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Phosphine–Borane Frustrated Lewis Pairs Derived from a 1,1′-Disubstituted Ferrocene Scaffold: Synthesis and Hydrogenation Catalysis

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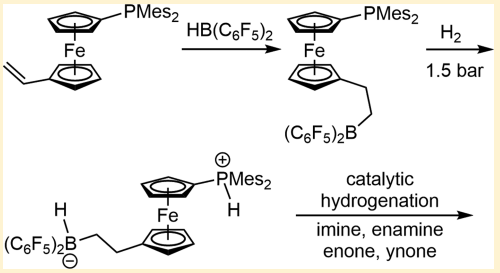
Supporting Information

ABSTRACT: (Dimesitylphosphino)ferrocene ($FcPMes_2$) (**1**) reacted with $HB(C_6F_5)_2$ (2 equiv) by disproportionation to give adduct $FcPMes_2 \cdot H_2B(C_6F_5)$ (**4**) plus $B(C_6F_5)_3$, whereas 1-(dimesitylphosphino)-1′-vinylferrocene (**2**) was cleanly hydroborated with $HB(C_6F_5)_2$ to afford $[Fe(\eta^5\text{-}C_5H_4PMes_2)(\eta^5\text{-}C_5H_4CH_2CH_2B(C_6F_5)_2)]$ (**7**). Compound **7** adopted an open non-interacting P/B frustrated Lewis pair (FLP) structure in the crystal state as well as in a solution. This frustrated Lewis pair heterolytically cleaved dihydrogen under mild conditions to give the respective zwitterionic $[P]H^+/[B]H^-$ phosphonium/hydroborate product, $[Fe(\eta^5\text{-}C_5H_4PHMes_2)\{\eta^5\text{-}C_5H_4CH_2CH_2BH(C_6F_5)_2\}]$ (**8**), which served as a catalyst for the hydrogenation of the electron-rich π-systems (imine, enamine) as well as the electron-deficient carbon–carbon double and triple bonds in some enones and an ynone under more forcing conditions (50 bar H_2 pressure, 50 °C).



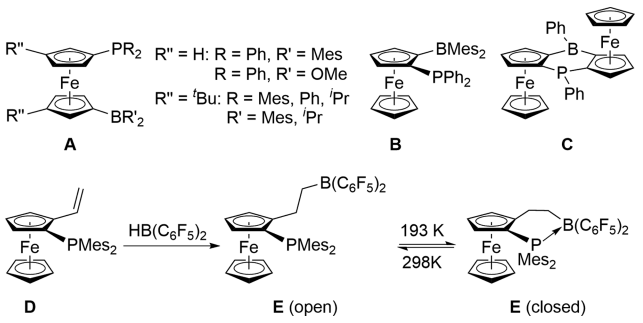
INTRODUCTION

Phosphine–borane frustrated Lewis pairs (P/B FLPs) have been the subject of recent interest, mainly due to their unorthodox reactivity and an ability to react with and activate small molecules such as H_2, CO, and CO_2.[1] The chemical properties of P/B FLPs strongly depend on the mutual positioning of the phosphine and borane moieties in their molecules and the substituents in the functional molecular parts that are controlling their steric and electronic properties. The majority of FLPs reported to date exploit simple organic fragments as the molecular backbone. In contrast, the use of organometallic fragments as molecular scaffolds for FLPs remains still rather scarce. Indeed, there have been reported examples of P/B FLPs derived from Group 4 metallocenes,[2] but the otherwise ubiquitous ferrocene moiety[3] has found only a limited use in the design of FLP-type molecules.

In the past few years, Bourissou,[4] Cantat,[5a] Diaconescu,[5b] and Hierso[5c] independently reported the synthesis of 1,1′-disubstituted (R_2B-/R_2P-)ferrocenes, compounds **A** (Chart 1), while Aldridge[6] prepared the isomeric 1,2-disubstituted (Mes_2B-/Ph_2P-)ferrocene, compound **B** (Chart 1). More recently, the family of ferrocene-based P/B FLPs was extended by the ring-fused bis-ferrocene derivative **C**.[7]

In order to increase molecular flexibility and thus possibly allow for interactions between the Lewis acidic and basic sites in the molecules of phosphinoferrocene boranes, some of us have utilized the hydroboration of ferrocene phosphino-alkenes **D**[8] with Piers' borane $[HB(C_6F_5)_2]$,[9] that directly provides planar-chiral FLPs of type **E** (see Chart 1).[10] Compound **E** and

Chart 1. Representative Examples of Phosphinoferrocene Boranes



a derivative activated molecular hydrogen and were used as catalysts for asymmetric hydrogenation of imines, leading to the corresponding amines with moderate enantioselectivity.[11] The promising reactivity of **E**-type compounds led us to extend our studies toward the isomeric compounds derived from the 1,1′-disubstituted ferrocene unit. The results of such investigations are reported herein.

RESULTS AND DISCUSSION

As the starting materials for this study, we employed (dimesitylphosphino)ferrocene (**1**) and 1-(dimesitylphosphino)-1′-vinylferrocene (**2**; Note: the synthesis and character-

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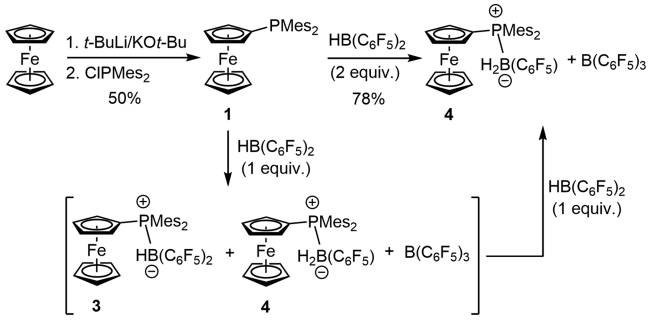
Organometallics XXXX, XXX, XXX–XXX

ization data of these two compounds are described in the Supporting Information). The former compound was prepared (Scheme 1) by lithiation of ferrocene with *tert*-butyl lithium in

Scheme 1. Synthesis of 1 and Its Reactions with $HB(C_6F_5)_2$



the presence of potassium *tert*-butoxide,[12] and subsequent reaction of the *in situ* generated lithioferrocene with chlorodimesitylphosphine. Following chromatographic purification, phosphine **1** was isolated as an orange solid and was characterized by the standard spectroscopic methods and by single-crystal X-ray diffraction analysis (Figure 1).

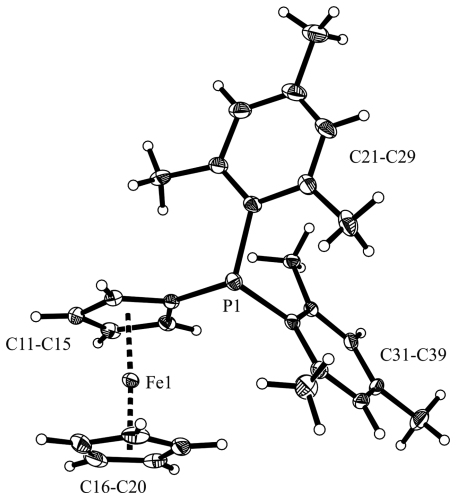


Figure 1. View of the molecular structure of compound **1** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): P1−C11, 1.817(5); P1−C21, 1.862(5); P1−C31, 1.844(5); $\Sigma P1^{CCC}$ = 314.9(2)°.

Piers reported that ferrocene reacts with $HB(C_6F_5)_2$ to give the bis(pentafluorophenyl)boryl ferrocene $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4B(C_6F_5)_2\}]$ with the releasing of dihydrogen.[13] Intrigued by this transformation, we performed the reaction of **1** with Piers' borane $HB(C_6F_5)_2$ to possibly obtain compounds $[Fe(\eta^5\text{-}C_5H_4PMes_2)\{\eta^5\text{-}C_5H_4B(C_6F_5)_2\}]$ (type **A**, Chart 1) or $[Fe(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_3(PMes_2)B(C_6F_5)_2\}]$ (type **B**, Chart 1). However, the reaction of **1** with 1 molar equiv of $HB(C_6F_5)_2$ in toluene-d_8 at room temperature led to a mixture containing the Lewis adduct $\mathbf{1}{\cdot}HB(C_6F_5)_2$ (**3**) but also $\mathbf{1}{\cdot}H_2B(C_6F_5)$ (**4**) and $B(C_6F_5)_3$ resulting from its redistribution reaction (Scheme 1). When the amount of $HB(C_6F_5)_2$ was increased to 2 equiv, the formation of **3** was suppressed, and compound **4**, the dominant ferrocene species in the reaction mixture, was isolated by crystallization as an orange solid in a 78% yield. The formation of adduct **4** was clearly manifested in the ^{31}P NMR spectrum through signal broadening and a shift to a lower field (compare δ_P −34.3 for **1** with +5.7 for **4**). The ^1H NMR signal of the equivalent BH_2 protons was observed as a broad singlet at δ_H 2.95, while the corresponding ^{11}B NMR resonance was found at δ_B −24.2. The formulation of **4** was independently corroborated by X-ray diffraction analysis (Figure 2).

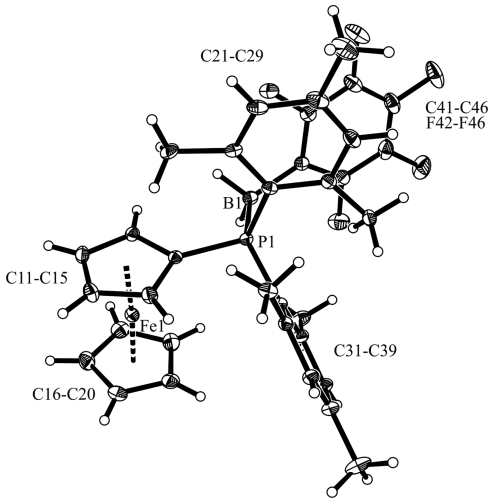


Figure 2. Molecular structure of compound **4** (thermal ellipsoids are shown with 15% probability). Selected bond lengths (Å) and angles (deg): P1−B1, 2.007(4); P1−C11, 1.798(3); P1−C21, 1.840(3); P1−C31, 1.846(3); C21−P1−B1, 102.5(2); C41−B1−P1, 115.1(2).

Since the reaction of **1** with $HB(C_6F_5)_2$ gave the unexpected P/B adduct **4**, we also investigated the interaction of **1** with $B(C_6F_5)_3$ (in situ). However, no similar reaction took place, indicating the formation of an intermolecular P/B FLP. Indeed, under 1.5 bar of H_2 atmosphere, the $\mathbf{1}/B(C_6F_5)_3$ system split dihydrogen to afford $[FcPHMes_2][HB(C_6F_5)_3]$ after 10 h, confirmed by NMR analysis (for details, see the Supporting Information).[14]

To avoid the formation of P/B adducts (such **3** and **4**), we introduced a vinyl substituent onto the ferrocene framework in position 1′ and employed it for the introduction of a $-B(C_6F_5)_2$ moiety through hydroboration. To this end, 1-(dimesitylphosphino)-1′-vinylferrocene (**2**) was synthesized by Wittig vinylation of 1-bromoferrocene-1′-carbaldehyde (**5**)[15] and lithiation/phosphinylation of the intermediate 1-bromo-1′-vinylferrocene (**6**). Gratifyingly, the reaction of **2** with $HB(C_6F_5)_2$ in pentane proceeded cleanly and rapidly to provide the anticipated hydroboration product **7**, which was isolated in a 90% yield (Scheme 2).

The NMR response of **7** suggested the presence of an intact $-PMes_2$ moiety (δ_P −34.8) and free terminal $-B(C_6F_5)_2$ unit (δ_B 72.9). The signals of the original vinyl moiety in **2** were replaced upon hydroboration by a pair of triplets at δ_H 2.15 and 2.39 and by signals at δ_C 32.9 and 24.5 in the ^1H and ^{13}C NMR spectra, respectively. The ^{19}F NMR spectrum showed three signals (*o*, *m*, *p*) with a relatively large $\Delta\delta^{19}F_{m,p}$ = 13.9 ppm chemical shift difference, as is typical of a trigonal planar boron coordination geometry in such a situation.

In addition to spectroscopic characterization, the structures of the starting material **2** and its hydroboration product **7** were determined by X-ray diffraction analysis (Figures 3 and 4). The structure of compound **7** confirms the presence of an open, non-interacting P/B FLP.[16] It contains the unchanged bulky

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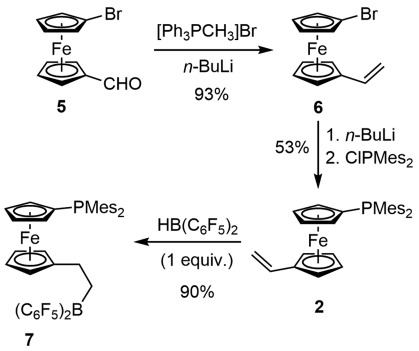
Scheme 2. Synthesis and Hydroboration of 2



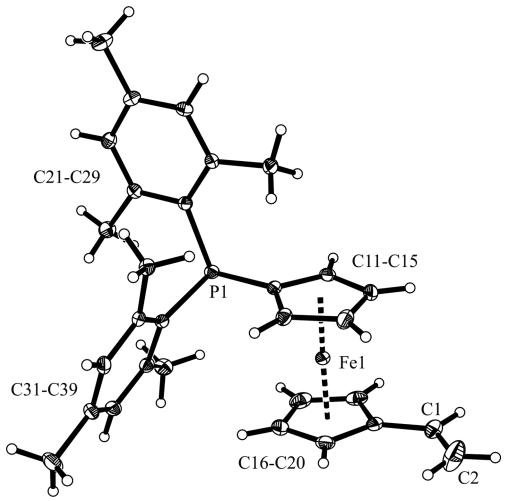


Figure 3. Molecular structure of compound **2** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): P1−C11, 1.818(2); P1−C21, 1.856(2); P1−C31, 1.853(2); C16−C1, 1.464(3); C1−C2, 1.301(3); C16−C1−C2, 125.6(2).

−$PMes_2$ unit at the C11−C15 cyclopentadienyl (Cp) ring of the central ferrocene unit. The substituents at the trigonal pyramidal phosphorus atom ($\Sigma P1^{CCC}$ = 314.4(1)°) are markedly rotated out of the parent Cp plane. The other Cp ring bears the $-CH_2CH_2B(C_6F_5)_2$ substituent formed by the hydroboration reaction. It shows a gauche conformation (θ C16−C1−C2−B1 = −62.5(4)°), which directs the borane away from the center of the ferrocene unit. The vectors of the pivotal C11−P1 and C16−C1 bonds at the eclipsed central metallocene moiety assume a gauche-like orientation (see Figure 4).

The P/B FLP **7** was next used for splitting dihydrogen.[1,17] For that purpose a solution of this compound in CD_2Cl_2 placed in a J. Young pressure NMR tube was exposed to H_2 (1.5 bar) at −5 °C (24 h). The formation of the $[P]H^+/[B]H^-$ splitting product **8** was nearly complete under these conditions (Scheme 3). We performed the reaction of **7** also with D_2 under analogous conditions and obtained the respective $[P]D^+/[B]D^-$ product **8-D_2** (see the Supporting Information for a comparison of the NMR spectra of compounds **8** and **8-D_2**).

The H_2 splitting product **8** is stable in solution at low temperature under the H_2 atmosphere but slowly loses dihydrogen at room temperature (see the Supporting Information for the NMR spectra obtained under various conditions that demonstrate reversible transformation of **7** into **8**).[18]

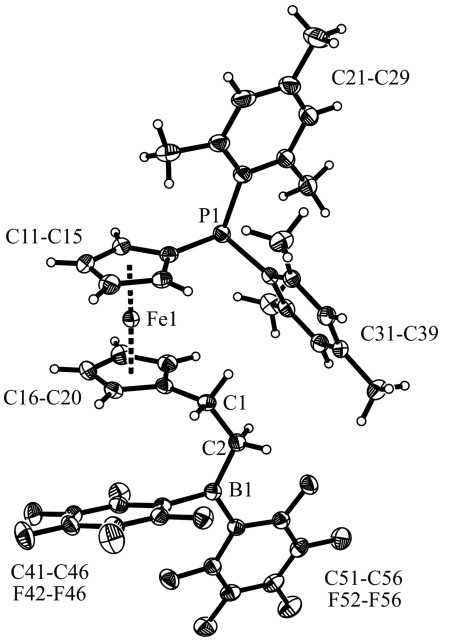
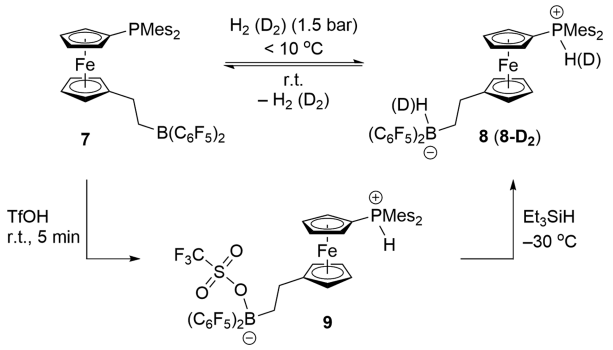


Figure 4. Projection of the molecular structure of compound **7** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C16−C1, 1.502(4); C1−C2, 1.542(4); C2−B1, 1.556(4); C11−P1, 1.815(3); C16−C1−C2, 112.8(3); C1−C2−B1, 119.2(3); $\Sigma P1^{CCC}$ = 314.4(1)°; $\Sigma B1^{CCC}$ = 359.9(3)°.

Scheme 3. Alternative Syntheses of the H_2 Splitting Product 8



Alternatively, the phosphonium/hydroborate **8** was prepared by introducing the proton at phosphorus and the hydride at boron in two separate steps. This method was used previously for the preparation of $[P]H^+/[B]H^-$ products that were sensitive to H_2 liberation.[19] In the present case, we first added 1 molar equiv of triflic acid to the in situ generated ferrocene P/B FLP **7** (see above). The addition reaction went to completion within a short period of time, and the product **9** could be precipitated at −30 °C. It was isolated as a yellow solid in 84% yield and fully characterized by elemental analysis and by NMR spectroscopy. Aside from the typical ferrocene signals and the resonances of the ethylene bridge, compound **9** showed the characteristic singlet of the triflate $-CF_3$ group at δ_F −79.2 and the *o*, *m*, *p* signals of the pair of $-C_6F_5$ substituents at the tetracoordinate boron [$\Delta\delta^{19}F_{m,p}$ = 5.0 ppm, ^{11}B: δ_B 6.3] in its ^{19}F NMR spectrum. The ^{31}P NMR resonance of compound **9** occurred at δ_P −13.7 (d, $^1J_{PH}$ = 495.0 Hz) with the corresponding ^1H NMR signal (PH) at δ_H 8.52.

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Organometallics XXXX, XXX, XXX−XXX

Subsequent triflate for hydride exchange was effected by treatment of **9** with excess (5-fold) of triethylsilane in dichloromethane at −30 °C. After several days of crystallization (pentane/CH_2Cl_2), orange yellow crystalline ferrocene phosphonium/hydroborate **8** was obtained. It was characterized by elemental analysis, by NMR spectroscopy, and also by X-ray diffraction. It showed a ^{11}B NMR resonance at δ_B −20.3 (d, $^1J_{BH}$ = 83.8 Hz) and a ^{31}P NMR feature at δ_P −13.6 (d, $^1J_{PH}$ = 492.0 Hz, with the associated ^1H NMR signal at δ_H 8.37). A single set of ^1H NMR signals due to the pair of mesityl groups at phosphorus and also the ^{19}F NMR signals of the enantiotopic $-C_6F_5$ substituents at boron [$\Delta\delta^{19}F_{m,p}$ = 2.3 ppm] was observed. The ethylene bridge connecting the boron Lewis acid with the ferrocene core gave rise to an AA′XX′ pattern at δ_H 1.92 and 0.93 (δ_C: 28.8 and 22.5).

The X-ray crystal structure analysis confirmed the presence of the $-P(H)^+Mes_2$ and $-CH_2CH_2B(H)^-(C_6F_5)_2$ substituents at the ferrocene core, mutually rotated into an anti position (derived from D_{5d} ferrocene conformation;[20] see Figure 5).

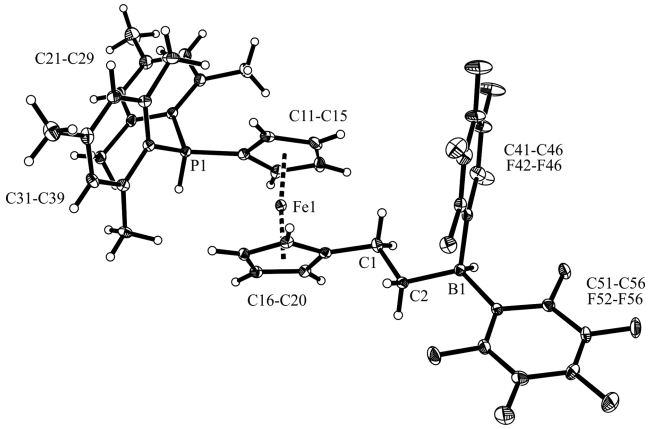
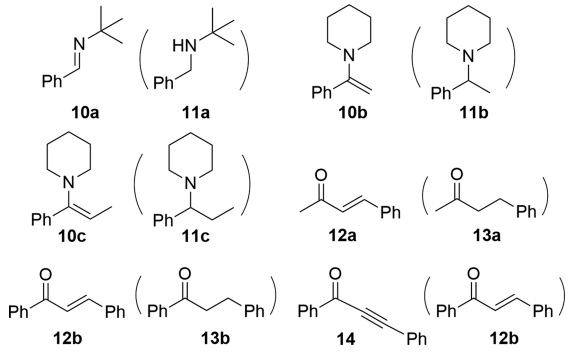


Figure 5. View of the molecular structure of the $[P]H^+/[B]H^-$ system **8** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (deg): C16−C1, 1.503(4); C1−C2, 1.535(4); C2−B1, 1.630(4); C11−P1, 1.766(3); C16−C1−C2, 115.1(2); C1−C2−B1, 109.8(2); $\Sigma P1^{CCC}$ = 339.9(1)°, $\Sigma B1^{CCC}$ = 333.7(2)°.

The $-CH_2CH_2-[B]$ moiety adopts an antiperiplanar arrangement with the bulky terminal $-B(C_6F_5)_2$ group diverted away from the ferrocene core (θ C16−C1−C2−B1 = −180.0(2)°). The B−H vector lies practically in the plane of the bonding Cp ring whereas the P−H bond in the $P(H)^+Mes_2$ moiety is directed inside the ferrocene unit.

The ferrocene-based P/B FLP was found to be an active hydrogenation catalyst, but it required relatively forcing reaction conditions. We carried out the catalytic hydrogenation reactions in benzene-d_6 solution at 50 °C (3 d) with a dihydrogen pressure of 50 bar using 10 mol % of **7** as a catalyst (see Table 1). The conversion was then determined by ^1H NMR spectroscopy. Under these conditions, we obtained quantitative hydrogenation of the C═N double bond of the bulky imine **10a** to tertiary amine **11a** (see Table 1) as well as of the enamine C═C double bonds of the piperidine-derived enamines **10b,c** (to afford the respective tertiary amines **11b,c**).[17,21] The P/B FLP catalyst **7** was also able to hydrogenate the electron-deficient C═C double bonds of the α,β-unsaturated ketones **12a,b** to give the respective saturated ketones **13a,b** under these conditions, albeit with markedly lower overall conversions. Even the conjugated ynone **14** could be hydrogenated into the respective conjugated eneone **12b** under these conditions,[22] but a rather low conversion was achieved in this case (see results in Table 1).

Table 1. Results of Catalytic Hydrogenation Mediated by 7 or 1/B(C$_6$F$_5$)$_3$



entry	substrate	product	conversion (%)
1[a]	**10a**	**11a**	>99
2[a]	**10b**	**11b**	>99
3[a]	**10c**	**10c**	>99
4[a]	**12a**	**13a**	38
5[a]	**12b**	**13b**	50
6[a]	**14**	**12b**	15
7[b]	**10a**	**11a**	>99
8[b]	**12b**	**13b**	>99 (84[c])

[a]Reagents and conditions: 0.3 mmol substrate, 10 mol % of catalyst **7**, C_6D_6 as solvent (1.5 mL), 50 bar of H_2, 50 °C, 3 d reaction time. Conversion was determined by ^1H NMR spectroscopy. [b]Reagents and conditions were the same except that 10 mol % of catalyst **1**/B(C$_6$F$_5$)$_3$ was used. [c]Isolated yield.

For a comparison, the catalytic hydrogenation tests were also performed with the intermolecular **1**/B(C$_6$F$_5$)$_3$ FLP system. Thus, quantitative hydrogenation of the C═N double bond in **10a** to give **11a** was achieved with this catalyst under the same reaction conditions (50 bar of H_2, 50 °C, 3 d). Remarkably, the **1**/B(C$_6$F$_5$)$_3$ FLP system was able to hydrogenate the C═C double bonds of **12b** to give **13b** in a quantitative conversion. As a representative sample, product **13b** was purified and isolated in a 84% yield by column chromatograph and fully characterized by NMR spectroscopy (for details, see the Supporting Information).

CONCLUSIONS

The bulky ferrocenyl-dimesitylphosphine **1** was shown to react with in a remarkable way with Pier's borane HB(C$_6$F$_5$)$_2$. It initially forms a Lewis adduct **1**·HB(C$_6$F$_5$)$_2$, which rapidly undergoes disproportionation to a mixture of **1**·H_2B(C$_6$F$_5$) (**4**) and B(C$_6$F$_5$)$_3$. Compound **4** becomes the dominant product when the amount of HB(C$_6$F$_5$)$_2$ is increased to 2 equiv. The role of the bulky phosphine moiety in this case consists in an efficient trapping of the H_2B(C$_6$F$_5$) component from the mixture by adduct formation, thereby shifting the equilibrium very effectively to the H_2B(C$_6$F$_5$) side. This procedure of generating the FcPMes$_2$/H_2B(C$_6$F$_5$) adduct may be viewed as a complement to Lancaster's $Me_2S/H_2B(C_6F_5)$ reagent.[23] We will see which of the characteristic $H_2B(C_6F_5)$ reactions[24] can be performed using the new ferrocene-derived reagent **4**.

The reaction between 1-(dimesitylphosphino)-1′-vinylferrocene (**2**) and HB(C$_6$F$_5$)$_2$ takes a different course, as expected. A clean hydroboration of the vinyl group conjugated

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with the ferrocene core is observed as long as the reaction is performed strictly under a 1:1 stoichiometry. The resulting phosphine−borane product **7** can be isolated in pure form and its spectroscopic data as well as the result of X-ray crystal structure analysis indicate the presence of a non-interacting P/B frustrated Lewis pair. Not unexpectedly, the ferrocene-derived P/B FLP **7** is a dihydrogen activator, although the dihydrogen cleavage reaction shows reversibility. Nevertheless, the **7**/H_2 system can be used as a FLP catalyst for the hydrogenation of a variety of organic π-systems, including a bulky imine and a couple of bulky enamines. Remarkably, the **7**/H_2 system can also serve as a catalyst for the selective hydrogenation of carbon−carbon multiple bonds in a small series of conjugated enones and ynones, although these reaction were markedly slower than the above-mentioned imine or enamine reductions and resulted in only partial conversions under our typical reaction conditions. The ferrocene-based FLP **7**/H_2 catalyst system thus seems to be suited to tackle both electron-rich as well as electron-poor organic C═N, C═C, and C≡C π-systems under suitable conditions as a functional main-group element hydrogenation catalyst.

A comparison of the new ferrocene-based P/B FLP system **7** with our previously reported 1,2-P/B disubstituted FLP system **E** (Chart 1)[10a] revealed the influence of the organometallic scaffold on the properties of these isomeric compounds. Whereas compound **7** possesses an open, nonbridged FLP structure in both the solid state and in solution, its planar-chiral isomer **E** shows an equilibrium of open and closed forms at variable temperature, with the open form, however, strongly favored at ambient temperature. We found that both the systems **7** and **E** are active dihydrogen splitting reagents and both can serve as hydrogenation catalysts, although the 1,2-isomer **E** is more active. Compound **7** needs significantly forcing conditions for the catalytic hydrogenations (50 bar, 50 °C, 3 d) to proceed satisfactorily, as compared to the previously reported system **E** (1.5 bar, r.t., 1 d).

EXPERIMENTAL SECTION

For general information, preparative details (including the synthesis of substrates **1** and **2**), and complete spectroscopic and structural data of all new compounds, see the Supporting Information.

Preparation of Compound 4. Compound **1** (91 mg, 0.2 mmol) and $HB(C_6F_6)_2$ (140 mg, 0.4 mmol) were mixed in toluene (3 mL) and the mixture was stirred for 12 h. Pentane (3 mL) was layered onto the resulting solution and the mixture was stored at −35 °C to provide orange crystals and white floe. The obtained mixture was recrystallized twice with toluene and pentane at −35 °C to yield pure adduct **4**. Yield: 99 mg, 78%.

^{1}H NMR (500 MHz, 223 K, CD_2Cl_2, 5.32 ppm): δ = 7.01 (s, 1H, *m*-Mes), 6.81 (s, 1H, *m*-Mes), 6.57 (s, 1H, *m*-Mes′), 6.55 (s, 1H, *m*-Mes′), 5.28 (s, 1H, Cp-H$^{\beta}$), 4.57 (s, 1H, Cp-H$^{\gamma}$), 4.49 (s, 1H, Cp-H$^{\gamma}$), 4.09 (s, 5H, C_5H_5), 4.03 (s, 1H, Cp-H$^{\beta}$), 3.03 (s, 3H, *o*-CH_3^{Mes}), 2.95 (very br s, 2H, BH_2), 2.27 (s, 3H, *p*-CH_3^{Mes}), 2.13 (s, 3H, *p*-$CH_3^{Mes′}$), 1.68 (s, 3H, *o*-CH_3^{Mes}), 1.58 (s, 3H, *o*-$CH_3^{Mes′}$), 1.48 (s, 3H, *o*-$CH_3^{Mes′}$). **^{13}C{^{1}H} NMR** (126 MHz, 223 K, CD_2Cl_2, 53.8 ppm): δ = 142.6 (d, $^2J_{PC}$ = 16.7 Hz, *o*-Mes), 141.4 (*o*-Mes), 140.5 (*p*-Mes), 140.1 (d, $^2J_{PC}$ = 13.4 Hz, *o*-Mes′), 139.5 (d, $^2J_{PC}$ = 4.1 Hz, *o*-Mes′), 139.2 (*p*-Mes′), 131.0 (d, $^3J_{PC}$ = 7.0 Hz, *m*-Mes), 130.4 (d, $^3J_{PC}$ = 10.2 Hz, *m*-Mes), 130.3 (d, $^3J_{PC}$ = 7.6 Hz, *m*-Mes′), 129.9 (d, $^3J_{PC}$ = 9.0 Hz, *m*-Mes′), 125.8 (d, $^1J_{PC}$ = 56.2 Hz, *i*-Mes), 125.6 (d, $^1J_{PC}$ = 51.1 Hz, *i*-Mes′), 76.8 (d, $^2J_{PC}$ = 14.2 Hz, Cp$^{\beta}$), 73.7 (d, $^2J_{PC}$ = 2.2 Hz, Cp$^{\beta}$), 72.4 (d, $^1J_{PC}$ = 65.3 Hz, *i*-Cp$^{\alpha}$), 72.0 (d, $^3J_{PC}$ = 7.1 Hz, Cp$^{\gamma}$), 71.9 (d, $^3J_{PC}$ = 8.0 Hz, Cp$^{\gamma}$), 69.9 (C_5H_5), 24.7 (*o*-CH_3^{Mes}), 24.4 (d, $^3J_{PC}$ = 4.5 Hz, *o*-CH_3^{Mes}), 24.0 (*o*-$CH_3^{Mes′}$), 22.9 (d, $^3J_{PC}$ = 7.2 Hz, *o*-$CH_3^{Mes′}$), 20.7 (*p*-CH_3^{Mes}), 20.4 (*p*-$CH_3^{Mes′}$). **^{11}B NMR** (160 MHz, 299 K, CD_2Cl_2): δ = −24.2 ($\nu_{1/2}$ ∼ 300 Hz). **^{11}B{^{1}H} NMR** (160 MHz, 299 K, CD_2Cl_2): δ = −24.2 ($\nu_{1/2}$ ∼ 200 Hz). **^{19}F NMR** (470 MHz, 299 K, CD_2Cl_2): δ = −127.2 (m, 2F, *o*-C_6F_6), −160.8 (m, 1F, *p*-C_6F_5), −166.4 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 5.6]. **^{31}P{^{1}H} NMR** (202 MHz, 299 K, CD_2Cl_2): δ = 5.7 ($\nu_{1/2}$ ∼ 120 Hz). Anal. Calc. for $C_{34}H_{33}FePBF_5$: C, 64.39; H, 5.24. Found: C, 64.73; H, 4.92. Mp 173 °C.

Preparation of Compound 7. Compound **2** (96 mg, 0.2 mmol) and $HB(C_6F_6)_2$ (69 mg, 0.2 mmol) were mixed in pentane (3 mL) and the resulting solution was stirred for 30 min. The reaction mixture was filtered and the solvent was removed in vacuo to afford compound **7** as an orange-red solid. Yield: 148 mg, 90%.

^{1}H NMR (600 MHz, 299 K, Benzene-d_6, 7.15 ppm): δ = 6.71 (d, $^4J_{PH}$ = 2.2 Hz, 4H, *m*-Mes), 4.30 (br s, 2H, Cp-H$^{\beta}$), 4.17 (br s, 2H, Cp-H$^{\gamma}$), 3.98 (br s, 2H, Cp-H$^{\beta′}$), 3.91 (br s, 2H, Cp-H$^{\gamma′}$), 2.41 (s, 12H, *o*-CH_3^{Mes}), 2.39 (t, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2), 2.15 (t, $^3J_{HH}$ = 8.0 Hz, 2H, BCH_2), 2.07 (s, 6H, *p*-CH_3^{Mes}). **^{13}C{^{1}H} NMR** (151 MHz, 299 K, Benzene-d_6, 128.0 ppm): δ = 147.0 (dm, $^1J_{FC}$ ∼ 244 Hz, C_6F_5), 143.4 (dm, $^1J_{FC}$ ∼ 262 Hz, C_6F_5), 142.5 (d, $^2J_{PC}$ = 15.0 Hz, *o*-Mes), 137.7 (*p*-Mes), 137.5 (dm, $^1J_{FC}$ ∼ 255 Hz, C_6F_5), 132.7 (d, $^1J_{PC}$ = 20.5 Hz, *i*-Mes), 130.5 (d, $^3J_{PC}$ = 3.0 Hz, *m*-Mes), 114.3 (br m, *i*-C_6F_5), 90.8 (*i*-Cp$^{\alpha′}$), 79.8 (d, $^1J_{PC}$ = 11.8 Hz, *i*-Cp$^{\alpha}$), 75.7 (d, $^2J_{PC}$ = 17.7 Hz, Cp$^{\beta}$), 71.5 (d, $^3J_{PC}$ = 4.0 Hz, Cp$^{\gamma}$), 69.2 (Cp$^{\beta′}$), 69.0 (Cp$^{\gamma′}$), 32.9 (br, BCH_2), 24.5 (CH_2), 23.5 (d, $^3J_{PC}$ = 15.2 Hz, *o*-CH_3^{Mes}), 20.8 (*p*-CH_3^{Mes}). **^{11}B{^{1}H} NMR** (192 MHz, 299 K, Benzene-d_6): δ = 72.9 ($\nu_{1/2}$ ∼ 1500 Hz). **^{19}F NMR** (564 MHz, 299 K, Benzene-d_6): δ = −130.3 (m, 2F, *o*-C_6F_6), −147.0 (t, $^3J_{FF}$ = 20.9 Hz, 1F, *p*-C_6F_5), −160.9 (m, 2F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 13.9]. **^{31}P{^{1}H} NMR** (243 MHz, 299 K, Benzene-d_6): δ = −34.8 ($\nu_{1/2}$ ∼ 2 Hz). Anal. Calc. for $C_{42}H_{34}FePBF_{10}$: C, 61.05; H, 4.15. Found: C, 61.14; H, 4.26. Mp 109 °C.

Preparation of Compound 8. (1) Preparation of **9**: A freshly prepared solution of compound **7** in pentane (2 mL), synthesized from **2** (100 mg, 0.21 mmol) and $HB(C_6F_5)_2$ (73 mg, 0.21 mmol; see the procedure above), was added to a solution of triflic acid (30.5 mg, 0.20 mmol) in pentane (1 mL). Immediately, a viscous liquid phase was formed. After stirring for 5 min at room temperature, the reaction mixture was cooled down to −30 °C. Then, the viscous mass was washed with pentane for several times (each 2 mL) until a yellow powder was obtained. Yield of **9**: 169 mg, 84%.

^{1}H NMR (600 MHz, 299 K, CD_2Cl_2, 5.32 ppm): δ = 8.52 (d, $^1J_{PH}$ = 495.0 Hz, 1H, PH), 7.07 (d, $^4J_{PH}$ = 3.6 Hz, 4H, *m*-Mes), 4.92 (s, 2H, Cp-H$^{\gamma}$), 4.58 (s, 2H, Cp-H$^{\beta}$), 4.27 (s, 2H, Cp-H$^{\beta′}$), 4.07 (s, 2H, Cp-H$^{\gamma′}$), 2.35 (s, 6H, *p*-CH_3^{Mes}), 2.34 (s, 12H, *o*-CH_3^{Mes}), 2.12 (m, 2H, CH_2), 1.54 (m, 2H, BCH_2). **^{13}C{^{1}H} NMR** (151 MHz, 299 K, CD_2Cl_2, 53.8 ppm): δ = 148.1 (dm, $^1J_{FC}$ ∼ 240 Hz, C_6F_5), 146.2 (d, $^4J_{PC}$ = 2.3 Hz, *p*-Mes), 143.3 (d, $^2J_{PC}$ = 10.6 Hz, *o*-Mes), 139.3 (dm, $^1J_{FC}$ ∼ 240 Hz, C_6F_5), 137.1 (dm, $^1J_{FC}$ ∼ 250 Hz, C_6F_5), 132.3 (d, $^3J_{PC}$ = 11.3 Hz, *m*-Mes), 121.9 (br m, *i*-C_6F_5), 119.2 (q, $^1J_{FC}$ = 316.0 Hz, CF_3), 113.1 (d, $^1J_{PC}$ = 86.1 Hz, *i*-Mes), 98.9 (*i*-Cp$^{\alpha′}$), 76.2 (d, $^3J_{PC}$ = 11.3 Hz, Cp$^{\gamma}$), 74.4 (d, $^2J_{PC}$ = 15.0 Hz, Cp$^{\beta}$), 71.0 (Cp$^{\beta′}$), 69.4 (Cp$^{\gamma′}$), 59.2 (d, $^1J_{PC}$ = 99.0 Hz, *i*-Cp$^{\alpha}$), 24.6 (br s, BCH_2), 24.5 (CH_2), 22.2 (d, $^3J_{PC}$ = 8.2 Hz, *o*-CH_3^{Mes}), 21.4 (d, $^5J_{PC}$ = 1.1 Hz, *p*-CH_3^{Mes}). **^{11}B{^{1}H} NMR** (192 MHz, 299 K, CD_2Cl_2): δ = 6.3 ($\nu_{1/2}$ ∼ 650 Hz). **^{19}F NMR** (564 MHz, 299 K, CD_2Cl_2): δ = −79.2 (s, 3F, CF_3), −134.5 (m, 4F, *o*-C_6F_6), −161.3 (t, $^3J_{FF}$ = 20.3 Hz, 2F, *p*-C_6F_5), −166.3 (m, 4F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 5.0]. **^{31}P{^{1}H} NMR** (243 MHz, 299 K, CD_2Cl_2): δ = −13.7 ($\nu_{1/2}$ ∼ 11 Hz). **^{31}P NMR** (243 MHz, 299 K, CD_2Cl_2): δ = −13.7 (d, $^1J_{PH}$ = 495.0 Hz). Anal. Calc. for $C_{43}H_{35}FeO_3PSBF_{13}$: C, 52.89; H, 3.61. Found: C, 52.20; H, 3.49. Mp 204 °C.

(2) Preparation of **8**: (route a) Neat Et_3SiH (60 mg, 5 equiv) was added to a cooled CH_2Cl_2 (0.3 mL) solution of compound **9** (97.6 mg, 0.1 mmol) at −30 °C in a small sized vial (2 mL). This vial was placed into a precooled (−30 °C) bigger vial (10 mL). Then, 2 mL of precooled (−30 °C) pentane was then added to the bigger vial to initiate crystallization. After several days, orange-red crystals were grown from the CH_2Cl_2/pentane system, which were suitable for X-ray diffraction analysis. The mixture was filtered to afford the orange-

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Organometallics XXXX, XXX, XXX−XXX

yellow solids, which were washed twice by cold pentane. Yield: 51 mg, 62%.

(route b) Compound 7 (17.0 mg, 0.02 mmol) was dissolved in CD_2Cl_2 (0.6 mL) and then transferred to a J. Young valve NMR tube. The solution was degassed with freeze−pump−thaw cycles and then exposed to dihydrogen atmosphere (1.5 bar). After storing the NMR tube for 24 h at −5 °C, the reaction mixture was characterized by NMR spectroscopy.

^{1}H NMR (600 MHz, 253 K, CD_2Cl_2, 5.32 ppm): δ = 8.37 (d, $^1J_{PH}$ = 492.0 Hz, 1H, PH), 7.01 (d, $^4J_{PH}$ = 4.3 Hz, 4H, *m*-Mes), 4.80 (br s, 2H, Cp-H$^{\gamma}$), 4.43 (s, 2H, Cp-H$^{\beta}$), 4.17 (s, 2H, Cp-H$^{\beta'}$), 4.07 (s, 2H, Cp-H$^{\gamma'}$), 2.52 (br s, 1H, BH), 2.29 (s, 6H, *p*-CH_3^{Mes}), 2.27 (br s, 12H, *o*-CH_3^{Mes}), 1.92 (m, 2H, CH_2), 0.93 (m, 2H, BCH_2). **^{13}C{^{1}H} NMR** (151 MHz, 253 K, CD_2Cl_2, 53.8 ppm): δ = 147.9 (dm, $^1J_{FC}$ ∼ 234 Hz, C_6F_5), 145.8 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Mes), 142.7 (d, $^2J_{PC}$ = 9.7 Hz, *o*-Mes), 137.2 (dm, $^1J_{FC}$ ∼ 242 Hz, C_6F_5), 136.2 (dm, $^1J_{FC}$ ∼ 246 Hz, C_6F_5), 131.9 (d, $^3J_{PC}$ = 11.1 Hz, *m*-Mes), 127.9 (br s, *i*-C_6F_5), 112.3 (d, $^1J_{PC}$ = 86.3 Hz, *i*-Mes), 99.7 (*i*-Cp$^{\alpha'}$), 76.1 (d, $^3J_{PC}$ = 11.1 Hz, Cp$^{\gamma}$), 73.7 (d, $^2J_{PC}$ = 15.0 Hz, Cp$^{\beta}$), 70.6 (Cp$^{\beta'}$), 69.3 (Cp$^{\gamma'}$), 57.9 (d, $^1J_{PC}$ = 98.1 Hz, *i*-Cp$^{\alpha}$), 28.8 (br s, CH_2), 22.5 (br s, BCH_2), 21.9 (d, $^3J_{PC}$ = 8.2 Hz, *o*-CH_3^{Mes}), 21.1 (d, $^5J_{PC}$ = 1.0 Hz, *p*-CH_3^{Mes}). **^{11}B{^{1}H} NMR** (192 MHz, 283 K, CD_2Cl_2): δ = −20.3 ($\nu_{1/2}$ ∼ 85 Hz). **^{11}B NMR** (192 MHz, 283 K, CD_2Cl_2): δ = −20.3 (d, $^1J_{BH}$ = 83.8 Hz). **^{19}F NMR** (564 MHz, 253 K, CD_2Cl_2): δ = −133.4 (m, 4F, *o*-C_6F_6), −164.6 (m, 2F, *p*-C_6F_5), −166.9 (m, 4F, *m*-C_6F_5). [$\Delta\delta^{19}F_{m,p}$ = 2.3]. **^{31}P{^{1}H} NMR** (243 MHz, 253 K, CD_2Cl_2): δ = −13.6 ($\nu_{1/2}$ ∼ 3 Hz). **^{31}P NMR** (243 MHz, 253 K, CD_2Cl_2): δ = −13.6 (d, $^1J_{PH}$ = 492.0 Hz). Anal. Calc. for $C_{42}H_{36}FePBF_{10}$: C, 60.90; H, 4.38. Found: C, 60.76; H, 4.26.

Typical Catalytic Hydrogenation Procedure. In a glovebox with an argon atmosphere, compound 7 (25 mg, 0.03 mmol) and *N*-benzylidene-*tert*-butylamine (48.3 mg, 0.3 mmol) were dissolved in C_6D_6 (1.5 mL) and the solution was transferred to an autoclave. The reaction mixture was stirred at 50 °C for 3 days under 50 bar of H_2 atmosphere. The conversion was estimated by ^{1}H NMR spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00363.

Details of the preparation and characterization of the new compounds (PDF)

Accession Codes

CCDC 1549039−1549043 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Organometallics XXXX, XXX, XXX−XXX