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Reaction of carbon oxides with an ethylene-bridged PH/B Lewis pair†

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The reaction of 2,4,6-tri(*tert*-butyl)phenyl vinyl phosphane with Piers' borane [$HB(C_6F_5)_2$] gave the ethylene-bridged PH/B frustrated Lewis pair (FLP) system. It is a monomer at high temperature (>323 K), but exists as an associated 12-membered macrocyclic trimer below 273 K. The PH/B FLP splits dihydrogen and serves as a metal-free hydrogenation catalyst. It adds carbon dioxide. It serves as a PH/B template for the reduction of carbon monoxide by the $HB(C_6F_5)_2$ borane to the formyl stage. The resulting six membered P/B/O containing heterocycle is opened upon treatment with pyridine and it reacts with benzaldehyde in a boron mediated Claisen-Tishchenko reaction.

Introduction

Intramolecular phosphane/borane pairs have played a major role in the development of the chemistry of reactive frustrated Lewis pairs (FLPs).[1,2] The ethylene-bridged vicinal system **1** may be regarded as the parent compound[3] of a series of internal FLPs, designed for metal-free small molecular binding and activation. Early on in the development the system **1** served to find novel pathways in the chemistry of the carbon oxides.[4] It was one of a pair of first P/B frustrated Lewis pairs to bind carbon dioxide,[5] and it was used to develop metal-free pathways for the conversion of carbon monoxide. Compound **1** served as one out of a small family of intramolecular FLPs to serve as a template for the reduction of the CO molecule to the formyl stage.[6] This was important as simple BH boranes cannot achieve that transformation. They form borane carbonyls instead, unless catalyzed.[7] Compound **1** adds nitric oxide (NO) to form a persistent FLPNO radical,[8] it splits dihydrogen and serves as a metal-free hydrogenation catalyst.

Subsequently, the BH, respectively PH functionalized ethylene-bridged relatives **2**–**4** had been prepared and their chemistry investigated.[9–11] They showed similar FLP behaviour toward small molecules as **1**, but some of the observed reaction pathways were determined by the presence of the BH or PH functional groups. Compound **3** stoichiometrically reduced CO to the formyl stage and CO_2 to the formaldehyde stage.[10] The PH/BH system **4** reacted with carbon monoxide by complete cleavage of the strong carbon oxygen bond.[11]

In a way the PH/B system **5** may be looked at as a missing link between the FLPs **3** and **4**. We have now prepared the ethylene-bridged PH/B compound **5** and investigated its behaviour toward a variety of small molecules, among them CO and CO_2. These results will be described in this account.

Results and discussion

Preparation of the PH/B FLP 5 and first reactions

Compound **5** was prepared by reacting Mes*P(H)vinyl with Piers' borane $[HB(C_6F_5)_2]$[12] in a 1 : 1 molar ratio (pentane, r.t., 15 h). This gave a suspension, and the product was isolated as a white solid in 90% yield by filtration (Scheme 2). The NMR and structural analysis revealed a strongly temperature dependent equilibrium between the monomer **5** and an associated cyclotrimeric structure $(\mathbf{5})_3$.[13] In the NMR spectra at r.t. both components are present in solution (C_6D_6: **5** : $(\mathbf{5})_3$ ~8 : 1). At 323 K only the monomer **5** was observed. It showed the typical heteronuclear magnetic resonance signals of an open, non-interacting P/B pair [^{11}B: δ 60.7, $\Delta\delta^{19}F_{m,p}$ = 12.6 ppm, ^{31}P: δ −56.2 (d, $^1J_{PH}$ ~ 250 Hz, ^{1}H: δ 5.33), in d_6-benzene] in addition to the typical ^{1}H/^{13}C NMR resonances of the –CH_2–CH_2– bridge and the bulky Mes* ligand at phosphorus.

At 273 K the spectrum of the associated structure was almost exclusively observed. We assume the analogous cyclotrimeric composition as it was observed in the solid state by X-ray diffraction (see below). In CD_2Cl_2 solution at 273 K compound $(\mathbf{5})_3$ showed a ^{31}P NMR signal at δ −12.8 (br d, $^1J_{PH}$ ~ 375 Hz, ^{1}H: δ 5.92) and a ^{11}B NMR resonance at *ca.* δ −3. There are the signals of the pairs of diastereotopic C_6F_5 substituents at boron. The rotation around the B-C_6F_5 vectors are hindered, so a total of each four ^{19}F NMR *o*- and *m*-C_6F_5 as well as two *p*-C_6F_5 signals were observed. The $\Delta\delta^{19}F_{m,p}$ separations are

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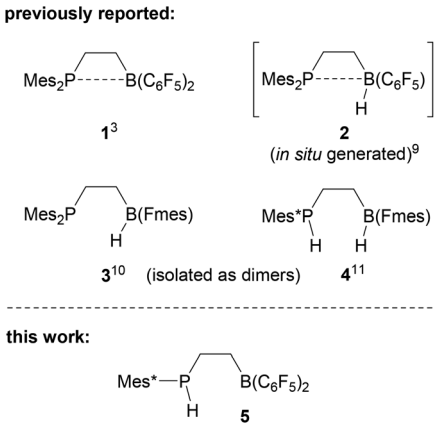
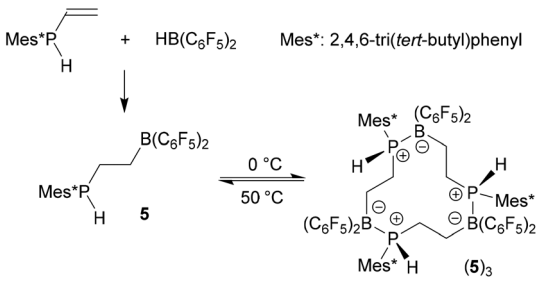


Scheme 1 Functionalized ethylene-bridged phosphorus/boron Lewis pairs (Mes = mesityl, Mes* = 2,4,6-tri(*tert*-butyl)phenyl, Fmes = 2,4,6-tris(trifluoromethyl)phenyl).



Scheme 2 Synthesis and aggregation of the PH/B FLP **5**.

small as it is typical for a four-coordinate borate-type situation. In the ^{1}H NMR spectrum pairs of PCH_2 and BCH_2 proton resonances were observed. The Mes*-P rotation is also hindered and, consequently, separate signals of the pairs *o*-^{t}Bu and the arene methine CH groups were monitored (the spectra are depicted in the ESI†).

Single crystals for the X-ray crystal structure analysis of $(\mathbf{5})_3$ were obtained from pentane at r.t. It shows that the FLP **5** has formed an associated cyclotrimeric structure featuring a twelve-membered heterocyclic core that contains three phosphorus and three boron atoms. It shows three newly formed P–B linkages with bond lengths of 2.091(5) Å (P1–B3), 2.131(4) Å (P2–B1) and 2.112(4) Å P3–B2. The P–C and B–C bond lengths are in a typical range (*e.g.*, P1–C1 1.857(4) Å, B1–C2 1.650(5) Å). The three connecting ethylene units show anti-periplanar conformations. The averaged bond angles at the heteroatoms amount to $\sum B1^{CCC}$ = 338.2° and $\sum P1^{BCC}$ = 354.8°, with the latter not deviating too much from co-planarity. The fourth substituent at P is hydrogen. In the solid state structure, the three P–H vectors are *all-cis* arranged. The molecule is close to (but not crystallographically) C_3 symmetric (see Fig. 1). The Mes* substituents at P are markedly bent (*e.g.* P1–C11···C14, averaged 24°) as it is often observed in Mes* containing phosphorus compounds.[14]

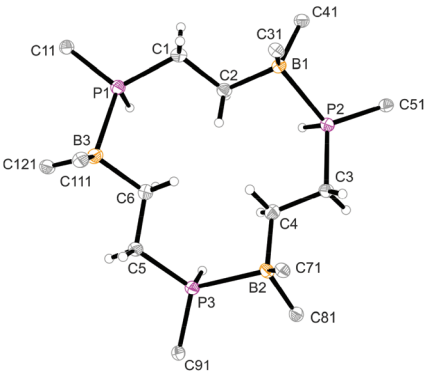
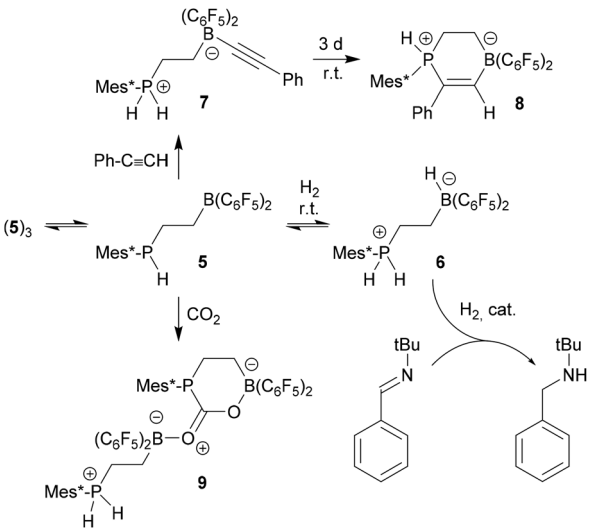


Fig. 1 A view of the macrocyclic molecular structure of the cyclotrimeric FLP associate $(\mathbf{5})_3$ (thermal ellipsoids at 30% probability; only the *ipso*-carbon atoms of the C_6F_5 groups at boron and the Mes* groups at phosphorus are shown).



Scheme 3 Typical FLP reactions of compound **5**.

The FLP **5** splits dihydrogen reversibly. Under ambient conditions it reacts in dichloromethane with H_2 to give a mixture of compounds **5**, $(\mathbf{5})_3$ and the dihydrogen splitting product **6** (*ca.* 49 : 30 : 20; ^{31}P) (Scheme 3). The product of heterolytic H_2/FLP splitting shows NMR signals of the [P]H_2 phosphonium [^{1}H: δ 7.33 (dm, $^1J_{PH}$ = 488.3 Hz, ^{31}P: δ −23.7 (t))] and the [B]H hydridoborate [^{11}B: δ −21.6 ($^1J_{BH}$ ∼ 85 Hz)] in addition to the typical NMR features of the Mes*$PCH_2CH_2B(C_6F_5)_2$ framework. The **5**/**6** equilibrium system serves as an active hydrogenation catalyst. The substrate *N*-*tert*-butyl-1-phenylmethanimine was rapidly reduced to benzyl-*tert*-butylamine by treatment with dihydrogen in the presence of 10 mol% of the FLP catalyst precursor **5** (CD_2Cl_2, 1.5 bar H_2, r.t., >99% conversion within 15 min).

Compound **5** reacts rapidly with phenylacetylene (Scheme 3). Consecutively, two typical FLP reactions were observed. Within 30 min at r.t. the C–H activation[15] product **7** was formed [NMR; ^{13}C: δ 97.1 (PhC≡), ^{1}H: δ 7.31 (ddd, $^1J_{PH}$ =

479.8 Hz, $[P]H_2^+$), ^{31}P: δ −21.8 (t), ^{11}B: δ −18.1]. Compound **7** was isolated in 95% yield. Upon storage of a pentane solution of compound **7** at r.t. for 3 days, crystals of the rearrangement product **8** were obtained in almost quantitative yield. We assume that the C–H activation reaction of **5** with phenylacetylene to give **7** is actually reversible and that then the regioselective 1,2-P/B addition[16] of the regenerated FLP **5** to the alkyne gave **8**. The heterocycle **8** was characterized by spectroscopy and by an X-ray crystal structure analysis (see the ESI† for details and the depicted structure).

Reaction of the FLP 5 with carbon dioxide

Compound **5** was exposed to carbon dioxide[5,17] (2.0 bar, heptane solution, 80 °C, 15 min). Slow cooling of the reaction mixture to r.t. gave colourless crystals of compound **9** that were isolated in 90% yield (Scheme 3). The X-ray crystal structure analysis (see Fig. 2) showed that the PH/B FLP had added to a C═O group of the CO_2 molecule to form a six-membered half-chair shaped heterocycle. It contains a tricoordinate phosphorus (P1) and a four-coordinate boron atom (B1). The remaining carbonyl function was trapped by the $B(C_6F_5)_2$ Lewis acid of a second molecule of **5** and a proton was transferred from P1 to P2 to form the observed adduct product **9**.

The NMR spectra (CD_2Cl_2, 299 K) of compound **9** show two sets of ^1H NMR signals of the Mes* groups of each component of the "dimer". A single broad ^{11}B NMR feature was observed at *ca.* δ 1.7, whereas two separate ^{31}P NMR signals were monitored [δ −20.8 (tm, $^1J_{PH}$ ~ 475 Hz, $[P]H_2^+$); δ −21.5 [P]-CO]. The $[P]H_2^+$ unit gives rise to a ^1H NMR resonance at δ 7.02. The carbonyl ^{13}C NMR signal of the former CO_2 building block inside the six-membered heterocyclic core was located at δ 196.0 (d, $^1J_{PC}$ = 37.4 Hz) (see the ESI† for further details).

Carbon monoxide reactions at the FLP template 5

Compound **5** itself did not react with carbon monoxide. However, in the presence of Piers' borane [$HB(C_6F_5)_2$] the CO molecule was reduced (2 bar CO, r.t., 12 h in dichloromethane) to give compound **11** (isolated in 95% yield after workup; Scheme 4).

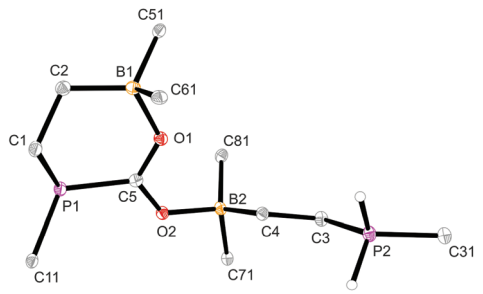


Fig. 2 Molecular structure of compound **9**, derived from the reaction of the FLP **5** with carbon dioxide (thermal ellipsoids at 30% probability; for clarity, only the *ipso* carbon atoms of the aryl substituents are depicted) Selected bond lengths (Å) and angles (°): C2–B1 1.608(3), B1–O1 1.593(3), O1–C5 1.282(2), C5–P1 1.835(2), C5–O2 1.277(2), O2–B2 1.549(3), C2–B1–O1 110.8(2), B1–O1–C5 127.6(2), C5–O2–B2 127.5(2), $\sum P1^{CCC}$ 320.1.

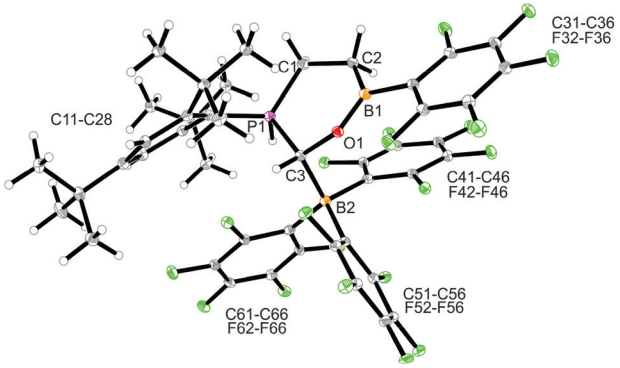
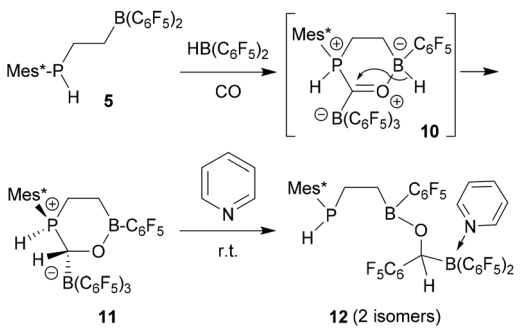


Fig. 3 Molecular structure of the CO reduction product **11**. Only one of the two independent molecules in the unit cell is depicted (thermal ellipsoids at 15% probability). Selected bond lengths (Å) and angles (°): P1A–C3A 1.838(3), C3A–B2A 1.681(5), C3A–O1A 1.453(4), O1A–B1A 1.349(4), B1A–C2A 1.573(5), C2A–C1A 1.546(5), C1A–P1A 1.822(3), P1A–C11A 1.814(3), C1A–P1A–C3A 109.8(2), C3A–O1A–B1A 128.3(3), O1A–B1A–C2A 123.8(3).

The X-ray crystal structure analysis of compound **11** (see Fig. 3) revealed that a six-membered heterocyclic core had been formed by formal addition of the CO carbon atom to phosphorus and the oxygen atom to the boron atom of the FLP reagent **5**. Carbon atom C3 has the bulky $B(C_6F_5)_3$ group attached and a hydrogen atom. The adjacent phosphorus atom P1 bears a hydrogen and represents a phosphonium unit. We note that the boron atom B1 has only one C_6F_5 substituent attached. The missing C_6F_5 group had apparently been transferred to B2 to build up the $B(C_6F_5)_3$ building block.

We assume a pathway that involves the intermediate formation of **10**. This may have been formed after C_6F_5 for H exchange between **5** and $HB(C_6F_5)_2$.[9,18] In a separate experiment we found that a sizable amount of $B(C_6F_5)_3$ was generated from **5** and $HB(C_6F_5)_2$ in the absence of CO under otherwise similar conditions. P/B FLP addition to the *in situ* generated borane carbonyl $(C_6F_5)_3B$-CO[7,19] might have provided a pathway of the straightforward formation of **10**. Internal hydride reduction of the activated endocyclic C═O unit would then directly open a pathway to **11** (see Scheme 4).

We note that compound **11** contains two stereogenic centers, one at phosphorus and one at the adjacent carbon



Scheme 4 Carbon monoxide reduction at the FLP template **5**.

atom C3. The isolated material contains only one of the possible diastereoisomers, namely the one that has the pair of the very bulky Mes* group at phosphorus and the $B(C_6F_5)_3$ substituent at the adjacent carbon atom *trans*-1,2-positioned.

In d_2-dichloromethane solution compound **11** shows PH phosphonium NMR signals at δ 6.87 (^{1}H) and δ −19.5 (^{31}P), respectively, with a $^1J_{PH} \sim 487$ Hz coupling constant. There are two ^{11}B NMR resonances at δ 43.6 (OBC_6F_5) and δ −11.5 ($B(C_6F_5)_3$). The ^{1}H NMR signals of two pairs of diastereotopic methylene hydrogens were observed for the [P]CH_2CH_2[B] unit, and the newly formed [P]CHO[B] unit gives rise to NMR resonances at δ 6.31 (^{1}H) and δ 69.0 (^{13}C), respectively. Both the bulky Mes*-[P] and the [C]-$B(C_6F_5)_3$ units show hindered rotation at 299 K.

The six-membered heterocyclic core of compound **11** was opened when treated with pyridine (CD_2Cl_2, r.t., 2 h). Workup involving crystallization from pentane gave the ring opened product **12**, which was isolated as colourless crystals in 80% yield (see Scheme 4). Compound **11** is thermally stable for quite some time at room temperature. Therefore, we assume that the rather fast **11** to **12** transformation is probably pyridine initiated, but the detailed mechanism of this reaction has remained unknown at this time.

The X-ray crystal structure analysis of compound **12** showed the acyclic framework that contained the heteroatoms P1, B1, O1 and B2 plus the pyridine donor attached at the latter boron atom. The internal B1–O1 bond is short indicating some π interaction.[20] The framework shows a sickle shaped conformation (see Fig. 4). The formation of compound **12** involved rupture of the phosphorus carbon bond and migration of one C_6F_5 substituent of the $B(C_6F_5)_3$ group from boron to the adjacent carbon atom. So, in the overall process the carbon monoxide molecule was converted to a [B]-CH(C_6F_5)-O-[B] moiety in these consecutive steps.[21] Compound **12** contains two chirality centers in the core chain. In the crystal the rel-3(*R*),(S)$_p$ diastereoisomer was observed.[22,23]

In solution (d_2-dichloromethane, 213 K) the NMR signals of two compounds were observed in a *ca.* 56 : 44 ratio. We assign to them the structures of the pair of possible diastereoisomers of compound **12**. The major isomer shows the signal of the [P]H moiety at δ 4.34 (^{1}H, $^1J_{PH}$ = 221.5 Hz) and δ −69.6 (^{31}P, both at 213 K). There is hindered rotation around the Mes*-P vector, giving rise to the observation of three ^{1}H NMR ^{t}Bu signals of **12**-major at δ 1.18 (*p*), 1.30, 1.35 (*o*) and two arene methine CH resonances. The C3–H NMR signal of **12**-major occurs at δ 6.74. The **12**-minor isomer shows the corresponding C3–H ^{1}H NMR signal at δ 6.79 (at 213 K) and the [P]H resonances at 4.62 (^{1}H, $^1J_{PH}$ = 221.5 Hz) and δ −69.0 (^{31}P). There are also the NMR signals of three separate ^{t}Bu substituents and a pair of arene CH signals. We observed a single set of pyridine NMR resonances and two ^{11}B NMR signals [299 K, δ 47.9 (BO), δ −0.9 (B-pyr)] (the spectra are depicted in the ESI†).

The reaction of compound **11** with benzaldehyde also proceeded with migration of a C_6F_5 group from boron to the adjacent carbonyl carbon atom. The reaction was carried out in a 1 : 2 molar ratio in d_2-dichloromethane at r.t. (48 h reaction time). The *in situ* NMR analysis indicated the formation of a 1 : 1 mixture of the products **14** and **15**, that were apparently formed in a borane mediated Claisen-Tishchenko[24] type disproportionation reaction (see Scheme 5). Compound **14** showed the signals of the Mes* substituent at phosphorus [PH: δ 4.77 ($^1J_{PH}$ = 221.1 Hz, ^{1}H), δ −65.9 (^{31}P)]. It features a ^{11}B NMR signal at 48.1 and shows the ^{1}H/^{13}C NMR resonances of the newly formed [B]-OCH_2-Ph methylene group at δ 5.10 (s, 2H, ^{1}H) and δ 70.5 (^{13}C). The ethylene-bridge shows the ^{1}H NMR signals of two pairs of diastereotopic hydrogen atoms (^{13}C NMR signals at δ 21.6, 19.5).

The phosphorus free compound **15** was isolated from a separate experiment and isolated as a colourless crystalline solid. It was characterized by an X-ray crystal structure analysis (crystals from pentane at r.t.). It shows the presence of a planar five-membered heterocyclic core with the phenyl substituent at carbon atom C2 oriented coplanar with the core (the two independent molecules found in the crystal are chemically equivalent). Both the O1–C2 (1.263(2) Å) and C2–O2 (1.297(2) Å) are short, indicating a delocalized structure (see Fig. 5).

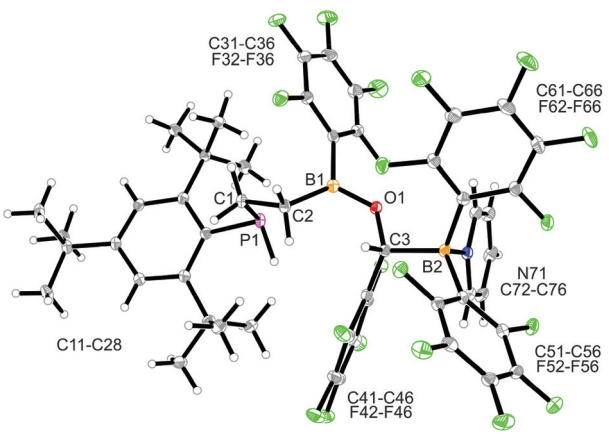
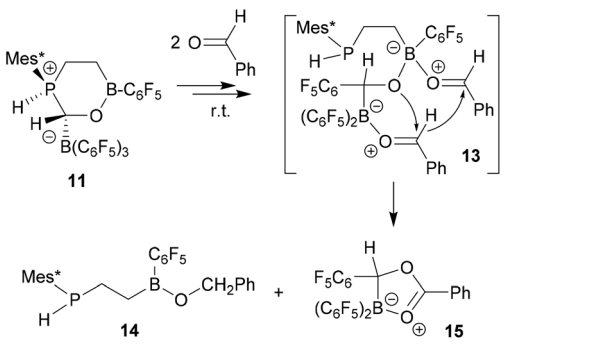


Fig. 4 Molecular structure of the ring-opened product **12** (thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (°): B2–N71 1.617(3), B2–C3 1.663(3), C3–O1 1.459(2), O1–B1 1.351(3), B1–C2 1.574(3), C2–C1 1.549(3), C1–P1 1.858(2), C1–P1–C11 102.3(1), $\sum B1^{OCC}$ 360.0, B1–O1–C3–B2–152.7(2), C2–B1–O1–C3–10.1(3), P1–C1–C2–B1 48.0(2).



Scheme 5 Reaction of compound **11** with benzaldehyde.

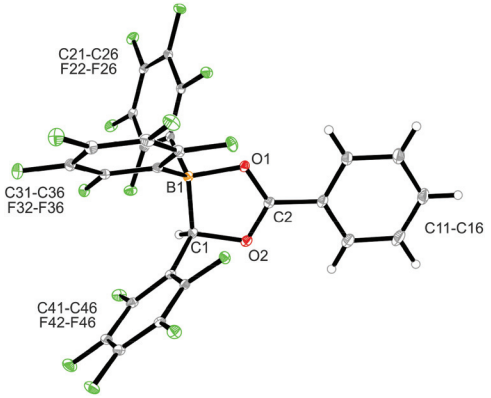


Fig. 5 A projection of the molecular structure of compound **15** (thermal ellipsoids at 15% probability, only molecule A of the pair of crystallographically independent molecules is depicted).

In solution (d_2-dichloromethane, 299 K) compound **15** shows a ^{11}B NMR resonance in the typical tetra-coordinated boron range (δ 4.4). The ^{1}H NMR resonance of the endocyclic C1–H hydrogen occurs at δ 6.88 (^{13}C: 80.6). There is a carbonyl ^{13}C NMR signal at δ 180.7. Compound **15** shows the ^{19}F NMR signals of three different C_6F_5 groups, one at carbon and two at boron.

Conclusion

The PH/B compound **5** is a rather active frustrated Lewis pair. The monomeric form has an open structure. Different from the very parent compound of this series, the $Mes_2PCH_2CH_2B(C_6F_5)_2$ system **1**[3] (see Scheme 1) compound **5** has no internal P···B interaction. However, that is offset at low temperature by the entropically favoured intermolecular P–B bond formation that led to the observation of the unique 12-membered macrocyclic associated structure $(\mathbf{5})_3$. The chemistry of the system is, however, dominated by the monomer. It undergoes a number of typical frustrated Lewis pair reactions. It rapidly cleaves dihydrogen and serves as a rather active metal-free hydrogenation catalyst. It C–H activates a terminal acetylene under kinetic control and forms a heterocyclic product by P/B addition to the carbon–carbon triple bond under thermodynamic control. The PH unit is indirectly involved in the FLP reaction with CO_2. The 2 : 1 FLP/CO_2 product is apparently stabilized by H^+-transfer to the second PH unit. In the CO reduction chemistry, the PH unit serves as the essential FLP Lewis base component, but its P-bonded hydrogen is not directly involved in the overall reaction, aside from influencing the rates of the reaction. Both the CO_2 as well as the CO chemistry at the PH/B FLP **5** show some new features, such as the benzaldehyde disproportionation reaction under borane control.

Conflicts of interest

The authors declare no competing financial interests.

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References

1 D. W. Stephan and G. Erker, *Top. Curr. Chem.*, 2013, **332**, 85–110.
2 (*a*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46–76; (*b*) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2015, **54**, 6400–6441; (*c*) J. Lam, K. M. Szkop, E. Mosaferi and D. W. Stephan, *Chem. Soc. Rev.*, 2019, **48**, 3592–3612.
3 P. Spies, G. Erker, G. Kehr, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072–5074.
4 D. W. Stephan and G. Erker, *Chem. Sci.*, 2014, **5**, 2625–2641.
5 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.
6 (*a*) M. Sajid, L.-M. Elmer, C. Rosorius, C. G. Daniliuc, S. Grimme, G. Kehr and G. Erker, *Angew. Chem., Int. Ed.*, 2013, **52**, 2243–2246; (*b*) M. Sajid, G. Kehr, C. G. Daniliuc and G. Erker, *Chem. – Eur. J.*, 2013, **21**, 1454–1457; (*c*) M. Sajid, A. Lawzer, W. Dong, C. Rosorius, W. Sander, B. Schirmer, S. Grimme, C. G. Daniliuc, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2013, **135**, 18567–18574; (*d*) M. Sajid, G. Kehr, C. G. Daniliuc and G. Erker, *Angew. Chem., Int. Ed.*, 2014, **54**, 1118–1121.
7 (*a*) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, 1937, **59**, 780–787; (*b*) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, 1957, **26**, 1118–1130; (*c*) R. C. Taylor, *J. Chem. Phys.*, 1957, **26**, 1131–1135; (*d*) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, 1966, **88**, 2606–2607; (*e*) M. Sajid, G. Kehr, C. G. Daniliuc and G. Erker, *Angew. Chem., Int. Ed.*, 2014, **53**, 1118–1121.
8 (*a*) A. J. P. Cardenas, B. J. Culotta, T. H. Warren, S. Grimme, A. Stute, R. Fröhlich, G. Kehr and G. Erker, *Angew. Chem., Int. Ed.*, 2011, **50**, 7567–7571; (*b*) M. Sajid, A. Stute, A. J. P. Cardenas, B. J. Culotta, J. A. M. Hepperle, T. H. Warren, B. Schirmer, S. Grimme, A. Studer, C. G. Daniliuc, R. Fröhlich, J. L. Petersen, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2012, **134**, 10156–10168; (*c*) R. Liedtke, F. Scheidt, J. Ren, B. Schirmer, A. J. P. Cardenas, C. G. Daniliuc, H. Eckert, T. H. Warren, S. Grimme, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2014, **136**, 9014–9027; (*d*) J. C. M. Pereira, M. Sajid, G. Kehr, A. Wright, B. Schirmer, Z. W. Qu, S. Grimme, G. Erker and P. Ford, *J. Am. Chem. Soc.*, 2014, **136**, 513–519.
9 M. Erdmann, C. Rösener, T. Holtrichter-Rößmann, C. G. Daniliuc, R. Fröhlich, W. Uhl, E. Würthwein, G. Kehr and G. Erker, *Dalton Trans.*, 2013, **42**, 709–718.
10 J. Li, C. G. Daniliuc, G. Kehr and G. Erker, *Angew. Chem., Int. Ed.*, 2019, **58**, 6737–6741.

11 Q. Sun, C. G. Daniliuc, C. Mück-Lichtenfeld, K. Bergander, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2020, **142**, 17260–17264.

12 (*a*) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem., Int. Ed.*, 1995, **34**, 809–811; (*b*) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492–5503; (*c*) see also: M. Hoshi, K. Shirakawa and M. Okimoto, *Tetrahedron Lett.*, 2007, **48**, 8475–8478; (*d*) X.-S. Tu, N.-N. Zeng, R.-Y. Li, Y.-Q. Zhao, D.-Z. Xie, Q. Peng and X.-C. Wang, *Angew. Chem., Int. Ed.*, 2018, **57**, 15096–15100.

13 For remotely related cyclooligomeric FLP derived macrocycles see e.g.: (*a*) L. Wang, S. Dong, C. G. Daniliuc, L. Liu, S. Grimme, R. Knitsch, H. Eckert, M. R. Hansen, G. Kehr and G. Erker, *Chem. Sci.*, 2018, **9**, 1544–1550; (*b*) X. Jie, C. G. Daniliuc, R. Knitsch, M. R. Hansen, H. Eckert, S. Ehlert, S. Grimme, G. Kehr and G. Erker, *Angew. Chem.*, 2019, **58**, 882–886.

14 (*a*) A. H. Cowley, N. C. Norman, M. Pakulski, G. Becker, M. Layh, E. Kirchner and M. Schmidt, *Inorg. Synth.*, 1990, **27**, 235–240; (*b*) Y. Hasegawa, G. Kehr, S. Ehrlich, S. Grimme, C. G. Daniliuc and G. Erker, *Chem. Sci.*, 2014, **5**, 797–803; (*c*) L. Wang, S. Zhang, Y. Hasegawa, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Commun.*, 2017, **53**, 5499–5502; (*d*) S. Dong, L. Wang, T. Wang, C. G. Daniliuc, M. Brinkkötter, H. Eckert, G. Kehr and G. Erker, *Dalton Trans.*, 2018, **47**, 4449–4454.

15 C. Jiang, O. Blacque and H. Berke, *Organometallics*, 2009, **29**, 125–133.

16 M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6594–6607.

17 See also: (*a*) I. Peuser, R. C. Neu, X. Zhao, M. Ulrich, B. Schirmer, J. A. Tannert, G. Kehr, R. Fröhlich, S. Grimme, G. Erker and D. W. Stephan, *Chem. – Eur. J.*, 2011, **17**, 9640–9650; (*b*) M. Pu and T. Privalov, *Chem. – Eur. J.*, 2013, **19**, 16512–16517; (*c*) M. Courtemanche, J. Larouche, M. Légaré, W. Bi, L. Maron and F. Fontaine, *Organometallics*, 2013, **32**, 6804–6811; (*d*) J. J. Chi, T. C. Johnstone, D. Voicu, P. Mehlmann, F. Dielmann, E. Kumacheva and D. W. Stephan, *Chem. Sci.*, 2017, **8**, 3270–3275; (*e*) X. Jie, Q. Sun, C. G. Daniliuc, R. Knitsch, M. R. Hansen, H. Eckert, G. Kehr and G. Erker, *Chem. – Eur. J.*, 2020, **26**, 1269–1273.

18 T. Wang, C. G. Daniliuc, C. Mück-Lichtenfeld, G. Kehr and G. Erker, *J. Am. Chem. Soc.*, 2018, **140**, 3635–3643.

19 For remotely related borane carbonyls see *e.g.*: (*a*) M. Finze, E. Bernhardt, A. Terheiden, M. Berkei, H. Willner, D. Chrsiten, H. Oberhammer and F. Aubke, *J. Am. Chem. Soc.*, 2002, **124**, 15385–15398; (*b*) H. Braunschweig, R. D. Dewhurst, F. Hupp, M. Nutz, K. Radacki, C. W. Tate, A. Vargas and Q. Ye, *Nature*, 2015, **522**, 327–330.

20 See for a comparison, see: (*a*) B. Pachaly and R. West, *J. Am. Chem. Soc.*, 1985, **107**, 2987–2988; (*b*) D. Vidovic, J. A. Moore, J. N. Jones and A. H. Cowley, *J. Am. Chem. Soc.*, 2005, **127**, 4566–4567; (*c*) Y. Yamamoto, M. Takizawa, X.-Q. Yu and N. Miyaura, *Angew. Chem., Int. Ed.*, 2008, **47**, 928–931; (*d*) C. Kleeberg, L. Dang, Z. Lin and T. B. Marder, *Angew. Chem., Int. Ed.*, 2009, **48**, 5350–5354; (*e*) Y. Shoji, N. Tanaka, K. Mikami, M. Uchiyama and T. Fukushima, *Nat. Chem.*, 2014, **6**, 498–503.

21 (*a*) A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron and O. Eisenstein, *J. Am. Chem. Soc.*, 2012, **134**, 10843–10851; (*b*) R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 4974–4977.

22 R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, 1970, **92**, 3090–3093.

23 See for a comparison: (*a*) C. Rosorius, G. Kehr, R. Fröhlich, S. Grimme and G. Erker, *Organometallics*, 2011, **30**, 4211–4219; (*b*) C. Rosorius, C. G. Daniliuc, R. Fröhlich, G. Kehr and G. Erker, *J. Organomet. Chem.*, 2013, **744**, 149–155; (*c*) C. Rosorius, J. Möricke, B. Wibbeling, A. C. McQuilken, T. H. Warren, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. – Eur. J.*, 2016, **22**, 1103–1113.

24 S. A. Morris and D. G. Gusev, *Angew. Chem., Int. Ed.*, 2017, **56**, 6228–6231 and references cited therein.

