Supplementary Data for:

Activation of H_2 by Frustrated Lewis Pairs Derived from *Mono- and Bis*-Phosphinoferrocenes and $B(C_6F_5)_3$

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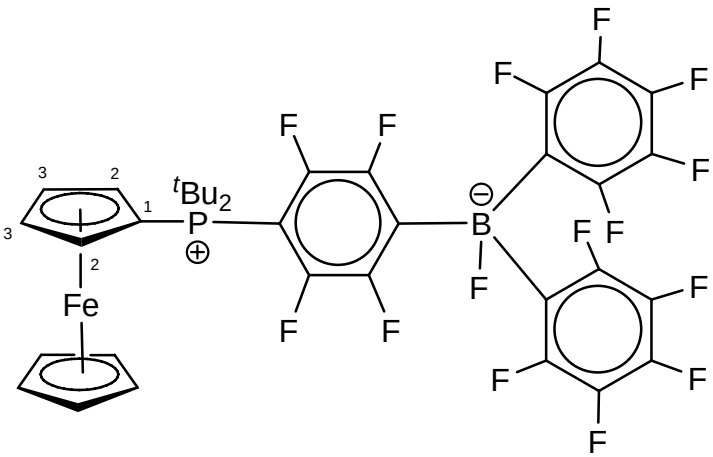
Experimental Section

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an Innovative Technologies or Vacuum Atmospheres inert atmosphere glove box. Solvents were purified employing a Grubbs' type column systems manufactured by Innovative Technology. ^1H, ^{13}C, ^{31}P, ^{11}B and ^{19}F NMR spectroscopy spectra were recorded on Varian 200, 300 and 400 MHz spectrometers. ^1H and ^{13}C NMR spectra are referenced to $SiMe_4$ using the residual solvent peak impurity of the given solvent. ^{31}P, ^{11}B and ^{19}F NMR spectra were referenced to 85% H_3PO_4, $Et_2O{\cdot}BF_3$, and $CFCl_3$ respectively. Chemical shifts are reported in ppm and coupling constants in Hz. CD_2Cl_2 and BrC_6D_5 were used as the NMR solvents after being dried over CaH_2, vacuum-transferred into Young bombs and freeze-pump-thaw degassed (three cycles)**.** Combustion analyses were performed in house employing a Perkin Elmer 2400 Series II CHNS Analyzer.

Cyclic voltammetry experiments were performed in a BASi RDE-2 cell stand for rotating disk electrochemical experiments, using a glassy carbon working electrode with a disk diameter of 3.0 mm, an aqueous Ag/AgCl reference electrode and a Pt and a Pt wire auxiliary electrode. The working electrode was polished with alumina (0.05 μm) and rinsed with deionised water prior to use. $[NBu_4][PF_6]$ or $[NBu_4][B(C_6F_5)_4]$[1] were used as the supporting electrolytes (0.1 M solutions). All the potentials were referenced versus ferrocene. All electrochemical data were acquired with a computer controlled BASi Epsilon EC potentiostat, using the Epsilon EC software.

Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4P{}^t\!Bu_2(C_6F_4)BF(C_6F_5)_2)]$ (1). A solution of $B(C_6F_5)_3$ (120 mg, 0.234 mmol) in 5 mL of CH_2Cl_2 was added to a solution of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4P{}^t\!Bu_2]$[2] (74 mg, 0.224 mmol) in 5 mL of CH_2Cl_2 at -35 ºC. After 3 h, the reaction went to completion and the solvent was evaporated under vacuum. The oily orange residue was washed with toluene (2 mL) and pentane (2 x 5 mL) and dried again under vacuum for a few hours to afford compound **1a** as an orange solid (173 m, 92%). Anal. Calcd. For $C_{36}H_{27}BF_{15}FeP$: C, 51.34; H, 3.23. Found: C, 51.02; H, 3.21 %.



$^{31}P\{^1H\}$ NMR (CD_2Cl_2): 64.3 (tt, J_{PF} = 5, 14). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): -0.5 (d, J_{BF} = 54). ^1H NMR (CD_2Cl_2): 4.90 (m, C_5H_4, 2H), 4.66 (br, C_5H_4, 2H), 4.45 (m, C_5H_5, 5H), 1.43 (d, J_{PH} = 17, *t*Bu, 18H). ^{19}F NMR (CD_2Cl_2): -117.8 (br, $C_6\mathit{F}_4$, 2F), -130.1 (br, $C_6\mathit{F}_4$, 2F), -135.8 (m, *o*-C_6F_5, 4F), -162.0 (t, J_{FF} = 21, *p*-C_6F_5, 2F), -166.8 (m, *m*-C_6F_5, 4F), -193.3 (d, br, J_{BF} = 55, B-*F*, 1F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, partial data): 150.1 (dm, J_{CF} = 230, C_6F_4), 148.7 (dm, J_{CF} = 240, *o*-C_6F_5), 147.0 (dm, J_{CF} = 245, C_6F_4), 139.6 (dm, J_{CF} = 240, *m*-C_6F_5), 137.3 (dm, J_{CF} = 255, *p*-C_6F_5), 76.1 (d, J_{PC} = 11, $C^{2/3}$-C_5H_4), 73.0 (d, J_{PC} = 10, $C^{3/2}$-C_5H_4), 72.6 (t, J_{FC} = 2, Cp), 64.3 (dt, J_{PC} = 82, J_{FC} = 4, C^1-C_5H_4), 40.8 (d, J_{PC} = 34, CH_3-*t*Bu), 29.1 (d, J_{PC} = 1, C-*t*Bu).

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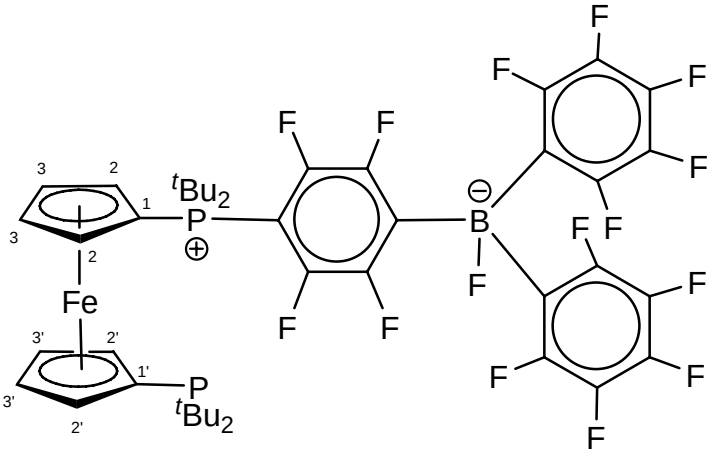
[1] R. J. LeSuer and William E. Geiger, Angew. Chem. Int. Ed., 2000, 39, 248.

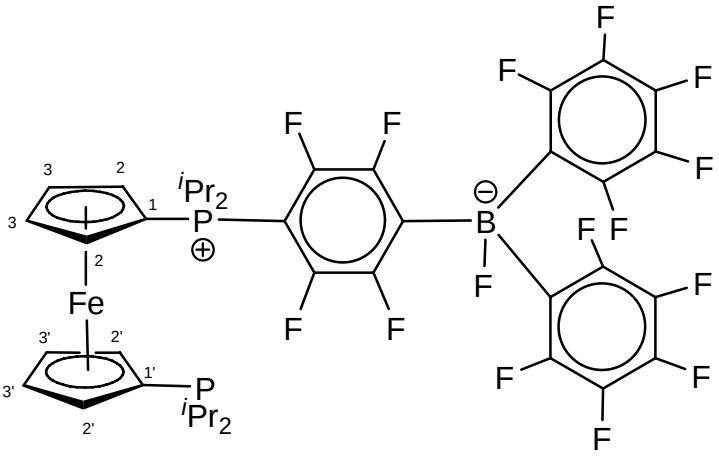
[2] K.-I. Fujita, M. Yamashita, F. Puschmann, M. Martínez Alvarez-Falcon, C. D.Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* 2006, **128**, 9044.

Synthesis of [(η^5-C_5H_4P*t*Bu_2)Fe(η^5-C_5H_4P*t*$Bu_2(C_6F_4)BF(C_6F_5)_2$)] (2). A solution of $B(C_6F_5)_3$ (256 mg, 0.500 mmol) in 5 mL of CH_2Cl_2 was added to a solution of 1,1'-Bis(di-*t*-butylphosphino)ferrocene (236 mg, 0.497 mmol) in 5 mL of CH_2Cl_2 at -35 ºC in the glovebox. After 3 h, the reaction went to completion and the solution was concentrated (1 mL) under vacuum. Then, 12 mL of pentane were added to precipitate the product, solvent mixture was decanted and the remaining oily orange solid was washed with more pentane (6 mL). After a few hours under vacuum compound **3** was afforded as an orange solid (470 mg, 96%).



Anal. Calcd. For $C_{44}H_{44}BF_{15}FeP_2$: C, 53.58; H, 4.50. Found: C, 53,43; H, 4,48 %.$^{31}P\{^1H\}$ NMR (CD_2Cl_2): 64.4 (tt, J_{PF} = 5, 14), 26.3 (s). ^1H NMR (CD_2Cl_2): 4.92, 4.69, 4.59, 4.51 (4 x m, 4 x br, C_5H_4, 4 x 2H), 1.46 (d, J_{PH} = 17, *t*Bu, 18H), 1.22 (d, J_{PH} = 11, *t*Bu, 18H). ^{19}F NMR (CD_2Cl_2): -118.0 (br, C_6F_4, 2F), -129.9 (br, C_6F_4, 2F), -135.9 (m, *o*-C_6F_5, 4F), -162.0 (t, J_{FF} = 21, *p*-C_6F_5, 2F), -166.9 (m, *m*-C_6F_5, 4F), -193.3 (br, B-*F*, 1F). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): -0.6 (d, J_{BF} = 54). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 150.2 (dm, J_{CF} = 250, C_6F_4), 148.7 (dm, J_{CF} = 240, *o*-C_6F_5), 147.0 (dm, J_{CF} = 250, C_6F_4), 139.6 (dm, J_{CF} = 250, *m*-C_6F_5), 137.2 (dm, J_{CF} = 240, *p*-C_6F_5), 84.0 (d, J_{PC} = 35, $C^{1'}$-C_5H_4), 77.4 (d, J_{PC} = 10, $C^{2/3}$-C_5H_4), 75.9 (d, J_{PC} = 10, $C^{2'/3'}$-C_5H_4), 75.3 (d, J_{PC} = 10, $C^{3/2}$-C_5H_4), 74.4 (s, $C^{3'/2'}$-C_5H_4), 64.3 (d, J_{PC} = 82, C^1-C_5H_4), 40.9 (d, J_{PC} = 34, C-*t*Bu), 33.5 (d, J_{PC} = 22, C-*t*Bu), 31.1 (d, J_{PC} = 13, CH_3-*t*Bu) 29.2 (s, CH_3-*t*Bu).

Synthesis of [(η^5-C_5H_4P*i*Pr_2)Fe(η^5-C_5H_4P*i*$Pr_2(C_6F_4)BF(C_6F_5)_2$)] (3). A solution of $B(C_6F_5)_3$ (90 mg, 0.175 mmol) in 3 mL of CH_2Cl_2 was added to a solution of 1,1'-Bis(di-*i*-propylphosphino)ferrocene (71 mg, 0.170 mmol) in 3 mL of CH_2Cl_2 at -35 ºC in the glovebox. After 2 h the reaction went to completion and the solution was concentrated (1 mL) under vacuum. Then, 10 mL of pentane were added to precipitate the product, solvent mixture was decanted and the remaining oily orange solid was washed with more pentane (6 mL). After a few hours under vacuum compound **3** was afforded as an orange solid (143 mg, 91 %).



Anal. Calcd. For $C_{40}H_{36}BF_{15}FeP_2$: C, 51.64; H, 3.90. Found: C, 51.41; H, 3.87 %. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 47.7 (tt, J_{PF} = 5, 11), 0.1 (s). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): -0.5 (d, J_{BF} = 53). ^1H NMR (CD_2Cl_2, 399.74 MHz): δ 4.84, 4.48, 4.43, 4.37 (4 x m, C_5H_4, 4 x 2H), 3.30, 1.91 (2 x m, CH-*i*Pr, 2 x 2H), 1.47, 1.06 (2 x m, CH_3-*i*Pr, 2 x 12H). ^{19}F NMR (CD_2Cl_2): -129.2, -129.5 (2 x m, C_6F_4, 2 x 2F), -135.8 (m, *o*-C_6F_5, 4F), -162.0 (t, J_{FF} = 19, *p*-C_6F_5, 2F), -166.9 (m, *m*-C_6F_5, 4F), -193.0 (br, B-*F*, 1F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 150.0 (dm, J_{CF} ~ 240, C_6F_4), 148.5 (dm, J_{CF} ~ 240, *o*-C_6F_5), 146.8 (dm, J_{CF} ~ 260, C_6F_4), 139.6 (dm, J_{CF} ~ 240, *p*-C_6F_5), 137.2 (dm, J_{CF} ~ 240, *m*-C_6F_5), 123.2 (br, *i*-C_6F_4), 93.5 (dm, $^1J_{CP}$ = 77, *p*-C_6F_4), 82.0 (d, J_{PC} = 25, $C^{1'}$-C_5H_4), 76.4 (d, br, J_{PC} = 10, $C^{2/3}$-C_5H_4), 74.7 (d, br, J_{PC} = 12, $C^{3/2}$-C_5H_4), 74.2 (d, J_{PC} = 9, $C^{2/3}$-C_5H_4), 72.9 (s, $C^{3/2}$-C_5H_4), 60.0 (d, J_{PC} = 83, C^1-C_5H_4), 27.0 (d, J_{PC} = 45, CH-*i*Pr), 23.9 (d, J_{PC} = 12, CH-*i*Pr), 20.3 (d, J_{PC} = 16, CH_3-*i*Pr), 20.0 (d, J_{PC} = 16, CH-*i*Pr), 18.2, 17.6 (2 x s, 2 x CH_3-*i*Pr).

Synthesis of [Fe(η^5-C_5H_4P*i*$Pr_2(C_6F_4)BH(C_6F_5)_2)_2$] (4). A solution of $B(C_6F_5)_3$ (275 mg, 0.537 mmol) in 4 mL of CH_2Cl_2 was added to a solution of 1,1'-Bis(di-*i*-propylphosphino)ferrocene (106 mg, 0.253 mmol) in 4 mL of CH_2Cl_2 at -35 ºC and left to reach room temperature progressively. Reaction was completed after 48 h stirring at room temperature. Then, hexane was added (10 mL) to precipitate the product. The supernatant was decanted and the orange precipitate thus obtained was washed with more hexane (2 x 5 mL) and dried under vacuum to afford **4** as an orange microcrystalline solid (350 mg, 96%). Anal. Calcd. for $C_{58}H_{36}B_2F_{30}FeP_2$: C, 48.30; H, 2.52. Found: C, 47.95; H, 2.43 %. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 47.0 (tt, J_{PF} = 5, 11). $^{11}B\{^1H\}$ NMR (CD_2Cl_2) -0.3 (br, 1B). ^1H NMR (CD_2Cl_2): 4.88, 4.58 (2 x m, 2 x C_5H_4, 2 x 4H), 3.25 (m, CH-*i*Pr, 4H), 1.43 (m, CH_3-*i*Pr, 24H). ^{19}F NMR (CD_2Cl_2): -127.7 (br, C_6F_4, 2F), -128.9 (m, C_6F_4, 2F), -136.0 (m, *o*-C_6F_5, 4F), -161.5 (t, J_{FF} = 19, *p*-C_6F_5, 2F), -166.6 (m, *m*-C_6F_5, 4F), -193.1 (br, B-F, 1F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, partial): 150.3 (dm, J_{CF} ~ 250, C_6F_4), 148.5 (dm, J_{CF} ~ 225, *o*-C_6F_5), 146.7 (dm, J_{CF} ~ 235, C_6F_4), 139.4 (dm, J_{CF} ~ 280, *p*-C_6F_5), 137.3 (dm, J_{CF} ~ 245, *m*-C_6F_5), 76.8 (d, J_{PC} = 10, $C^{2/3}$- C_5H_4), 75.5 (d, J_{PC} = 10, $C^{3/2}$-C_5H_4), 65.1 (d, J_{PC} = 89, C^1-C_5H_4), 27.0 (d, J_{PC} = 44, CH-*i*Pr), 18.0, 17.6 (2 x s, 2 x CH_3-*i*Pr) ppm.

Synthesis of [(η^5-C_5H_4P*t*Bu_2)Fe(η^5-C_5H_4P*t*$Bu_2(C_6F_4)BH(C_6F_5)_2$] (5). 31 mg (0.328 mmol) of $ClSiMe_2(H)$ were added to a solution of 50 mg of compound **3** (0.051 mmol) in 3 mL of CH_2Cl_2. After stirring for 1 h at room temperature, reaction went to completion. Solvent was removed under vacuum and the product extracted with a 1 to 4 CH_2Cl_2 / pentane mixture, filtered through celite and dried under vacuum to afford compound **5** as an orange solid. Yield 37 mg (75 %). Anal. Calcd. For $C_{44}H_{45}BF_{14}FeP_2$: C, 54.57; H, 4.68. Found: C, 54.36; H, 4.61 %. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 63.8 (tt, J_{PF} = 5, 14), 26.3 (s). ^{11}B NMR (CD_2Cl_2): -25.0 (d, J_{BH} = 87). ^1H NMR (CD_2Cl_2): 4.89 (m, C_5H_4, 2H), 4.67 (s, C_5H_4, 2H), 4.57 (m, C_5H_4, 2H), 4.49 (s, C_5H_4, 2H), 4.20-3.20 (br, B-H, 1H), 1.44 (d, J_{PH} = 17, ^{t}Bu, 18H), 1.21 (d, J_{PH} = 11, ^{t}Bu, 18H). ^{19}F NMR (CD_2Cl_2): -119.0 (br, C_6F_4, 2F), -129.0 (m, C_6F_4, 2F), -134.0 (d, J_{FF} = 23, *o*-C_6F_5, 4F), -164.1 (t, J_{FF} = 20, *p*-C_6F_5, 2F), -166.9 (m, *m*-C_6F_5, 4F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 150.5 (dm, J_{CF} ~ 240, C_6F_4), 148.8 (dm, J_{CF} ~ 240, *o*-C_6F_5), 146.9 (dm, J_{CF} ~ 255, C_6F_4), 138.7 (dm, J_{CF} ~ 245, *p*-C_6F_5), 138.7 (dm, J_{CF} ~ 250, *m*-C_6F_5), 125.0-123.0 (br, *i*-C_6F_4), 91.4 (dm, $^1J_{CP}$ ~ 70, *p*-C_6F_4), 83.9 (d, J_{PC} = 36, $C^{1'}$-C_5H_4), 77.4 (d, J_{PC} = 10, $C^{2/3}$-C_5H_4), 75.9 (d, J_{PC} = 9, $C^{2'/3'}$-C_5H_4), 75.2 (d, J_{PC} = 9, $C^{3/2}$-C_5H_4), 74.4 (s, $C^{3'/2'}$-C_5H_4), 65.1 (d, J_{PC} = 81, C^1-C_5H_4), 40.8 (d, J_{PC} = 34, C-*t*Bu), 33.5 (d, J_{PC} = 22, C-*t*Bu), 31.1 (d, J_{PC} = 13, CH_3-*t*Bu) 29.2 (s, CH_3-*t*Bu).

Synthesis of [{η^5-$C_5H_4P^tBu_2$-C_6F_4-$BH(C_6F_5)_2$}Fe(η^5-$C_5H_4P^tBu_2H$)][$HB(C_6F_5)_3$] (6). Solid $B(C_6F_5)_3$ (29 mg, 0.057 mmol) and compound **5** (55 mg, 0.057 mmol) were dissolved in 6 mL of CH_2Cl_2 and charged into a 100 mL storage flask. Solution was frozen with liquid N_2, evacuated and filled with H_2 (4 atm. approx.). After reaching room temperature, the solution was left stirring for 3 h and then the product was precipitated with hexanes (10 mL), the supernatant was decanted and the product was washed with more hexanes (2 x 5 mL) and dried under vacuum to afford compound **6** as an orange solid (60 mg, 71%). Anal. Calcd. For $C_{62}H_{47}B_2F_{29}FeP_2$: C, 50.23; H, 3.20. Found: C, 49.95; H, 3.19 %. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 62.1 (m), 47.6 (s). ^{31}P NMR (CD_2Cl_2): δ 62.1 (m), 47.6 (dm, $^1J_{PH}$ ~ 460). $^{11}B\{^1H\}$ NMR (CD_2Cl_2,): -25.1 (br, 2B). ^{11}B NMR (CD_2Cl_2): -25.1 (d, $J_{BH} \sim J_{B'H} \sim 77$, 2B). ^1H NMR (CD_2Cl_2): 5.89 (d, br, $^1J_{PH}$ = 464, P-H, 1H), 5.21, 5.14, 4.76, 4.70 (4 x s, 4 x br, C_5H_4, 4 x 2H), 4.20-3.20 (2 x m, 2 x B-H, 2 x 1H), 1.47 (d, J_{PH} = 17, *t*Bu, 18H), 1.45 (d, J_{PH} = 18, *t*Bu, 18H). ^{19}F NMR (CD_2Cl_2): -114.3, -119.8 (2 x br, C_6F_4, 2 x 1F), -127.2 (br, C_6F_4, 2F), -133.8 (d, J_{FF} = 21, *o*-C_6F_5, 4F), -134.0 (d, J_{FF} = 21, *o*-C_6F_5, 6F), -163.6 (t, J_{FF} = 20, *p*-C_6F_5, 2F), -164.5 (t, J_{FF} = 20, *p*-C_6F_5, 3F), -167.2 (m, *m*-C_6F_5, 4F), -167.6 (m, *m*-C_6F_5, 6F) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 150.7 (dm, $J_{CF} \sim 230$, C_6F_4), 148.7 (dm, $J_{CF} \sim 230$, *o*-C_6F_5), 146.6 dm, $J_{CF} \sim 255$, C_6F_4), 138.8 (dm, $J_{CF} \sim 245$, *p*-C_6F_5), 138.4 (dm, $J_{CF} \sim 245$, *p*-C_6F_5), 137.1 (dm, $J_{CF} \sim 250$, *m*-C_6F_5), 127.0-123.0 (br, *i*-C_6F_4), 90.4 (dm, $^1J_{CP} \sim 70$, *p*-C_6F_4), 79.4 (d, J_{PC} = 8, $C^{2'/3'}$-Cp), 78.5 (s, $C^{3'/2'}$-Cp), 76.3 (d, J_{PC} = 9, $C^{2,3}$-C_5H_4), 74.9 (d, J_{PC} = 9, $C^{3/2}$-C_5H_4), 69.0 (d, J_{PC} = 78, $C^{1/1'}$-C_5H_4), 60.9 (d, J_{PC} = 77, $C^{1'/1}$-C_5H_4), 41.0 (d, J_{PC} = 32, C-*t*Bu), 35.6 (d, J_{PC} = 35, C-*t*Bu), 28.8, 28.7 (2 x s, 2 x CH_3-*t*Bu).

Synthesis of [(η^5-C_5Ph_5)Fe(η^5-C_5H_4P*t*Bu_2H)][$HB(C_6F_5)_3$] (7). Solid $B(C_6F_5)_3$ (105 mg, 0.205 mmol) and [(η^5-C_5Ph_5)Fe(η^5-$C_5H_4P^tBu_2$)] 141 mg (0.198 mmol) were dissolved in 4 mL of CH_2Cl_2 and charged into a 50 mL storage flask. Solution was frozen with liquid N_2, evacuated and filled with H_2 (4 atm. approx.). The solution was left to reach room temperature progressively and was stirred for 2 h. Then pentane was added (12 mL) to precipitate the product. The solvent mixture was decanted and the product was washed with a CH_2Cl_2 / pentane (1 to 3) mixture and pentane (2 x 5 mL). After drying under vacuum, compound **7** was obtained as a red solid (200 mg, 83 %). Red crystals suitable for an X-ray analysis were grown by vapour diffusion of pentane into a concentrated solution of **8** in CH_2Cl_2 at

room temperature. Anal. Calcd. for $C_{66}H_{49}BF_{15}FeP$: C, 64.73; H, 4.03. Found: C, 64.33; H, 4.16 % $^{31}P\{^1H\}$ NMR (CD_2Cl_2,): 49.1. ^{31}P NMR (CD_2Cl_2): 49.0 (dm, $^1J_{PH}$ = 446). $^{11}B\{^1H\}$ NMR (CD_2Cl_2,): 25.4. ^{11}B NMR (CD_2Cl_2): 25.4 (d, J_{BH} = 90). ^1H NMR (CD_2Cl_2): 7.30-7.05 (m, Ph, 25H), 5.51 (d, $^1J_{PH}$ = 445, P-H, 1H), 5.06, 4.94 (2 x m, C_5H_4, 2 x 2H), 3.63 (q, J_{BH} = 90, B-H, 1H), 1.17 (d, J_{PH} = 18, *t*Bu, 18H). ^{19}F NMR (CD_2Cl_2):-134.3 (d, J_{FF} = 23, *o*-C_6F_5, 6F), -165.1 (t, J_{FF} = 21, *p*-C_6F_5, 3F), -168.0 (m, *m*-C_6F_5, 6F). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 148.8 (dm, J_{CF} = 235, *o*-C_6F_5), 138.3 (dm, J_{CF} = 245, *p*-C_6F_5), 137.1 (dm, J_{CF} = 240, *m*-C_6F_5), 134.1 (s, *i*-C-Ph), 132.8, 128.2 (2 x s, *o*/*m*-C-Ph), 126.9 (s, *p*-C-Ph), 90.7 (s, C_5Ph_5), 81.0 (d, J_{PC} = 9, $C^{2/3}$-C_5H_4), 79.1 (d, J_{PC} = 9, $C^{3/2}$-C_5H_4), 60.5 (d, J_{PC} = 78, C^1-C_5H_4), 36.0 (d, J_{PC} = 35, *t*Bu), 28.5 (s, *t*Bu). X-ray: Space group Triclinic, P-1, a = 11.9830(2) Å, b = 21.9410(4) Å c = 22.8040(4) Å, α = 71.3220(11)°, β = 84.4670(11) °, γ = 80.923(1) °, V = 5601.96(17) $Å^3$, Z = 4, μ = 0.390 mm^{-1}, measured reflections = 25496, independent reflections = 1663, parameters = 186, Rint = 0.0602, R = 0.0635, Rw = 0.1482, GOF = 0.996.