

Supporting Information for

A CO-derived Fe Dicarbyne that Releases Olefin upon Hydrogenation

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Table of Contents

S2	Experimental procedures
S6	DFT calculations
S12	Cyclic voltammogram
S12	EPR spectrum
S13	Mössbauer spectra
S14	X-ray diffraction details

General Considerations. All manipulations were carried out using standard Schlenk or glovebox techniques under an atmosphere of dinitrogen. Solvents were degassed and dried by sparging with N₂ gas and passage through an activated alumina column. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. Reagents were purchased from commercial vendors and used without further purification unless otherwise noted. Complex **1** was synthesized according to a literature procedure.¹ Elemental analyses were performed by Midwest Microlab (Indianapolis, IN) and Robertson Microlit Laboratories (Ledgewood, NJ).

NMR, IR, EPR, and UV/vis spectroscopic measurements. ¹H, ¹³C, ³¹P, and ¹¹B NMR spectra were collected at room temperature on either a Varian 400 MHz or a Varian 500 MHz spectrometer. ¹H and ¹³C spectra were referenced to residual solvent resonances. ³¹P spectra were referenced to external 85% phosphoric acid ($\delta = 0$ ppm). ¹¹B spectra were referenced to BF₃•Et₂O (0 ppm). UV-vis measurements were performed with a Cary 50 instrument with Cary WinUV software. IR measurements were obtained as thin films formed by evaporation using a Bruker Alpha Platinum ATR spectrometer with OPUS software. EPR spectra were recorded on a Bruker EMS spectrometer at ca. 1 mM concentrations. IR measurements were obtained in KBr pellets using a Bio-Rad Excalibur FTS 3000 spectrometer with Varian Resolutions Pro software.

X-ray Crystallography. X-ray diffraction studies were carried out at the Caltech Division of Chemistry and Chemical Engineering X-ray Crystallography Facility on a Bruker three-circle SMART diffractometer with a SMART 1K CCD detector. Data were collected at 100K using Mo K α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct or Patterson methods using SHELXS and refined against F^2 on all data by full-matrix least squares with SHELXL-97.² All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 (1.5 for methyl groups) times the Ueq of the atoms to which they are bonded. One of the P'Pr₂ groups in **4** is disordered over two positions with an occupancy ratio that was refined to ~3:2. The resulting model fit the data set highly satisfactorily (see Table S3).

Mössbauer Spectroscopy. Spectra were recorded on a spectrometer from SEE Co (Edina, MN) operating in the constant acceleration mode in a transmission-geometry. Spectra were recorded with the temperature of the sample maintained at 5 K. The sample was kept in an SVT-400 dewar from Janis (Wilmington, MA), at zero field. Application of a magnetic field of 54 mT parallel to the γ -beam did not cause detectable changes in the spectra recorded at 5 K. The quoted isomer shifts are relative to the centroid of the spectrum of a metallic foil of α -Fe at room temperature. Samples were prepared by grinding polycrystalline material into a fine powder and then mounted in a cup fitted with a screw cap as a boron nitride pellet. Data analysis was performed using the program WMOSS and quadrupole doublets were fit to Lorentzian lineshapes.

Synthetic procedures

(DPB)Fe(CO)₂ (2): A red-brown solution of [(DPB)Fe]₂(μ-1,2-N₂) (**1**, 524.2 mg, 0.482 mmol) in THF (20 mL) was subjected to three freeze-pump-thaw cycles and subsequently exposed to 1 atm CO. The solution was vigorously stirred until the color changed to red-orange (about 15 min.). Consumption of **1** was monitored by ¹H NMR spectroscopy of aliquots. Extended reaction times result in overcarbonylation to give (DPB)Fe(CO)₃ (**3**), so the reaction should be monitored diligently. After complete consumption of **1**, vacuum was applied to the solution giving a dark red residue. Residual THF was removed by addition of Et₂O (5 mL) and drying *in vacuo*. The resulting red solids were washed with cold Et₂O (5 x 2mL) to give **2** (420.0 mg, 0.717 mmol, 74%). An additional batch of **2** may be obtained by concentration of the Et₂O washings into HMDSO (51.9 mg, 0.0886 mmol, 9%). Single crystals suitable for X-ray diffraction analysis may be obtained by concentration of a saturated Et₂O solution. ¹H NMR (400 MHz, C₆D₆) δ 8.63 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 6.7 Hz, 1H), 7.16-7.00 (m, 6H), 6.89 (t, *J* = 7.2 Hz, 1H), 6.42 (d, *J* = 7.3 Hz, 1H), 2.44 (dh, *J* = 14.6, 7.3 Hz, 2H), 1.50-1.40 (m, 4H), 1.28 (dd, *J* = 14.9, 6.9 Hz, 3H), 1.27-1.19 (m, 4H), 1.10 (dd, *J* = 15.3, 6.9 Hz, 3H), 0.95 (dd, *J* = 19.5, 7.6 Hz, 3H), 0.88 (dd, *J* = 11.6, 7.2 Hz, 3H), 0.65 (dd, *J* = 13.4, 7.2 Hz, 3H), 0.36 (dd, *J* = 16.4, 7.5 Hz, 3H). ¹¹B NMR (128 MHz, C₆D₆) δ 11.5. ¹³C NMR (101 MHz, C₆D₆) δ 220.9 (dd, *J* = 23.3, 17.6 Hz), 214.4-213.6 (m), 165.1, 151.6, 146.2, 146.1, 141.6, 141.2, 136.8, 136.6, 135.7, 131.0, 129.6, 129.0, 126.4, 126.3, 125.2, 117.0, 98.5, 98.4, 30.1 (d, *J* = 18.1 Hz), 28.6 (dd, *J* = 28.4, 12.7 Hz), 26.7 (d, *J* = 16.3 Hz), 22.1, 22.1, 20.8, 19.3, 18.7, 18.2, 18.1, 17.8. ³¹P NMR (162 MHz, C₆D₆) δ 90.6 (d, *J* = 65.3 Hz), 54.6 (d, *J* = 65.3 Hz). UV/vis (toluene, nm {M⁻¹ cm⁻¹}): 482 {sh, 2000}. Elemental analysis for C₃₂H₄₁BFeO₂P₂: calc. C 65.65, H 7.05, N 0; found C 65.48, H 7.14, N <0.02. IR of (DPB)Fe(¹²CO)₂ (cm⁻¹): 1908, 1863. IR of (DPB)Fe(¹³CO)₂ (cm⁻¹): 1868, 1824.

(DPB)Fe(CO)₃ (3): A J. Young NMR tube was charged with (DPB)Fe(CO)₂ (**2**, 22.0 mg, 0.0375 mmol) and 0.7 mL C₆D₆ under N₂. After three freeze-pump-thaw cycles, 1 atm CO was added and the NMR tube was rotated at RT for 1 hr. The solution changed from red-orange to very pale yellow and NMR and IR spectroscopies showed quantitative conversion to **3**. Solutions and colorless powders of **3** slowly reconvert to **2** under 1 atm N₂ or vacuum. As such, **3** is best studied in solution under 1 atm CO. Colorless single crystals suitable for X-ray diffraction analysis may be obtained by concentration of an Et₂O solution into HMDSO (with a small contamination of red-orange crystals of (DPB)Fe(CO)₂). ¹H NMR (400 MHz, C₆D₆) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.26-6.91 (m, 9H), 6.88-6.76 (m, 2H), 2.73 (m, 2H), 2.38 (m, 2H), 1.25 (m, 12H), 1.06 (m, 12H). ¹¹B NMR (128 MHz, C₆D₆) δ 20.25. ¹³C NMR (101 MHz, C₆D₆) δ 217.6 (t, *J* = 26.2 Hz), 215.8 (t, *J* = 30.8 Hz), 213.6 (t, *J* = 10.7 Hz), 166.7, 157.8, 141.9-139.6 (m), 135.8, 132.6 (t, *J* = 8.6 Hz), 129.3, 128.8, 126.6, 125.7, 123.7, 31.4 (t, *J* = 11.5 Hz), 26.7-26.0 (m), 20.4, 20.1, 18.9, 16.9. ³¹P NMR (162 MHz, C₆D₆) δ 87.5. Elemental analysis data were not obtained due to the instability of (DPB)Fe(CO)₃ with respect to CO loss when not stored under 1 atm CO. IR of (DPB)Fe(¹²CO)₃ (cm⁻¹): 2002 (w), 1932 (vs).

(DPB-H)Fe(H)(CO)₂ (4): A J. Young NMR tube was charged with (DPB)Fe(CO)₂ (**2**, 24.3 mg, 0.0415 mmol) and 0.7 mL C₆D₆ under N₂. After three freeze-pump-thaw cycles, 1 atm H₂ was added and the NMR tube was rotated at RT for 1 hr. The solution changed from red-orange to

very pale green and NMR and IR spectroscopies showed quantitative conversion to **4**. Solvent was removed in vacuo and the resulting colorless solids were extracted into n-pentane. Recrystallization by evaporation of this solution into HMDSO afforded large, polychroic (magenta, teal, green) single crystals suitable for X-ray diffraction (23.0 mg, 0.0391 mmol, 94%). ^1H NMR (400 MHz, C_6D_6) δ 7.76 (d, J = 6.9 Hz, 2H), 7.12 (m, 9H), 7.00 (m, 3H), 2.40 (m, 2H), 2.13 (m, 2H), 1.04 (m, 18H), 0.88 (m, 6H), -7.73 (td, J = 54.4, 7.6 Hz, 1H, Fe–H), -17.00 (br m, 1H, Fe–H–B). ^{11}B NMR (128 MHz, C_6D_6) δ 11.8. ^{13}C NMR (101 MHz, C_6D_6) δ 217.4, 214.8, 162.9, 155.5, 139.5 (t, J = 25.8 Hz), 134.1, 132.8 (t, J = 7.3 Hz), 128.6, 128.5, 126.8, 125.4, 124.6, 30.6 (t, J = 8.3 Hz), 28.2 (t, J = 16.2 Hz), 18.9, 18.6, 18.4, 18.4. ^{31}P NMR (162 MHz, C_6D_6) δ 93.0. UV/vis (toluene, nm $\{\text{M}^{-1}\text{cm}^{-1}\}$): 332 {sh, 900}. Elemental analysis for $\text{C}_{32}\text{H}_{43}\text{BFeO}_2\text{P}_2$: calc. C 65.33, H 7.37, N 0; found C 65.03, H 7.26, N <0.02. IR of (DPB–H)Fe(H)(^{13}CO) $_2$ (cm^{-1}): 2080 (br, Fe–H–B), 1815 (s, C–O asym.), 1752 (s, C–O sym.).

[K(benzo-15-c-5) $_2$][(DPB)Fe(CO) $_2$] (5): A red-orange solution of (DPB)Fe(CO) $_2$ (**2**, 28.6 mg, 0.0488 mmol) in THF (3 mL) was stirred over excess K until the solution turned inky yellow (<5 min.). The solution was decanted from the K onto benzo-15-crown-5 (28.8 mg, 0.107 mmol). Solvent was removed in vacuo to provide a brown residue that was washed with Et $_2$ O (3 x 1 mL) and C_6H_6 (3 x 1 mL). Diffusion of n-pentane into a THF solution afforded single crystals of the title compound (53.1 mg, 0.0457 mmol, 94%). ^1H NMR (300 MHz, THF) δ 8.73, 8.58, 8.17, 5.70, 5.54, 3.16, 2.75, -0.04 (v br). Solution magnetic moment by Evans method (THF, RT): 1.7 μ_{B} . Elemental analysis for $\text{C}_{60}\text{H}_{81}\text{BFeKO}_{12}\text{P}_2$: calc. C 62.02, H 7.03, N 0; found C 61.71, H 7.15, N <0.02. UV/vis (THF, nm $\{\text{M}^{-1}\text{cm}^{-1}\}$): 750 (br), 950 (br). IR of [K(benzo-15-c-5) $_2$][(DPB)Fe(^{12}CO) $_2$] (cm^{-1}): 1857, 1791. IR of [K(benzo-15-c-5) $_2$][(DPB)Fe(^{13}CO) $_2$]: 1815, 1752.

[K(benzo-15-c-5) $_2$][(DPB)Fe(CO) $_2$] (6): Due to its extremely high air and moisture sensitivity, ((DPB)Fe(CO) $_2$)(K(THF) $_x$) $_2$ is best generated *in situ* (by stirring a THF solution of (DPB)Fe(CO) $_2$ (**2**) over excess K for 6 hr.) and used immediately. A cation-encapsulated species was generating for NMR, IR, and XRD characterization according to the following procedure. A red-orange solution of (DPB)Fe(CO) $_2$ (**2**, 12.9 mg, 0.0219 mmol) in THF- d_8 (0.7 mL) was stirred over K for 6 hr. The solution initially changed to inky yellow and subsequently to dark red-brown. The solution was decanted from the K unto benzo-15-crown-5 (24.7 mg, 0.0921 mmol) and transferred to a J. Young tube for NMR characterization. Vapor diffusion of Et $_2$ O into this THF solution afforded dark solids from which a single crystal was selected for XRD analysis. ^1H NMR (300 MHz, THF- d_8) δ 7.14–6.99 (m, 4H), 6.80 (m, 18H), 6.60 (m, 4H), 6.50 (t, J = 7.2 Hz, 2H), 6.36 (t, J = 5.8 Hz, 1H), 3.91 (br s, 16H), 3.72 (br s, 16H), 3.63 (br s, 32H), 2.28 (br s, 2H), 2.03 (br s, 2H), 1.22 (br s, 6H), 1.06 (br s, 6H), 0.90 (br s, 6H), 0.77 (br s, 6H). ^{11}B NMR (160 MHz, THF- d_8) δ 14.1. ^{13}C NMR (126 MHz, THF- d_8) δ 244.7 (t, J = 10.5 Hz), 244.1 (t, J = 17.5 Hz), 183.1, 159.8, 154.1, 141.1, 137.4, 130.3, 128.9 (t, J = 23.8 Hz), 126.4 (d, J = 47.1 Hz), 124.4, 122.4, 118.9 (d, J = 44.0 Hz), 75.3, 74.7, 73.8, 73.3, 37.8 (d, J = 20.7 Hz), 35.3–34.1 (m), 30.8, 26.8–26.0 (m), 26.0–25.0 (m), 24.0. ^{31}P NMR (121 MHz, THF- d_8) δ 102.4. IR of [K(benzo-15-c-5) $_2$][(DPB)Fe(^{12}CO) $_2$] (cm^{-1}): 1738, 1659. IR of [K(benzo-15-c-5) $_2$][(DPB)Fe(^{13}CO) $_2$] (cm^{-1}): 1696, 1620.

(DPB)Fe(COSiMe₃)₂ (8**):** A red-orange solution of (DPB)Fe(CO)₂ (**2**, 20.8 mg, 0.0354 mmol) in THF (2 mL) was stirred over K for 6 hr. The solution initially changed to inky yellow and subsequently to dark red-brown. The solution was cooled to -78 °C and then added dropwise to a precooled (-78 °C) 0.4 M toluene solution of TMSOTf (0.185 mL, 0.0743 mmol). The cold solution immediately turned to a lighter brown. After stirring for 15 min. at -78 °C, the solution was brought to RT and solvent was removed in vacuo. Residual THF and toluene was removed by addition of n-pentane (2 mL) followed by drying in vacuo. The resulting solids were dissolved in n-pentane (2 mL) and filtered through Celite to afford a brown solution. Removal of the solvent in vacuo afforded brown solids (18.0 mg) with compositions that are typically 85-90% **8** and 10-15% **2** as judged by ¹H and ³¹P NMR spectroscopy. In solution, **8** converts to **2** over several days; as such, samples of **8** are best prepared immediately before use. Brown, single crystals of **8** (contaminated by single crystals of **8**) may be obtained by evaporation of a concentrated SiMe₄ solution into HMDSO. ¹H NMR (400 MHz, C₆D₆) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 6.9 Hz, 2H), 7.46-7.35 (m, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.08 (m, 3H), 6.96 (t, *J* = 7.3 Hz, 2H), 2.55-2.41 (m, 2H), 2.16 (dq, *J* = 13.8, 6.9 Hz, 2H), 1.27 (m, 12H), 1.02 (dd, *J* = 13.2, 7.2 Hz, 6H), 0.79 (dd, *J* = 13.2, 6.9 Hz, 6H), 0.12 (s, 9H), -0.08 (s, 9H). ¹³C NMR (101 MHz, C₆D₆) δ 261.9 (td, *J* = 9.0, 3.1 Hz), 230.2 (d, *J* = 3.1 Hz), 165.4, 159.3, 143.2-142.9 (m), 139.6, 139.1, 138.5, 138.3, 131.1, 125.5, 125.2, 123.8, 123.0, 28.9 (d, *J* = 24.5 Hz), 27.4 (d, *J* = 10.7 Hz), 20.8, 19.9, 19.6, 19.2 (*J* = 4.1 Hz), -0.1, -1.0. ³¹P NMR (162 MHz, C₆D₆) δ 87.5 (for ¹³C-labeled sample: d, *J* = 9.0 Hz). ¹¹B NMR (128 MHz, C₆D₆) δ 6.4. UV/vis (toluene, nm {M⁻¹ cm⁻¹}): 480 {sh, 1100}. Elemental analysis data were not obtained due to the thermal instability of (DPB)Fe(COSiMe₃)₂.

Hydrogenation of (DPB)Fe(COSiMe₃)₂ (8**):** Three samples of freshly-prepared **8** (~7 mg each) were mixed with ferrocene (~2 mg each), dissolved in C₆D₆ (~0.7 mL each), and added to separate J. Young tubes. A ¹H NMR spectrum was recorded for each sample to determine the relative amounts of **8** (as judged by two the aryl resonances at 7.90 and 7.51 ppm) and Fc. The samples were subjected to three freeze-pump-thaw cycles and exposed to 1 atm H₂. The brown solutions turned yellow over a period of 15 min. at which time another ¹H NMR spectrum was recorded. Yields of Z-1,2-bis(trimethylsiloxy)ethylene (**10**) were determined by integrating the olefinic resonance (a singlet in natural-abundance ¹²C samples and a complicated multiplet in ¹³C-enriched samples) against Fc. The identity of Z-1,2-bis(trimethylsiloxy)ethylene was established by comparison with an independently prepared, authentic sample.³ The three runs gave yields of 45, 42, and 41%, for an average of 43%.

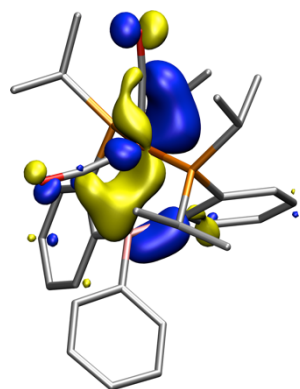
Hydrogenation of (DPB)Fe(¹²COSiMe₃)₂ in the presence of (DPB)Fe(¹³COSiMe₃)₂: An approximately equal molar ratio of **8**-¹²C and **8**-¹³C (~5 mg each) were dissolved in C₆D₆ (0.7 mL) and added to a J. Young NMR tube. After rotating for 30 min. under 1 atm H₂, ¹H NMR spectroscopy showed only **10**-¹²C¹²C and **10**-¹³C¹³C with no **10**-¹²C¹³C.

DFT calculations

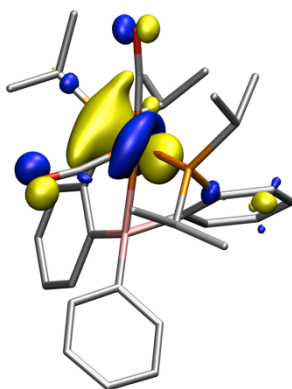
Single point energy calculations were undertaken using Gaussian09 Revision B.01⁴ at the M06L/6-311+g(d) level with geometries taken from X-ray structure coordinates. Molecular orbitals and spin density surfaces shown with 0.05 and 0.004 e Å⁻³ isosurfaces. Orbital energies are set relative to the HOMO. Only MOs with significant Fe- or B-character are shown.

Chart S1. DFT study of **2**: molecular orbital analysis

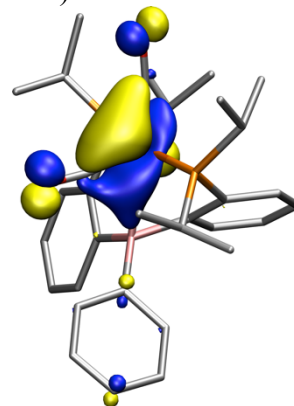
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HOMO-1 (-0.8 eV)



HOMO-2 (-0.9 eV)



HOMO-3 (-1.2 eV)

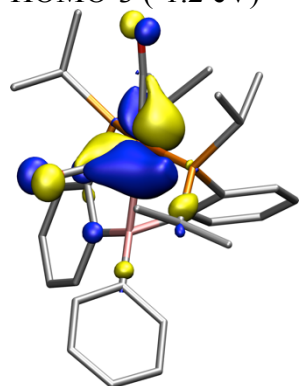
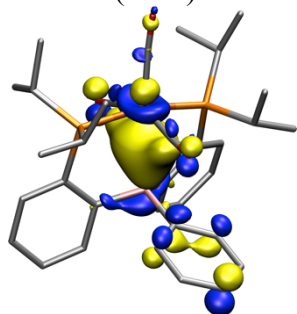
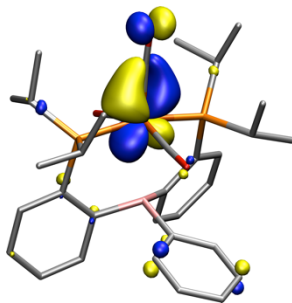


Chart S2. DFT study of **3**: molecular orbital analysisFrontier molecular orbitals

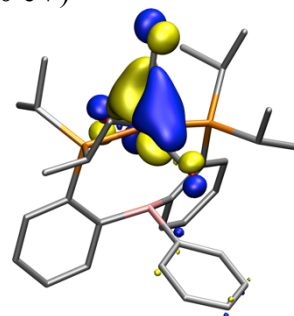
HOMO (0 eV)



HOMO-2 (-0.9 eV)



HOMO-4 (-1.0 eV)



HOMO-6 (-1.0 eV)

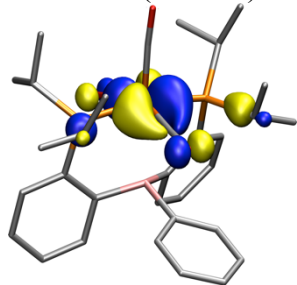
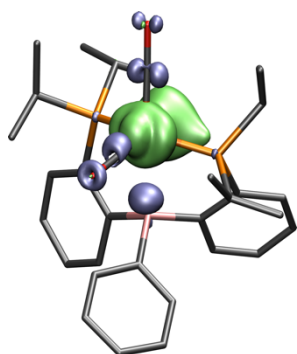
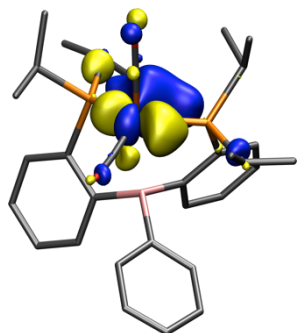
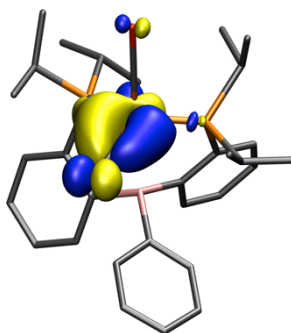
**Chart S3.** DFT study of **5**: spin density analysisSpin density

Chart S4. DFT study of **6**: molecular orbital analysisFrontier molecular orbitals

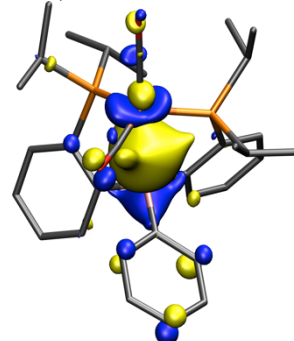
HOMO (0 eV)



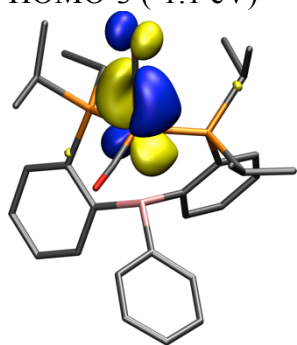
HOMO-1 (-0.4 eV)



HOMO-2 (-0.5 eV)



HOMO-3 (-1.1 eV)



HOMO-4 (-1.3 eV)

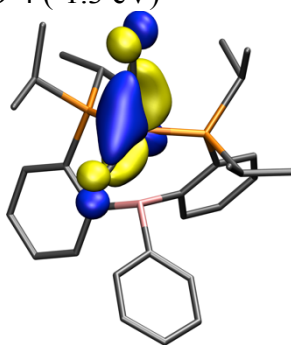
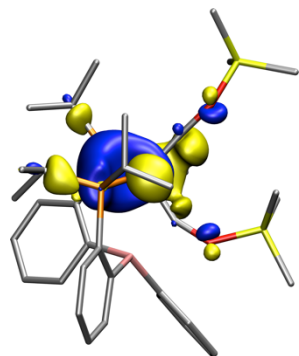


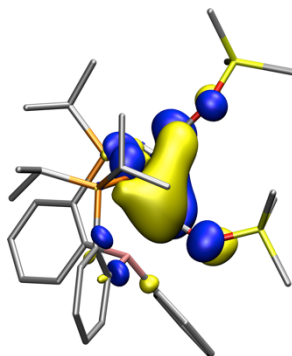
Chart S5. DFT study of **8**: molecular orbital analysis

Frontier molecular orbitals

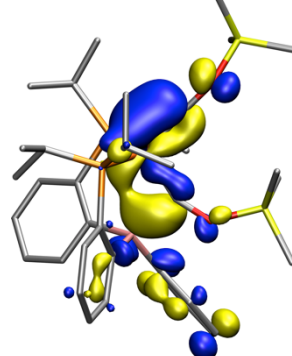
HOMO (0 eV)



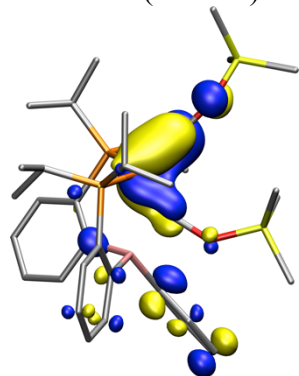
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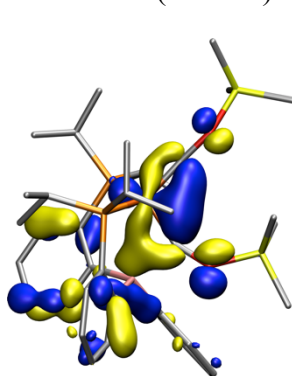
HOMO-2 (-1.1 eV)



HOMO-4 (-1.7 eV)



HOMO-10 (-2.3 eV)



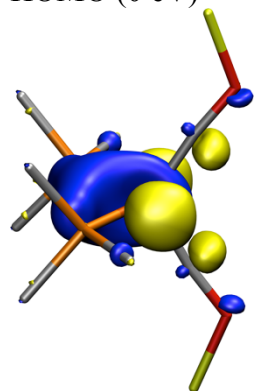
^{13}C NMR chemical shift calculations

The ^{13}C NMR chemical shifts for the carbyne carbons with and without an interaction with the borane were calculated to be 249 and 228 ppm, respectively, using the GIAO method.⁴ As such, we tentatively assign the experimentally observed signals at 261.9 and 230.2 ppm accordingly.

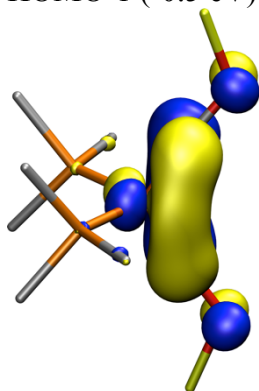
Chart S6. DFT study of **9**: molecular orbital analysis (reproduced from Figure 1)

Frontier molecular orbitals

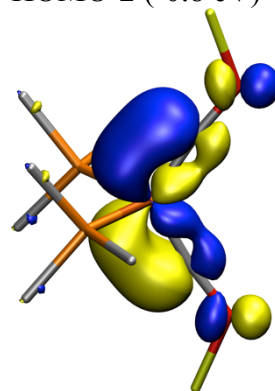
HOMO (0 eV)



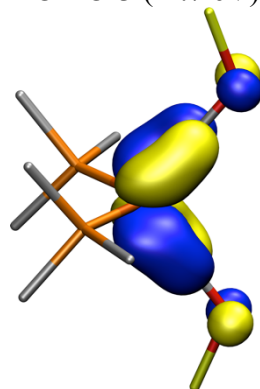
HOMO-1 (-0.5 eV)



HOMO-2 (-0.8 eV)



HOMO-3 (-1.7 eV)



HOMO-4 (-1.7 eV)

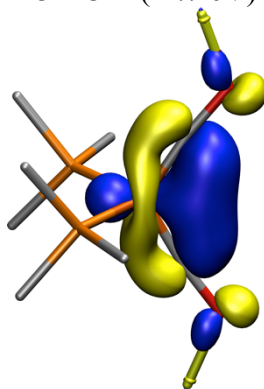
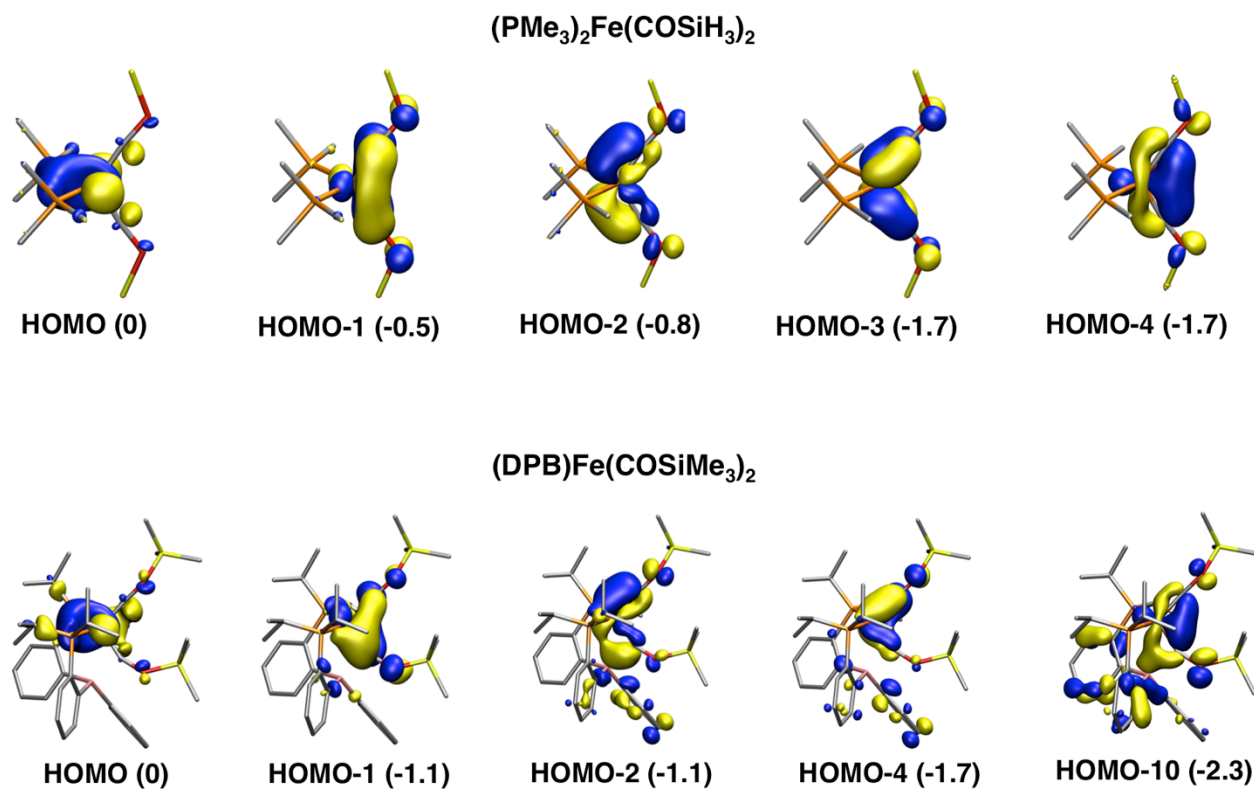
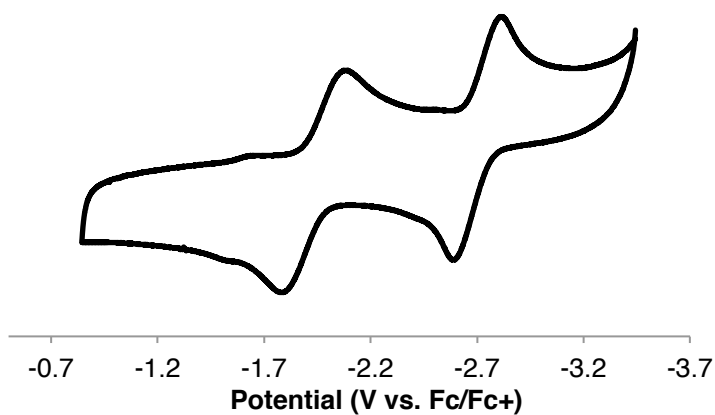


Chart S7. Comparison of frontier molecular orbitals of **8** (top) and **9** (bottom).



Cyclic voltammagram



. Cyclic voltammagram of **2** recorded in THF with 0.3 M Bu₄NPF₆ electrolyte at 100 mV s⁻¹.

EPR spectrum

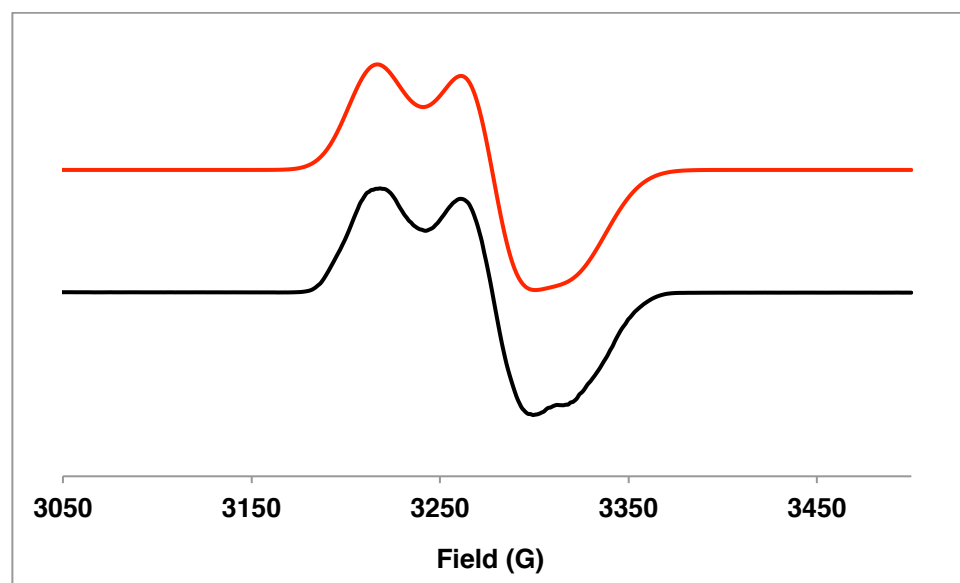


Figure S. Experimental (black) and simulated (red) X-band EPR spectrum of [K(benzo-15-c-5)₂][(DPB)Fe(CO)₂] **5** recorded at 77 K in 2-MeTHF. Fit parameters: $g = [2.111, 2.070, 2.042]$.

Mössbauer spectra

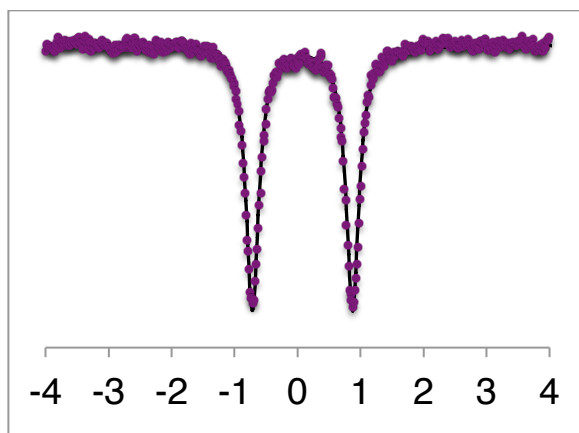


Figure S2. Mössbauer spectrum of **2** recorded at 4 K. Fit parameters: $\delta = -0.078 \text{ mm s}^{-1}$, $|\Delta E_q| = 1.59 \text{ mm s}^{-1}$, linewidth = 0.25 mm s^{-1} .

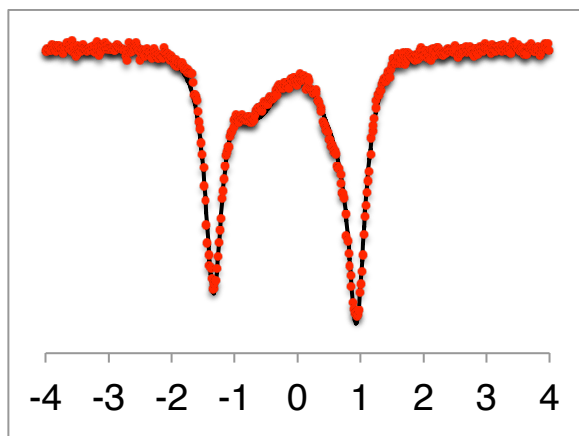


Figure S3. Mössbauer spectrum of **8** recorded at 4 K. Fit parameters for major component (**8**, 68%): $\delta = -0.200 \text{ mm s}^{-1}$, $|\Delta E_q| = 2.27 \text{ mm s}^{-1}$, linewidth = 0.32 mm s^{-1} . Minor components (including some **2**) likely arising from exposure to air and moisture during sample handling were satisfactorily fit as a single, broad doublet (32%): $\delta = 0.001 \text{ mm s}^{-1}$, $|\Delta E_q| = 1.29 \text{ mm s}^{-1}$, linewidth = 0.82 mm s^{-1} .

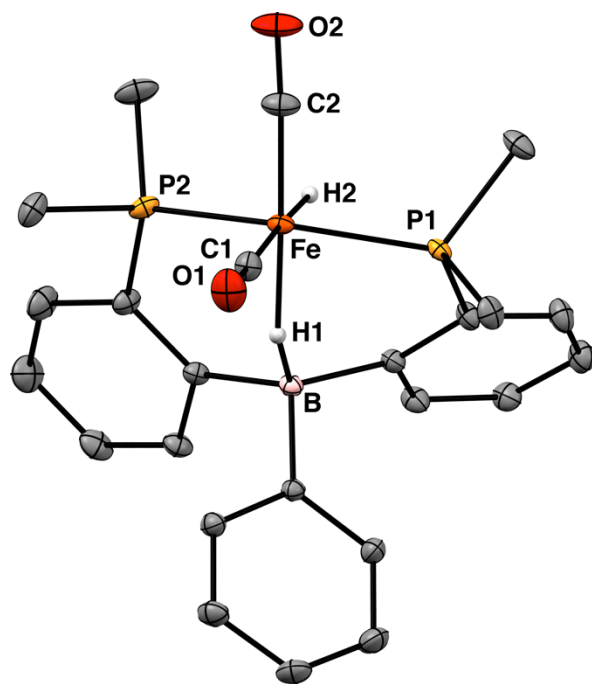
X-ray structure of **4**

Figure SX. Displacement ellipsoid (50%) representation of **4**. P^iPr_2 groups are truncated and H atoms are omitted for clarity. The P^iPr_2 fragment for P1 is disordered over two positions; only the major component is shown. Selected distances and angles: Fe–B = 2.7426(6) Å; Fe–P1 = 2.249(2) Å; Fe–P2 = 2.2146(2) Å; Fe–C1 = 1.7970(5) Å; Fe–C2 = 1.7466(6) Å; $\angle(P1-Fe-P2) = 150.71(5)^\circ$; $\Sigma\angle(C-B-C) = 340^\circ$.

X-ray diffraction tablesTable S1. Crystal data and structure refinement for **2**.

Identification code	(DPB)Fe(CO) ₂	
Empirical formula	C ₃₂ H ₄₁ B Fe O ₂ P ₂	
Formula weight	586.25	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.8731(10) Å	$\alpha = 90^\circ$
	b = 9.0298(5) Å	$\beta = 110.704(2)^\circ$
	c = 21.5015(12) Å	$\gamma = 90^\circ$
Volume	3064.4(3) Å ³	
Z	4	
Density (calculated)	1.271 Mg/m ³	
Absorption coefficient	0.623 mm ⁻¹	
F(000)	1240	
Crystal size	0.40 x 0.30 x 0.30 mm ³	
Theta range for data collection	1.29 to 39.03°	
Index ranges	-29 ≤ h ≤ 29, -15 ≤ k ≤ 15, -37 ≤ l ≤ 37	
Reflections collected	187067	
Independent reflections	17354 [R(int) = 0.0933]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8351 and 0.7886	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	17354 / 0 / 351	
Goodness-of-fit on F ²	1.075	
Final R indices [I > 2σ(I)]	R1 = 0.0528, wR2 = 0.1146	
R indices (all data)	R1 = 0.0927, wR2 = 0.1320	
Largest diff. peak and hole	1.514 and -0.498 e Å ⁻³	

Table S2. Crystal data and structure refinement for **3**.

Identification code	(DPB)Fe(CO) ₃	
Empirical formula	C ₃₃ H ₄₁ B Fe O ₃ P ₂	
Formula weight	614.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.1059(5) Å	$\alpha = 90^\circ$
	b = 16.9341(7) Å	$\beta = 92.838(2)^\circ$
	c = 18.0259(9) Å	$\gamma = 90^\circ$
Volume	3081.1(3) Å ³	
Z	4	
Density (calculated)	1.324 Mg/m ³	
Absorption coefficient	0.626 mm ⁻¹	
F(000)	1296	
Crystal size	0.39 x 0.32 x 0.23 mm ³	
Theta range for data collection	2.26 to 47.13°	
Index ranges	-20 ≤ h ≤ 20, -34 ≤ k ≤ 34, -37 ≤ l ≤ 25	
Reflections collected	423493	
Independent reflections	28099 [R(int) = 0.0543]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	28099 / 0 / 369	
Goodness-of-fit on F ²	1.043	
Final R indices [I > 2σ(I)]	R1 = 0.0302, wR2 = 0.0871	
R indices (all data)	R1 = 0.0499, wR2 = 0.0921	
Largest diff. peak and hole	1.574 and -0.440 e Å ⁻³	

Table S3. Crystal data and structure refinement for **4**.

Identification code	(DPB–H)Fe(H)(CO) ₂	
Empirical formula	C ₃₂ H ₄₃ B Fe O ₂ P ₂	
Formula weight	588.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5324(6) Å	α = 98.981(3)°
	b = 9.7170(7) Å	β = 99.435(3)°
	c = 17.8890(16) Å	γ = 105.950(2)°
Volume	1535.9(2) Å ³	
Z	2	
Density (calculated)	1.272 Mg/m ³	
Absorption coefficient	0.622 mm ⁻¹	
F(000)	624	
Crystal size	0.34 x 0.28 x 0.28 mm ³	
Theta range for data collection	2.23 to 48.60°	
Index ranges	-20 ≤ h ≤ 19, -19 ≤ k ≤ 19, -37 ≤ l ≤ 37	
Reflections collected	196119	
Independent reflections	29527 [R(int) = 0.0410]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8451 and 0.8164	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	29527 / 451 / 427	
Goodness-of-fit on F ²	1.015	
Final R indices [I > 2σ(I)]	R1 = 0.0333, wR2 = 0.0924	
R indices (all data)	R1 = 0.0515, wR2 = 0.0976	
Largest diff. peak and hole	1.050 and -0.482 e Å ⁻³	

Table S4. Crystal data and structure refinement for **5**.

Identification code	[K(benzo-15-crown-5) ₂][(DPB)Fe(CO) ₂]	
Empirical formula	C ₆₀ H ₈₁ B Fe K O ₁₂ P ₂	
Formula weight	1161.95	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.736(3) Å	$\alpha = 90^\circ$
	b = 11.266(2) Å	$\beta = 92.526(10)^\circ$
	c = 31.692(9) Å	$\gamma = 90^\circ$
Volume	5969(2) Å ³	
Z	4	
Density (calculated)	1.293 Mg/m ³	
Absorption coefficient	0.435 mm ⁻¹	
F(000)	2468	
Crystal size	0.35 x 0.12 x 0.04 mm ³	
Theta range for data collection	1.73 to 32.68°	
Index ranges	-25 ≤ h ≤ 24, -16 ≤ k ≤ 16, -46 ≤ l ≤ 46	
Reflections collected	196722	
Independent reflections	20375 [R(int) = 0.0930]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9828 and 0.8625	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	20375 / 0 / 702	
Goodness-of-fit on F ²	0.919	
Final R indices [I > 2σ(I)]	R1 = 0.0375, wR2 = 0.0756	
R indices (all data)	R1 = 0.0807, wR2 = 0.0833	
Largest diff. peak and hole	0.438 and -0.534 e Å ⁻³	

Table S5. Crystal data and structure refinement for **6**.

Identification code	[K(benzo-15-crown-5) ₂] ₂ [(DPB)Fe(CO) ₂]	
Empirical formula	C ₄₆ H _{64.50} B _{0.50} Fe _{0.50} K O _{11.50} P	
Formula weight	904.88	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.3954(14) Å	α = 96.728(4)°
	b = 14.7510(12) Å	β = 96.954(2)°
	c = 24.5846(14) Å	γ = 115.227(2)°
Volume	4604.3(6) Å ³	
Z	4	
Density (calculated)	1.305 Mg/m ³	
Absorption coefficient	0.361 mm ⁻¹	
F(000)	1928	
Crystal size	0.30 x 0.30 x 0.20 mm ³	
Theta range for data collection	1.66 to 42.89°	
Index ranges	-27<=h<=27, -28<=k<=27, -46<=l<=46	
Reflections collected	340219	
Independent reflections	64746 [R(int) = 0.0551]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9314 and 0.8995	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	64746 / 0 / 1098	
Goodness-of-fit on F ²	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0472, wR2 = 0.1091	
R indices (all data)	R1 = 0.0857, wR2 = 0.1242	
Largest diff. peak and hole	1.257 and -1.146 e Å ⁻³	

Table S6. Crystal data and structure refinement for **8**.

Identification code	(DPB)Fe(COSiMe ₃) ₂	
Empirical formula	C ₃₈ H ₅₉ B Fe O ₂ P ₂ Si ₂	
Formula weight	732.63	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.6336(12) Å	α = 90.693(2)°
	b = 18.0101(17) Å	β = 103.060(3)°
	c = 18.2534(13) Å	γ = 90.701(3)°
Volume	4045.0(6) Å ³	
Z	4	
Density (calculated)	1.203 Mg/m ³	
Absorption coefficient	0.541 mm ⁻¹	
F(000)	1568	
Crystal size	0.28 x 0.22 x 0.10 mm ³	
Theta range for data collection	1.79 to 37.12°	
Index ranges	-21 ≤ h ≤ 21, -29 ≤ k ≤ 30, -30 ≤ l ≤ 30	
Reflections collected	299923	
Independent reflections	39962 [R(int) = 0.0678]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9478 and 0.8632	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	39962 / 0 / 857	
Goodness-of-fit on F ²	0.948	
Final R indices [I > 2σ(I)]	R1 = 0.0379, wR2 = 0.0907	
R indices (all data)	R1 = 0.0688, wR2 = 0.0984	
Largest diff. peak and hole	1.159 and -0.743 e Å ⁻³	

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