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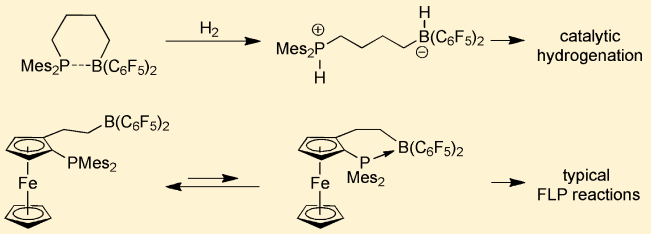
Internal Adduct Formation of Active Intramolecular C_4-bridged Frustrated Phosphane/Borane Lewis Pairs

Xiaowu Wang, Gerald Kehr, Constantin G. Daniliuc, and Gerhard Erker*

Organisch-Chemisches Institut der Universität Münster, Correnstrasse 40, 48149 Münster, Germany.

Supporting Information

ABSTRACT: The tetramethylene-bridged $PMes_2/B(C_6F_5)_2$ frustrated Lewis pair (FLP) **8** was prepared by hydroboration of $Mes_2P{-}(CH_2)_2CH{=}CH_2$ with $HB(C_6F_5)_2$. It is an active FLP that splits dihydrogen under mild conditions and, consequently, serves as a metal-free hydrogenation catalyst for a variety of substrates. It also reacts typically with terminal acetylenes. The C_4-bridged FLP **23** was prepared by $HB(C_6F_5)_2$ hydroboration of 1-dimesitylphosphino-2-vinylferrocene. It represents a rare example of a FLP where the equilibrium between the open form and the closed internal P/B adduct form is experimentally observable. It also shows a variety of typical FLP reactions, including dihydrogen splitting. The FLPs **8** and **23** (open form) and many precursors and products were characterized by X-ray diffraction.

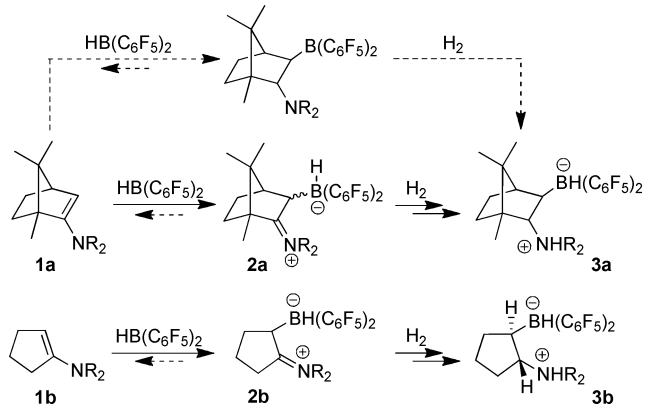


INTRODUCTION

Frustrated Lewis pairs (FLPs) have pairs of active Lewis acids and bases in solution that provide the opportunity to observe their joint reaction with added substrates.[1,2] Such cooperative or synergistic FLP reactions have been observed upon exposure of, e.g. respective phosphane/[3,4] or amine/[5]borane pairs to dihydrogen resulting in heterolytic cleavage of the H_2 molecule, often providing a basis for developing metal-free catalytic hydrogenation reactions.[6−8] FLPs also have been observed to add to alkenes[9] or alkynes,[10,11] to carbonyl compounds[12] including carbon dioxide,[13] to SO_2,[14] and even to nitrogen oxides.[15] Recently, the reduction of carbon monoxide to the formyl stage has been achieved at a frustrated Lewis pair template.[16]

Steric hindrance (and sometimes special electronic features[17]) have been used to hinder deactivating strong Lewis acid/Lewis base adduct formation between the frustrated Lewis pair components. However, that does not imply that FLPs must be completely devoid of any Lewis acid (LA)/Lewis base (LB) interaction or even adduct formation. Actually, weak LA/LB van der Waals contacts seem to be essential in the reactions of intermolecular FLPs with small molecules to avoid the "termolecularity trap".[18] Also intramolecular FLPs often feature pronounced Lewis acid/base interactions,[5b,19] although recently we have described a few geminal and vicinal FLP examples that seem to have no measurable LA/LB contacts.[16a,20] Lewis acid/Lewis base interaction can go to extremes in active FLPs. Examples are the systems **1a,b** where the addition of the strongly Lewis acidic $HB(C_6F_5)_2$ reagent has resulted in the quantitative formation of the strong B-Lewis acid/enamine C-Lewis base adducts **2**, that were isolated and characterized by X-ray diffraction.[21] Nevertheless, these systems split dihydrogen under mild reaction conditions to give the zwitterionic products **3**, probably via reversal of the LA/LB adduct formation followed by hydroboration under rapid equilibrium conditions (see Scheme 1).

Scheme 1



Most vicinal P/B and N/B FLPs that we had contributed to the literature show weak internal adduct formation. From dynamic ^{19}F NMR spectroscopy the activation barriers for ring-opening were determined at $\Delta G^{\ddagger} \approx 12$ to 14 kcal·mol^{-1} for chiral variants of such systems.[5b,19] It was thought that the typical FLP reactions of systems such as **4** took place via their nonobserved open isomers **5** (see Scheme 2).[22]

We had also prepared the corresponding trimethylene-bridged P/B system **7** but have so far not found any indication of typical FLP activity.[23] We have now prepared the next

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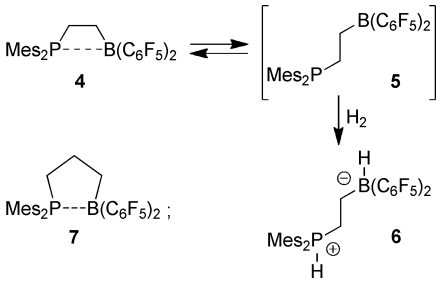
Scheme 2

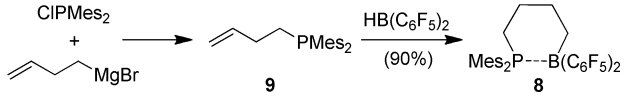


member in this series, the tetramethylene-bridged P/B FLP **8** and found it to be an active frustrated Lewis pair. We here report its characterization and some typical reactions, and we have prepared a closely related C_4-bridged P/B FLP where we were able to experimentally observe both the open and the closed form of an active frustrated Lewis pair.

RESULTS AND DISCUSSION

The Tetramethylene-Bridged P/B FLP 8. The synthesis of the tetramethylene-bridged phosphane/borane FLP **8** was rather straightforward. The reaction of the butenyl magnesium bromide Grignard reagent with dimesitylchlorophosphane gave butenyldimesitylphosphane (**9**) in reasonable yield. This was then reacted with Piers' borane $[HB(C_6F_5)_2]$.[24] A clean hydroboration reaction ensued with the usual anti-Markovnikov regiochemistry to yield the P/B system **8** (see Scheme 3). Compound **8** was isolated as a white solid in 90% yield.

Scheme 3



Both the compounds **9** and **8** were characterized by X-ray diffraction. Compound **9** features a tricoordinate phosphorus center with a typical trigonal pyramidal geometry with a sum of C−P−C bond angles of 316.3° (values given for one of the independent molecules of **9** in the crystal, see Figure 1). The individual P−C bond lengths were found in a very narrow range between 1.851(2) Å (P1A−C21A) and 1.857(2) Å (P1A−C11A). The P1A−C1A bond length amounts to 1.856(2) Å. The P-bonded butenyl group was found in an extended conformation (C1A−C2A 1.533(3) Å, C2A−C3A 1.494(3) Å, C3A−C4A 1.292(4) Å, dihedral angles P1A−C1A−C2A−C3A 172.7(1)°, C1A−C2A−C3A−C4A 126.3(3)°). In solution, compound **9** shows the typical NMR features of the terminal vinyl group and a ^{31}P NMR resonance at δ −22.5.

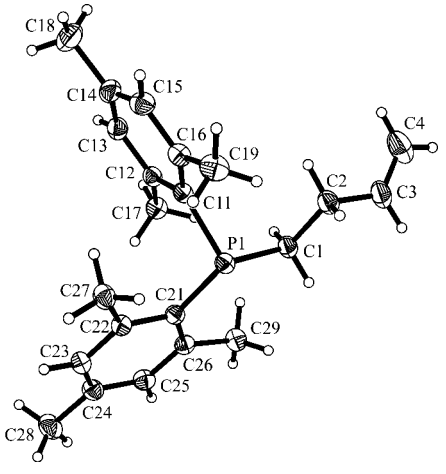


Figure 1. View of the molecular structure of butenyldimesitylphosphane **9** (thermal ellipsoids are shown with 30% probability).

The X-ray crystal structure analysis of compound **8** shows a tetramethylene chain that has a $PMes_2$ group and a $B(C_6F_5)_2$ substituent attached at its ends (P1−C1 1.855(2) Å, B1−C4 1.636(3) Å). There is a marked bonding contact between the boron Lewis acid and the phosphorus Lewis base (B1−P1 2.113(2) Å) which is, however, located at the long end of related B−P systems.[25] In the crystal, compound **8** exhibits a chairlike conformation of its framework with a close to *gauche* C1−P1−B1−C4 dihedral angle of 44.9(2)° (see Figure 2).

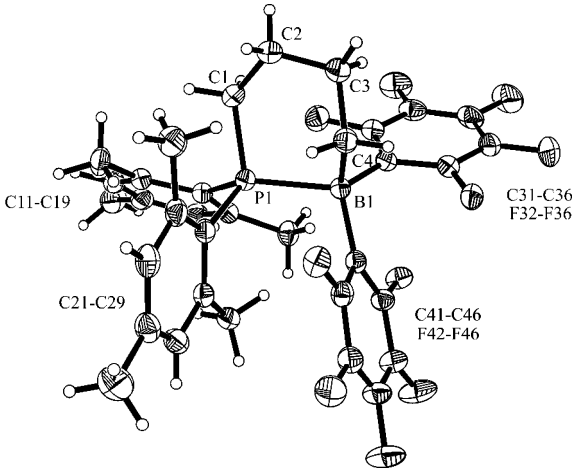


Figure 2. View of the molecular structure of compound **8** (thermal ellipsoids are shown with 30% probability).

In solution, compound **8** shows heteronuclear magnetic resonance signals at δ −5.8 (^{11}B) and δ 3.3 (^{31}P), respectively. It exhibits a set of four ^{13}C NMR signals of the tetramethylene linker at δ 23.1, 23.1, 21.2, and 18.6 (br). Compound **8** features dynamic NMR spectra probably due to conformational inversion of the heterocyclohexane chair conformation of the six-membered core-ring structure concomitant with "freezing" of the P−C(mesityl) and B−C_6F_5 rotation at low temperature on the respective NMR time scales. Consequently, we have observed a total of six mesityl methyl ^{1}H NMR signals at low temperature and four *m*-arene proton resonances (the spectra are depicted in the SI). Similarly, we have monitored a decoalescence of the three broad *o*,*p*,*m*-C_6F_5 ^{19}F NMR signals observed at 299 K to eventually give four well-separated *o*-F resonances, two *p*-F signals and four *m*-F signals of the pair of C_6F_5 substituents at boron. From the *p*-F coalescence, we have obtained a Gibbs-activation energy value of $\Delta G^{\ddagger}$(268 K) = 11.5 ± 0.3 kcal·mol^{-1} for this conformational equilibration process of compound **8**.

Despite the fact that compound **8** shows an internal adduct structure in both the crystal and in solution, it reacted with dihydrogen. A solution of **8** in dichloromethane was exposed to a H_2 atmosphere (1.5 bar) at ambient temperature for 30 min, and the mixture was kept under H_2 at −30 °C for 2 d to give a

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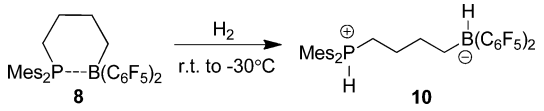
crystalline material (50% isolated) which was identified as the product **10** of heterolytic splitting of dihydrogen by compound **8** (see Scheme 4).

Scheme 4



The zwitterionic complex **10** was characterized by X-ray diffraction, by spectroscopy, and by C,H-elemental analysis. In solution it shows the ^{31}P NMR doublet of the [$PHMes_2^+$] moiety at δ −11.9 within the typical large coupling constant of $^1J_{PH} \approx 486$ Hz (corresponding ^{1}H NMR feature at δ 7.82). The ^{11}B NMR signal of **10** occurs at δ −20.9 ($^1J_{BH} \approx 80$ Hz). Compound **10** shows three ^{19}F NMR resonances of the pair of symmetry equivalent C_6F_5 substituents at δ −134.0 (*o*), −164.6 (*p*), and −166.8 (*m*) with a small $\Delta\delta^{19}$F(*m*,*p*) shift difference of 2.2 that is typical of a borate anion structure. The hydrogen splitting reaction by **10** was confirmed by its reaction with dideuterium to yield compound **10**-D_2. It shows the ^{31}P/^{11}B NMR signals of the [$PDMes_2^+$] unit at δ −11.7 ($^1J_{PD}$ = 73 Hz) and of the [$BD(C_6F_5)_2^-$] moiety at δ −21.0 ($\nu_{1/2} \approx 85$ Hz) (for details see the SI).

The X-ray crystal structure analysis of compound **10** (see Figure 3) shows an extended acyclic structure. The [Mes_2PH^+]

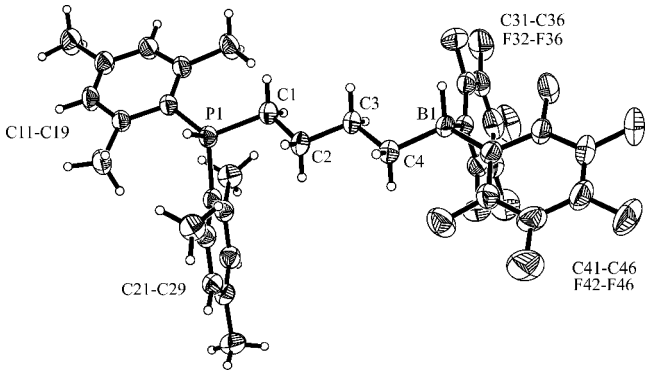


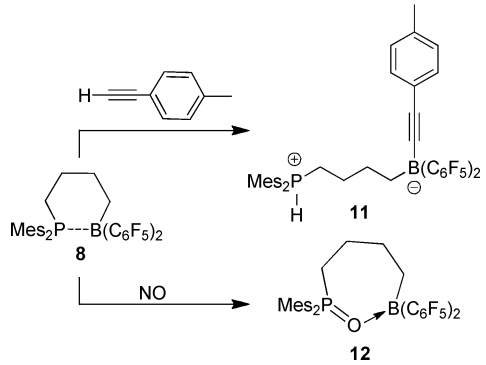
Figure 3. Molecular structure of the zwitterionic compound **10** (thermal ellipsoids are shown with 30% probability).

phosphonium substituent is bonded to carbon at one end of the C_4-chain (C1−P1 1.807(4) Å, sum of heavy atom bond angles at phosphorus: $\sum P^{ccc}$ 339.9°) and the [$(C_6F_5)_2BH^-$] hydridoborate unit to the other C-terminus (B1−C4 1.632(6) Å, $\sum B^{ccc}$ 334.9°). The central heavy atom chain is found in a close all-anti-periplanar conformation (dihedral angles P1−C1−C2−C3 −179.6(3)°, C1−C2−C3−C4 −179.5(4)°, C2−C3−C4−B1 −179.2(4)°).

Many zwitterionic hydridoborate/phosphonium pairs derived from the heterolytic splitting of dihydrogen by internal P/B frustrated Lewis pairs were shown to be able to transfer the H^+/H^- pair to a variety of suitable substrates, and some of them have served as active catalysts in hydrogenation reactions. In a small series of qualitative experiments, we were able to show that the [PH^+]/[BH^-] zwitterion **10** can also transfer H^+/H^- and serve as a metal-free hydrogenation catalyst. We carried out catalytic hydrogenations of bulky imines, enamines, and also of alkenylferrocene derivatives by *in situ* generated **10** using between 5 and 10 mol % of the FLP/H_2 catalyst system **10**/H_2 (for details see the SI).

We have also carried out a few other FLP reactions with the tetramethylene-bridged P/B system **8**. Active FLPs usually react with terminal acetylenes by (sometimes) competing addition or deprotonation reactions. The latter was observed when compound **8** was treated with *p*-tolylacetylene in dichloromethane. The reaction went to completion during 1 h, and we isolated the product **11** as a white solid in 78% yield (Scheme 5). It shows the typical ^{1}H NMR [Mes_2PH^+] doublet at δ 7.38

Scheme 5



($^1J_{PH}$ = 475.5 Hz, corresponding ^{31}P NMR resonance at δ −10.7), and a borate type ^{11}B NMR feature at δ −18.2. There is a single set of ^{19}F NMR signals of the pair of C_6F_5 substituents at boron with a small $\Delta\delta^{19}$F(*m*,*p*) value of 2.4. We have monitored one of the ^{13}C NMR signals of the [B]−C≡C−Ar unit at δ 94.1, and we have located the four ^{13}C NMR signals of the bridging tetramethylene moiety at δ 29.0, 27.0, 24.8, and 22.3 (for details see the SI).

We had shown that a variety of vicinal P/B FLPs (**4**, see Scheme 2) undergo P/B addition to the nitrogen atom of nitric oxide (NO) under mild conditions to yield the respective persistent FLP-NO aminoxyl radicals.[15b,c] Alternatively, phosphanes are known to react with NO to give the corresponding phosphanoxide plus N_2O.[26] Compound **8** shows a typical free phosphane reactivity toward NO. Treatment of **8** with nitric oxide (−78 °C to −30 °C) overnight gave a blue solution from which workup produced a white solid (89%) that was shown to be the phosphanoxide derivative **12** by X-ray diffraction (Scheme 5). In the crystal compound **12** shows a heterocyclic seven membered ring structure. It contains a phosphanoxide (P1−O1 1.536(3) Å). Its oxygen atom is internally coordinated to the $B(C_6F_5)_2$ group[27] (B1−O1 1.570(5) Å, angle P1−O1−B1 129.9(2)°) (see Figure 4).

In solution, compound **12** shows a typical ^{31}P NMR signal of a phosphanoxide (δ 64.7). It shows the typical set of ^{19}F NMR *o*-, *p*-, *m*-signals of the pair of symmetry-equivalent C_6F_5 groups at boron with a small $\Delta\delta^{19}$F(*m*,*p*) = 4.5 ppm shift difference. The ^{13}C NMR resonance of the bridging tetramethylene unit of **12** were located at δ 34.3 ($^1J_{PC}$ = 55.5 Hz), δ 23.4 ($^2J_{PC}$ = 5.1 Hz), δ 29.0, and δ 24.4 (br).

A C_4-bridged P/B FLP at the Ferrocene Framework. We prepared a couple of related C_4-bridged P/B-FLPs derived from a respective ferrocene framework. Our synthesis followed a pathway that had been developed previously by Kagan[28] and by Stěpnička.[29] It started with the enantiomerically pure acetal (*S*,*S*)-**14** that was derived from ferrocene carbaldehyde by the "Kagan method" (see Scheme 6). Directed *o*-metalation

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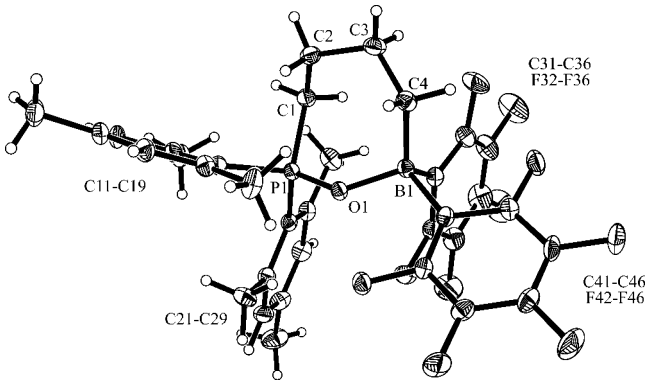
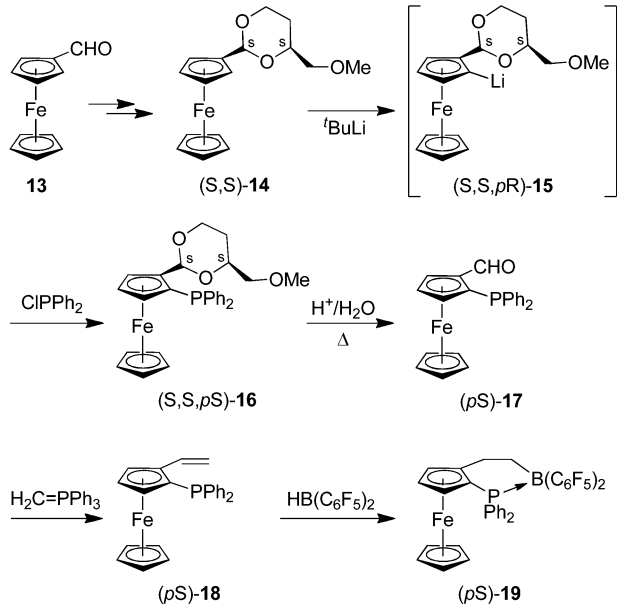


Figure 4. Molecular structure of compound **12** (thermal ellipsoids are shown with 30% probability).

Scheme 6



followed by treatment with diphenylchlorophosphane gave the (S,S,*p*S)-**16** acetal in high diastereomeric excess as described by Kagan.[28] Hydrolysis followed by Wittig olefination of the resulting aldehyde (*p*S)-**17** eventually yielded the *o*-diphenylphosphanyl(vinyl)ferrocene (*p*S)-**18** highly enantiomerically enriched as described by Stěpnička.[29]

Compound (*p*S)-**18** was then reacted with Piers' borane [$HB(C_6F_5)_2$]. A clean hydroboration of the vinyl-substituent was observed with anti-Markovnikov regioselectivity to give the P/B system (*p*S)-**19** which was isolated as an orange solid in close to quantitative yield. Compound (*p*S)-**19** was characterized by X-ray diffraction (single crystals were obtained from benzene/heptane at r.t.). The X-ray crystal structure analysis confirmed the 1,2-substitution pattern at the "upper" ferrocene Cp-ring and the regioselective hydroboration of the pendant vinyl substituent. The most prominent structural feature of compound (*p*S)-**19** is the presence of a strong P−B bond between the PPh_2 Lewis base and the $B(C_6F_5)_2$ Lewis acid (P1−B1 2.046(2) Å). The resulting six-membered heterocyclic ring system exihibits a distorted cyclohexene-type half-chair conformation (see Figure 5) with pairs of chemically inequivalent phenyl substituents at phosphorus and C_6F_5 groups at boron (θ B1−C12−C11−C2 75.6 (2)°).

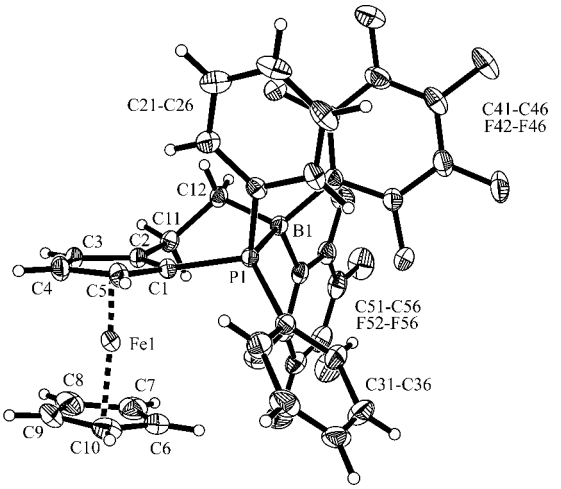
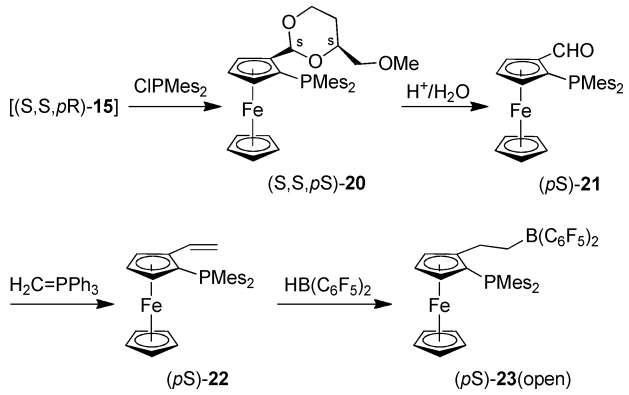


Figure 5. View of the molecular structure of compound (*p*S)-**19** (thermal ellipsoids are shown with 30% probability).

The NMR spectra of compound (*p*S)-**19** indicate that the P−B bond is retained in solution. The complex features a ^{31}P NMR resonance at δ +3.4 and a sharp ^{11}B NMR signal at δ −10.7. The latter is typical of tetra-coordinated borane in this environment. Consequently, we have observed a pair of sharp ^{19}F NMR signals of the *p*-F atoms of the pair of inequivalent C_6F_5 groups at boron (δ −157.9 and δ −158.7) and a corresponding pair of *m*-C_6F_5 signals of 2-fold relative intensity at δ −163.8 and −164.5. Compound (*p*S)-**19** features the $^1H/^{13}C$ NMR signals of a pair of inequivalent phenyl groups at phosphorus and a set of ^1H NMR signals of the CH_2-CH_2-[B] moiety at δ 2.58 (m, 2H) and δ 1.98, 1.85 (each m, each 1H).

We prepared the related $PMes_2$ containing ferrocene-based FLP by an analogous route. It started with the *in situ* generated lithio-ferrocene derivative (S,S,*p*R)-**15** (see Scheme 6) that was quenched with $ClPMes_2$ to give (S,S,*p*S)-**20** (see Scheme 7). Compound (S,S,*p*S)-**20** was characterized by X-ray diffraction, and its stereochemical features were confirmed (see Figure 6).

Scheme 7



Acid-catalyzed hydrolysis then gave (*p*S)-**21**. It shows a ^{31}P NMR signal at δ −41.9 and the typical $^1H/^{13}C$ NMR resonances of the carbaldehyde function at δ 10.63/192.3 [(IR (C=O stretch): $\tilde{\nu}$ = 1671 cm^{-1})]. Complex (*p*S)-**21** was also characterized by X-ray diffraction. It shows the pair of *o*-$PMes_2$ and CHO functional groups attached at the "upper"

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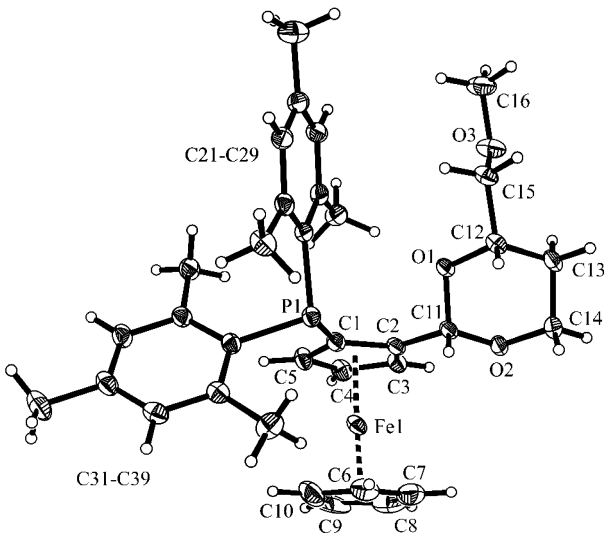

Figure 6. Molecular structure of compound (S,S,*p*S)-**20** (thermal ellipsoids are shown with 30% probability).

ferrocene-Cp ring (see Figure 7). The plane of the aldehyde is rotated slightly out of the Cp-ring plane (C11−O1 1.194(4) Å,

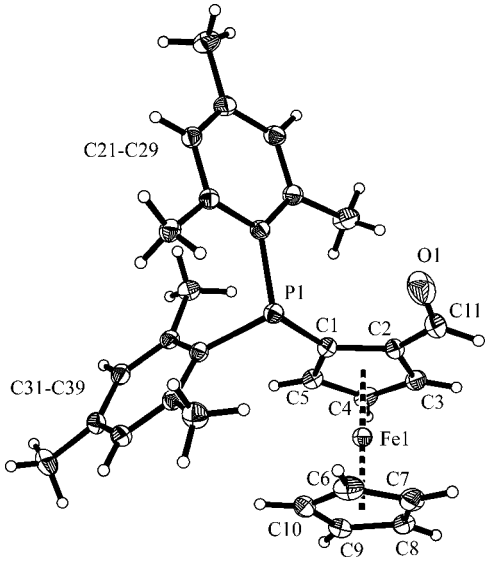

Figure 7. View of the molecular structure of compound (*p*S)-**21** (thermal ellipsoids are shown with 30% probability).

θ C3−C2−C11−O1 167.5(3)°) and the carbonyl oxygen atom is pointing toward the adjacent phosphorus (C1−P1 1.824(2) Å).

Wittig olefination of the aldehyde function in (*p*S)-**21** gave the vinylferrocene derivative (*p*S)-**22** in good yield (97%) [$[\alpha]^{20}_{D}$ = +324; (*p*S)-**18**: $[\alpha]^{20}_{D}$ = +343[29]]. It shows the typical ^{1}H NMR AMX pattern of the vinyl group [δ 6.94, 5.45, 5.09; ^{13}C: δ 134.1 (HC=, $^{3}J_{PC}$ = 14.4 Hz), δ 111.9 ($^{4}J_{PC}$ = 2.4 Hz, =CH_2)] and a ^{31}P NMR resonance at δ −40.9. Complex (*p*S)-**22** was also characterized by an X-ray crystal structure analysis (see Figure 8). It features the vinyl group in a conformation showing away from the phosphorus (C11−C12 1.317(5) Å, θ C1−C2−C11−C12 −152.2(3)°).

Addition of Piers' borane [$HB(C_6F_5)_2$] to (*p*S)-**22** resulted in a clean hydroboration of the vinyl CH=CH_2 double bond with

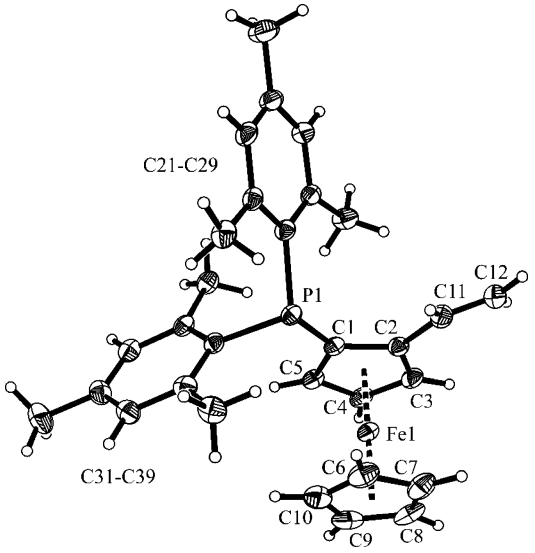

Figure 8. Molecular structure of complex (*p*S)-**22** (thermal ellipsoids are shown with 30% probability).

anti-Markovnikov orientation to give the ferrocene-derived frustrated Lewis pair (*p*S)-**23** in close to quantitative yield. The X-ray crystal structure analysis revealed an open structure. Contrary to its PPh_2 analogue (*p*S)-**19** (see above), complex (*p*S)-**23** does not show any appreciable interaction between the bulky $PMes_2$ Lewis base (P1−C1 1.811(7) Å) and the $B(C_6F_5)_2$ Lewis acid (C12−B1 1.559(1) Å). The boron center is planar tricoordinate ($\sum B^{CCC}$ = 359.8°). The Cp−CH_2−CH_2−$B(C_6F_5)_2$ unit features a gauche like conformation (θ C2−C11−C12−B1 73.7(9)°) that has the C11−C12 vector pointing away from the phosphorus atom. Actually, the P and B atoms in compound (*p*S)-**23** are separated by 5.837 Å (see Figure 9).

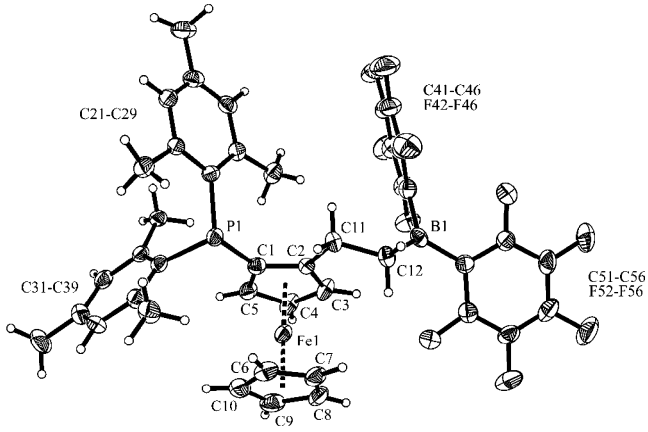

Figure 9. A view of the molecular structure of the FLP (*p*S)-**23** in the crystal (thermal ellipsoids are shown with 30% probability).

Compound (*p*S)-**23** shows temperature dependent NMR spectra. These indicate an equilibrium of the open FLP structure (*p*S)-**23**(open) with the internally P···B coordinated adduct structure (*p*S)-**23**(closed). This system shows dynamic NMR spectra demonstrating a strongly temperature dependent **23**(open) ⇄ **23**(closed) equilibrium situation. At high temperature the open form is favored as expected (probably mostly entropically controlled), whereas with decreasing

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temperature an increasing equilibrium amount of the closed isomer is being observed. This is best illustrated with the temperature dependent ^{19}F NMR spectra. At ambient conditions, we have monitored three slightly broadened ^{19}F NMR $B(C_6F_5)_2$ resonances [298 K, CD_2Cl_2 solution, 564 MHz: δ −129.8 (*o*), δ −148.6 (*p*), δ −161.8 (*m*)]. On lowering the temperature these signals broaden and show a slight shifting. Below 223 K, we start to observe the signals of a second species that rapidly increases in intensity with decreasing temperature. Figure 10 shows the ^{19}F NMR

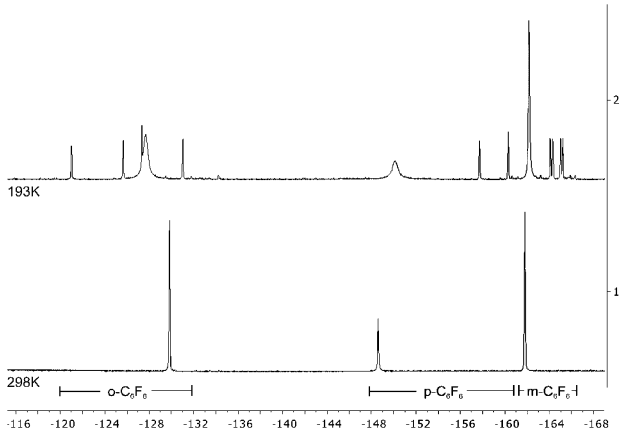
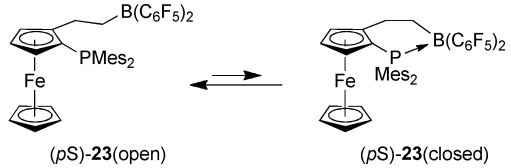


Figure 10. ^{19}F NMR (564 MHz, CD_2Cl_2) spectra of the (*pS*)-**23**(open), (closed) mixture of isomers at 193 K (2) and 298 K (1).

spectrum at 193 K. It features the three broad signals of the (*pS*)-**23**(open) isomer [δ −127.7 (*o*), δ −150.1 (*p*), δ −162.2 (*m*)] with a large $\Delta\delta^{19}F(m,p)$ separation of 12.1 that is typical for a Lewis acidic tricoordinate $R-B(C_6F_5)_2$ situation (see Scheme 8). The second species is likely the (*pS*)-**23**(closed)

Scheme 8



isomer. In contrast to the open isomer, it features the ^{19}F NMR resonances of a pair of nonequivalent C_6F_5 groups at boron and "frozen" rotation about the $B-C_6F_5$ vectors of both on the ^{19}F NMR time scale. Consequently, we observe a total of four *o*-, two *p*- and four *m*-C_6F_5 ^{19}F NMR signals of (*pS*)-**23**(closed) (see Figure 10) (for further details see the SI). The ^{19}F NMR $\Delta\delta^{19}F(m,p)$ = 4.7, 4.9 of the (*pS*)-**23**(closed) isomer is small, as it is expected for a tetra-coordinated borane situation.[30] We have observed corresponding temperature dependent spectral changes in the ^{1}H, ^{31}P and ^{11}B NMR spectra of compound (*pS*)-**23**. At 193 K the mixture of the (*pS*)-**23** (open)/(closed) isomers shows a pair of ^{31}P NMR signals (63: 37) at δ −33.4 and +11.5 whereas at 298 K one resonance at δ −42.8 was observed. The (*pS*)-**23**(closed)/(*pS*)-**23**(open) equilibrium was characterized by a van't Hoff plot (depicted in the SI). This equilibrium is characterized by the thermodynamic parameters of ΔH° = 4.7 ± 0.2 kcal·mol^{-1} and ΔS° = +25.9 ± 0.2 cal·mol^{-1}·K^{-1}.

Reactions of the Ferrocene-Derived FLP (*pS*)-23. We first reacted the FLP (*pS*)-**23** with typical N- and C-donor ligands. Treatment of the ferrocene-derived FLP with pyridine in a 1:1 molar ratio in pentane at r.t. gave a yellow precipitate of the [B]−pyridine adduct (*pS*)-**24** that was isolated in 88% yield. Compound (*pS*)-**24** features the $^{1}H/^{13}C$ NMR signals of the pyridine moiety and of a pair of diastereotopic mesityl substituents at phosphorus. Actually the rotation around the P−Mes vectors are "frozen" on the 600 MHz ^{1}H NMR time scale at 233 K so that we have observed a total of six methyl group signals and four *m*-CH signals of the $PMes_2$ unit in compound (*pS*)-**24**. Similarly, we have observed the ^{19}F NMR resonances of a pair of diastereotopic C_6F_5 groups at boron. The remaining heteronuclear magnetic resonance signals of compound (*pS*)-**24** occur at δ −44.0 (^{31}P) and δ −1.8 (^{11}B), respectively.

Compound (*pS*)-**24** was characterized by X-ray diffraction. In the crystal, compound (*pS*)-**24** features a tetracoordinated boron atom that has the pyridine unit bonded to it (B1−N13 1.632(5) Å). The B1−C12−C11−C2 unit shows a close to antiperiplanar conformational arrangement (θ −177.9(3)°) (see Figure 11 and Scheme 9).

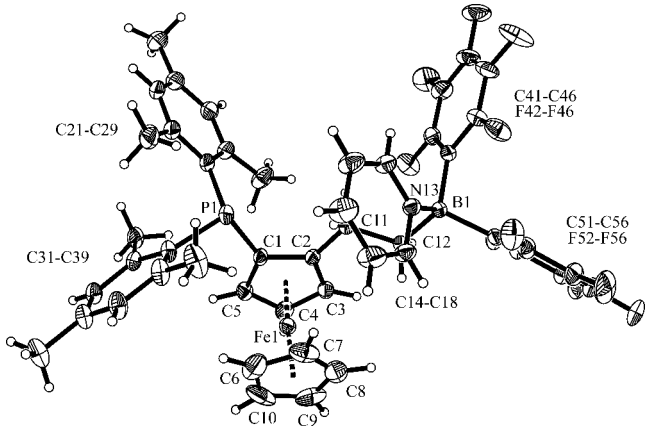
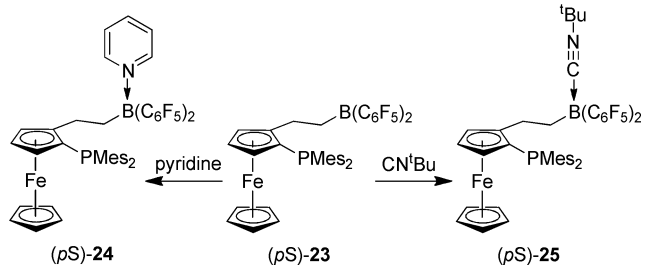


Figure 11. Molecular structure of compound (*pS*)-**24** (thermal ellipsoids are shown with 30% probability).

Scheme 9



Treatment of (*pS*)-**23** with *tert*-butylisocyanide gave a similar adduct. We isolated compound (*pS*)-**25** as an yellow solid in >80% yield. It was also characterized by X-ray diffraction (see Figure 12). In the crystal, the newly formed [B]−C≡N−^{t}Bu moiety is linear [B1−C13 1.621(1) Å, C13−N14 1.141(9) Å, angles B1−C13−N14 173.6(9)°, C13−N14−C15 171.4(9)°]. The ^{13}C NMR isonitrile signal of (*pS*)-**25** was located at δ 116.8 as a broad resonance. Complex (*pS*)-**25** shows an isonitrile IR band at $\tilde{\nu}$ = 2289 cm^{-1}.

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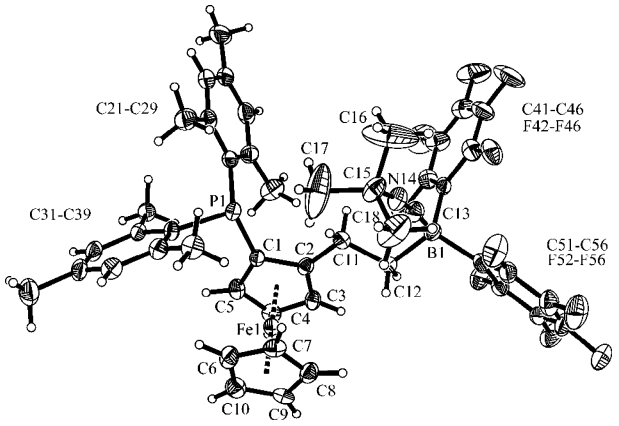
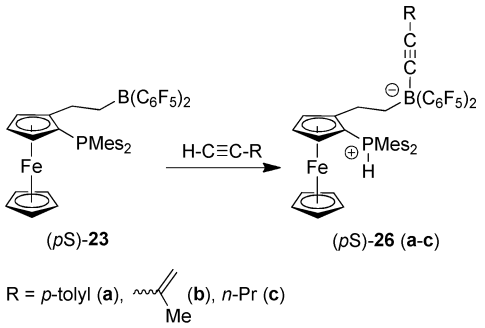


Figure 12. Molecular structure of compound (*p*S)-**25** [thermal ellipsoids are shown with 30% probability; only one molecule (molecule A) from two found in the asymmetric unit is shown].

Many intramolecular P/B FLPs react with terminal acetylenes by deprotonation and formation of the respective phosphonium cation/alkynyl borate anion zwitterions.[31] Compound (*p*S)-**23** reacted analogously. In three different experiments, we treated complex (*p*S)-**23** with *p*-tolylacetylene, with 2-methylbutenyne and with 1-pentyne. In each case we have observed the formation of the corresponding zwitterionic phosphonium/alkynylborate systems and isolated the respective complexes (*p*S)-**26 a-c** (see Scheme 10).

Scheme 10



As a typical example compound (*p*S)-**26a** shows a ^{11}B NMR signal at δ −18.9 and a ^{31}P NMR doublet at δ −18.9 ($^{1}J_{PH} \approx$ 500 Hz). The corresponding ^{1}H NMR PH signal occurs at δ 8.55. The acetylene ^{13}C NMR resonances were located at δ 110.3 (BC≡) and δ 94.2 (≡C-[p-tolyl]) respectively. Compounds (*p*S)-**26b** and (*p*S)-**26c** show similar NMR signals (see the SI).

The *p*-tolylacetylene-derived compound (*p*S)-**26a** was characterized by X-ray diffraction (see Figure 13). It shows the acetylene moiety bonded to the boron atom [B1−C41 1.603(7) Å, C41−C42 1.196(7) Å]. The boron center is pseudotetrahedrally coordinated.

The intramolecular frustrated Lewis pair (*p*S)-**23** reacts rapidly with dihydrogen at ambient conditions (r.t., 1.5 bar H_2). From a pentane solution, a yellow precipitate was formed. We isolated the [PH$^+$][BH$^-$] containing compound (*p*S)-**27** in >70% yield. Compound (*p*S)-**27** turned out to be rather sensitive in solution.[32] Some of the NMR features of the product of heterolytic splitting of dihydrogen by the FLP (*p*S)-**23** were obtained from *in situ* experiments without workup.

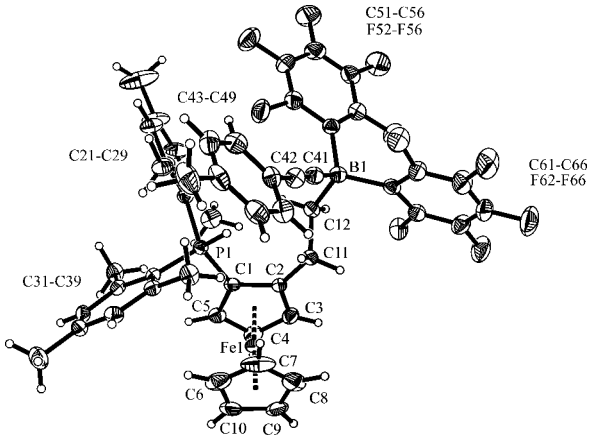
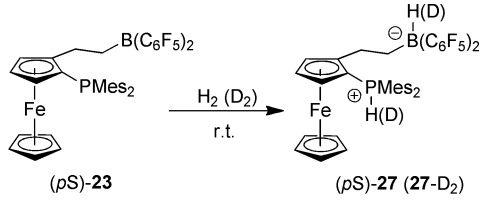


Figure 13. Molecular structure of compound (*p*S)-**26a** (thermal ellipsoids are shown with 30% probability).

Compound (*p*S)-**27** exhibits a ^{31}P NMR signal at δ −18.8 (d, $^{1}J_{PH}$ = 496.1 Hz). The ^{19}F NMR spectrum shows typical signals of a tetracoordinated borate signal. The ^{11}B NMR spectrum indicates the presence of a [BH$^-$] unit (δ −20.5, d, $^{1}J_{BH} \approx$ 85 Hz). We have also reacted (*p*S)-**23** with D_2 and obtained the corresponding [PD$^+$]/[BD$^-$] product (*p*S)-**27**-D_2. It shows the expected 1:1:1 intensity triplet ^{31}P NMR signal and the ^{2}D NMR [PD$^+$] doublet and a broad [BD$^-$] signal (for details see the SI) (see Scheme 11).

Scheme 11



The FLP (*p*S)-**23** serves as a hydrogenation catalyst via its dihydrogen splitting product (*p*S)-**27**. We have briefly tested it in the successful catalytic hydrogenation of selected imines and enamine examples. In most cases, the substrates were rapidly hydrogenated using 5−20 mol % of the FLP catalyst. Hydrogenation of *N-tert*-butylacetophenone imine gave the corresponding amine in up to 26% ee (for details see the SI). Although this represents only a relatively small asymmetric induction exerted by the planary chiral FLP catalyst, it nevertheless proves that the intact FLP (*p*S)-**23**, respectively its dihydrogen activation product (*p*S)-**27**, is responsible for this hydrogenation process. We assume a mechanistic scheme of iminium ion formation by initial protonation followed by hydride transfer. Therefore, the (*p*S)-**23** system not unexpectedly was able to catalytically hydrogenate vinylferrocene to give ethylferrocene.

Eventually we reacted the ferrocene-derived system (*p*S)-**23** with nitrogen monoxide (see Scheme 12). Similar to the reaction behavior of the tetramethylene-bridged $PMes_2$/$B(C_6F_5)_2$ system **8** (see above) this also marked the limits of (*p*S)-**23** in cooperative FLP chemistry. Instead of synergistic P/B addition as it had been observed for the ethylene-bridged $PMes_2$/$B(C_6F_5)_2$ system **4**, the phosphane and borane functionality in (*p*S)-**23** react additively, i.e. each is acting independently. Consequently, the phosphane of (*p*S)-**23** was

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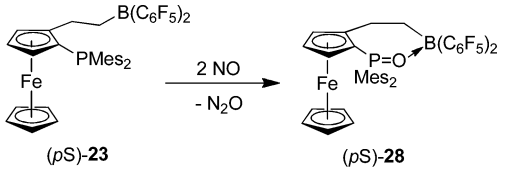
Scheme 12



oxidized upon exposure to NO to give the respective phosphanoxide which was then κO-bonded to the internal boron Lewis acid to give the product (*pS*)-**28**, which was isolated as a pale-yellow solid in 79% yield.

Complex (*pS*)-**28** shows the ^{19}F NMR signals of a pair of diasterotopic C_6F_5 groups at boron. The rotation around the P-mesityl vectors is slow on the ^{1}H NMR time scale, so we have observed a total of six methyl group signals and four arene methine protons of the pair of mesityl groups at the $P(O)Mes_2$ function of (*pS*)-**28**. The ^{11}B NMR resonance of (*pS*)-**28** is at δ 3.6 and the ^{31}P NMR signal is at δ 58.6.

CONCLUSIONS

We had reported about the highly reactive ethylene-bridged FLP **4** that has undergone a great variety of typical FLP reactions, including selective small-molecule activation and binding.[22,33] Since the next homologue, the trimethylene-linked $PMes_2/B(C_6F_5)_2$ system **7**, turned out to be an unreactive FLP (for reasons that are presently not clear), one might not have expected quite reactive FLP behavior of the next homologue, the tetramethylene-bridged $PMes_2$, $B(C_6F_5)_2$ system **8**. However, **8** is a very reactive FLP. It cleaves dihydrogen and activates it for metal-free catalytic hydrogenation, deprotonates alkynes with formation of the respective phosphonium/alkynylborate products. The ferrocene-derived FLP (*pS*)-**23** behaves similarly. In this very exceptional case of a C_4-bridged $PMes_2/B(C_6F_5)_2$ FLP we can experimentally observe the reversible P−B adduct formation/dissociation reaction by its temperature-dependent NMR spectra. This constitutes a very rare case where the open (active) and closed (dormant) structures of an intramolecular frustrated Lewis pair have become experimentally observable. These two C_4-bridged intramolecular P/B FLP systems serve to markedly extend the structural and conceptional scope of active intramolecular FLP systems and frameworks. They will probably help us design a variety of active FLP systems for future applications of frustrated Lewis chemistry.

EXPERIMENTAL SECTION

Preparation of Compound 8. Compound **9** (8.6 mmol, 2.80 g, 1 equiv) and $HB(C_6F_5)_2$ (8.6 mmol, 2.99 g, 1 equiv) were suspended in pentane (20 mL) and stirred for 1 h at ambient temperature. The resulting clouded suspension was filtered, and the clear filtrate was dried in vacuo to yield compound **8** (7.7 mmol, 5.20 g, 90%) as a pale-yellow solid which was crystallized in toluene. Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of **8** in toluene at −30 °C. Mp: 151 °C. Anal. Calcd for $C_{34}H_{30}BF_{10}P$: C, 60.92; H, 4.51. Found: C, 61.05; H, 4.76. ^{1}H NMR (600 MMR, 193 K, [D_2]-dichloromethane): δ = 6.96 (m, 1H, *m*-Mes^A), 6.86 (m, 1H, *m*-Mes^B), 6.73 (m, 1H, *m*′-Mes^B), 6.40 (m, 1H, *m*′-Mes^A), 3.14, 2.36, 2.23, 1.89, 1.57, 0.84 (each m, each 1H, CH_2), 2.81 (s, 3H, *o*-CH_3^{MesA}), 2.45 (br d, $^4J_{PH}$ = 4.2 Hz, 3H, *o*-CH_3^{MesB}), 2.17 (s, 3H, *p*-CH_3^{MesA}), 2.15 (s, 3H, *p*-CH_3^{MesB}), 2.06 (s, 3H, *o*′-CH_3^{MesB}), 1.44, 1.00 (each m, each 1H, BCH_2), 1.14 (s, 3H, *o*′-CH_3^{MesA}). ^{13}C{^{1}H} NMR (151 MHz, 193 K, [D_2]-dichloromethane): δ = 142.0 (d, $^2J_{PC}$ = 14.3 Hz, *o*-Mes^B), 141.5 (d, $^2J_{PC}$ = 11.9 Hz, *o*′-Mes^A), 140.9 (br, *o*-Mes^A), 140.3 (d, $^4J_{PC}$ = 2.2 Hz, *p*-Mes^A), 140.2 (br, *o*′-Mes^B), 139.5 (d, $^4J_{PC}$ = 1.8 Hz, *p*-Mes^B), 131.0 (d, $^3J_{PC}$ = 6.4 Hz, *m*′-Mes^B), 130.8 (d, $^3J_{PC}$ = 8.0 Hz, *m*-Mes^A), 129.9 (d, $^3J_{PC}$ = 9.4 Hz, *m*′-Mes^A), 129.5 (d, $^1J_{PC}$ = 45.3 Hz, *i*-Mes^B), 128.9 (d, $^3J_{PC}$ = 8.9 Hz, *m*-Mes^B), 123.0 (dd, $^1J_{PC}$ = 45.8 Hz, *J* = 2.1 Hz, *i*-Mes^A), 25.1 (d, $^3J_{PC}$ = 2.2 Hz, *o*-CH_3^{MesA}), 24.4 (m, *o*-CH_3^{MesB}), 23.12 (d, J_{PC} = 3.3 Hz)^t, 23.07 (d, J_{PC} = 37.1 Hz)^t, 21.2 (br)(CH_2), 23.0 (d, $^3J_{PC}$ = 6.4 Hz, *o*′-CH_3^{MesA}), 21.8 (d, $^3J_{PC}$ = 3.2 Hz, *o*′-CH_3^{MesB}), 20.07 (d, $^5J_{PC}$ = 0.9 Hz, *p*-CH_3^{MesA}), 20.13 (d, $^5J_{PC}$ = 0.5 Hz, *p*-CH_3^{MesB}), 18.6 (br, BCH_2), [C_6F_5 not listed. ^{t} tentatively assigned]. ^{11}B{^{1}H} NMR (192 MHz, 193 K, [D_2]-dichloromethane): δ = −5.8 ($\nu_{1/2}$ ≈ 1400 Hz). ^{19}F NMR (564 MHz, [D_2]-dichloromethane, 193 K): δ = −126.0 (m, *o*), −127.5 (m, *o*″), −158.0 (br t, $^3J_{FF}$ = 19.5 Hz, *p*), −165.0 (m, *m*), −165.1 (m, *m*′)(each 1F, $C_6F_5^B$) [$\Delta\delta^{19}F_{mp}$ = 5.0, 5.1], −124.5 (m, *o*), −130.2 (m, *o*″), −159.8 (t, $^3J_{FF}$ = 21.3 Hz, *p*), −164.0 (m, *m*′), −164.6 (m, *m*)(each 1F, $C_6F_5^A$) [$\Delta\delta^{19}F_{mp}$ = 4.2, 4.8]. ^{31}P{^{1}H} NMR (243 MHz, 193 K, [D_2]-dichloromethane): δ = 3.3 ($\nu_{1/2}$ ≈ 30 Hz).

Preparation of Compound 10. The P/B FLP **8** (0.12 mmol, 80.0 mg, 1 equiv) was dissolved in dichloromethane (2 mL), and the solution was degassed by freeze−pump−thaw cycles (two times). Then H_2 gas (1.5 bar) was pressed to the solution for 30 min at ambient temperature. The reaction mixture was stored in the refrigerator at −30 °C for 2 d. Batches of crystals were formed at the bottom of the vessel. Solvent was removed in vacuum, and the obtained solid was dried at low temperature (∼0 °C) *in vacuo* to give a white powder (0.06 mmol, 40.0 mg, 50%). Crystals suitable for the X-ray crystal structure analysis were obtained from a toluene solution of **10** at −30 °C in an H_2 atmosphere (1.5 bar). Mp: 111 °C. Anal. Calcd for $C_{34}H_{32}BF_{10}P$: C, 60.73; H, 4.80. Found: C, 61.05; H, 4.76. ^{1}H NMR (600 MMR, 243 K, [D_2]-dichloromethane): δ = 7.82 (br dt, $^1J_{PH}$ = 482.6 Hz, $^3J_{HH}$ = 6.3 Hz, 1H, PH), 6.98 (d, $^3J_{PH}$ = 3.9 Hz, 4H, *m*-Mes), 2.76 (br m, 2H, PCH_2), 2.33 (s, 12H, *o*-CH_3^{Mes}), 2.29 (s, 6H, *p*-CH_3^{Mes}), 1.65, 1.24, 0.81 (each br m, each 2H, CH_2), n.o. (BH). ^{13}C{^{1}H} NMR (151 MHz, 243 K, [D_2]-dichloromethane): δ = 145.9 (*p*-Mes), 143.0 (d, $^2J_{PC}$ = 9.9 Hz, *o*-Mes), 131.7 (d, $^2J_{PC}$ = 11.7 Hz, *m*-Mes), 111.2 (d, $^1J_{PC}$ = 81.3 Hz, *i*-Mes), 32.1, 28.1, n.o. (each br, CH_2), 24.5 (br d, $^1J_{PC}$ = 40.1 Hz, PCH_2), 22.0 (d, $^3J_{PC}$ = 7.2 Hz, *o*-CH_3^{Mes}), 21.1 (*p*-CH_3^{Mes}), [C_6F_5 not listed]. ^{11}B NMR (192 MHz, 299 K, [D_2]-dichloromethane): δ = −20.9 (d, $^1J_{BH}$ ≈ 78 Hz). ^{19}F NMR (564 MHz, 243 K, [D_2]-dichloromethane): δ = −134.0 (br m, 2F, *o*-C_6F_5), −164.6 (br t, $^3J_{FF}$ = 20.3 Hz, 1F, *p*-C_6F_5), −166.8 (br m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 2.2]. ^{31}P NMR (243 MHz, 243 K, [D_2]-dichloromethane): δ = −11.9 (br d, $^1J_{PH}$ ≈ 486 Hz, $\nu_{1/2}$ ≈ 40 Hz).

Preparation of Compound 10-D_2. A solution of compound **8** (0.35 mmol, 240 mg, 1 equiv) in dichloromethane (5 mL) was degassed by freeze−pump−thaw cycles (two times). Then D_2 gas (2 bar) was pressed to the solution for 30 min. The reaction mixture was stirred overnight. Solvent was quickly evaporated in vacuum, and the obtained solid was dried at low temperature *in vacuo* to give compound **10**-D_2 (0.16 mmol, 113 mg, 47%) as a white powder. ^{1}H NMR (600 MHz, 299 K, [D_2]-dichloromethane): δ = 7.06 (d, $^4J_{PH}$ = 4.2 Hz, 4H, *m*-Mes), 2.88, 1.78, 1.43, 0.88 (each m, each 2H, CH_2), 2.41 (s, 12H, *o*-CH_3^{Mes}), 2.35 (s, 6H, *p*-CH_3^{Mes}). ^{11}B{^{1}H} NMR (192 MHz, 299 K, [D_2]-dichloromethane)): δ = −21.0 ($\nu_{1/2}$ ≈ 80 Hz). ^{19}F NMR (564 MHz, 299 K, [D_2]-dichloromethane): δ = −133.7 (m, 2F, *o*-C_6F_5), −165.5 (t, $^3J_{FF}$ = 19.9 Hz, 1F, *p*-C_6F_5), −167.5 (m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{mp}$ = 2.0]. ^{31}P{^{1}H} NMR (243 MHz, 299 K, [D_2]-dichloromethane)): δ = −11.7 (1:1:1 t, $^1J_{PD}$ = 73.0 Hz, $\nu_{1/2}$ ≈ 5 Hz).

Preparation of Compound (*pS*)-23. *NMR Characterization.* Compound (*pS*)-**22** (0.05 mmol, 24.0 mg, 1 equiv) was reacted with $HB(C_6F_5)_2$ (0.05 mmol, 17.3 mg, 1 equiv) in deuterated dichloromethane (0.5 mL) at room temperature for 30 min to give compound (*pS*)-**23** (100% conversion). [Comment: two compounds were observed in CD_2Cl_2 solution at 193 K, which were tentatively assigned as the "open" and "closed" FLP structure]. ^{1}H NMR (600 MHz, 193 K, [D_2]-dichloromethane): δ[major] = 7.00 (d, $^4J_{PH}$ = 4.9 Hz), 6.81 (br), 6.54 (br), 6.51 (br, each 1H, *m*-Mes), 4.30, 4.22, 4.04 (each br m, each 1H, C_5H_3), 3.93 (s, 5H, C_5H_5), 2.83, 2.34 (each br m, each 1H, CH_2), 2.80, 2.23, 2.07, 1.87, 1.80, 1.56 (each s, each 3H, CH_3^{Mes}), 2.35,

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2.02 (each m, each 1H, BCH_2). δ[minor] = 7.03, 6.82, 6.81, 6.49(each br, each 1H, *m*-Mes), 4.04 (2H), 3.83 (1H, each br m, C_5H_3), 4.12 (s, 5H, C_5H_5), 3.71 (s), 2.46 (s), 2.26 (d, $^3J_{PH}$ = 6.3 Hz), 2.22 (s), 2.19 (s), 0.99 (s) (each 3H, CH_3^{Mes}), 3.03, 1.90 (each br m, each 1H, CH_2), 1.90 (br m), 1.27 (br dm, $^3J_{PH}$ = 37.7 Hz)(each 1H, BCH_2). $^{11}B\{^1H\}$ NMR (192 MHz, 298 K, [D_2]-dichloromethane): δ = 72.6 ($\nu_{1/2} \approx$ 1200 Hz). ^{19}F NMR (564 MHz, 193 K, [D_2]-dichloromethane): δ[major, ~70% mol] = −127.7 (br, 2F, *o*-C_6F_5), −150.1 (br, 1F, *p*-C_6F_5), −162.2 (br, 2F, *m*-C_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 12.1]. δ[minor, ~30% mol] = −121.0, −131.0 (each m, *o*), −160.3 (br t, $^3J_{FF}$ = 21.0 Hz, *p*), −165.0, −165.2 (each m, *m*) (each 1F, C_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 6.4, 6.6], −125.7, −127.4 (each m, *o*), −157.7 (br t, $^3J_{FF}$ = 19.8 Hz, *p*), −164.1 −164.3 (each m, *m*) (each 1F, C_6F_5)[$\Delta\delta^{19}F_{p,m}$ = 4.7, 4.9]. ^{19}F NMR (564 MHz, 298 K, [D_2]-dichloromethane): δ = −129.8 (br m, 2F, *o*-C_6F_5), −148.6 (br, 1F, *p*-C_6F_5), −161.8 (br m, 2F, *m*-C_6F_5) [$\Delta\delta^{19}F_{p,m}$ = 13.2]. $^{31}P\{^1H\}$ NMR (243 MHz, 193 K, [D_2]-dichloromethane): δ = −33.4 ($\nu_{1/2} \approx$ 750 Hz, ~63% mol, "open" structure), 11.5 ($\nu_{1/2} \approx$ 40 Hz, ~37% mol, "closed" structure). $^{31}P\{^1H\}$ NMR (243 MHz, 298 K, [D_2]-dichloromethane): δ = −42.8 ($\nu_{1/2} \approx$ 55 Hz).

*Isolation of Compound (pS)-**23**.* Compound (*p*S)-**22** (0.1 mmol, 48.0 mg, 1 equiv) was reacted with $HB(C_6F_5)_2$ (0.1 mmol, 34.6 mg, 1 equiv) in pentane (7.0 mL) at room temperature for 30 min to give a red-orange solution. The red-orange solution was kept in the refrigerator at −30 °C. Crystals suitable for the X-ray crystal structure analysis were obtained from a solution of (*p*S)-**23** in pentane at −30 °C. Quick removal of the pentane solution by pipet and drying of the resultant red-orange solid in vacuum gave compound (*p*S)-**23** (0.07 mmol, 61.0 mg, 74%). Mp: 176 °C. Anal. Calcd for $C_{42}H_{34}BF_{10}FeP$: C, 61.05; H, 4.15. Found: C, 59.96; H, 3.94.

Preparation of Compound (*p*S)-27. *NMR Characterization.* In a Schlenk vessel (10 mL), compound (*p*S)-**22** (0.05 mmol, 24.0 mg, 1 equiv) was reacted with $HB(C_6F_5)_2$ (0.05 mmol, 17.3 mg, 1 equiv) in CD_2Cl_2 (0.5 mL) at room temperature for 30 min to give an orange solution. Afterward the solution was exposed to an H_2 gas atmosphere (1.5 bar). Within 1 min, a bright yellow solution was formed. The solution was stirred for another 20 min in the presence of an H_2 gas atmosphere (1.5 bar). Then the solution was immediately transferred to a NMR tube and sealed. The sample was immediately characterized by NMR experiments. ^1H NMR (600 MHz, 193 K, [D_2]-dichloromethane): δ = 8.45 (d, $^1J_{PH}$ = 495.4 Hz, 1H. PH), 7.21 (d, $^4J_{PH}$ = 3.8 Hz, 1H, *m*-Mes^a), 7.01 (br, 1H, *m*′-Mes^a), 6.93 (d, $^4J_{PH}$ = 3.5 Hz, 1H, *m*-Mes^b), 6.76 (d, $^4J_{PH}$ = 3.3 Hz, 1H, *m*′-Mes^b), 4.86, 4.62, 4.16 (each br, each 1H, C_5H_3), 4.13 (s, 5H, C_5H_5), 2.86 (s, 3H, *o*-CH_3^{Mesa}), 2.33 (s, 3H, *p*-CH_3^{Mesa}), 2.203 (s, 3H, *p*-CH_3^{Mesb}), 2.198 (s, 3H, *o*-CH_3^{Mesb}), 2.18 (m, 2H, CH_2), 2.11 (s, 3H, *o*′-CH_3^{Mesa}), 1.74 (s, 3H, *o*′-CH_3^{Mesb}), 0.94, 0.85 (each br, each 1H, BCH_2), n.o. (BH). $^{13}C\{^1H\}$ NMR (151 MHz, 193 K, [D_2]-dichloromethane): δ = 145.3 (*p*-Mes^a), 144.7 (*p*-Mes^b), 143.8 (d, $^2J_{PC}$ = 10.1 Hz, *o*′-Mes^b), 142.3 (d, $^2J_{PC}$ = 10.3 Hz, *o*′-Mes^a), 141.4 (d, $^2J_{PC}$ = 19.2 Hz, *o*′-Mes^a), 141.3 (d, $^2J_{PC}$ = 21.4 Hz, *o*-Mes^b), 131.9 (d, $^3J_{PC}$ = 12.1 Hz, *m*′-Mes^b), 131.6 (d, $^3J_{PC}$ = 11.7 Hz, *m*′-Mes^a), 130.7 (d, $^3J_{PC}$ = 10.5 Hz, *m*-Mes^a), 130.5 (d, $^3J_{PC}$ = 10.5 Hz, *m*-Mes^b), 111.7 (d, $^1J_{PC}$ = 89.8 Hz, *i*-Mes^a), 110.8 (d, $^1J_{PC}$ = 82.1 Hz, *i*-Mes^b), 99.7 (d, J_{PC} = 12.1 Hz), 75.6 (d, J_{PC} = 10.0 Hz), 72.6 (d, J_{PC} = 11.0 Hz), 71.9 (d, J_{PC} = 14.1 Hz), 56.9 (d, J_{PC} = 96.3 Hz)(C_5H_3), 70.5 (C_5H_5), 28.8 (br, CH_2), 23.4 (br, BCH_2), 21.9 (d, $^3J_{PC}$ = 10.5 Hz, *o*-CH_3^{Mesa}), 21.8 (d, $^3J_{PC}$ = 3.3 Hz, *o*′-CH_3^{Mesb}), 21.5 (d, $^3J_{PC}$ = 6.8 Hz, *o*′-CH_3^{Mesa}), 21.0 (*p*-CH_3^{Mesa}), 20.50 (*p*-CH_3^{Mesb}), 20.49 (d, $^3J_{PC}$ = 8.6 Hz, *o*-CH_3^{Mesb}), [C_6F_5 not listed]. ^{11}B NMR (192 MHz, 273 K, [D_2]-dichloromethane): δ = −20.5 (d, $^1J_{BH} \approx$ 85 Hz)(diluted sample ~0.0125 mmol/mL). ^{19}F NMR (564 MHz, 193 K, [D_2]-dichloromethane): δ = −134.2 (m, 4F, *o*-C_6F_5); −163.9, −164.0 (each br m, each 1F, *p*-C_6F_5); −166.0, −166.2 (each m, each 2F, *m*-C_6F_5). ^{31}P NMR (243 MHz, 193 K, [D_2]-dichloromethane): δ = −18.8 (d, $^1J_{PH}$ = 496.1 Hz).

*Isolation of Compound (pS)-**27**.* Compound (*p*S)-**22** (0.05 mmol, 24.0 mg, 1 equiv) was reacted with $HB(C_6F_5)_2$ (0.05 mmol, 17.3 mg, 1 equiv) in pentane (10 mL) at room temperature for 30 min to give an orange solution. Afterward the solution was exposed to an H_2 gas atmosphere (1.5 bar). Within 1 min, a bright-yellow solid was formed. The solution was stirred for another 5 min in the presence of an H_2 gas atmosphere (1.5 bar). Then all volatiles were removed *in vacuo* and the resulting pale-yellow solid was washed twice with pentane (2 × 1 mL) to give compound (*p*S)-**27** (0.036 mmol, 30.0 mg, 73%) as a pale-yellow solid. Dec: 150 °C. Anal. Calcd for $C_{42}H_{36}BF_{10}FeP$: C, 60.90; H, 4.38. Found: C, 60.10; H, 4.08.

Preparation of Compound (*p*S)-27-D_2. *NMR Characterization.* In a Schlenk vessel (10 mL) compound (*p*S)-**22** (0.1 mmol, 48.0 mg, 1 equiv) was reacted with $HB(C_6F_5)_2$ (0.1 mmol, 34.6 mg, 1 equiv) in CD_2Cl_2 (1 mL) at room temperature for 30 min to give an orange solution. Afterward, 1.5 bar D_2 gas was exposed to the reaction solution. A bright-yellow solution was formed immediately. The solution was stirred for another 20 min in the presence of a D_2 gas atmosphere (1.5 bar). The solution was immediately transferred to a NMR tube and sealed. The sample was promptly characterized by NMR experiments. ^1H NMR (600 MHz, 193 K, [D_2]-dichloromethane): δ = 7.21 (d, $^4J_{PH}$= 5.1 Hz), 7.00 (d, $^4J_{PH}$ = 4.2 Hz), 6.93 (d, $^4J_{PH}$ = 4.3 Hz), 6.76 (d, $^4J_{PH}$ = 4.3 Hz)(each 1H, *m*-Mes), 4.86, 4.62, 4.16 (each br, each 1H, C_5H_3), 4.13 (s, 5H, C_5H_5), 2.86 (3H), 2.33 (3H), 2.20 (6H), 2.11 (3H), 1.74 (3H) (each s, CH_3^{Mes}), 2.18 (m, 2H, CH_2), 0.93, 0.82 (each m, each 1H, BCH_2). ^2H NMR (92 MHz, 193 K, [D_2]-dichloromethane): 8.46 (br d, $^1J_{PD}$ = 73.6 Hz, PD), 2.50 (br, BD). ^{11}B NMR (192 MHz, 193 K, [D_2]-dichloromethane): δ = −21.1 ($\nu_{1/2} \approx$ 350 Hz). ^{19}F NMR (564 MHz, 193 K, [D_2]-dichloromethane): δ = −134.2 (m, 4F, *o*-C_6F_5); −163.9, −164.0 (each br m, each 1F, *p*-C_6F_5); −166.0, −166.1 (each m, each 2F, *m*-C_6F_5) [$\Delta\delta_{mp}$ = 2.1]. $^{31}P\{^1H\}$ NMR (243 MHz, 193 K, [D_2]-dichloromethane): δ = −19.2 (1:1:1 t, $^1J_{PD}$ = 73.4 Hz).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and physical characterization of the new compounds, hydrogenation reactions, crystallographic data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

erker@uni-muenster.de

kehrald@uni-muenster.de

Notes

The authors declare no competing financial interest.

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