Supporting Information

Stabilization of Pentaphospholes as $\eta^5$-Coordinating Ligands
Christoph Riesinger, Gábor Balázs, Michael Bodensteiner, and Manfred Scheer*

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Experimental procedures

General considerations

All manipulations were carried out using standard Schlenk techniques at a Stock apparatus under N₂ as an inert gas or in a glove box with Ar atmosphere. All glassware was dried with a heat gun (600 °C) for at least 1 h prior to use. α-DFB was distilled from P₂O₅, CD₂Cl₂ was distilled from CaH₂ and other solvents were directly taken from an MBraun SPS-800 solvent purification system and degassed at room temperature. Solution ¹H (400.130 MHz), ¹²C (100.627 MHz), ¹³F (376.498 MHz), ²⁹Si (79.485 MHz) and ³¹P (161.976 MHz) NMR spectra were recorded at an Avance400 (Bruker) spectrometer using (H₂)₄Si (¹H, ¹³C, ²⁹Si), CFCl₃ (¹³F) or 85% phosphoric acid (³¹P), respectively, as external standards. Chemical shifts (Δ) are provided in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). Chemical shifts and coupling constants for all ³¹P(¹H) and ³¹P NMR spectra were derived from spectral simulation using the built-in simulation package of TopSpin4.0. The following abbreviations are used: s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, t = triplet, td = triplet of doublets br = broad and m = multiplet. ESI mass spectra were recorded at the internal mass spectrometry department using a ThermoQuest Finnigan TSQ 7000 mass spectrometer and peak assignment was performed using the Molecular weight calculator 6.50.¹¹ Elemental analysis of the products was conducted by the elemental analysis department at the University of Regensburg using an Elementar Vario EL. The starting materials Cp*Fe(η⁵-P₅) (1),¹² [(Et₃Si)₅(μ-H)][B(C₆F₅)₄] [³] and B(C₆F₅)₃ [⁴] were synthesized following literature procedures. All other chemicals were purchased from commercial vendors.

Synthesis

[Cp*Fe(η⁵-P₅SiEt₃)][B(C₆F₅)₄] (2)

Addition of a colourless solution of [(Et₃Si)₅(μ-H)][B(C₆F₅)₄] [³] (156 mg, 0.171 mmol, 1 eq.) in 3 mL of α-DFB (1,2-difluorobenzene, C₆H₅F₂) to a green solution of [Cp*Fe(η⁵-P₅)] [²] (59 mg, 0.171 mmol, 1 eq.) in 3 mL of α-DFB at room temperature immediately resulted in a greenish brown reaction solution. After stirring this solution for 1 h 30 mL of n-pentane were added under vigorous stirring, which resulted in the precipitation of [Cp*Fe(η⁵-P₅SiEt₃)][B(C₆F₅)₄] (2) as a light greenish brown powder. 2 was washed two times with 20 mL of n-pentane each, then dried under reduced pressure (10⁻³ mbar) and isolated as a light greenish brown powder (134 mg, 0.12 mmol, 71%). Crystallisation from a solution in α-DFB (2 mL) which was layered with n-hexane (18 mL) leads to the formation of dark green crystals of 2 as large plates.

Yield: 134 mg (0.12 mmol, 71%)

Elemental Analysis: calc. (%) for [Cp*Fe(η⁵-P₅SiEt₃)][B(C₆F₅)₄] (C₄₀H₃₀BF₂₀Si₃P₃Fe): C: 42.13 H: 2.65

ESI (+) MS (α-DFB): m/z (%) = 346.9 (55%) [Cp*Fe(η⁵-P₅H)]⁺, 345.9 (40%) [Cp*Fe(η⁵-P₅)]⁺, 156.1 (100%) [Et₃Si(MeCN)]⁻, 115.1 (13%) [Et₃Si⁺ (acetonitrile arises from the cleansing solution of the mass spectrometer)

NMR (r. t., α-DFB): ¹H ppm = 1.13 (t, ³JHH = 7.6 Hz, 9 H, Si(CH₂CH₃)₃), 1.25 (q, ³JHH = 7.6 Hz, 6 H, Si(CH₂CH₃)₃), 1.32 (br, 15 H, Cp⁺)
Yield: 38 mg (0.037 mmol, 74 %)

Elemental Analysis: calc. (%) for [Cp*Fe(η^5-P₃H)]|B(C₆F₅)₄| (C₄H₁₆BF₂₀P₃Fe): C: 39.80 H: 1.57

found (%): C: 40.28 H: 1.72

ESI(+) MS (o-DFB):

NMR (t. t., CD₂Cl₂):

| Compound | δ ppm (J) |
|----------|-----------|
| 1H | 1.55 (s, 15 H, Cp*) |

NMR (-30°C, CD₂Cl₂):

| Compound | δ ppm (J) |
|----------|-----------|
| 1H | 1.53 (s, 15 H, Cp*) |

NMR (30°C, o-DFB):

| Compound | δ ppm (J) |
|----------|-----------|
| 1H | 1.00 (t, J₉-H = 7.8 Hz, 9 H, Si(CH₂CH₃)₃), 1.08 (q, J₉-H = 7.8 Hz, 6 H, Si(CH₂CH₃)₃), 1.18 (s, 15 H, Cp*) |

[19F][1H] δ ppm = -167.67 (t, 3J₁-F = 20 Hz, 8 F, m-C₆F₅), -163.90 (t, 3J₁-F = 18 Hz, 4 F, p-C₆F₅), -132.55 (br, 8 F, o-C₆F₅)

[31P][1H] δ ppm = 87.6 (br), 102.7 (br), 149.8 (br)

[19F][1H] δ ppm = -167.30 (t, 3J₁-F = 18 Hz, 8 F, m-C₆F₅), -163.50 (t, 3J₁-F = 18 Hz, 4 F, p-C₆F₅), -132.80 (br, 8 F, o-C₆F₅)

[31P][1H] δ ppm = -60.9 (br), 112.6 (br), 179.6 (br)

[23Si][1H] δ ppm = 42 (d, J₉-Si-P = 60.7 Hz)

[Cp*Fe(η^5-P₃H)][B(C₆F₅)₄] (3)

[Cp*Fe(η^5-P₃SiEt₃)][B(C₆F₅)₄] (2, 114 mg, 0.1 mmol, 1 eq.) was dissolved in 4 mL of o-DFB and H₂O (1 μL, 0.05 mmol, 0.5 eq.) was added with a syringe. The resulting mixture was stirred for 1 h, upon which a gradual colour change from brownish green to clear red could be observed. 20 mL of n-pentane were added to precipitate a brownish red powder, which was then washed three times with 10 mL of n-pentane each. After drying under reduced pressure (10⁻³ mbar) [Cp*Fe(η^5-P₃H)][B(C₆F₅)₄] (3) could be isolated as a pale brownish red powder. Recrystallisation of 3 from o-DFB (4 mL) solution layered with n-hexane (32 mL) gave after 5 days large red blocks, suitable for single crystals X-ray analysis.
[Cp*Fe(η⁵-P₅Me)][FB(C₆F₅)₃]-[HFB(C₆F₅)₃]_{0.5} (4a)

Cp*Fe(η⁵-P₅) (1, 70 mg, 0.2 mmol, 1 eq.) and [Me₂O][BF₄] (30 mg, 0.2 mmol, 1 eq.) were weighed into a Schlenk flask and 6 mL of o-DFB was added ([Me₂O][BF₄] does not dissolve). Then a solution of B(C₆F₅)₃ [H] (102 mg, 0.2 mmol, 1 eq.) in 2 mL of o-DFB was added. Upon stirring the resulting mixture for 3 h a gradual colour change from clear green to brownish red could be observed (after 2 hours there was no solid [Me₂O][BF₄] left in the flask). 30 mL of n-pentane were added to precipitate a brownish red oil, which was washed three times with 20 mL of n-pentane each. Recrystallisation from o-DFB (5 mL) solution by layering with n-pentane (20 mL) gave after two weeks [Cp*Fe(η⁵-P₅Me)][FB(C₆F₅)₃] (4a) as brownish red stick-shaped crystals.

Yield: 147 mg (0.127 mmol, 64%)

Elemental Analysis: 39.42 H: 1.61

calc. (%) for [Cp*Fe(η⁵-P₅Me)][FB(C₆F₅)₃]-[H][FB(C₆F₅)₃]_{0.5} (C₃H₁₈.₅B₁.₅F₂₂FeP₅): C: found (%): C: 39.16 H: 1.79

ESI(+) MS: m/z (%) = 360.9 (100%) [Cp*Fe(η⁵-P₅Me)]⁺, 377.9 (25%) [Cp*Fe(η⁵-P₅Me)+OH]⁺, 326.2 (60%) unidentified species

ESI(-) MS: m/z (%) = 531.0 (90%) [FB(C₆F₅)₃]⁻, 1100.9 (35%) ([FB(C₆F₅)₃]₂[H₂F](H₂O))⁻, 1080.0 (100%) ([FB(C₆F₅)₃]₃[H(O)]⁻, 1059.0 (20%) [FB(C₆F₅)₃]⁺O⁻.

NMR (r. t., CD₂Cl₂): ¹H δ ppm = 1.69 (s, 15 H, Cp⁺), 2.68 (dt, 2Jₘ-P₅ = 11.2 Hz 2Jₘ-P₅X = 3.8 Hz, 3 H, P₅CH₃)

¹¹B(¹H) δ ppm = -0.1 (br, [FB(C₆F₅)₃]⁻)

¹³C(¹H) δ ppm = 1.8 (dt, ¹Jₘ-P = 15.9 Hz, ²Jₘ-P = 4.5 Hz, P₅CH₃), 11.1 (s, C₅(CH₂)₃), 97.8 (s, C₅(CH₂)₃), 117.3 (br, [H][FB(C₆F₅)₃]_{penta}), 122.6 (br, [FB(C₆F₅)₃]_{penta}), 137.1 (br, [FB(C₆F₅)₃]_{meta}), 140.0 (br, [FB(C₆F₅)₃]_{ortho}), 141.2 (br, [H][FB(C₆F₅)₃]_{para}), 148.2 (br, [FB(C₆F₅)₃]_{para}). The determination of coupling constants for the [FB(C₆F₅)₃]⁻ anion is hampered by strong overlap and broadening of the signals.

¹⁹F δ ppm = -184.25 (br, 1.5F, [FB(C₆F₅)₃]⁻[H][FB(C₆F₅)₃]), -166.32 (m, 6 F, [FB(C₆F₅)₃]_{meta}), -164.67 (m, 3 F, [H][FB(C₆F₅)₃]_{meta}), -161.46 (t, 3F-F = 20.1 Hz, 3 F, [FB(C₆F₅)₃]_{para}), -157.91 (m, 1.5 F, [H][FB(C₆F₅)₃]_{para}) -135.62 (m, 6, 6 F, [FB(C₆F₅)₃]_{ortho}, -135.34 (m, 3 F, [H][FB(C₆F₅)₃]_{ortho})
SUPPORTING INFORMATION

$^{31}$P[1H] δ ppm = 78.74 (m, $\delta_{J_{FB-PB}} = 607.74$ Hz, $\delta_{J_{FP-PA}} = 605.96$ Hz, $\delta_{J_{FP-PA}} = 462.34$ Hz, $\delta_{J_{FP-PA}} = 448.15$ Hz, $\delta_{J_{FP-PA}} = -61.40$ Hz, $\delta_{J_{FP-PA}} = -48.99$ Hz, $\delta_{J_{FP-PA}} = 42.11$ Hz, $\delta_{J_{FB-PX}} = 607.74$ Hz, $\delta_{J_{FB-PX}} = 605.96$ Hz, $\delta_{J_{FB-PX}} = 11.82$ Hz, $\delta_{J_{FB-PX}} = 9.42$ Hz, $\delta_{J_{FB-PX}} = 448.15$ Hz, $\delta_{J_{FB-PX}} = 448.15$ Hz, $\delta_{J_{FB-PX}} = 9.42$ Hz, 2P, P$^{\alpha\alpha}$)

$^{31}$P δ ppm = 78.73 (m, $\delta_{J_{FB-PB}} = 607.66$ Hz, $\delta_{J_{FP-PA}} = 606.05$ Hz, $\delta_{J_{FP-PA}} = 461.98$ Hz, $\delta_{J_{FP-PA}} = 448.49$ Hz, $\delta_{J_{FP-PA}} = -60.90$ Hz, $\delta_{J_{FP-PA}} = -49.45$ Hz, $\delta_{J_{FP-PA}} = 42.11$ Hz, $\delta_{J_{FP-PA}} = 3.59$ Hz, $\delta_{J_{FP-PA}} = 2.87$ Hz, 2P, P$^{\alpha\alpha}$), 111.79 (m, $\delta_{J_{FB-PX}} = 607.66$ Hz, $\delta_{J_{FB-PX}} = 606.05$ Hz, $\delta_{J_{FB-PX}} = 10.72$ Hz, $\delta_{J_{FB-PX}} = 10.47$ Hz, $\delta_{J_{FB-PX}} = 11.33$ Hz, 1P, P$^{\beta}$), 114.24 (m, $\delta_{J_{FB-PX}} = 466.34$ Hz, $\delta_{J_{FB-PX}} = 448.15$ Hz, $\delta_{J_{FB-PX}} = 405.90$ Hz, $\delta_{J_{FB-PX}} = 9.42$ Hz, 2P, P$^{\alpha\alpha}$)

$[\text{Cp}^*\text{Fe}(\eta^5-P_5\text{Me})][\text{B(C_6F_5)}_4]$ (4b)

Cp*Fe(η$^5$-P$^5$-Me) (1, 70 mg, 0.2 mmol, 1 eq.) was weighed into a Schlenk flask and 4 mL of α-DFB and MeOTf (22 μL, 0.2 mmol, 1 eq.) were added. After stirring the solution for 1 h a solution of [(Li(OEt)$_2$)][B(C$_6$F$_5$)$_4$] (167 mg, 0.2 mmol, 1 eq.) in 2 mL of α-DFB was added. Upon stirring the resulting mixture for 3 h a gradual colour change from clear green to brownish red could be observed and the solution was then stirred for another 15 h. Then, 30 mL of n-pentane were added to precipitate a brownish red solid, which was washed three times with 10 mL of n-pentane each. 2 mL of CH$_2$Cl$_2$ were added and the resulting red solution was filtered from the forms white precipitate (LiOTf). Layering this red solution with 16 mL of n-pentane and storing it at room temperature afforded [Cp*Fe(η$^5$-P$^5$-Me)][B(C$_6$F$_5$)$_4$] (4b) as brownish red block shaped crystals after one day.

Yield: 135 mg (0.13 mmol, 65%)

Elemental Analysis: calc. (%) for [Cp*Fe(η$^5$-P$^5$-Me)][B(C$_6$F$_5$)$_4$] (C$_{35}$H$_{18}$BF$_{20}$P$_5$Fe): C: 40.42 H: 1.74

found (%): C: 40.97 H: 1.92

ESI(+): m/z (%) = 360.9 (20%) [Cp*Fe(η$^5$-P$^5$-Me)]$^+$, 474.0 (80%) unidentified species, 326.2 (30%) unidentified species, 187.2 (100%) unidentified species

ESI(-): m/z (%) = 679.0 (100%) [B(C$_6$F$_5$)$_4$]$^-$

NMR (r. t., CD$_2$Cl$_2$):

$^1$H δ ppm = 1.69 (s, 15 H, Cp$^*$), 2.68 (dt, $^2$J$_{H-H}$ = 11.2 Hz $^3$J$_{H-H}$ = 3.8 Hz, 3 H, P$_5$CH$_3$)

$^{11}$B[1H] δ ppm = -16.9 (s, [B(C$_6$F$_5$)$_4$]$^-$)

$^{13}$C[1H] δ ppm = 1.8 (dt, $^1$J$_{C-P}$ = 15.9 Hz, $^2$J$_{C-P}$ = 4.5 Hz, P$_5$CH$_3$), 11.1 (s, C$_5$(CH$_3$)$_5$), 97.8 (s, C$_5$(CH$_3$)$_5$), 123.7 (br, gem-C$_5$(CH$_3$)$_5$), 136.3 (dm, $^1$J$_{C-F}$ = 274 Hz, o-C$_6$F$_5$), 138.2 (dm, $^1$J$_{C-F}$ = 245 Hz, p-C$_6$F$_5$), 148.2 (dm, $^1$J$_{C-F}$ = 243 Hz, m-C$_6$F$_5$)

$^{19}$F δ ppm = -167.11 (t, $^3$J$_{F-F}$ = 19 Hz, 8 F, m-C$_6$F$_5$), -163.26 (t, $^3$J$_{F-F}$ = 19 Hz, 4 F, p-C$_6$F$_5$), -132.74 (br, 8 F, o-C$_6$F$_5$)

$^{31}$P[1H] δ ppm = 78.74 (m, $\delta_{J_{FB-PB}} = 607.74$ Hz, $\delta_{J_{FB-PB}} = 605.96$ Hz, $\delta_{J_{FP-PA}} = 462.34$ Hz, $\delta_{J_{FP-PA}} = 448.15$ Hz, $\delta_{J_{FP-PA}} = -61.40$ Hz, $\delta_{J_{FP-PA}} = -48.99$ Hz, $\delta_{J_{FP-PA}} = 42.11$ Hz, $\delta_{J_{FB-PX}} = 607.74$ Hz, $\delta_{J_{FB-PX}} = 605.96$ Hz, $\delta_{J_{FB-PX}} = 11.82$ Hz, $\delta_{J_{FB-PX}} = 9.42$ Hz, $\delta_{J_{FB-PX}} = 448.15$ Hz, $\delta_{J_{FB-PX}} = 448.15$ Hz, $\delta_{J_{FB-PX}} = 9.42$ Hz, 2P, P$^{\alpha\alpha}$)

$^{31}$P δ ppm = 78.73 (m, $\delta_{J_{FB-PB}} = 607.66$ Hz, $\delta_{J_{FB-PB}} = 605.05$ Hz, $\delta_{J_{FP-PA}} = 461.98$ Hz, $\delta_{J_{FP-PA}} = 448.49$ Hz, $\delta_{J_{FP-PA}} = -60.90$ Hz, $\delta_{J_{FP-PA}} = -49.45$ Hz, $\delta_{J_{FP-PA}} = 42.11$ Hz,
NMR spectroscopic investigations

\([\text{Cp}^*\text{Fe}(&\eta^5-\text{P}_5\text{SiEt}_3))][\text{B}(\text{C}_6\text{F}_5)_4]\) (2)

\([\text{Cp}^*\text{Fe}(&\eta^5-\text{P}_5\text{SiEt}_3))][\text{B}(\text{C}_6\text{F}_5)_4]\) (2) is highly unstable towards hydrolysis and reacts even with traces of water left on the surface of meticulously dried glassware (heated to 600 °C at 10⁻³ mbar for 3 h and then stored in a glove box for 7 days). Thus, exposing isolated 2 to fresh glassware/solvents usually leads to partial decomposition. As 2 shows highly dynamic behaviour in solution at room temperature, we carried out a VT NMR study (Figure S 1) of this compound by preparing it in the NMR tube itself. However, the stoichiometry of the reaction could not be accurately controlled under these circumstances and there was residual 1 left in the reaction mixture, which can be clearly seen in the \(^{31}P\{^1\text{H}\}\) NMR spectra (Figure S 1).

When a crystalline sample of 2 is dissolved in \(\alpha\)-DFB in a NMR tube and then subjected to NMR spectroscopic analysis, the respective \(^{31}P\{^1\text{H}\}\) NMR spectrum (at –30 ºC) reveals small signs of degradation (Figure S 2), but obviously there is no 1 left in the sample. While these degradation products may imply the impurity of 2, elemental analysis (\textit{vide supra}) confirmed the purity of 2. Simulation of this spectrum allowed the determination of the coupling constants (Table S 1) within the cyclo-P₅SiEt₃ ligand in 2. In accordance with the observed signal in the \(^{29}\text{Si}\{^1\text{H}\}\) NMR spectrum (Figure S 3, \(^{1}J_{PM-Si} = 60\) Hz), simulation of the \(^{29}\text{Si}\) satellites in the \(^{31}P\{^1\text{H}\}\) NMR spectrum yields a \(^{1}J_{PM-Si}\) coupling constant of 62.1 Hz.
**Figure S 2**: Experimental (top) and simulated (bottom) $^{31}$P-$^1$H NMR spectrum of isolated 2 in o-DFB at 243 K and assignment of the spin system (left); * = 3, which is formed due to the slightest traces of H$_2$O in the NMR tube. * = unidentified side product.

**Table S 1**: Spectral parameters of the $^{31}$P-$^1$H NMR spectrum of 2 in o-DFB (toluene-$d_8$ capillary) recorded at 243 K extracted from spectral simulation.

| $J$ / Hz | $\delta$ / ppm |
|---------|-----------------|
| $^1J_{PA'/PA}$ | 435.2/421.92 | $\delta_{PA'/PA}$ | 146.28 |
| $^1J_{PM-PX'/X}$ | 558.5/557.9 | $\delta_{PM}$ | 101.69 |
| $^1J_{PA-PA'}$ | 415.1 | $\delta_{PA'}$ | 84.31 |
| $^2J_{PA'-PA}$ | $-54.9/-46.3$ | $\delta_{PA}$ | 62.1 |
| $^2J_{PM-PX}$ | 14.1/10.9 | $\delta_{PM}$ | 22.2 |
| $^2J_{PX-PX'}$ | 62.1 | $\delta_{PX'}$ | 16.6 |
Figure S3: $^{29}$Si($^1$H) NMR spectra of 2 in o-DFB recorded at different temperatures; The spectrum at 243 K was collected with 2000, the one at 253 K with 4000 scans.
Similarly to 2, \([\text{Cp}^*\text{Fe(}\eta^5-\text{P}_5\text{H})][\text{B(C}_6\text{F}_5)_4]\) (3) is highly moisture sensitive and easily reacts with traces of moisture left on the surface of glass ware. Thus, small impurities of 1 and an unidentified product, already formed during hydrolysis of 2, can be detected in the NMR spectra of isolated 3. 2 also expresses significant dynamic behaviour in \(\text{CD}_2\text{Cl}_2\) solution at room temperature as seen from the respective \(^{31}\text{P}\) NMR spectra. VT \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopic investigations (Figure S 4) however show that this dynamic behaviour is not expressed at lower temperatures and at \(-80\, ^\circ\text{C}\) a well resolved spectrum is observed (Figure S 5). Spectral simulation of the latter revealed the coupling constants (Table S 2) within the cyclo-P\(_5\)H ligand and the additional coupling (Table S 3) to the proton of this ligand can be observed in the respective \(^{31}\text{P}\) NMR spectrum (Figure S 6). Accordingly, the \(^1\text{H}\) NMR spectrum of 3 in \(\text{CD}_2\text{Cl}_2\) recorded at room temperature only shows a broad resonance for the cyclo-P\(_5\)H ligand but at \(-80\, ^\circ\text{C}\) a well resolved doublet can be observed (Figure S 7). As both, the \(^{11}\text{B}\) and \(^{19}\text{F}\) NMR spectra (at r. t.) of 3 do not show similar signs of dynamic effects, we do not attribute this behaviour to exchange of the proton between 1 and the \([\text{B(C}_6\text{F}_5)_4]\)– anion. Furthermore, we observed the formation of small quantities of 3 in other reactions involving the electrophilic functionalisation of 1 as well, and the respective \(^{31}\text{P}\) NMR spectra are already well resolved at room temperature. It has to be noted that in these cases no traces of free 1 are detected in the \(^1\text{H}\) or \(^{31}\text{P}\) NMR spectra. Thus, we attribute the highly dynamic behaviour of isolated 3 to the small quantities of 1, which are formed upon exposure to fresh glass ware (when dissolved in the NMR tube). This dynamic process can then be understood as a constant “bond-braking/bond-forming” mechanism and based upon the above we exclude a mechanism, in which the proton would migrate around a single molecule of 1.

**Figure S 4:** \(^{31}\text{P}\{^1\text{H}\}\) VT NMR spectra of 3 in \(\text{CD}_2\text{Cl}_2\). The spin system is labelled according to the Scheme in Figure S 5, * = residual 1, which is probably formed due to slight traces of moisture on the NMR tube and • = trace impurities of an unidentified side product.
Figure S 5: Experimental (top) and simulated (bottom) $^{31}$P$[^1]$H) NMR spectrum of 3 in CD$_2$Cl$_2$ at 193 K and assignment of the spin system (right); * = residual 1 and • = trace impurities of an unidentified side product.

Table S 2: Spectral parameters of the $^{31}$P$[^1]$H) NMR spectrum of 3 in CD$_2$Cl$_2$ recorded at 193 K extracted from spectral simulation.

| $J$/ Hz | $\delta$/ ppm |
|--------|---------------|
| $^1$J$_{PA'/PM'/M}$ | 436.76/427.80 | $^1$J$_{PA'/PM'/M}$ | 183.95 |
| $^1$J$_{PA'/PX}$ | 517.37/516.60 | $^1$J$_{PA'/PM'/M}$ | 107.75 |
| $^3$J$_{PM/PM'}$ | 416.61 | $^2$J$_{PM'/PM}$ | 107.75 |
| $^2$J$_{PA'/PM'/M}$ | $^2$J$_{PA'/PM'/M}$ | $^2$J$_{PA'/PM'/M}$ | $^2$J$_{PA'/PM'/M}$ |
| $^2$J$_{PM'/PX}$ | 5.67/3.19 | $^2$J$_{PM'/PX}$ | $^2$J$_{PM'/PX}$ |
| $^2$J$_{PA'/A'}$ | 18.16 | $^2$J$_{PA'/A'}$ | 18.16 |
| R-factor (%) | 9.9 |
Figure S 6: Experimental (top) and simulated (bottom) $^{31}$P NMR spectrum of 3 in CD$_2$Cl$_2$ at 193 K and assignment of the spin system (right); * = residual 1 and • = trace impurities of an unidentified side product.

Table S 3: Spectral parameters of the $^{31}$P NMR spectrum of 3 in CD$_2$Cl$_2$ recorded at 193 K extracted from spectral simulation.

| $J$/ Hz | $\delta$/ ppm |
|---------|---------------|
| $^{1}J_{PA/A'/PM/M'}$ | 436.75/428.24 | $^{pA/A'}$ | 183.96 |
| $^{1}J_{PA/A'-PX}$ | 516.99/516.94 | $^{pM'/M'}$ | 107.67 |
| $^{1}J_{PM/M'-PM}$ | 416.91 | $^{pX}$ | -64.14 |
| $^{2}J_{PA/A'/PM'/M}$ | $-63.45/-52.76$ | | |
| $^{2}J_{PM/M'-PX}$ | 5.32/4.20 | | |
| $^{2}J_{PA-X}$ | 18.53 | | |
| $^{1}J_{PX-H}$ | 315.82 | | |

R-factor (%) | 1.2
Figure S7: $^1$H VT NMR spectrum of 3 in CD$_2$Cl$_2$. * = residual 1, Cp* is the signal arising from the Cp* ligand in 3 and • = residual CH$_2$Cl$_2$. 
In contrast to 2 and 3, [Cp*Fe(η⁵-P₅Me)][X] (4a/b) do not show signs of dynamic behaviour in CD₂Cl₂ at room temperature. Thus, the corresponding NMR spectra can easily be obtained (depicted are only the ones for 4a, as those obtained for 4b are similar) and show the expected signals for the cation 4⁺ in the ¹H (Figure S 10), ¹³C{¹H} (Figure S 11), ³¹P (Figure S 9) and ³¹P{¹H} (Figure S 8) NMR spectra. The coupling constants within the cyclo-P₅Me ligand could be obtained by simulation (Table S 4 and S 5) of the ³¹P and ³¹P{¹H} NMR spectra and extracted from the ¹H and ¹³C{¹H} NMR spectra. The ¹⁹F and ¹⁹F{¹H} and ¹¹B NMR spectra of 4a reveal two sets of signals for species containing the B(C₆F₅)₃ moiety, of which one can clearly be attributed to the [FB(C₆F₅)₃]⁻ anion. In accordance with the solid state structure of 4a and the obtained ESI(-) mass spectra, we attribute the second set of signals to B(C₆F₅)₃•HF. The respective ¹⁹F and ¹¹B NMR spectra of 4b reveal the sole presence of the [B(C₆F₅)₄]⁻ anion, which is in agreement with the solid state structure of this compound and the respective mass spectra and elemental analysis.

Figure S 8: Experimental (top) and simulated (bottom) ³¹P{¹H} NMR spectrum of 4a in CD₂Cl₂ at r. t. and assignment of the spin system (left).

Table S 4: Spectral parameters of the ³¹P{¹H} NMR spectrum of 4a in CD₂Cl₂ recorded at r. t. extracted from spectral simulation.

| J/ Hz       | δ/ ppm |
|-------------|--------|
| ¹J_PA/P%',PX/X' | 462.34/448.15 | pA'/X' | 114.24 |
| ¹J_PB-PX/X'   | 607.74/605.96  | pB     | 111.79 |
| ¹J_PA-PX'     | 405.82      | pX/X'  | 78.74  |
| ²J_PA/P%',PX/X | −61.40/−48.99 |        |        |
| ²J_PA/P%'PB   | 11.82/9.42  |        |        |
| ²J_PX/X'      | 42.11      |        |        |
| R-factor (%)  | 2.9       |        |        |
Figure S 9: Experimental (top) and simulated (bottom) $^{31}$P NMR spectrum of 4a in CD$_2$Cl$_2$ at r. t. and assignment of the spin system (left).

Table S 5: Spectral parameters of the $^{31}$P NMR spectrum of 4a in CD$_2$Cl$_2$ recorded at r.t. extracted from spectral simulation.

| $J$/ Hz       | $\delta$/ ppm |
|---------------|---------------|
| $^{1}J_{PA/A'-PX/X}$ | 461.98/448.49 | $^{p^{A/A'}}$ 114.23 |
| $^{1}J_{PB-PX/X'}$ | 607.66/606.05 | $^{p^B}$ 111.79 |
| $^{1}J_{PA-PA'}$ | 405.90        | $^{p^{X/X'}}$ 78.73 |
| $^{2}J_{PA/A'-PX/X}$ | $-60.90/-49.45$ |
| $^{2}J_{PA/A'-PB}$ | 10.72/10.47   |
| $^{2}J_{PX/X'}$ | 42.11         |
| $^{2}J_{PB-H(Me)}$ | 11.33         |
| $^{3}J_{PX/X'-H(Me)}$ | 3.59/2.87     |
| R-factor (%)   | 1.4           |
**Figure S 10:** $^1$H NMR spectrum of 4a in CD$_2$Cl$_2$ at r.t.; “Cp*” and “Me” mark the signals for the respective protons in 4 and * is the signal from residual CH$_2$Cl$_2$.

**Figure S 11:** $^{13}$C($^1$H) NMR spectrum of 4a in CD$_2$Cl$_2$ at r.t.; “Cp*” and “Me” mark the signals for the respective protons in 4. • marks the signals for the [FB(C$_6$F$_5$)$_3$] anion and H[FB(C$_6$F$_5$)$_3$] and * is the solvent residual signal.
Additional NMR spectroscopic investigations

MeOH quenching

In search of milder quenching reagents for 2 to form 3, we thought MeOH would be a suitable substrate. Adding MeOH (0.1 mmol, 4 μL, 1 eq.) to a solution of 2 (0.1 mmol, 114 mg, 1 eq.) in o-DFB (4 mL) leads to the desired colour change to red within seconds. The solvent was then removed under reduced pressure and the red residue dissolved in 1 mL of CD$_2$Cl$_2$. Subjecting this sample to low temperature (−80 °C) NMR spectroscopic studies (Figure S 12) revealed the presence of both, 3$^+$ and 4$^+$ in solution. As this product mixture could however not be separated, MeOH seems unsuitable for preparing salts of either 3$^+$ or 4$^+$, respectively.

Figure S 12: $^{31}$P NMR spectrum of the reaction solution of 2 and MeOH in CD$_2$Cl$_2$ recorded at 193 K, which indicates the formation of two species, namely 3 and 4 (assignment according to colour scheme).
Rigaku on and absorption correction were performed with the CrysAlisPro software. Structure solution and refinement was conducted in Olex2 (1.3 release) with ShelXT(7) (solution) and ShelXL-2014(8) (least squares refinement (F2)) or olex2.refine (Gauss-Newton). All non-H atoms were refined with anisotropic displacement parameters and H atoms were treated as riding models with isotropic displacement parameters.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for 2, 3, 4a and 4b are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-2022440, CCDC-2022441, CCDC-2022442 and CCDC-2022443, respectively.

Table S 6: X-ray crystallographic data on all crystallographically characterised compounds.

| Compound | 2[B(C6F5)4] | 3[B(C6F5)4] | 4a | 4b |
|----------|-------------|-------------|----|----|
| Empirical formula | CuH3BF6Fe3PfSi | CuH3BF6Fe3PfFe | CuH3BF6Fe3PfFeP4 | CuH3BF6Fe3PfFe |
| Formula weight | 1140.24 | 1025.98 | 9258.95 | 1040.00 |
| Temperature/K | 123(2) | 123.00(10) | 89.9(4) | 123(2) |
| Crystal system | monoclinic | triclinic | monoclinic | triclinic |
| Space group | a/A | P21 | Cc | Pt |
| a/A | 17.8234(4) | 10.3611(2) | 24.7070(2) | 10.4794(3) |
| b/A | 18.3720(4) | 12.6558(2) | 29.0546(2) | 12.6253(4) |
| c/A | 28.7731(7) | 14.0360(3) | 47.1012(3) | 14.3041(4) |
| α/° | 90 | 94.696(2) | 90 | 85.003(2) |
| β/° | 106.895(3) | 90.099(2) | 93.720(10) | 88.481(2) |
| γ/° | 109 | 98.632(2) | 90 | 83.202(2) |
| Volume/Å³ | 9017.34(4) | 1813.41(6) | 3373.7(4) | 1871.81(10) |
| Z | 8 | 2 | 4 | 2 |
| μ/mm⁻¹ | 1.680 | 1.879 | 1.823 | 1.845 |
| F(000) | 653 | 4.964 | 5.957 | 6.471 |
| Crystal size/mm³ | 4560.0 | 1012.0 | 18255.0 | 1028.0 |
| Radiation | CuKα (λ = 1.7073) | CuKβ (λ = 1.39222) | CuKα (λ = 1.54184) | CuKα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.816 to 58.202 | 5.706 to 148.828 | 7.154 to 148.394 | 7.076 to 144.032 |
| Index ranges | -24 ≤ h ≤ 16, -21 ≤ k ≤ 23, -38 ≤ l ≤ 37 | -14 ≤ h ≤ 14, -17 ≤ k ≤ 16, -19 ≤ l ≤ 19 | -30 ≤ h ≤ 29, -36 ≤ k ≤ 36, -58 ≤ l ≤ 55 | -12 ≤ h ≤ 9, -15 ≤ k ≤ 14, -16 ≤ l ≤ 17 |
| Reflections collected | 17646 | 28663 | 142942 | 20735 |
| Independent reflections | 10205 [Rint = 0.0032, Rrestr = 0.0044] | 9759 [Rint = 0.0029, Rrestr = 0.0027] | 53933 [Rint = 0.0035, Rrestr = 0.0029] | 7190 [Rint = 0.0039, Rrestr = 0.0036] |
| Data/restraints/parameters | 10205/0/621 | 9759/0/559 | 53933/1050/5338 | 7190/0/603 |
| Goodness-of-fit on F² | 1.050 | 1.039 | 1.051 | 1.021 |
| Final R indexes | R1 = 0.0429, wR2 = 0.0835 | R1 = 0.0340, wR2 = 0.0913 | R1 = 0.0578, wR2 = 0.1553 | R1 = 0.0406, wR2 = 0.1098 |
| Final R indexes [all data] | R1 = 0.0590, wR2 = 0.0897 | R1 = 0.0354, wR2 = 0.0926 | R1 = 0.0632, wR2 = 0.1621 | R1 = 0.0424, wR2 = 0.1116 |
| Largest diff. peak/hole / e Å³ | 0.46/-0.35 | 0.56/-0.53 | 1.26/-0.45 | 0.55/-0.49 |
Large green prism shaped crystals of [Cp*Fe(η⁵-P₅SiEt₃)][B(C₆F₅)₄] (2) are obtained by layering a concentrated solution in o-DFB with n-hexane (1:7) and storing it at room temperature for two weeks. 2 crystallises in the monoclinic space group I2/a with one cation and one anion in the asymmetric unit (Figure S 13).

**Figure S 13:** Solid state structure of 2; Depicted is the asymmetric unit and ADPs (anisotropic displacement parameters) are drawn at 50% probability; Selected bond lengths and angles: d(P1-P2) = 2.1062(9) Å, d(P2-P3) = 2.1177(9) Å, d(P3-P4) = 2.1216(10) Å, d(P4-P5) = 2.1145(9) Å, d(P1-P5) = 2.0993(9) Å, d(P1-Fe) = 2.3010(7) Å, d(P2-Fe) = 2.3947(7) Å, d(P3-Fe) = 2.3852(7) Å, d(P4-Fe) = 2.3855(7) Å, d(P5-Fe) = 2.3979(7) Å, d(P1-Si) = 2.3085(9) Å, \( \angle(P1-P2-P3) = 101.70(3) ^\circ \), \( \angle(P2-P3-P4) = 109.91(4) ^\circ \), \( \angle(P3-P4-P5) = 110.02(4) ^\circ \), \( \angle(P4-P5-P1) = 101.83(4) ^\circ \), \( \angle(P5-P1-P2) = 116.02(4) ^\circ \), \( \angle(Si-P1-P2) = 123.82(4) ^\circ \), \( \angle(Si-P1-P5) = 120.14(4) ^\circ \), \( \angle(Si-P1-Fe) = 140.16(4) ^\circ \), \( \angle(P4-P5-P2-P1) = 172.31(8) ^\circ \), \( \angle(P3-P2-P5-P1) = -172.54(6) ^\circ \).
Large red crystalline blocks of \([\text{Cp}^*\text{Fe(}\eta^5\text{-P}_5\text{H})][\text{B(C}_6\text{F}_5)_4]\) (3) are obtained by layering a concentrated solution in \(\sigma\)-DFB with \(n\)-hexane (1:10) and storing it at \(-30^\circ\text{C}\) for five days. 3 crystallises in the triclinic space group \(P\overline{1}\) with one cation and one anion in the asymmetric unit (Figure S 14).

Figure S 14: Solid state structure of 3; Depicted is the asymmetric unit and ADPs are drawn at 50% probability; Selected bond lengths and angles: d(P1-P2) = 2.1241(6) Å, d(P2-P3) = 2.1179(7) Å, d(P3-P4) = 2.1295(8) Å, d(P4-P5) = 2.1155(7) Å, d(P1-P5) = 2.1242(7) Å, d(P1-Fe) = 2.3729(5) Å, d(P2-Fe) = 2.3076(5) Å, d(P3-Fe) = 2.3903(5) Å, d(P4-Fe) = 2.3926(5) Å, d(P5-Fe) = 2.3067(5) Å, d(P1-H1) = 1.29(3) Å, \(\angle\)(P1-P2-P3) = 99.84(3)\(^\circ\), \(\angle\)(P2-P3-P4) = 110.11(3)\(^\circ\), \(\angle\)(P3-P4-P5) = 109.73(3)\(^\circ\), \(\angle\)(P4-P5-P1) = 100.17(3)\(^\circ\), \(\angle\)(P5-P1-P2) = 114.44(3)\(^\circ\), \(\angle\)(H1-P1-P2) = 108.24(17)\(^\circ\), \(\angle\)(H1-P1-P5) = 112.14(14)\(^\circ\), \(\angle\)(H1-Fe) = 102.24(14)\(^\circ\), \(\delta\)(P2-P5-P1-H1) = -124.5(18)\(^\circ\), \(\delta\)(P4-P2-P5-P1) = -154.77(4)\(^\circ\), \(\delta\)(P3-P5-P2-P1) = 154.62(4)\(^\circ\).
[Cp*Fe(\eta^5-P_5Me)][FB(C_6F_5)_3] \textsuperscript{(4a)} (4a) crystallises as a [H][FB(C_6F_5)_3] solvate from o-DFB solution layered with n-hexane (1:6) after 4 days at room temperature. The obtained dark red to brown block shaped crystals adopt the space group \textit{Cc} with eight formula units and four equivalents of [H][FB(C_6F_5)_3] in the asymmetric unit (Figure S 15). Together with the acid, two equivalents of the anion [FB(C_6F_5)_3]– form a dianionic agglomerate, in which the exact position of the proton could not be determined. Furthermore, several of the cations [Cp*Fe(\eta^5-P_5Me)]\textsuperscript{+} are disordered. The disorder for these cations could however only be resolved for the Fe atoms and the P\textsubscript{5}Me ligand (distance and ADP restraints were applied), but the disorder within the Cp\textsuperscript{*} ligands of these cations could not be resolved. Thus, one of the cations, which was not disordered is discussed regarding its structure.

\textbf{Figure S 15}: Asymmetric unit of \textit{4a} [H][FB(C_6F_5)_3]_{\text{0.5}} with the cation discussed structurally marked in red (left), the respective cation (top right) and one of the dianionic aggregates [H][FB(C_6F_5)_3]_{2\text{–}} (bottom right); ADPs are drawn at the 50 % probability level; Selected bond lengths and angles: d(P1\textendash P2) = 2.108(4) Å, d(P2\textendash P3) = 2.101(4) Å, d(P3\textendash P4) = 2.123(5) Å, d(P4\textendash P5) = 2.084(5) Å, d(P1\textendash P5) = 2.106(4) Å, d(P1\textendash Fe) = 2.306(3) Å, d(P2\textendash Fe) = 2.351(3) Å, d(P3\textendash Fe) = 2.382(3) Å, d(P4\textendash Fe) = 2.364(3) Å, d(P5\textendash Fe) = 2.354 (3) Å, d(P1\textendash C) = 1.799(11) Å, \(\delta(P1\textendash P2\textendash P3) = 100.31(16)^\circ\), \(\delta(P2\textendash P3\textendash P4) = 110.09(19)^\circ\), \(\delta(P3\textendash P4\textendash P5) = 110.70(20)^\circ\), \(\delta(P4\textendash P5\textendash P1) = 100.58(18)^\circ\), \(\delta(P5\textendash P1\textendash P2) = 116.37(18)^\circ\), \(\delta(C\textendash P1\textendash P2) = 121.3(4)^\circ\), \(\delta(C\textendash P1\textendash P5) = 116.5(4)^\circ\), \(\delta(C\textendash P1\textendash P1\textendash Fe) = 122.0(4)^\circ\), \(\delta(P2\textendash P5\textendash P1\textendash C) = -153.6(4)^\circ\), \(\delta(P4\textendash P2\textendash P5\textendash P1) = -165.4(2)^\circ\), \(\delta(P3\textendash P5\textendash P2\textendash P1) = 164.7(2)^\circ\).
[Cp*Fe(η⁵-P₅Me)][B(C₆F₅)₄] (4b) crystallises as dark red blocks from concentrated CH₂Cl₂ solutions, layered with n-pentane (1:10) and stored for one day at room temperature. The formed crystals adopt the triclinic space group P1 with one cation and one anion in the asymmetric unit (Figure S 16). Disorder within the cyclo-P₅Me ligand was refined using distance and ADP constraints and restraints.

![Figure S16: Asymmetric unit of 4b, with only one part of the disordered cation displayed; ADPs are drawn at the 50% probability level; Selected bond lengths and angles: d(P1-P2) = 2.131(9) Å, d(P2-P3) = 2.260(4) Å, d(P3-P4) = 2.110(6) Å, d(P4-P5) = 2.050(5) Å, d(P1-P5) = 2.170(3) Å, d(P1-Fe) = 2.282(7) Å, d(P2-Fe) = 2.291(2) Å, d(P3-Fe) = 2.390(4) Å, d(P4-Fe) = 2.380(4) Å, d(P5-Fe) = 2.350(3) Å, d(P1-C) = 1.750(1) Å, ∠(P1-P2-P3) = 99.80(1)°, ∠(P2-P3-P4) = 108.30(2)°, ∠(P3-P4-P5) = 113.0(2)°, ∠(P4-P5-P1) = 102.9(2)°, ∠(C-P1-P2) = 114.4(8)°, ∠(P1-P2-P1) = 120.3(4)°, ∠(C-P1-P5) = 117.3(9)°, ∠(C-P1-Fe) = 119.2(4)°, ∠(P2-P5-P1-C) = −148.9(9)°, ∠(P4-P2-P5-P1) = −166.0(2)°, ∠(P3-P5-P2-P1) = 164.8(2)°.]

Figure S16: Asymmetric unit of 4b, with only one part of the disordered cation displayed; ADPs are drawn at the 50% probability level; Selected bond lengths and angles: d(P1-P2) = 2.131(9) Å, d(P2-P3) = 2.260(4) Å, d(P3-P4) = 2.110(6) Å, d(P4-P5) = 2.050(5) Å, d(P1-P5) = 2.170(3) Å, d(P1-Fe) = 2.282(7) Å, d(P2-Fe) = 2.291(2) Å, d(P3-Fe) = 2.390(4) Å, d(P4-Fe) = 2.380(4) Å, d(P5-Fe) = 2.350(3) Å, d(P1-C) = 1.750(1) Å, ∠(P1-P2-P3) = 99.80(1)°, ∠(P2-P3-P4) = 108.30(2)°, ∠(P3-P4-P5) = 113.0(2)°, ∠(P4-P5-P1) = 102.9(2)°, ∠(C-P1-P2) = 114.4(8)°, ∠(P1-P2-P1) = 120.3(4)°, ∠(C-P1-P5) = 117.3(9)°, ∠(C-P1-Fe) = 119.2(4)°, ∠(P2-P5-P1-C) = −148.9(9)°, ∠(P4-P2-P5-P1) = −166.0(2)°, ∠(P3-P5-P2-P1) = 164.8(2)°.
General remarks

DFT calculations were performed using the Gaussian09 software package. The geometry optimizations were performed at the B3LYP/def2-TZVP level of theory with PCM solvent correction for CH₂Cl₂. The gas phase energy values for the calculation of proton affinities were obtained on the B3LYP/def2-TZVPD level of theory without solvent correction. Orbital interaction schemes were created using single point calculations at the B3LYP/def2-TZVP level of theory (PCM solvent correction for CH₂Cl₂) and the AOMix program. Magnetic shielding tensors were calculated at the PBE0/aug-pcSseg-2 level of theory (PCM solvent correction for CH₂Cl₂). NICS(0/1/-1)zz values and ring critical points were derived using Multiwfn. The basis sets def2-TZVPD and aug-pcSseg-2 were generated with the help of the open access “basis set exchange” web page.

Proton and methyl cation affinities of 1

As we were experimentally unsuccessful in direct protonation of 1 with acids, such as H[BF₄] in ether or [H(OEt₂)][TEF], we computed the gas phase proton affinities of 1 and Et₂O at the B3LYP/def2-TZVPD level of theory (pre optimized structures at B3LYP/def2-TZVP level of theory). For the latter, we assumed formation of the [H(OEt₂)]+ cation, as it is found in the crystal structure of [H(OEt₂)][TEF]. Proton affinities (PA) were calculated using equation 1. For 1 we calculated a proton affinity of 875.42 kJ/mol, which is 11.31 kJ/mol lower than that found for Et₂O (886.73 kJ/mol), thus yielding a theoretical explanation for our experimental finding that 1 cannot be protonated in the presence of Et₂O.

\[ PA = \Delta E_{\text{el}} + \Delta E_{\text{vib}} + \frac{5}{2}RT \]  (1)

Additionally, we computed the methyl cation affinity of 1 according to Scheme SI 1 at the B3LYP/def2-TZVP level of theory with implicit solvent correction (PCM model for CH₂Cl₂ implemented in Gaussian09). Thus, we calculated a methyl cation affinity of 355.27 kJ/mol for 1.

Scheme S 1: Reaction equation used for calculating the methyl cation affinity of 1.

Reaction energetics for the formation of 2, 3 and 4

The molecular structures of all involved species for the reactions yielding 2, 3 and 4 were optimized at the B3LYP/def2-TZVP level of theory with implicit solvent correction (PCM model for CH₂Cl₂ implemented in Gaussian09). Reaction enthalpies were then extracted by summation across all involved species according to equations 2, 3 and 4.

\[
\begin{align*}
\text{[Cp*Fe(\eta^1-P₅)]} + [(\text{Et}_3\text{Si})(\mu-H)]^- & \rightarrow \text{[Cp*Fe(\eta^1-P₅\text{SiEt}_3)]}^- + \text{Et}_3\text{SiH} & (2) \\
2\text{[Cp*Fe(\eta^1-P₅\text{SiEt}_3)]}^- + \text{H}_2\text{O} & \rightarrow 2\text{[Cp*Fe(\eta^1-P₅\text{H})]^-} + (\text{Et}_3\text{Si})\text{O} & (3) \\
\text{[Cp*Fe(\eta^1-P₅)]} + [\text{Me}_2\text{O}]^- & \rightarrow \text{[Cp*Fe(\eta^1-P₅\text{Me})]^-} + \text{Me}_2\text{O} & (4)
\end{align*}
\]
NBO analysis[24] was performed on the pre-optimized (B3LYP[10]/def2-TZVP[11]), PCM solvent correction for CH₂Cl₂[12] molecular structures of 2, 3 and 4 using the NBO6.0[24] software package and its implementation in Gaussian09[9] (Figure S 17). Wiberg bond indices (WBI) and orbital energies for the respective P1-R (R= SiEt₃ (2), H (3) and Me (4)) bond have also been obtained from these calculations. While the WBIs suggest proper single bonds for 3 (0.92) and 4 (0.97), the one for the P1-Si bond in 2 (0.69) is significantly lower, which may hint towards the dative character of this bond. This is also represented in the orbital contributions for the discussed bonds:
P1-Si (NBO 71) in 2: s(P1) = 27%, p(P1) = 47%, s(Si) = 4%, p(Si) = 22%, overall contribution (P1: 75%, Si: 25%)
P1-H (NBO 57) in 3: s(P1) = 6%, p(P1) = 47%, s(H) = 45%, overall contribution (P1: 54%, H: 46 %)
P1-Me (NBO 60) in 4: s(P1) = 14%, p(P1) = 30%, s(C) = 14%, p(C) = 42%, overall contribution (P1: 44%, C: 56%)

Additional Mulliken population analysis on the optimized structures of 2, 3 and 4 revealed the charge distribution for these compounds. Summation of the partial charges on the \{\text{Cp*Fe(η⁵-P₅)}\} moiety and the respective substituent R (R = SiEt₃ (2), H (3), Me (4)) shows that the charge transfer from the substituent is much less pronounced in 2 than it is in 3 and 4 (Table S 17). This goes in hand with a more polar P–Si bond in 2 and more covalent P–H and P–C bonds in 3 and 4.

**Table S 7:** Summed up Mulliken charges of the \{\text{Cp*Fe(η⁵-P₅)}\} moiety and the respective substituent (R) for the compounds 2, 3 and 4.

| Compound | \{\text{Cp*Fe(η⁵-P₅)}\} | R |
|----------|-------------------------|---|
| 2 (R = SiEt₃) | 0.627 | 0.373 |
| 3 (R = H) | 0.889 | 0.111 |
| 4 (R = Me) | 0.908 | 0.092 |

**Figure S 17:** P1-R bonding NBOs of 2 (R = SiEt₃, left), 3 (R = H, middle) and 4 (R = Me, right), the respective orbital energies and WBIs.
Orbital interaction in 3

The orbital interaction diagram (Figure S 18) for $3^+$ has been created using single point calculations performed at the B3LYP/def2-TZVP level of theory (PCM solvent correction for $\text{CH}_2\text{Cl}_2$) using Gaussian09 and the AOMix program. The geometries of $3^+$ and free cyclo-$\text{P}_5\text{H}$ were optimized at the same level of theory and the fragments $\{\text{Cp}^*\text{Fe}\}^+$ and bent cyclo-$\text{P}_5\text{H}$ were extracted from the optimized structure of $3^+$. As indicated by the schematic representations of the MOs in Figure S 18, the P1 atom (the one the H atom is bonded to) in the bent geometry of cyclo-$\text{P}_5\text{H}$ has strong contributions to the HOMO-1 (37b, the atomic contribution of P1 is $p(P1) = 34\%$), which itself shows strong overlap MOs of the $\{\text{Cp}^*\text{Fe}\}^+$ fragment to form the HOMO-2 (86, $p(P1) < 10\%$) and HOMO-7 (81, $p(P1) = 14\%$) of $3^+$. This strong contribution manifests the cyclo-$\text{P}_5\text{H}$ ligands hapticity in $3^+$ as $\eta^5$. Orbital energies of selected MOs of the $\{\text{Cp}^*\text{Fe}\}^+$ fragment, $3^+$, bent cyclo-$\text{P}_5\text{H}$ and planar cyclo-$\text{P}_5\text{H}$ are provided in Table S 8.

![Figure S 18: Orbital interaction diagram for $3^+$ as parted into the $\{\text{Cp}^*\text{Fe}\}^+$ fragment and the cyclo-$\text{P}_5\text{H}$ ligand (left box) and changes in the molecular orbitals of the cyclo-$\text{P}_5\text{H}$ ligand upon bending into the geometry found in $3^+$.

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SUPPORTING INFORMATION

WILEY-VCH
NICS values for cyclo-P₃H

We calculated the NICS values\(^{[17]}\) for the bent geometry of the cyclo-P₃H ligand found in 3* to assess its aromaticity and compared them with the values obtained for the planar geometry of hypothetical free cyclo-P₃H and two geometries of [cyclo-P₅]⁻ for which a highly aromatic character can safely be stated (Table S 9). Calculation of these NICS values\(^{[17]}\) has been performed on optimized (B3LYP\(^{[10]}\)/def2-TZVP\(^{[11]}\), PCM solvent correction for CH₂Cl₂\(^{[12]}\)) molecular structures of free cyclo-P₃H, [cyclo-P₅]⁻, the bent geometry of the cyclo-P₃H ligand in 3* and the coordinated [cyclo-P₅]⁻ ligand in 1. Calculation of magnetic shielding tensors for dummy atoms placed at the centre (ring critical point), 1 Å above this centre and 1 Å below this centre have been performed on the PBE0\(^{[15]}\)/aug-cc-PVQZ level of theory. MultiWFN was used to obtain the ring critical point for these species and to extract the corresponding NICS(0/1/1/3) values.\(^{[16]}\) The obtained values show clearly that the aromatic character of cyclo-P₃H is retained upon bending into the geometry found in 3*. While the decrease in all three NICS values is larger for this bending, than what is found for the geometric changes within the [cyclo-P₅]⁻ upon coordination, the obtained NICS values are still negative indicating a high degree of aromaticity for the system.

\[\text{Table S 9: NICS(0/1/1/3) of various species whose aromaticity can safely be stated and those obtained for the bent geometry of the cyclo-P₃H ligand in 3*, revealing decreased aromaticity for this geometry, while maintaining the largest part of it.}\]

| Species | NICS(0) | NICS(0) | NICS(1) | NICS(-1) |
|---------|---------|---------|---------|---------|
| cyclo-P₃H (bent) | -13.10 | -20.96 | -31.71 | -30.92 |
| cyclo-P₃H (free) | -17.03 | -27.92 | -37.19 | -37.19 |
| [cyclo-P₅]⁻ (ligand) | -15.95 | -31.90 | -39.98 | -39.98 |
| [cyclo-P₅]⁻ (free) | -16.25 | -33.12 | -41.10 | -41.10 |
### optimized geometries

\( [\text{Cp}^*\text{Fe}(\eta^5-P_5)] \)

**B3LYP/def2TZVP:** Energies/H = \(-3360.782830\), Enthalpies/H = \(-3360.781885\), Free Energies/H = \(-3360.850077\), ZPVE/ kJ/mol = 610.65

**B3LYP/def2TZVPD:** Energies/H = \(-3360.781850\), Enthalpies/H = \(-3360.780905\), Free Energies/H = \(-3360.848996\), ZPVE/ kJ/mol = 610.99

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| Fe   | 0.0907820 | 0.0001340 | -0.0004200|
| P    | 1.6788700 | 0.7449760 | -1.6476410|
| P    | 1.6790230 | 1.7963410 | 0.1985620 |
| P    | 1.6811750 | -1.5701960| 0.8927190 |
| P    | 1.6810900 | 0.3653270 | 1.7686030 |
| C    | -1.6470920| -1.2064340| -0.1482740|
| C    | -1.6458170| -0.5151290| 1.1023450 |
| C    | -1.6481730| 1.0637610 | -0.5868840|
| C    | -1.6486720| -0.2306910| -1.1922690|
| C    | -1.7384330| -1.1484940| 2.4533840 |
| C    | -1.7394940| 1.9787350 | 1.8493280 |
| C    | -1.7441380| 2.3700220 | -1.3074480|
| C    | -1.7428180| -2.6872710| -0.3305700|
| C    | -1.7448980| -0.5142630| -2.6570370|
| H    | -1.2575250| -2.1255810| 2.4751130 |
| H    | -1.2581930| 1.6953900 | 2.7896440 |
| H    | -1.2949470| -3.0087260| -1.2700400|
| H    | -1.2582440| 3.1731220 | -0.7545040|
| H    | -1.2499760| -3.2266820| 0.4774400 |
| H    | -2.7880280| -1.2899790| 2.7293270 |
| H    | -1.2716310| -1.4601910| -2.9175540|
| H    | -2.7928810| -2.9957100| -0.3419380|
| H    | -2.7891990| 2.2055810 | 2.0603880 |
| H    | -1.2771270| 0.2688120 | -3.2524780 |
| H    | -1.2679960| 2.8971080 | 1.5019960 |
| H    | -2.7953310| -0.5759870| -2.9580780 |
| H    | -1.2886150| 2.3207090 | -2.2956440|
| H    | -2.7943510| 2.6478750 | -1.4405750|
SUPPORTING INFORMATION

$[\text{Cp}^*\text{Fe}^{\eta^5-P_5\text{SiEt}_3}]^+$ ($2^+$)

B3LYP/def2TZVP: Energies/H = $-3887.722003$, Enthalpies/H = $-3887.721059$, Free Energies/H = $-3887.814994$, ZPVE/ kJ/mol = 1136.93

\begin{verbatim}
Fe   1.324578 -0.105551 -0.01182
P   -0.914722 -0.777765 -0.188888
P   0.177455 -0.935106 -1.99369
P   0.076203 -1.533599  1.52032
P   1.898082 -2.015912 -1.396412
P   1.839168 -2.370392  0.700751
Si  -3.112785  0.094463 -0.09863
C   2.307397  1.093776  1.442468
C   3.239954  0.705871  0.430627
C   1.55396  1.925941 -0.579785
C   2.773663  1.220552 -0.819064
C   1.270175  1.85319  0.81993
C   4.540497  0.00663  0.656949
H   4.506235 -0.646025  1.527479
H   5.326095  0.748261  0.830226
H   4.837324 -0.590924 -0.203514
C   3.502029  1.150219 -2.121502
H   4.13132   0.2646   -2.189214
H   4.150825  2.025417 -2.222592
H   2.820703  1.148185 -2.970875
C   2.464362  0.864308  2.910268
H   1.503788  0.82441  3.421166
H   3.037595  1.686606  3.348901
H   3.001334 -0.058823  3.122852
C   0.79581   2.720816 -1.592454
H   0.883369  2.296632 -2.591463
H   1.194082  3.739091  1.63154
H  -0.261801  2.791557 -1.346823
C   0.180934  2.577919  1.541019
H  -0.646598  2.833557  0.882695
H   0.576967  3.514831  1.944076
H  -0.208486  2.004178  2.380835
C  -3.132935  1.618566 -1.202432
H  -2.62671   2.429273 -0.671658
H  -2.532046  1.411211 -2.091744
C  -3.403039  0.40641  1.733059
H  -3.170102 -0.511719  2.279406
H  -2.684808  1.155178  2.076175
C  -4.124468 -1.323748 -0.805484
H  -5.147569 -0.939047 -0.888352
H  -3.793828 -1.495469  1.83414
C  -4.540369  2.072646  1.632609
\end{verbatim}
[\textit{Cp'^{*}\textit{Fe(\eta^5-\textit{P}_5\textit{H})}^+] (3^+)\]

B3LYP/def2TZVP: Energies/H = -3361.177444, Enthalpies/H = -3361.176500, Free Energies/H = -3361.245504, ZPVE/ kJ/mol = 633.43
### SUPPORTING INFORMATION

|   |   |   |   |
|---|---|---|---|
| H | -2.88467 | -1.783146 | -2.331128 |
| H | -1.376962 | 1.14654 | -3.047645 |
| H | -2.869726 | 1.769762 | -2.35695 |

\[ \text{[Cp}^*\text{Fe(η}^5\text{-P}_3\text{Me})]^+ (4^+) \]

B3LYP/def2TZVP: Energies/H = -3400.488573, Enthalpies/H = -3400.487629, Free Energies/H = -3400.560708, ZPVE/ kJ/mol = 710.48

### Coordinates

\begin{align*}
\text{Fe} & : [-0.048181, -0.108942, -0.000338] \\
\text{P} & : [2.215598, 0.369174, 0.004563] \\
\text{P} & : [1.551908, -0.48332, 1.803392] \\
\text{P} & : [1.542083, -0.476443, 1.811754] \\
\text{P} & : [0.562034, -2.203472, 1.145221] \\
\text{P} & : [0.556989, -2.199831, 1.072762] \\
\text{C} & : [-1.738676, 0.430048, 1.165216] \\
\text{C} & : [-2.168144, -0.313232, 0.022747] \\
\text{C} & : [-1.76121, 0.430048, 1.165216] \\
\text{C} & : [-1.090194, 1.594041, 0.725368] \\
\text{C} & : [-1.075564, 1.611484, -0.703409] \\
\text{C} & : [-3.000569, -1.553601, -0.044674] \\
\text{C} & : [-2.099575, 0.046328, 2.55607] \\
\text{C} & : [-0.617682, 2.6817, 1.634897] \\
\text{C} & : [-2.049564, 0.105319, 2.589917] \\
\text{C} & : [-0.584533, 2.721977, 1.574631] \\
\text{H} & : [-2.814251, -2.153539, -0.933829] \\
\text{H} & : [-2.824082, -2.17752, 0.829972] \\
\text{H} & : [-2.177259, -1.030084, 2.700158] \\
\text{H} & : [-1.299397, 0.50337, -3.271394] \\
\text{H} & : [-0.149796, 2.287391, 2.53641] \\
\text{H} & : [-2.126819, -0.967729, 2.757636] \\
\text{H} & : [-4.059813, -1.279946, -0.069655] \\
\text{H} & : [-0.154783, 2.350812, -2.504045] \\
\text{H} & : [-3.01045, 0.551599, 2.862724] \\
\text{H} & : [-3.06687, 0.485073, 2.819038] \\
\text{H} & : [0.161678, 3.337322, -1.075416] \\
\text{H} & : [-1.363706, 0.432302, 3.25986] \\
\text{H} & : [-1.421174, 3.374844, -1.839835] \\
\text{H} & : [0.089993, 3.346967, 1.144418] \\
\text{H} & : [-1.470564, 3.290047, 1.94933] \\
\text{C} & : [3.015034, 2.009543, -0.000786] \\
\text{H} & : [4.088394, 1.864807, 0.112851] \\
\text{H} & : [2.811106, 2.502442, -0.949323] \\
\text{H} & : [2.635181, 2.608825, 0.823737]
\end{align*}
$[(\text{Et}_3\text{Si})_2(\mu-\text{H})]^+$

B3LYP/def2TZVP: Energies/H = −1054.628352, Enthalpies/H = −1054.627408, Free Energies/H = −1054.704688, ZPVE/ kJ/mol = 1063.67
SUPPORTING INFORMATION

\[
\begin{align*}
\text{Si} & : 1.5219690, -0.0479420, 0.0473920 \\
\text{Si} & : -1.7476380, -0.0700230, -0.0742810 \\
\text{H} & : -0.1132820, 0.0023400, -0.0049920
\end{align*}
\]

\(\text{Et}_3\text{SiH}\)

B3LYP/def2TZVP: Energies/H = \(-527.701140\), Enthalpies/H = \(-527.700196\), Free Energies/H = \(-527.750313\), ZPVE/\(\text{kJ/mol}\) = 536.82

\[
\begin{align*}
\text{C} & : -2.4019700, -0.7208310, -0.8476060 \\
\text{H} & : -3.4169770, 1.1259300, -0.8501840 \\
\text{H} & : -1.8348750, -1.2611950, -1.6087120 \\
\text{H} & : -2.4677930, 0.3202470, -1.1688570 \\
\text{C} & : -1.7537420, 1.6274940, 0.6626620 \\
\text{H} & : -0.4649440, 2.0498300, 1.4077280 \\
\text{C} & : -0.0031530, 2.3120570, -0.6944270 \\
\text{H} & : -1.0232180, 2.1733050, -1.0572570 \\
\text{H} & : 0.1741680, 3.3885130, -0.6296490 \\
\text{H} & : 0.6700440, 1.9178790, -1.4590170 \\
\text{C} & : 1.1634450, -1.1118580, -0.5255240 \\
\text{H} & : 0.9691870, -2.1881490, -0.4619500 \\
\text{H} & : 0.8607980, -0.8169600, -1.5358580 \\
\text{C} & : 2.6634850, -0.8441910, -0.3345200 \\
\text{H} & : 3.2648030, -1.3870300, -1.0667940 \\
\text{H} & : 2.9066540, 0.2164340, -0.4442180 \\
\text{H} & : 3.0000280, -1.1511490, 0.6586140 \\
\text{Si} & : 0.0340670, -0.2560300, 0.7262260 \\
\text{H} & : 0.4736040, -0.6704430, 2.0938450
\end{align*}
\]

\((\text{Et}_3\text{Si})_2\text{O}\)

B3LYP/def2TZVP: Energies/H = \(-1129.581330\), Enthalpies/H = \(-1129.580386\), Free Energies/H = \(-1129.663504\), ZPVE/\(\text{kJ/mol}\) = 1045.45

\[
\begin{align*}
\text{C} & : 3.2793150, 2.3347630, 0.5481400 \\
\text{H} & : 3.3415830, 3.4005500, 0.7817670 \\
\text{H} & : 3.8144230, 2.1768720, -0.3907850 \\
\text{H} & : 3.8264180, 1.8014710, 1.3276550 \\
\text{C} & : 1.8189940, 1.8678180, 0.4521850 \\
\text{H} & : 1.3066710, 2.0623630, 1.4013990 \\
\text{H} & : 1.2929020, 2.4743300, -0.2939760 \\
\text{C} & : 1.9586300, -1.1407690, 1.3708520 \\
\text{H} & : 1.5110590, -2.1048500, 1.1044620 \\
\text{H} & : 1.4342300, -0.8177640, 2.2771950
\end{align*}
\]
### SUPPORTING INFORMATION

|  |  |  |
|---|---|---|
| C | 3.4505170 | -1.3402440 | 1.6783160 |
| H | 3.9208800 | -0.4194080 | 2.0280320 |
| H | 3.5990450 | -2.0933140 | 2.4562870 |
| H | 4.0033560 | -1.6722920 | 0.7965850 |
| C | 2.4153460 | -0.3657910 | -1.6075630 |
| H | 2.1403820 | 0.3847640 | -2.3574380 |
| H | 3.4897980 | -0.2337060 | -1.4401430 |
| H | 2.4607150 | -2.5481220 | -1.4584910 |
| H | 1.0817250 | -1.9241290 | -2.3560080 |
| Si | 1.5044340 | 0.0632300 | -0.0132110 |
| O | -0.1105540 | -0.1130330 | -0.3000330 |
| C | -2.6729550 | -1.2054590 | -0.9213600 |
| H | -3.7425990 | -1.9957060 | -0.8077140 |
| H | -2.4363290 | -1.0904520 | -1.9903290 |
| C | -2.3767040 | -2.6494250 | -0.4905920 |
| H | -2.9522040 | -3.3706320 | -1.0763680 |
| H | -1.3199600 | -2.8932760 | -0.6187070 |
| H | -2.6235760 | -2.8136720 | 0.5608070 |
| C | -2.2173840 | 1.8374560 | -0.6313760 |
| H | -3.2790570 | 1.9819990 | -0.4018000 |
| H | -1.6834610 | 2.5854190 | -0.0341140 |
| C | -1.9719510 | 2.0977680 | -2.1248240 |
| H | -2.5481060 | 1.4141920 | -2.7523290 |
| H | -2.2551120 | 3.1147590 | -2.4077310 |
| H | -0.9190920 | 1.9672990 | -2.3841580 |
| C | -2.0043660 | 0.0205790 | 1.8612210 |
| H | -1.6138550 | -0.9437110 | 2.2042320 |
| H | -1.3743040 | 0.7790160 | 2.3396040 |
| C | -3.4583730 | 0.1857920 | 2.3298360 |
| H | -4.1099990 | -0.5780550 | 1.8990550 |
| H | -3.5405690 | 0.1055870 | 3.4165970 |
| H | -3.8659330 | 1.1584570 | 2.0453400 |
| Si | -1.7133340 | 0.1313440 | -0.0008660 |

**H$_2$O**

B3LYP/def2TZVP: Energies/H = -76.445378, Enthalpies/H = -76.444434, Free Energies/H = -76.465863, ZPVE/ kJ/mol = 55.42
**Supporting Information**

\[
\text{Me}_2\text{O}
\]

B3LYP/def2TZVP: Energies/H = \(-155.012573\), Enthalpies/H = \(-155.012573\), Free Energies/H = \(-155.042385\), ZPVE/ kJ/mol = 208.17

\[
\begin{align*}
C & \quad 1.1762010 \quad -0.1960170 \quad 0.0000000 \\
H & \quad 2.0261580 \quad 0.4851680 \quad 0.0003490 \\
H & \quad 1.2290150 \quad -0.8347970 \quad -0.8905680 \\
H & \quad 1.2286910 \quad -0.8353050 \quad 0.8901390 \\
C & \quad -1.1762010 \quad -0.1960170 \quad 0.0000000 \\
H & \quad -1.2286050 \quad -0.8354300 \quad 0.8906520 \\
H & \quad -2.0261580 \quad 0.4851680 \quad 0.0005280 \\
H & \quad -1.2291010 \quad -0.8346710 \quad -0.8906520 \\
O & \quad 0.0000000 \quad 0.5902590 \quad -0.0000030 \\
\end{align*}
\]

\[
\text{[Me}_3\text{O}]^+
\]

B3LYP/def2TZVP: Energies/H = \(-194.684233\), Enthalpies/H = \(-194.683289\), Free Energies/H = \(-194.718687\), ZPVE/ kJ/mol = 317.88

\[
\begin{align*}
C & \quad -0.4519470 \quad -1.3591690 \quad 0.0651410 \\
H & \quad 0.2637340 \quad -2.0420890 \quad -0.3780480 \\
H & \quad -1.4330190 \quad -1.4753870 \quad -0.3807600 \\
H & \quad -0.4835490 \quad -1.4480290 \quad 1.1485390 \\
C & \quad -0.9520730 \quad 1.0704720 \quad 0.0653180 \\
H & \quad -1.0096680 \quad 1.1450250 \quad 1.1487880 \\
H & \quad -0.5687210 \quad 1.9791350 \quad -0.3847650 \\
H & \quad -1.9013910 \quad 0.7869130 \quad -0.3746420 \\
C & \quad 1.4037020 \quad 0.2885640 \quad 0.0652530 \\
H & \quad 1.9960770 \quad -0.5029690 \quad -0.3787610 \\
H & \quad 1.6384320 \quad 1.2488740 \quad -0.3795850 \\
H & \quad 1.4954570 \quad 0.3068040 \quad 1.1487120 \\
O & \quad 0.0005700 \quad 0.0003150 \quad -0.2929350 \\
\end{align*}
\]

cyclo-P_5H (free)

B3LYP/def2TZVP: Energies/H = \(-1707.509978\), Enthalpies/H = \(-1707.509034\), Free Energies/H = \(-1707.548299\), ZPVE/ kJ/mol = 41.90

\[
\begin{align*}
P & \quad -0.0001190 \quad -1.4181550 \quad -1.0583310 \\
P & \quad -0.0001190 \quad -1.4181550 \quad 1.0583310 \\
P & \quad -0.0001190 \quad 0.5490970 \quad -1.8160170 \\
P & \quad 0.0004610 \quad 1.5416710 \quad 0.0000000 \\
H & \quad 0.0002280 \quad 2.9467030 \quad 0.0000000 \\
P & \quad -0.0001190 \quad 0.5490970 \quad 1.8160170 \\
\end{align*}
\]
SUPPORTING INFORMATION

[cyclo-P$_5$]$^-$ (free)

B3LYP/def2TZVP: Energies/H = -1707.08315, Enthalpies/H = -1707.082210, Free Energies/H = -1707.12035, ZPVE/ kJ/mol = 20.55

\[
\begin{array}{ccc}
  \text{P} & -1.1419970 & 1.3794220 \\
  \text{P} & 0.9591780 & 1.5122790 \\
  \text{P} & -1.6650010 & -0.6597200 \\
  \text{P} & 1.7348780 & -0.4448980 \\
  \text{P} & 0.1129430 & -1.7870840 \\
\end{array}
\]

\[\text{B3LYP/def2TZVPD: Energies/H = -467.587972, Enthalpies/H = -467.587028, Free Energies/H = -467.647942, ZPVE/ kJ/mol = 747.04} \]

\[
\begin{array}{ccc}
  \text{C} & -3.1023330 & 0.2879020 \\
  \text{H} & -3.8415050 & -0.1960270 \\
  \text{H} & -3.6119460 & 1.0854360 \\
  \text{H} & -2.7320280 & -0.4359030 \\
  \text{C} & -1.9706760 & 0.8936160 \\
  \text{H} & -2.3151640 & 1.0854360 \\
  \text{H} & -1.2379890 & -1.5643740 \\
  \text{C} & -1.7525980 & 0.8936160 \\
  \text{H} & -2.8145840 & -0.4359030 \\
  \text{H} & -1.6240570 & 1.3730670 \\
  \text{C} & -1.0540250 & -1.8423010 \\
  \text{H} & -1.4804990 & -2.1563740 \\
  \text{H} & -1.1996680 & 1.3730670 \\
  \text{H} & 0.0138510 & -0.1960270 \\
  \text{C} & 1.8827490 & 1.3730670 \\
  \text{H} & 2.9264090 & 1.3730670 \\
  \text{H} & 1.8317850 & 1.3730670 \\
  \text{C} & 1.7866550 & -0.1960270 \\
  \text{H} & 2.0499060 & 0.2420540 \\
  \text{H} & 0.9794340 & -0.1960270 \\
  \text{C} & 2.9734440 & -2.1563740 \\
  \text{H} & 3.3539090 & -2.0751200 \\
  \text{H} & 3.8018620 & -0.4359030 \\
  \text{H} & 2.6946810 & -0.4359030 \\
  \text{C} & 2.8120800 & -0.4359030 \\
  \text{H} & 1.7947480 & 1.3730670 \\
  \text{H} & 0.2110030 & 1.3730670 \\
  \text{H} & 1.3002120 & 1.3730670 \\
  \text{O} & -1.2063090 & -0.1960270 \\
  \text{O} & 1.1970970 & 1.3730670 \\
  \text{H} & -0.0881420 & 0.2420540 \\
\end{array}
\]
SUPPORTING INFORMATION

$\text{Et}_2\text{O}$

B3LYP/def2TZVPD: Energies/H = \(-233.619297\), Enthalpies/H = \(-233.618353\), Free Energies/H = \(-233.656271\), ZPVE/ $\text{kJ/mol} = 357.00$

|  | $\text{C}$ | $\text{H}$ | $\text{H}$ | $\text{H}$ | $\text{C}$ | $\text{H}$ | $\text{H}$ | $\text{O}$ |
|---|---|---|---|---|---|---|---|---|
| $\text{E}_{\text{H}}$ | -2.3794560 | 0.4127000 | 0.0000070 | | | | | |
| $\text{E}_{\text{H}}$ | -2.3689380 | 1.0517910 | -0.8841620 | | | | | |
| $\text{E}_{\text{H}}$ | -3.3079000 | -0.1617670 | 0.0000240 | | | | | |
| $\text{E}_{\text{H}}$ | -2.3689160 | 1.0518080 | 0.8841620 | | | | | |
| $\text{E}_{\text{H}}$ | -1.1845980 | -0.5178840 | 0.0000000 | | | | | |
| $\text{E}_{\text{H}}$ | -1.2034130 | -1.1709230 | -0.8849940 | | | | | |
| $\text{E}_{\text{H}}$ | -1.2033920 | -1.1709070 | 0.8850070 | | | | | |
| $\text{E}_{\text{H}}$ | 1.1845980 | -0.5178840 | 0.0000020 | | | | | |
| $\text{E}_{\text{H}}$ | 1.2033930 | -1.1709030 | 0.8850100 | | | | | |
| $\text{E}_{\text{H}}$ | 1.2034120 | -1.1709270 | -0.8849900 | | | | | |
| $\text{E}_{\text{H}}$ | 2.3794560 | 0.4127000 | 0.0000060 | | | | | |
| $\text{E}_{\text{H}}$ | 3.3079000 | -0.1617670 | 0.0000280 | | | | | |
| $\text{E}_{\text{H}}$ | 2.3689400 | 1.0517870 | -0.8841650 | | | | | |
| $\text{E}_{\text{H}}$ | 2.3689140 | 1.0518120 | 0.8841590 | | | | | |
| $\text{O}$ | 0.0000000 | 0.2577750 | -0.0000210 | | | | | |
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