbon dioxide.

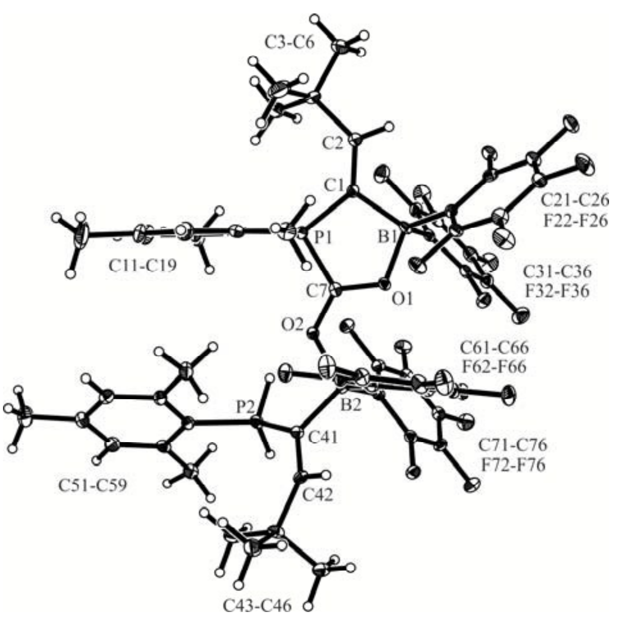


Fig. 2 Molecular structure of the CO_2 addition product **16b** (thermal ellipsoids are shown with 15 % probability). Selected bond lengths (Å) and angles (°): P1–C1 1.805(5), C1–B1 1.639(8), C1–C2 1.330(7), B1–O1 1.580(6), O1–C7 1.277(6), C7–O2 1.274(6), O2–B2 1.559(7), B2–C41 1.639(7), C41–P2 1.792(5), C41–C42 1.333(7), C42–C43 1.513(7); B1–O1–C7 113.6(4), O1–C7–O2 121.7(5), C7–O2–B2 124.1(4), B2–C41–P2 112.0(3), C41–P2–C51 123.9(2), $\Sigma P1^{CCC}$ = 307.6(2).

Consequently, the phosphorus atom P2 has a pair of hydrogen atoms bonded whereas the other phosphorus atom P1 is tri-coordinated. Inside the five-membered core heterocycle we find almost identical C7–O1/O2 bond lengths indicating a delocalized structure of this moiety. Due to the chiral trivalent phosphorus unit P1, compound **16b** shows the ^{1}H NMR signals of a pair of diastereotopic PH_2 hydrogens at δ 6.61 ($^{1}J_{PH}$ = 479.7 Hz) and 6.40 ($^{1}J_{PH}$ = 486.8 Hz) in CD_2Cl_2 solution as well as the ^{19}F NMR signals of a total of four differentiated C_6F_5 groups at the pair of boron atoms [^{11}B: δ 7.2 and 1.9; ^{31}P: δ −17.7 and −60.3 (td, $^{1}J_{PH}$ = 482.9 Hz, $^{3}J_{PH}$ = 70.5 Hz); ^{13}C: δ 205.2 (br d, $^{1}J_{PC}$ = 5.6 Hz, C7); for details see the Supporting Information].

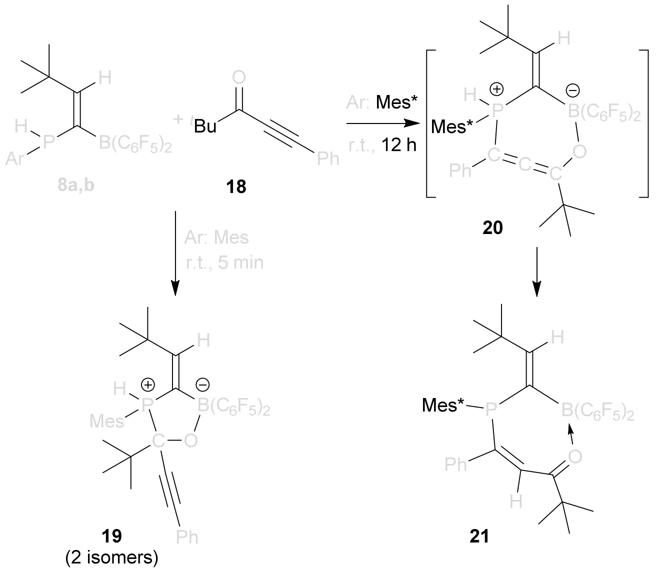
Compound **8a** reacted analogously with CO_2. Again the product formation occurred with a FLP/CO_2 stoichiometry of 2:1 and we isolated the twofold addition product **16a** in 60% yield (Scheme 4). Compound **16a** was shown by X-ray diffraction to have an analogous structure to **16b**. It shows similar NMR data [^{1}H: δ 7.61 ($^{1}J_{PH}$ = 504.8 Hz) and 7.10 ($^{1}J_{PH}$ = 477.9 Hz); ^{31}P: δ −4.5 and −48.3; ^{11}B: δ 4.2 and 1.8; ^{13}C: δ 201.0 (C7), ^{19}F: at 233 K compound **16a** shows a total of twenty resonances; we note that two of the *ortho*-F signals show a rather large through space $^{TS}J_{FF}$ coupling constant of ca. 70 Hz;[17] for details see the Supporting Information].

We were able to trap the alleged intermediate **15** by the phosphane-free strong boron Lewis acid $B(C_6F_5)_3$. For that reason $B(C_6F_5)_3$ (1 molar equiv.) was added to a pentane solution of in situ generated compound **8a** and subsequent exposure to CO_2 (2 bar) for 1 h at r.t. produced compound **17** as a white precipitate. The product was isolated in 71% yield and characterized by C,H elemental analysis and by spectroscopy [^{1}H NMR: δ 8.24 ($^{1}J_{PH}$ = 484.3 Hz, PH), 6.78 ($^{3}J_{PH}$ = 68.6 Hz, =CH); ^{13}C: δ 175.9 ($^{1}J_{PC}$ = 117.6 Hz, [P]-CO_2); ^{31}P: δ −26.8 (dd, $^{1}J_{PH}$ = 484.3 Hz, $^{3}J_{PH}$ = 68.6 Hz); ^{11}B: δ 12.1 and 4.9, for further details see the Supporting Information]. In an in situ NMR experiment we noticed that the $B(C_6F_5)_3$/CO_2 FLP adduct **17** over 3 days at r.t. had partially converted to the CO_2 addition product **16a**.

The FLP **8b** (Ar: Mes) reacted rapidly with the α,β-unsaturated ynone **18** in the often observed 1,2-P/B carbonyl addition mode (r.t., pentane, 5 min) to give the substituted five-membered heterocyclic product **19** (Scheme 5) (isolated in 84% yield as a mixture of two stereoisomers, see the Supporting Information for the characterization of the compounds including the X-ray crystal structure analysis of one isomer). The P/B FLP **8a** reacted in a remarkably different way with the ynone **18**. Stirring the reaction mixture of **8a** and **18** for 12 h in pentane at r.t. gave a dark purple solution after filtration, from which the product **21** crystallized at −35 °C. We isolated the red crystalline product in 76% yield (Scheme 5). It was characterized by C,H elemental analysis, by NMR spectroscopy and by X-ray diffraction. The X-ray crystal structure analysis revealed the formation of the seven-membered heterocycle (Fig. 3). We assume that it was formed by initial 1,4-PB FLP addition to the ynone forming the allenic boron enolate intermediate **20**.[18] This reactive intermediate contains a phosphonium Brønsted acid and an enolate carbon base. Consequently, proton transfer takes place to eventually give the observed product **21**, formed by sequential transformation of the acetylic carbon-carbon triple bond of the substrate **18** to the Z-configurated olefinic double bond in **21**. The ^{1}H NMR spectrum shows the olefinic hydrogen signal at δ 6.07 ($^{3}J_{PH}$ = 30.3 Hz, −C(Ph)=CH−) [^{13}C: δ 168.4 ($^{1}J_{PC}$ = 63.9 Hz), 116.3 ($^{2}J_{PC}$ = 5.5 Hz); ^{31}P: δ 60.2; ^{11}B: δ 3.9]. The ^{13}C NMR carbonyl resonance of the newly formed conjugated enone, coordinated to the boron Lewis acid, occurs at δ 199.3

View Article Online
DOI: 10.1039/C7DT02315D

($^3J_{PC}$ = 13.3 Hz); for further details of the characterization of compound **21** see the Supporting Information.



Scheme 5 Reaction of the FLPs with a conjugated ynone.

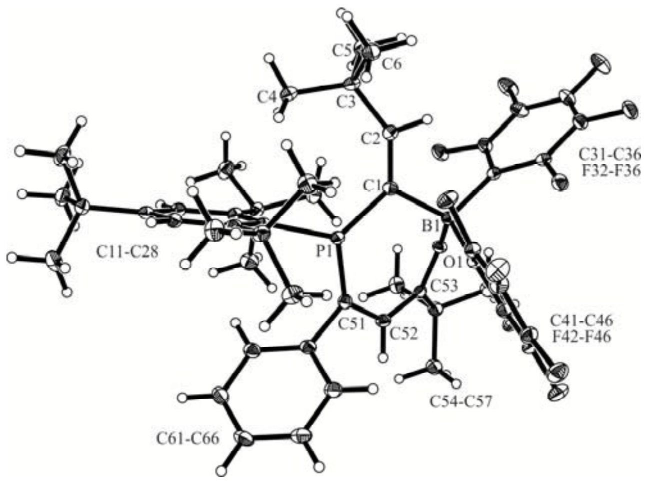


Fig 3 Molecular structure of the ynone reaction product **21** (thermal ellipsoids are shown with 30 % probability). Selected bond lengths (Å) and angles (°): P1−C1 1.786(3), C1−B1 1.649(4), B1−O1 1.538(3), O1−C53 1.288(3), C53−C52 1.395(4), C52−C51 1.406(4), C51−P1 1.736(3); P1−C1−B1 111.1(2), C1−B1−O1 108.4(2), B1−O1−C53 132.5(2), C53−C52−C51 128.7(2), C52−C51−P1 131.0(2), $\Sigma P1^{CCC}$ = 351.1(1).

Conclusions

Alkenyl and alkynyl phosphanes usually undergo hydroboration with Piers' borane [$HB(C_6F_5)_2$] to give the respective vicinal P/B systems. Many syntheses of C_2-bridged P/B FLPs rely on that regioselectivity.[11] This strong regiocontrol of the hydroboration reaction on the other hand had so far precluded the easy synthesis of the missing alkylidene-bridged geminal P/B FLPs by the hydroboration pathway. Our new systems **8**, therefore, represent a remarkable exception. Moreover, the system is characterized by the joint presence of the strong $B(C_6F_5)_2$ Lewis acid function plus the strong P(H)Aryl Lewis base in close spacial proximity. In addition, the secondary phosphane in the systems **8** serves as a latent Brønsted acid, which becomes active through the generation of the respective phosphonium cation upon cooperative substrate addition. This may lead to new reactivities toward carbonyl compounds as we have seen it in the reaction of **8a** with the ynone **18**. The combination with the latent [P]H$^+$ Brønsted acid also causes the $B(C_6F_5)_2$ FLP component to appear more Lewis acidic in conjunction with the phosphonium Brønsted acid under equilibrium conditions as we have seen it in the reaction of the systems **8** with carbon dioxide. We shall investigate if this H$^+$/$B(C_6F_5)_2$ cooperation might direct us toward new applications in frustrated Lewis pair chemistry.

Experimental section

For general information and the spectroscopic and structural data of these new compounds see the Supporting Information.

Preparation of compound 8a

After stirring the white suspension of compound **7a** (180 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 5 min, the formed yellow solution was stirred for 1 h at room temperature to finally give a red solution (with a little bit solid material). The solution was filtered and then all volatiles of the obtained red filtrate were removed in vacuo to give an orange solid. Yield: 318 mg, 90%. Anal. calc. for $C_{36}H_{40}PBF_{10}$ (704.5 g mol^{-1}): C, 61.38; H, 5.72. Found: C, 61.62; H, 5.74.

Preparation of compound 8b

After stirring the white suspension of compound **7b** (116 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room temperature for 5 min, the formed yellow solution was stirred for 12 h at room temperature to finally give a yellow solution (with a little bit solid material). The solution was filtered and then all volatiles of the obtained yellow filtrate were removed in vacuo to give a yellow solid. Yield: 246 mg, 85%. Anal. calc. for $C_{27}H_{22}PBF_{10}$ (578.2 g mol^{-1}): C, 56.08; H, 3.84. Found: C, 56.38; H, 3.95.

Preparation of compound 16a

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 1 h, the resulting red suspension was filtered to give a clear red solution which was exposed to CO_2 gas (2.0 bar). After the reaction mixture was stirred at room temperature for 12 h a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 218 mg, 60%. Anal. calc. for $C_{73}H_{80}P_2B_2O_2F_{20}$ (1453.0 g mol^{-1}): C, 60.35; H, 5.55. Found: C, 60.28; H, 5.48.

Preparation of compound 16b

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) in pentane (5 mL) at room

View Article Online
DOI: 10.1039/C7DT02815D

temperature for 12 h, the resulting yellow suspension was filtered to give a clear yellow solution which was exposed to CO_2 gas (2.0 bar). After the reaction mixture was stirred at room temperature for 12 h a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: Yield: 195 mg, 65%. Anal. calc. for $C_{55}H_{44}P_2B_2O_2F_{20}$ (1200.5 g mol^{-1}): C, 55.03; H, 3.69. Found: C, 55.48; H, 4.06.

Preparation of compound 19

After stirring a mixture of compound **7b** (116 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 10 h, the resulting yellow suspension was filtered to give a clear yellow solution. Then one equiv. of 4,4-dimethyl-1-phenylpent-1-yn-3-one (93 mg, 0.5 mmol) was added and after stirring for 5 min a white precipitate was formed. The resulting suspension was filtered. The collected solid was washed twice with pentane (2×5 mL) and dried in vacuo to give a white solid. Yield: 321 mg, 84%. Anal. calc. for $C_{40}H_{36}PBOF_{10}$ (764.5 g mol^{-1}): C, 62.84; H, 4.75. Found: C, 62.76; H, 4.49.

Preparation of compound 21

After stirring a mixture of compound **7a** (180 mg, 0.5 mmol) and $HB(C_6F_5)_2$ (173 mg, 0.5 mmol) in pentane (3 mL) at room temperature for 1 h, the resulting red suspension was filtered to give a clear red solution. Then one equiv. of 4,4-dimethyl-1-phenylpent-1-yn-3-one (93 mg, 0.5 mmol) was added and after stirring for 12 h a dark purple suspension was formed which was filtered. The filtrate was stored at −35 °C to give dark red crystal. Yield: 339 mg, 76%. Anal. calc. for $C_{49}H_{54}PBOF_{10}$ (0.5 CH_2Cl_2): C, 63.71; H, 5.94. Found: C, 63.98; H, 5.90.

Acknowledgements

Financial support from the European Research Council is gratefully acknowledged.

Notes and references

1 (a) Frustrated Lewis Pair Chemistry I: Uncovering and Understanding, *Top. Curr. Chem.*, ed. G. Erker and D. W. Stephan, Heidelberg, 2013, vol. 332; (b) Frustrated Lewis Pair Chemistry II: Expanding the Scope, *Top. Curr. Chem.*, ed. G. Erker and D. W. Stephan, Heidelberg, 2013, vol. 334; (c) D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2015, **54**, 6400-6441; *Angew. Chem.*, 2015, **127**, 6498-6541; (d) D. W. Stephan, *Science*, 2016, **354**, aaf7229.

2 (a) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072-5074; (b) G. Kehr, S. Schwendemann and G. Erker, *Top. Curr. Chem.*, 2013, **332**, 45-84.

3 For selected examples of the geminal compound type **1**: (a) C. Appelt, H. Westenberg, F. Bertini, A. W. Ehlers, J. C. Slootweg, K. Lammertsma and W. Uhl, *Angew. Chem. Int. Ed.*, 2011, **50**, 3925-3928; *Angew. Chem.*, 2011, **123**, 4011-4014; (b) C. Appelt, J. C. Slootweg, K. Lammertsma and W. Uhl, *Angew. Chem. Int. Ed.*, 2012, **51**, 5911-5914; *Angew. Chem.*, 2012, **124**, 6013-6016; (c) S. Roters, C. Appelt, H. Westenberg, A. Hepp, J. C. Slootweg, K. Lammertsma and W. Uhl, *Dalton Trans.*, 2012, **41**, 9033-9045; (d) C. Appelt, J. C. Slootweg, K. Lammertsma and W. Uhl, *Angew. Chem. Int. Ed.*, 2013, **52**, 4256-4259; *Angew. Chem.*, 2013, **125**, 4350-4353; (e) W. Uhl and E.-U. Würthwein, *Top. Curr. Chem.*, 2013, **334**, 101-119; (f) W. Uhl, C. Appelt, J. Backs, H. Westenberg, A. Wollschläger and J. Tannert, *Organometallics*, 2014, **33**, 1212-1217; (g) M. Devillard, R. Declercq, E. Nicolas, A. W. Ehlers, J. Backs, N. Saffon-Merceron, G. Bouhadir, J. C. Slootweg, W. Uhl and D. Bourissou, *J. Am. Chem. Soc.*, 2016, **138**, 4917-4926.

4 For compound **2** see: L. Keweloh, H. Klöcker, E.-U. Würthwein and W. Uhl, *Angew. Chem. Int. Ed.*, 2016, **55**, 3212-3215; *Angew. Chem.*, 2016, **128**, 3266-3269.

5 For $R_2P{-}CH_2{-}AlR'_2$ systems see also: (a) J. Boudreau, M. A. Courtemanche and F. G. Fontaine, *Chem. Commun.*, 2011, **47**, 11131-11133; (b) F. Bertini, F. Hoffmann, C. Appelt, W. Uhl, A. W. Ehlers, J. C. Slootweg and K. Lammertsma, *Organometallics*, 2013, **32**, 6764-6769.

6 For compound **3** see: (a) X. Xu, R. Fröhlich, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2012, **48**, 6109-6111; (b) X. Xu, G. Kehr, C. G. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2013, **135**, 6465-6476.

7 For compounds **4** and **5** see: (a) A. Stute, G. Kehr, R. Fröhlich and G. Erker, *Chem. Commun.*, 2011, **47**, 4288-4290; (b) C. Rosorius, G. Kehr, R. Fröhlich, S. Grimme and G. Erker, *Organometallics*, 2011, **30**, 4211-4219; (c) A. Stute, G. Kehr, C. G. Daniliuc, R. Fröhlich and G. Erker, *Dalton Trans.*, 2013, **42**, 4487-4499; (d) C. Rosorius, C. G. Daniliuc, R. Fröhlich, G. Kehr and G. Erker, *J. Organomet. Chem.*, 2013, **744**, 149-155.

8 For compound **6** see: (a) F. Bertini, V. Lyaskoyskyy, B. J. J. Timmer, F. J. J. de Kanter, M. Lutz, A. W. Ehlers, J. C. Slootweg and K. Lammertsma, *J. Am. Chem. Soc.*, 2012, **134**, 201-204; (b) J. Yu, G. Kehr, C. G. Daniliuc, C. Bannwarth, S. Grimme and G. Erker, *Org. Biomol. Chem.*, 2015, **13**, 5783-5792; (c) K. Samigullin, I. Georg, M. Bolte, H.-W. Lerner and M. Wagner, *Chem. Eur. J.*, 2016, **22**, 3478-3484.

9 For other geminal FLP examples see: (a) F. G. Fontaine, J. Boudreau and M.-H. Thibault, *Eur. J. Inorg. Chem.*, 2008, 5439-5454; (b) F. Lavigne, E. Maerten, G. Alcaraz, N. Saffon-Merceron, C. Acosta-Silva, V. Branchadell and A. Baceiredo, *J. Am. Chem. Soc.*, 2010, **132**, 8864-8865; **S/B**: (c) Y. Gloaguen, G. Alcaraz, A.-F. Pécharman, E. Clot, L. Vendier and S. Sabo-Etienne, *Angew. Chem. Int. Ed.*, 2009, **48**, 2964-2968; *Angew. Chem.*, 2009, **121**, 3008-3012; (d) C. A. Tanur and D. W. Stephan, *Organometallics*, 2011, **30**, 3652-3657; **N/B**: (e) L. Zhao, H. Li, G. Lu, F. Huang, C. Zhang and Z.-X. Wang, *Dalton Trans.*, 2011, **40**, 1929-1937; (f) E. Theuergarten, J. Schlosser, D. Schluns, M. Freytag, C. G. Daniliuc, P. G. Jones and M. Tamm, *Dalton Trans.*, 2012, **41**, 9101-9110; (g) É. Dorkó, E. Varga, T. Gáti, T. Holczbauer, I. Pápai, H. Mehdi and T. Soós, *Synlett*, 2014, **25**, 1525-1528; (h) D. Yepes, P. Jaque and I. Fernández, *Chem. Eur. J.*, 2016, **22**, 18801-18809; **N/Al**: (i) W. Zheng, C. Pi and H. Wu, *Organometallics*, 2012, **31**, 4072-4075; **P/Si**: (j) B. Waerder, M. Pieper, L. A. Korte, T. A. Kinder, A. Mix, B. Neumann, H.-G. Stammler and N. W. Mitzel, *Angew. Chem. Int. Ed.*, 2015, **54**, 13416-13419; *Angew. Chem.*, 2015, **127**, 13614-13617; **P/X (X = Ge, Sn, Pb)**: (k) J. Schneider, K. M. Krebs, S. M. Freitag, K. Eichele, H. Schubert and L. Wesemann, *Chem. Eur. J.*, 2016, **22**, 9812-9826; (l) J. Schneider, C. P. Sindlinger, S. M. Freitag, H. Schubert and L. Wesemann, *Angew. Chem. Int. Ed.*, 2017, **56**, 333-337; *Angew. Chem.*, 2017, **129**, 339-343.

10 (a) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 809-811; *Angew. Chem.*, 1995, **107**, 895-897; (b) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492-5503.

11 For reactions of substituted alkynyl phosphanes with $[HB(C_6F_5)_2]$ or $[B(C_6F_5)_3]$ giving vicinal P/B FLP systems see e.g.:

View Article Online
DOI: 10.1039/C7DT02315D

(a) P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem. Int. Ed.*, 2008, **47**, 7543-7546; *Angew. Chem.*, 2008, **120**, 7654-7657; (b) O. Ekkert, G. Kehr, R. Fröhlich and G. Erker, *J. Am. Chem. Soc.*, 2011, **133**, 4610-4616; (c) O. Ekkert, G. G. Miera, T. Wiegand, H. Eckert, B. Schirmer, J. L. Petersen, C. G. Daniliuc, R. Fröhlich, S. Grimme, G. Kehr and G. Erker, *Chem. Sci.*, 2013, **4**, 2657-2664.

12 (a) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124-1126; (b) A. Schnurr, H. Vitze, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2010, **29**, 6012-6019; (c) A. Schnurr, M. Bolte, H.-W. Lerner and M. Wagner, *Eur. J. Inorg. Chem.*, 2012, 112-120; (d) J. S. Reddy, B.-H. Xu, T. Mahdi, R. Fröhlich, G. Kehr, D. W. Stephan and G. Erker, *Organometallics*, 2012, **31**, 5638-5649.

13 (a) X. Xu, G. Kehr, C. G. Daniliuc and G. Erker, *J. Am. Chem. Soc.*, 2014, **136**, 12431-12443; (b) L. E. Longobardi, V. Wolter and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2015, **54**, 809-812; *Angew. Chem.*, 2015, **127**, 823-826.

14 For examples of CO_2 binding by FLPs see: (a) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2009, **48**, 6643-6646; *Angew. Chem.*, 2009, **121**, 6770-6773; (b) A. M. Chapman, M. F. Haddow and D. F. Wass, *J. Am. Chem. Soc.*, 2011, **133**, 18463-18478; (c) D. Voicu, M. Abolhasani, R. Choueiri, G. Lestari, C. Seiler, G. Ménard, J. Greener, A. Guenther, D. W. Stephan and E. Kumacheva, *J. Am. Chem. Soc.*, 2014, **136**, 3875-3880; (d) D. W. Stephan and G. Erker, *Chem. Sci.*, 2014, **5**, 2625-2641; (e) S. Bontemps, *Coord. Chem. Rev.*, 2016, **308**, 117-130.

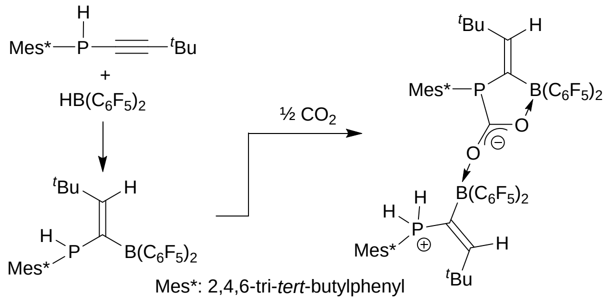
15 For FLP mediated CO_2 reduction see: (a) A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem. Int. Ed.*, 2009, **48**, 9839-9843; *Angew. Chem.*, 2009, **121**, 10023-10027; (b) A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660-10661; (c) G. Ménard and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2011, **50**, 8396-8399; *Angew. Chem.*, 2011, **123**, 8546-8549; (d) M. J. Sgro and D. W. Stephan, *Angew. Chem. Int. Ed.*, 2012, **51**, 11343-11345; *Angew. Chem.*, 2012, **124**, 11505-11507; (e) M. A. Courtemanche, M. A. Legare, L. Maron and F. G. Fontaine, *J. Am. Chem. Soc.*, 2013, **135**, 9326-9329; (f) A. E. Ashley and D. O'Hare, *Top. Curr. Chem.*, 2013, **334**, 191-217; (g) M. A. Courtemanche, M. A. Légaré, L. Maron and F. G. Fontaine, *J. Am. Chem. Soc.*, 2014, **136**, 10708-10717.

16 For rare examples of bis-borane binding to CO_2, see e.g.: (a) X. Zhao and D. W. Stephan, *Chem. Commun.*, 2011, **47**, 1833-1835; (b) Y.-L. Liu, G. Kehr, C. G. Daniliuc and G. Erker, *Chem. Sci.*, 2017, **8**, 1097-1104.

17 (a) F. B. Mallory, *J. Am. Chem. Soc.*, 1973, **95**, 7747-7752; (b) F. B. Mallory, C. W. Mallory and M.-C. Fedarko, *J. Am. Chem. Soc.*, 1974, **96**, 3536-3542; (c) A. D. Buckingham and J. E. Cordle, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 994-1014; (d) J. Hilton and L. H. Sutcliffe, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1975, **10**, 27-39; (e) J. W. Emsley, L. Phillips and V. Wray, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1976, **10**, 83-756; (f) L. Ernst, K. Ibrom, K. Marat, R. H. Mitchell, G. J. Bodwell and G. W. Buschnell, *Chem. Ber.*, 1994, **127**, 1119-1124; (g) W. D. Arnold, J. Mao, H. Sun and E. Oldfield, *J. Am. Chem. Soc.*, 2000, **122**, 12164-12168; (h) T. Tuttle, J. Gräfenstein and D. Cremer, *Chem. Phys. Lett.*, 2004, **394**, 5-13; (i) P. Espinet, A. C. Albéniz, . A. Casares and J. M. Martínez-Ilarduya, *Coord. Chem. Rev.*, 2008, **252**, 2180-2208; (j) see also: S. Berger, S. Braun, H.-O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, Band 4, *^{19}F-NMR-Spektroskopie*, Thieme-Verlag, Stuttgart, 1994.

18 See for a comparison: (a) B.-H. Xu, G. Kehr, R. Fröhlich, B. Wibbeling, B. Schirmer, S. Grimme and G. Erker, *Angew. Chem. Int. Ed.*, 2011, **50**, 7183-7186; *Angew. Chem.*, 2011, **123**, 7321-7324; (b) B.-H. Xu, R. Yanez, H. Nakatsuka, M. Kitamura, R. Fröhlich, G. Kehr and G. Erker, *Chem. Asian J.*, 2012, **7**, 1347-1356.

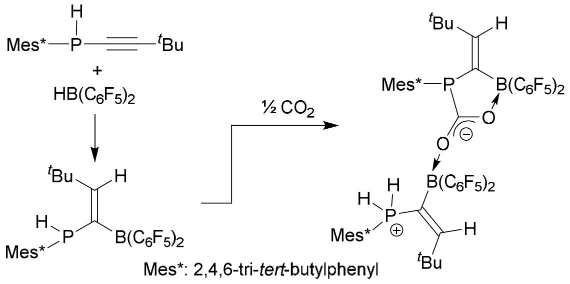
TOC



Hydroboration of a secondary alkynyl phosphane gives a geminal P/B frustrated Lewis pair that reacts with carbon dioxide

View Article Online
DOI: 10.1039/C7DT02315D

TOC



Hydroboration of a secondary alkynyl phosphane gives a geminal P/B frustrated Lewis pair that reacts with carbon dioxide